CHEMISTRY
A European Journal

A Journal of
ChemPubSoc Europe

Accepted Article

Title: Polymer-supported palladium (II) carbene complexes: catalytic activity, recyclability and selectivity in C-H acetoxylation of arenes

Authors: Maitham H. Majeed, Payam Shayesteh, Reine Wallenberg, Axel R. Persson, Niclas Johansson, Lei Ye, Joachim Schnadt, and Ola F. Wendt

To be cited as: *Chem. Eur. J.* 10.1002/chem.201700777

Link to VoR: http://dx.doi.org/10.1002/chem.201700777

Supported by
ACES

WILEY-VCH

Polymer-supported palladium (II) carbene complexes: catalytic activity, recyclability and selectivity in C–H acetoxylation of arenes

Maitham H. Majeed,[a] Payam Shayesteh,[b] L. Reine Wallenberg,[a,c] Axel R. Persson,[a,c] Niclas Johansson,[b] Lei Ye,[d] Joachim Schnadt,[b] and Ola F. Wendt*[a]

Abstract: Heterogeneous catalysts for selective oxidation of C–H bonds were synthesized by co-polymerization of new N-heterocyclic carbene-palladium(II) (NHC-Pd(II)) monomers with divinylbenzene. The polymer-supported NHC-Pd(II) catalyses undirected C–H acetoxylation of simple and methylated arenes as well as polyarenes, with similar or superior efficiency compared to their homogeneous analogues. In particular, the regioselectivity has been improved in the acetoxylation of biphenyl and naphthalene compared to the best homogeneous catalysts. The new polymer-supported catalysts maintain the original oxidation state of Pd(II) after repeated catalytic reactions, and exhibit no significant leaching of palladium. In addition, the new catalysts have been successfully recovered and reused without loss of activity over several cycles of reactions.

Introduction

The selective oxidation of undirected C–H bonds can simplify the functionalization of hydrocarbons and is therefore potentially very useful in the synthesis of both fine and bulk chemicals.[1] Thus, it can help in reducing waste in large scale transformations, and in the synthesis of more complex molecules it can enable late stage functionalization. So far, the most successful approach to the selective oxidation of C–H bonds has been ligand-directed C–H functionalization where a heteroatom controls the regioselectivity.[2,3] However, although some progress has been made,[4,5] there are still no general, regioselective methods for the functionalization of simple alkanes or arenes neither by homogeneous nor heterogeneous catalysts. To address this shortcoming substantial research efforts have been devoted during several decades to developing Pd catalysts for the undirected C−H acetoxylation of arenes using different oxidants.[6-8] One successful strategy has been the use of Pd(OAc)$_2$ as a catalyst, PhI(OAc)$_2$ as an oxidant, and pyridine derivatives as supporting ligands,[9] a system that catalyses the acetoxylation of undirected arenes via non-radical pathways.[10] As a ligated alternative to the Pd acetate catalyst in C–H activation NHC-Pd complexes have been reported recently.[11-18] The ligand adds stability to the system due to the strong NHC-M interaction, and it also enables functionalization and ligand control.[15,19,20] Moreover, to further catalyst separation and recovery the NHC-M complex can be heterogenized.[21] Indeed, the development of stable heterogeneous catalysts would substantially facilitate any industrial application.[22] There are many examples of supported Pd(II) catalysts,[23-26,27] and polymer-supported NHC-Pd complexes have been successfully used in many applications and for different chemical transformations, and advances in support strategies have been made recently.[26,28-35] However, metal leaching, reduction of the Pd(II) species during preparation steps and catalysis and aggregation of Pd(0) nanoparticles inside the polymer matrixes remains an unsolved problem in many cases.[36,37] However, although directed C–H activation over supported Pd complexes has been reported, there are no examples of the application of such catalysts for undirected C–H activation reactions.[38-41]

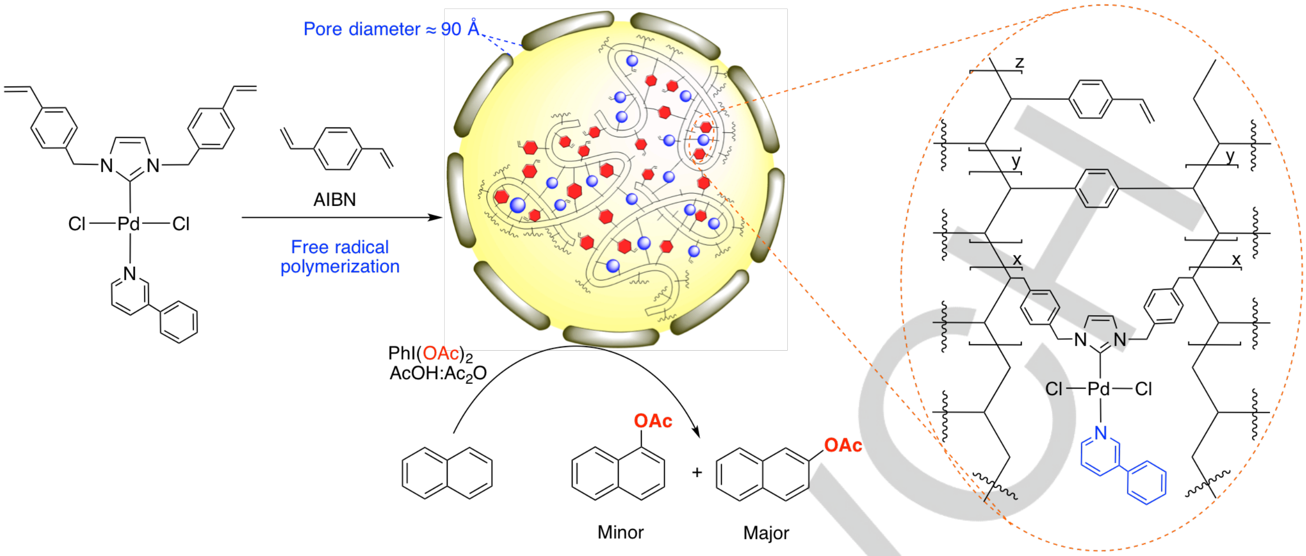
Here we report on the synthesis and characterization of a Pd(II) containing polymeric material based on the co-polymerization of polymerizable arms in the structure of an N-heterocyclic carbene ligand and divinylbenzene (Scheme 1). Our concept gave a material which is stable towards reduction and recyclable with no or little loss in activity. Its reactivity and regioselectivity in the C–H oxidation of arenes is reported together with the effect of various stabilizing pyridine ligands. Productivity is on par with the corresponding homogeneous catalysts and selectivity is in many cases substantially better.

Results and Discussion

Monomers: Synthesis and Characterization. Imidazolium chloride precursors [bmim]Cl **1a** and [bvbim]Cl **1b** were synthesized according to previously reported procedures.[42-45] We chose these precursors based on that they either have one (**1a**) or two (**1b**) polymerizable arms to investigate whether

---

[a] *M. H. Majeed, Prof. L. R. Wallenberg, A. R. Persson, Prof. O. F. Wendt*
Centre for Analysis snd Synthesis, Department of Chemistry, Lund University
Box 124, SE-221 00, Lund (Sweden)
E-mail: ola.wendt@chem.lu.se
[b] *P. Shayesteh, N. Johansson, Prof. J. Schnadt*
Division of Synchrotron Radiation Research, Department of Physics, Lund University
Box 118, SE-221 00, Lund (Sweden)
[c] *Prof. L. R. Wallenberg, A. R. Persson*
National Center for High Resolution Electron Microscopy, Lund University
Box 124, SE-221 00, Lund (Sweden)
[d] *Prof. L. Ye*
Centre for Applied Life Sciences, Department of Chemistry, Lund University
Box 124, SE-221 00, Lund (Sweden)



Scheme 1. Polymerized NHC-Pd(II) monomer can catalyse C-H acetoxylation of undirected arene.

this leads to a difference in stability or selectivity. In particular, the degree of cross-linking is expected to vary with the number of vinyl groups in the monomer. Direct metallation using literature procedures afforded $[Ag(bmim)_2]_2[Ag_2Cl_4]$ **2a**[46] and Ag[bvbim]Cl complex **2b** in good yield (Figure 1). ^{13}C NMR spectra showed the characteristic carbene signals at 180.7 ppm and 180.9 ppm for **2a** and **2b**, respectively.[46-50] The use of silver intermediates precluded any radical polymerization of the vinyl moiety at an earlier stage; some other protocols use harsh reaction conditions where such unwanted side reactions could occur.[51] Transmetallation with $PdCl_2(PhCN)_2$ gave NHC-Pd(II) dimers **3a** and **3b** (Ref. 47 and Figure 1), which showed broad signals in the ^{1}H NMR spectra due to the dynamic equilibrium between monomeric and dimeric species as previously shown.[16] Adding pyridine derivatives cleaved the dimer and afforded NHC-Pd complexes **4a**, **4b**, **5a**, **5b** and **6b** in excellent yield with one **(a)** or two-vinyl **(b)** moieties and 3-phenylpyridine **(4)**, 4-phenylpyridine **(5)**, and 9-chloroacridine **(6)** as stabilizing ligands, respectively (cf. Figure 1 and Scheme 2). They were characterized by ^{1}H and ^{13}C NMR spectroscopy and elemental analysis. All signals were sharp and, again, characteristic carbene signals around 150 ppm were observed in the ^{13}C NMR spectra in $CDCl_3$.[51,52] Slow diffusion of n-hexane into a DCM solution of the complexes gave X-ray quality crystals and an X-ray diffraction (XRD) analysis confirmed the molecular structures of **4a**, **5a**,[47] **4b** and **6b**. They are given in Figures 1 and S1; all details including selected bond distances and angles are, likewise, found in the supporting information.

Polymers: Synthesis and Characterization. Palladium monomers **4a**, **4b**, **5a**, **5b**, and **6b** were co-polymerized with divinylbenzene (DVB) using precipitation polymerization which has been previously shown to give microspheres.[53-55] The polymerization conditions did not influence similar palladium complexes without polymerizable arms, *i.e.* the metal centre is not influenced by *e.g.* the free radical initiator AIBN (see SI for details). The polymerization gave polymers **7a**, **7b**, **8a**, **8b** and **9b**, respectively (Scheme 2).

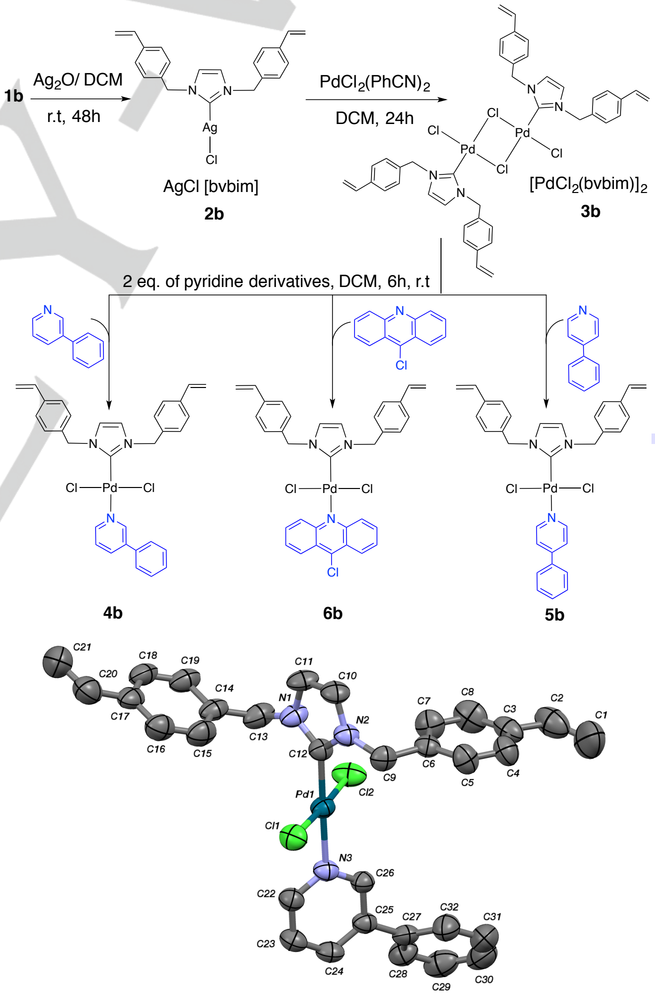
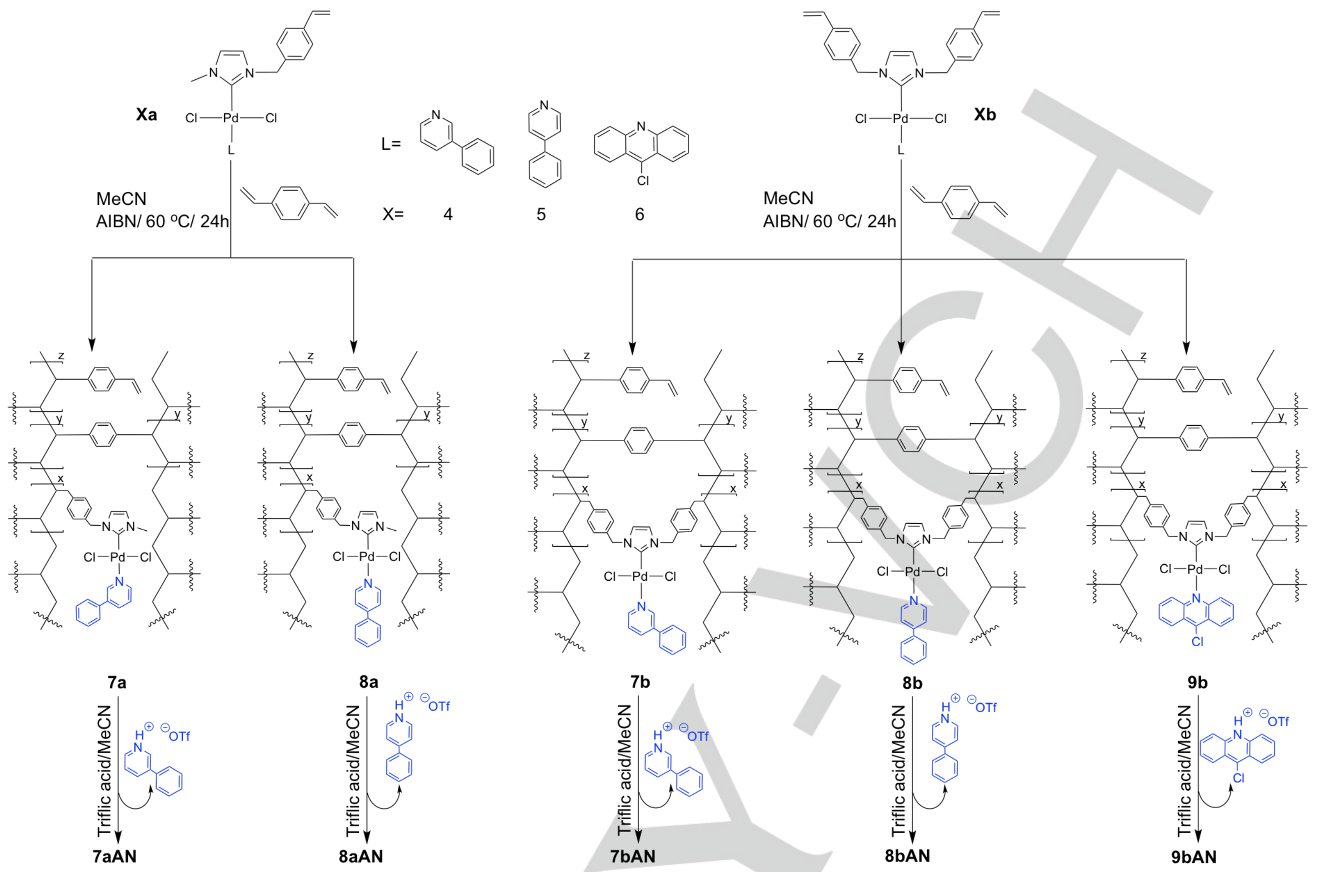


Figure 1. Synthesis of NHC-Pd(II) monomers and crystal structure of **4b** with thermal ellipsoids displayed at 50% probability. Hydrogen atoms have been omitted for clarity.



Scheme 2. Precipitation polymerization of NHC-Pd(II) monomers and pyridine derivatives removing step from the microspheres.

Neat acetonitrile or a mixture of acetonitrile and toluene, which are near θ-solvents for DVB type polymers, were used. These solvents are known to form a clean surface of microspheres of 2-5 µm and to create porous polymer beads, which is very important for catalysis.[56-59] The Pd:DVB ratio was 1:4 and the total monomer concentration used in this study was ~ 2% (w/v) of the solvent; all preparation details are given in the supporting information, Table S3. In order to study the impact of the pyridine ligands on the catalytic performance they were removed through protonation in one series of catalysts, giving the acetonitrile adducts **7aAN**, **7bAN**, **8aAN**, **8bAN**, and **9bAN** (Scheme 2). This procedure in principle renders the metal centres of the **a** and **b** series identical. However, the different catalysts within each series (**a** and **b**) could still display different activities and selectivities, since the use of the different pyridines could have induced differences in the shape of the polymer cavity.

All polymers were characterized by an Inductively coupled plasma (ICP) analysis. For selected polymers we also performed Solid state NMR spectroscopy (SS-NMR), High resolution transmission electron microscopy (HRTEM), X-ray energy-dispersive spectroscopy (XEDS), and X-ray photoelectron spectroscopy (XPS). The solid-state ^{13}C-Cross polarization magic angle spinning (CP-MAS) spectra are almost identical for the different polymers except a shoulder peak which is present near 150 ppm for the pyridine polymers, but absent in the acetonitrile series. This is shown in Figure S2 for **7a** and **7aAN** and provides good evidence for the success of the washing process. Figure S3 in the supporting information show similar details for polymers **8b** and **8bAN**, respectively. Peaks near 30, 41, and 55 ppm are assigned to the aliphatic CH$_3$-, CH$_2$-, and CH- carbons for the NHC-Pd(II) and poly-DVB skeleton. Unreacted vinyl linkers in the poly-DVB skeleton exhibit two peaks around 113 and 138 ppm assigned to the terminal and internal carbons respectively.[60] Aromatic phenyl, aromatic phenylpyridine, aromatic poly-DVB skeleton and C10, C11 of the imidazolyl show resonances near 129, 138 and 146 ppm, respectively. HRTEM images were recorded for polymer **7bAN**. EDX data show a low, but detectable level of Pd and Cl inside the particles of **7bAN** (Figure S4a and S4b), whereas the concentrations of those two elements were below the detection limit outside the particles. Furthermore, HRTEM images showed no metallic palladium particles in the polymer (Figure 2a and 2b) This was confirmed by Fast Fourier transform (FFT) analysis of HRTEM images which revealed no spots corresponding to lattice fringes. The palladium found is thus homogeneously dispersed and presumably molecular, although no information on the oxidation state can be inferred. Using bright-field STEM mode, an EDX mapping of the edge of the particles of **7bAN** was performed. Again, Pd and C are clearly visible (as brighter areas) in the particles, while the area outside the particles contains very little Pd and C (supporting information Figure S6).

To confirm the previous results (and address the issue of oxidation state), **7b** was treated with ascorbic acid to reduce any Pd(II) to Pd(0). Powder X-ray diffraction (PXRD) patterns were recorded for the native polymers and compared with that of the reduced polymer **7b(red)**. The PXRD patterns of the native polymers are featureless, but the PXRD curve of **7b(red)** shows peaks at 40°, 47° and 67° which can be assigned to the (111), (200), and (220) crystal planes of Pd(0) particles in the polymer matrix (Figure S5a). These results demonstrate the presence of Pd(II) in the native polymer which only upon reduction gives Pd(0) particles.[61] To further characterize and investigate the elemental composition, oxidation state, and coordination environment of the Pd species in the monomer and fresh polymer XPS was employed. Pd 3d core level spectra of the monomer **4b** and polymers **7b** and **7bAN** show the Pd $3d_{5/2}$ and Pd $3d_{3/2}$ peaks at approximately 340 and 345.5 eV binding energy in agreement with the energies expected for a Pd(II) species (Figure 2c).[62] A small shift to lower binding energy between the lines of **4b** and **7b** is seen as the result of the polymerization and concomitant change in Pd environment, while the shift to somewhat higher binding energy between **7b** and **7bAN** likely is related to the replacement of phenylpyridine by acetonitrile. The occurrence of a small shoulder at ca. 337.5 eV, which is still within the Pd(II) region, can probably be explained by a variation of the chemical environment of the Pd ion.[63,64] More importantly, there are no peaks which correspond to the binding energies of Pd in the metallic state. This confirms that no reduction to Pd(0) takes place during the polymer

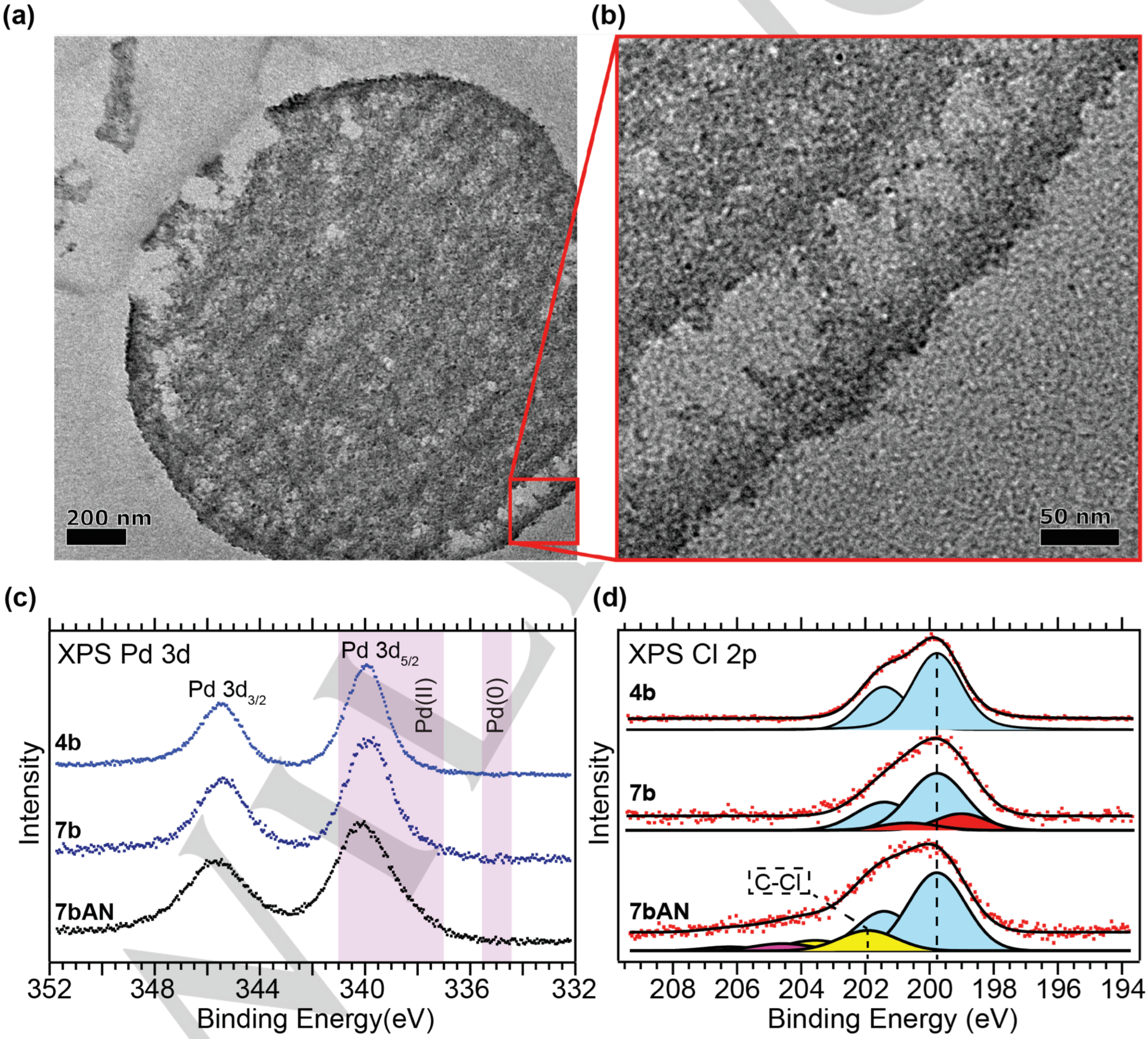
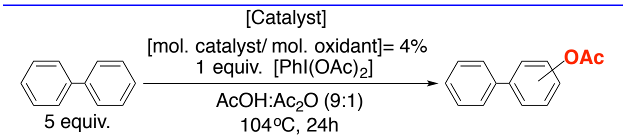


Figure 2. (a) and (b) TEM-images of 7bAN. (c) and (d) Pd 3d and Cl 2p XP spectra of the indicated samples.

Table 1. NHC-Pd(II) polymer-catalysed C-H acetoxylation of biphenyl.



Entry	[Cat.][a]	Temp. (°C)	Yield[b] (%)	Selectivity (%)		
				o-	m-	p-
1	8bAN	70	Trace	-	-	-
2	8bAN	92	18	-	39	61
3	8bAN	104	45	12	43	45
4	8bAN	115	28	22	32	46
5	8bAN	125	28	22	32	46
6	8bAN	135	30	27	30	43
7	None	104	0	-	-	-
8	PE-iPr[c]	104	44	13	41	46
9	8aAN	104	56[d]	13	41	46
10	7aAN	104	45	13	29	58
11	7aAN[e]	104	53	13	40	47
12	7bAN	104	50	12	42	46
13	7bAN[e]	104	56	14	41	45
14	7bAN[f]	104	51	14	41	45
15	7bAN[g]	104	46	13	41	46
16	9bAN	104	53	13	41	45
17	9bAN[e]	104	47	15	38	47
18	Pd(OAc)$_2$	104	58[h]	10	46	44

[a] Pd loading described in table S3. [b] Yield and selectivity were determined by GC using a calibration curve based on decane as an internal standard. [c] PE-ipr= PEPPSI-iPr (5 mol%). [d] TON≈ 14. [e] [Oxidant]= MesI(OAc)$_2$. [f] Reaction time=48h, [g] Reaction time= 72h, [h] 2 mol% of Pd(OAc)$_2$ and 2 mol% of pyridine (1:1 ratio of [Pd] to [pyr]; catalyst loading relative to oxidant) Ref. [79].

synthesis and washing steps.[65,66] For comparison, the XP spectrum of **7b(red)** shows peaks at ca. 335 and 340.3 eV binding energy corresponding to the binding energy of Pd(0) (Figure S14). The Cl 2p$_{3/2}$ and Cl 2p$_{1/2}$ peaks at 199.8 and 201.4 eV are clearly visible for monomer **4b** (Figure 2d). In addition, the Cl 2p X-ray photoelectron (XP) spectrum of **7b** exhibits an additional component to lower energy. The presence of several components can probably be attributed to the larger variation of chemical environments upon polymerization. A corresponding line broadening due to polydispersity is observed in the Pd 3d spectrum of **7b**. In the Cl 2p spectrum of polymer **7bAN** a high binding energy species at ca. 201.9 eV is found. Such high Cl 2p energies are typical for C-Cl bonds and thus are an indication that H-Cl addition to the vinyl groups occurs to some extent during washing with triflic acid.[67-69] The N 1s spectra for **4b**, **7b**, and **7bAN** are shown in Figure S7. The high energy peaks (ca. 402.4 eV) are related to the imidazole nitrogen atoms,[62,70] and the lower energy peaks (ca. 401.7 eV) are associated with the phenylpyridine nitrogen. The ratio between the imidazole and phenylpyridine peaks is 2:1 as expected. Peak broadening towards lower and higher binding energies is observed in the N 1s spectra of **7b** and **7bAN**; as above it can be assigned to the variation of the N chemical environment by polymerization and washing steps.[71-73] Polymers **7b** and **7bAN** are spherical particles within a size range of several hundred nm to 4 µm according to Scanning electron microscopy (SEM) (Figures S5b, S5c, S5d, and S5e). In general, the polymer beads were found to have a more uniform size distribution after removing the phenylpyridine, probably due to loss of the nanospheres (less than 1 µm) during the washing process. Details of the N$_2$ adsorption experiment and ICP analyses of all polymers are given in the supporting information, Figure S16 and Table S3. There were no considerable differences in the palladium loading, which is between 6-8 %. Thermogravimetric analysis (TGA) shows that all polymers possess a high thermal stability up to 200 °C (see Figure S8a and S8b for details).

Activity in C–H activation. Homogeneous Pd(II) catalysts are active in both ligand-directed[3,75-77] and non-directed C–H bond acetoxylation,[4,10,78-80] mainly using Pd(OAc)$_2$ as a catalyst, pyridines as ancillary ligands, and PhI(OAc)$_2$ as an oxidant. As a benchmark for the activity and selectivity of our palladium-containing polymers we chose the non-directed C–H acetoxylation of arenes, and for the optimization of reaction conditions we used biphenyl as the substrate, so that there would also be a selectivity issue. A PEPPSI-iPr[52] catalyst was employed as a reference homogeneous catalyst. Although monomers **4**-**6** would have been preferred these are not stable towards polymerization under the reaction conditions. It is expected that the electronic properties of PEPPSI-iPr are not substantially different than those of **4**-**6**.[81,82] The initial screening of oxidants using polymer **8bAN** as catalyst revealed that only PhI(OAc)$_2$ and MesI(OAc)$_2$ gave any turnover in the reaction with 45% and 49% yields, respectively (Table S4). We clearly observed that the catalysis reaction proceeded without formation of chlorinated biphenyl products. Traces of phenyl iodide were, however, detected in the Gas chromatography (GC) analysis. Subsequently, we tested different temperatures (Table 1, entries 1-6). The results show traces of acetoxybiphenyl derivatives at 70 °C and 18% yield at 92 °C with a ca 61:39 regioselectivity in favour of the *para*-substituted over the *meta*-substituted. The yield of acetoxybiphenyl derivatives increased to 45% (Table 1, entry 3) at 104 °C with a decrease in the regioselectivity to ca. 45:43 for *para*- and *meta*-substituted positions, while *ortho*-substituted biphenyl was formed as a minor product due to the steric hindrance in the biphenyl substrate. At higher temperatures the yield decreased (entries 4-6); this decrease could be attributed to the decomposition of PhI(OAc)$_2$ in the reaction mixture in accordance with a previous study.[83] There is no reaction in the absence of catalyst (entry 7).

The homogeneous PEPPSI-iPr (5 mol %) catalyst shows very similar productivity and selectivity as **8bAN** (entry 8) and the same is true for Pd(OAc)$_2$/pyridine (1:1), a known homogeneous Pd(II) system with high activity in C–H oxygenation of arenes (entry 18).[79] Comparing the different polymeric catalyst all NHC-Pd(II)(MeCN) polymers in general afforded higher yield of acetoxybiphenyl products compared to the NHC-Pd(II)(pyridine derivative) polymers (Table S5, entries 1-9). However, **7bAN** and **8bAN** show comparable activity to **7b** and **8b** respectively in the presence of PhI(OAc)$_2$. No prominent differences were observed in the regioselectivities among the polymeric catalysts except for **7aAN** (Table 1, entry 10), which exhibited a regioselectivity of ca. 58:29 for *para*- and *meta*-substituted positions as opposed to the ca 1:1 selectivity for the other types of catalysts including the homogeneous one. $MesI(OAc)_2$ increased the yields compared to $PhI(OAc)_2$ except for **9bAN** (Table 1, entry 17) when used as an oxidant with the acetonitrile series of polymers. However, with the pyridine containing polymers a decrease of the yields was observed using $MesI(OAc)_2$ as an oxidant (Table S5, entries 1-9). The origin of this observation is likely connected to an increased steric congestion in the pyridine derivatives. The use of various pyridine ligands was introduced to probe if there is any effect on the polymer cavity induced by the different pyridines. An increase in yields was identified when **7a** and **7b** were used in the reaction compared to **8a** and **8b** (Table S5, Entries 1, 3-7). This is possibly due to the creation of a larger cavity when using the 3-phenylpyridine during polymerization. There was no significant influence of increase of the reaction time on the yield of acetoxybiphenyl derivatives (Table 1, entries 14 and 15).

The fact that the polymer bound catalysts behave similarly as the molecular catalysts in terms of oxidation state and reactivity suggests a similar reaction mechanism as previously proposed for molecular Pd(II) systems.[16]

Reusability and Heterogeneity. All the polymer-based catalysts **7**-**9** were evaluated for recyclability and they can all be separated easily from the reaction mixture by a simple centrifugation process. We chose to investigate **7b** further since this gave the best turnover in the catalysis (Table S5). Additionally, we also tested **7bAN** for recyclability to shed some light on the issue of pyridine vs. acetonitrile ligand. Thus, the recovered **7b** was shaken with 5 mL of 3-phenylpyridine/DCM solutions for 30 min after each cycle and then washed with MeCN to remove the remaining non-bonded phenylpyridines, a procedure which, however, was not entirely effective for all cycles as can be seen from the shifts in the N 1s spectra in Figure S7. **7bAN** was shaken only with MeCN solvent. The so-treated catalysts were dried and used directly for the next reaction cycle. Both **7b** and **7bAN** were found to be effective in four cycles (probably in more, but this was not tested) of the acetoxylation reaction. No significant change in the productivity and selectivity of the recovered catalysts was observed (Figure 3c and supporting information Figure S9), and importantly the kinetic profile for the four runs was more or less identical (Figure 3d). The slight increase of activity that is observed could possibly mean that the polymer material opens up during the reaction giving a better access to the palladium and therefore a slightly higher activity. The catalysis stops almost completely after eight hours and ^1H NMR spectroscopy showed no traces of $PhI(OAc)_2$ in the catalysis mixture. However, in terms of mass balance what has not been converted to acetoxylated product is almost exclusively unreacted starting material. Thus, upon addition of 1 additional equivalent of $PhI(OAc)_2$ into the reaction vessel after eight hours, the reaction continues and the yield of

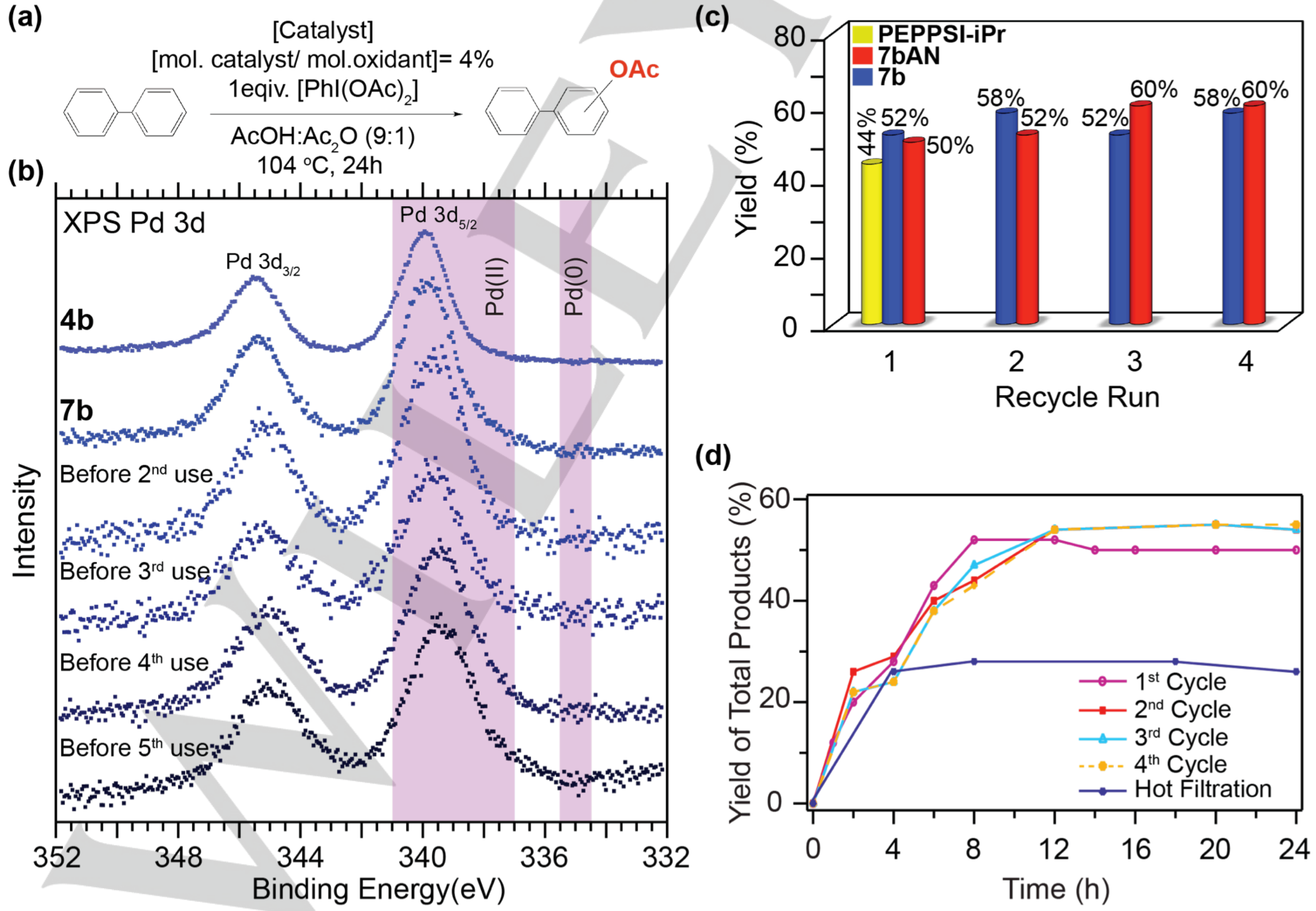
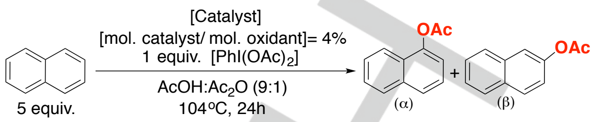


Figure 3. (a) C-H acetoxylation reaction of biphenyl over **7b** and **7bAN** catalysts using $PhI(OAc)_2$ as an oxidant. (b) Pd 3d XP spectra of **4b**, **7b** fresh and **7b** after each reuse. (c) Reusability and productivity of **7b** and **7bAN**; the results are compared to those for a [PEPPSI-iPr] catalyst at 5 mol%. (d) Time profile and hot filtration study of **7b**-catalyzed C-H acetoxylation of biphenyl.

10.1002/chem.201700777

acetoxybiphenyl derivatives approximately doubles (Table S5, entry 10). The yields are thus primarily controlled by the access to oxidant not by the stability of the catalyst. In line with this the recycled catalysts have (within error) the same activity as the fresh one. A hot filtration test (Figure 3d) underlines the heterogeneous nature of the catalyst with a complete inhibition of the activity after removal of the solid catalyst. These results were supported with results from an ICP-OES analysis, in which only a small leaching of Pd from the polymer is detected after each catalytic cycle (Pd wt% = 6.58, 6.52, 6.41, and 6.30 after the 1st, 2nd, 3rd, and 4th catalytic cycle, respectively). To probe the palladium oxidation state after catalysis, **7b** was analysed by XPS. The Pd $3d_{5/2}$ and Pd $3d_{3/2}$ binding energies of **7b** after each catalytic cycle (ca. 339.3 and 344.6 eV, respectively) showed only a small shift compared to those of the monomer and fresh polymer (Figure 3b). This shift is probably related to ligand exchange between chloride and acetate. It is clear, however, from the spectra that the palladium remains in oxidation state (II) for all cycles. Similar results were obtained for **7bAN** after the fourth catalytic cycle (Figure S15). Subsequently, we focused our attention to the Cl 2p core level of **7b** after each catalytic cycle, which showed significant broadening in the spectral features and shifts by 2 eV toward higher binding energies compared to the spectra of the monomer and fresh polymer (supporting information Figure S10). The spectrum can be convoluted into two peaks, one corresponding to a Pd-Cl species (with a Cl $2p_{3/2}$ binding energy of 199.8 eV) and a second Cl $2p_{3/2}$ peak at 201.9 eV, which can be assigned to a C-Cl species according to literature.[67-69] In order to understand this remarkable change in Cl 2p binding energy, we also characterized **7b** before and after catalysis with SS-NMR spectroscopy. ^{13}C CP-MAS NMR spectra (which were performed at two different spinning rates to differentiate between peaks and side bands) revealed a new peak after catalysis at 169.8 ppm, which corresponds to (C=O) of an acetate group (supporting information Figure S11 and S12).[84-87] In contrast, the peaks related to terminal and internal carbons of vinyl linkers at ca. 113 and 138 ppm respectively observed for the fresh catalyst are absent after catalysis (supporting information Figure S12). For comparison the biphenyl acetoxylation reaction was carried out in the presence of poly(divinylbenzene) under the described reaction conditions. This gave no conversion of biphenyl but, again, ^{13}C CP-MAS NMR spectra showed a sharp peak from an acetate group at 169.5 ppm and the intensities of carbon peaks related to vinyl linkers were reduced (supporting information Figure S13). These data suggest that $PhI(OAc)_2$ can functionalize unreacted vinyl groups (but not aromatic groups) in the absence of a catalyst. In the presence of a catalyst we therefore suggest that all remaining vinyl groups in the polymer are acetoxylated or chlorinated during catalysis. These results were supported by elemental analysis of **7b** after catalysis, which confirmed that the ratio between Pd:Cl is almost 1:2 (85% of Cl is still present in the catalyst). Thus, the majority of the chlorine, ca. 75% according to the XPS results, have been transferred to the polymer matrix, while the rest is still coordinated to Pd; ca 15 % have been washed out from the catalyst according to the ICP analysis.

Table 2. Polymer catalysed C–H acetoxylation of naphthalene.



Entry	[Catalyst][a]	Yield[b] (%)	Selectivity (%) (α : β)
1	None	0	-
2	PEPPSI-iPr[c]	36	44:56
3	PEPPSI-iPr[c,d]	33	33:67
4	7b	18	28:72
5	7bAN	25	56:44
6	7b[d]	18	17:83
7	7bAN[d]	26	54:46
8	8b[d]	15	20:80
9	8bAN[d]	19	47:53
10	8bAN[d,e]	9	11:89
11	$Pd(OAc)_2$/Acridine[79]	88	20:80
12	$Pd(OAc)_2$/FPCA[80]	69	29:71

[a] Pd loading described in Table S3. [b] Yield and selectivity were determined by GC using a calibration curve and based on decane as an internal standard. [c] [PEPPSI-iPr]= 5 mol%, [d] [Oxidant]= $MesI(OAc)_2$, [e] 1 equiv. of 4-Phenylpyridine/Pd added to the reaction mixture. [80] FPCA= 6-Fluoropicolinic acid.

Oxidation of naphthalene and other arenes. We further investigated the scope of C–H acetoxylation for other arenes using the optimized reaction conditions. With naphthalene as a substrate (Table 2) the polymeric catalysts showed a significant increase in selectivity compared to homogeneous ones. Thus, PEPPSI-iPr showed no regioselectivity using $PhI(OAc)_2$ as an oxidant, while a moderate regioselectivity of ca 33:67 in favour of the β-substitution was observed with $MesI(OAc)_2$ (Table 2, entries 2 and 3). This is in line with other homogenous catalysts such as $Pd(OAc)_2$ and sulfinyl-NHC−Pd complexes reported previously.[16,79] On the other hand, the polymeric catalysts are significantly better with a regioselectivity in favour of acetoxylation at the β-position of ca 28:72 using **7b**/$PhI(OAc)_2$ (Table 2, entry 4). This improvement in selectivity was diminished significantly using **7bAN**, in slight favour of acetoxylation at the α-position (α:β = 56:44) (Table 2, entry 5). For the acetonitrile-supported systems no improvement in selectivity was obtained using $MesI(OAc)_2$, but for **8b** and **7b** the bulky oxidant gave an even better selectivity of α:β = 20:80 and 17:83, respectively. Thus, the presence of phenylpyridines increase the selectivity substantially and this goes hand in hand with a decreased activity. To confirm the improved selectivity one equiv. of 4-phenylpyridine (with respect to Pd) was added to the reaction mixture using **8bAN**. As expected this gave a lower activity compared to previously reported $Pd(OAc)_2$ systems (Table 2, entries 11 and 12), but a dramatically increased selectivity (11:89) (Table 2, entry 10). In general the polymeric catalysts showed lower activity than the homogeneous ones. Finally, we tested catalyst **8b** under the optimized reaction conditions in C–H acetoxylation of mono- and polycyclic arene substrates. It exhibited modest yields but a higher selectivity (compared with PEPPSI-iPr) when employed to the acetoxylation of pyrene. For simple aromatic substrates the polymeric catalyst offered only a modest improvement in terms of selectivity but surprisingly enough some improvement in terms of activity in the acetoxylation of toluene (Table S6).

Conclusions

The development of a catalytically active, reusable and selective NHC-Pd(II) polymer based on co-polymerization of divinyl benzene with vinyl moieties in the structure of the N-heterocyclic carbene ligand is described. Characterization of the NHC-Pd(II) polymers showed the presence of Pd(II) species in the native polymer without any trace of Pd(0) nanoparticles. The catalytic activity and selectivity in direct acetoxylation of unactivated C–H bonds in arenes was evaluated for all polymers with and without phenylpyridine as supporting ligands on the palladium. The presence of phenylpyridines increased the selectivity and decreased the activity of the polymers, reaching a 9:1 selectivity in the acetoxylation of naphtalene. While the catalysis stops almost completely after eight hours due to decomposition of the oxidant it can be restarted through addition of fresh oxidant and there is no indication that the catalyst loses its activity. Thus, it can be recycled four times without any loss of activity, but likely it will be effective for many more cycles. Moreover, the catalyst was shown to be truly heterogeneous in a hot filtration test. No significant leaching of Pd from the polymer after each catalysis cycle was detected. The supported polymer contains reactive vinyl moieties in the backbone of the polymer, and these are acetoxylated or chlorinated during catalysis. The present system is the first heterogeneous catalyst for acetoxylation of non-functionalized arenes. The heterogeneous nature of these catalysts could open up for continuous flow catalysis.

Experimental Section

Procedure for the acetoxylation of biphenyl catalysed by *N*HC-Pd(II) heterogeneous catalysts.

The catalytic reactions were performed in a glass-threaded vial with magnetic stirring bar, which was loaded up with biphenyl (0.2 g, 1.29 mmol, 5 equiv.), $PhI(OAc)_2$ (0.083 g, 0.25 mmol, 1 equiv.), catalyst (4 mol% proportion to the amount of the oxidant), glacial acetic acid (4.5 mL), and acetic anhydride (0.5 mL) and sealed tightly by using a screw cap. The mixture was stirred at ambient temperature for 10 min before it was heated to 104 °C using a heating block. At the end of the reaction the vessel was cooled to room temperature, and the catalyst was separated by centrifugation. The mixture was diluted with Et_2O (5 mL), shaken for 2 min, and extracted with saturated aqueous solution of K_2CO_3 (9M in distilled water, 3×2mL). The organic layer was then separated and the solvent was removed by evaporation. DCM (1.2 mL) and decane (20 µl, as an internal standard for quantitative GC analysis) were added to the resulting solids and analysed by GC.

Recyclability, heterogeneity and time study experiments

Recycling Experiment. The acetoxylation reaction was carried out under the same reaction conditions as described above. The reaction mixture was centrifuged after it had reached room temperature. The remaining solid was washed with a pyridine derivative/DCM solution (1×5 mL) and MeCN (3×10 mL), dried, and reused for the following run. Using these conditions, the recyclability study was performed at designated reaction times (2 h, 4 h, 6 h, 8 h, 12 h, 20 h, and 24 h).
Hot Filtration test. The acetoxylation reaction was carried out under identical reaction conditions as described above. After 4 h (yield 28%) the catalyst was filtered off at the reaction temperature (104 °C) and the catalyst free filtrate was allowed to stir under identical reaction conditions. The GC analysis of the products after 8 h, 18 h, and 24 h revealed no further acetoxylation of biphenyl (GC final yield 26%).

Acknowledgements

Financial support from the Swedish Research Council (contract no. 621-2012-5815), the Knut and Alice Wallenberg Foundation, and the Royal Physiographic Society is gratefully acknowledged.

Keywords: *N*-heterocyclic carbenes • Palladium(II) • Polymer supported Pd(II) • C–H activation • Undirected acetoxylation

[1] R. Giri, J. Liang, J. G. Lei, J. J. Li, D. H. Wang, X. Chen, I. C. Naggar, C. Guo, B. M. Foxman, J. Q. Yu, *Angew. Chem. Int. Ed.* **2005**, *44*, 7420.
[2] T. W. Lyons, M. S. Sanford, *Chem. Rev.* **2010**, *110*, 1147.
[3] S. R. Neufeldt, M. S. Sanford, *Acc. Chem. Res.* **2012**, *45*, 936.
[4] J. B. Gary, A. K. Cook, M. S. Sanford, *ACS Catal.* **2013**, *3*, 700.
[5] N. Kuhl, M. N. Hopkinson, J. Wencel-Delord, F. Glorius, *Angew. Chem. Int. Ed.* **2012**, *51*, 10236.
[6] L. Eberson, L. Gomezgon, *Chem. Commun.* **1971**, 263.
[7] L. Eberson, L. Gomezgon, *Acta. Chem. Scand.* **1973**, *27*, 1255.
[8] L. Eberson, L. Jonsson, *Chem. Commun.* **1974**, 885.
[9] T. Yoneyama, R. H. Crabtree, *J. Mol. Catal. A: Chem.* **1996**, *108*, 35.
[10] A. K. Cook, M. S. Sanford, *J. Am. Chem. Soc.* **2015**, *137*, 3109.
[11] D. Meyer, M. A. Taige, A. Zeller, K. Hohlfeld, S. Ahrens, T. Strassner, *Organometallics* **2009**, *28*, 2142.
[12] M. Muehlhofer, T. Strassner, W. A. Herrmann, *Angew. Chem. Int. Ed.* **2002**, *41*, 1745.
[13] D. Munz, T. Strassner, *Inorg. Chem.* **2015**.
[14] B. M. Prince, T. R. Cundari, *Organometallics* **2012**, *31*, 1042. M. G. Organ, *Chem. Eur. J* **2010**, *16*, 10844.
[15] P. L. Arnold, M. S. Sanford, S. M. Pearson, *J. Am. Chem. Soc.* **2009**, *131*, 13912.
[16] F. Tato, A. Garcia-Dominguez, D. J. Cardenas, *Organometallics* **2013**, *32*, 7487.
[17] S. P. Desai, M. Mondal, J. Choudhury, *Organometallics* **2015**, *34*, 2731.
[18] E. Bolbat, O. F. Wendt, *Eur. J. Org. Chem.* **2016**, *20*, 3395.
[19] R. Credendino, L. Falivene, L. Cavallo, *J. Am. Chem. Soc.* **2012**, *134*, 8127.
[20] M. N. Hopkinson, C. Richter, M. Schedler, F. Glorius, *Nature* **2014**, *510*, 485.
[21] I. Karame, M. Boualleg, J. M. Camus, T. K. Maishal, J. Alauzun, J. M. Basset, C. Coperet, R. J. Corriu, E. Jeanneau, A. Mehdi, C. Reye, L. Veyre, C. Thieuleux, *Chem.: Eur. J.* **2009**, *15*, 11820.
[22] M. P. Conley, C. Coperet, C. Thieuleux, *ACS Catal.* **2014**, *4*, 1458.
[23] H. Duan, M. Li, G. Zhang, H. Duan, J. R. Gallagher, Z. Huang, Y. Sun, Z. Luo, H. Chen, J. T. Miller, R. Zou, A. Lei, Y. Zhao, *ACS Catal.* **2015**, *5*, 3752.

[24] T. Park, A. J. Hickman, K. Koh, S. Martin, A. G. Wong-Foy, M. S. Sanford, A. J. Matzger, *J. Am. Chem. Soc.* **2011**, *133*, 20138.

[25] Santoro, S.; Kozhushkov, S. I.; Ackermann, L.; Vaccaro, L. *Green Chem.* **2016**, *18*, 3471.

[26] Y. M. A. Yamada, S. M. Sarkar, Y. Uozumi, *J. Am. Chem. Soc.* **2012**, *134*, 3190.

[27] X. Li, R. V. Zeeland, R. V. Maligal-Ganesh, Y. Pei, G. Power, L. Stanley, W. Huang, *ACS Catal.* **2016**, *6*, 6324.

[28] K. V. S. Ranganath, S. Onitsuka, A. K. Kumar, J. Inanaga, *Catal. Sci. Technol.* **2013**, *3*, 2161.

[29] K. V. Bukhryakov, C. Mugemana, K. B. Vu, V. O. Rodionov, *Org. Lett.* **2015**, *17*, 4826.

[30] S. J. Xu, K. P. Song, T. Li, B. Tan, *J. Mater. Chem. A* **2015**, *3*, 1272.

[31] W. J. Sommer, M. Weck, *Coord. Chem. Rev.* **2007**, *251*, 860.

[32] B. Tamami, F. Farjadian, S. Ghasemi, H. Allahyari, *New J. Chem.* **2013**, *37*, 2011.

[33] E. Mohammadi, B. Movassagh, *J. Organomet. Chem.* **2016**, *822*, 62.

[34] C. A. Witham, W. Huang, C. Tsung, J. N. Kuhn, G. A. Somorjai, F. D. Toste, *Nat. Chem.* **2010**, *2*, 36.

[35] W. Huang, J. H. Liu, P. Alayoglu, Y. Li, C. A. Witham, C. Tsung, F. D. Toste, G. A. Somorjai, *J. Am. Chem. Soc.* **2010**, *132*, 16771.

[36] M. Pagliaro, V. Pandarus, R. Ciriminna, F. Beland, P. D. Cara, *Chem. Cat. Chem.* **2012**, *4*, Cp27.

[37] M. Arpad, *Chem. Rev.* **2011**, *111*, 2251.

[38] P. C. Perumgani, S. P. Parvathaneni, S. Keesara, M. R. Mandapati, *Appl. Organometal. Chem.* **2016**, 1.

[39] H. Fei, S. M. Cohen, *J. Am. Chem. Soc.* **2015**, *137*, 2191.

[40] V. Pascanu, F. Carson, M. V. Solano, J. Su, X. Zou, M. J. Johansson, B. Martín-Matute, *Chem.: Eur. J.* **2016**, *22*, 3729.

[41] L. Lee, J. He, J. Yu, C. W. Jones, *ACS Catal.* **2016**, *6*, 5245.

[42] J. H. Kim, J. W. Kim, M. Shokouhimehr, Y. S. Lee, *J. Org. Chem.* **2005**, *70*, 6714.

[43] D. Zhao, Z. Fei, W. H. Ang, P. J. Dyson, *Small* **2006**, *2*, 879.

[44] C. Fu, L. Meng, Q. Lu, Z. Fei, P. J. Dyson, *Adv. Funct. Mater.* **2008**, *18*, 857.

[45] S. Ghazali-Esfahani, H. Song, E. Paunescu, F. D. Bobbink, H. Liu, Z. Fei, G. Laurenczy, M. Bagherzadeh, N. Yan, P. J. Dyson, *Green Chem.* **2013**, *15*, 1584.

[46] X. Y. Lu, F. Chen, W. F. Xu, X.-T. Chen, *Inorg. Chim. Acta* **2009**, *362*, 5113.

[47] M. H. Majeed, O. F. Wendt, *Acta Cryst.* **2016**, E72, 534-537.

[48] I. J. B. Lin, C. S. Vasam, *Coord. Chem. Rev.* **2007**, *251*, 642.

[49] U. Hintermair, U. Englert, W. Leitner, *Organometallics* **2011**, *30*, 3726.

[50] S. Warsink, J. A. Venter, A. Roodt, *J. Organomet. Chem.* **2015**, *775*, 195.

[51] A. Chartoire, X. Frogneux, A. Boreux, A. M. Z. Slawin, S. P. Nolan, *Organometallics* **2012**, *31*, 6947.

[52] J. Nasielski, N. Hadei, G. Achonduh, E. A. Kantchev, C. J. O'Brien, A. Lough, M. G. Organ, *Chem.: Eur. J* **2010**, *16*, 10844.

[53] L. Ye, R. Weiss, K. Mosbach, *Macromolecules* **2000**, *33*, 8239.

[54] C. Cacho, E. Turiel, A Martin-Esteban, C. Perez-Conde, C. Camara, *J. Chromatogr. B* **2004**, *802*, 347.

[55] B. Y. Zu, G. Q. Pan, X. Z. Guo, Y. Zhang, H. Q. Zhang, *J. Polym. Sci. Pol. Chem.* **2009**, *47*, 3257.

[56] K. Li, H. D. H. Stover, *J. Polym. Sci. Pol. Chem.* **1993**, *31*, 3257.

[57] J. S. Downey, R. S. Frank, W. H. Li, H. D. H. Stover, *Macromolecules* **1999**, *32*, 2838.

[58] W. H. Li, K. Li, H. D. H. Stover, *J. Polym. Sci. Pol. Chem.* **1999**, *37*, 2295.

[59] W. H. Li, H. D. H. Stover, *J. Polym. Sci. Pol. Chem.* **1999**, *37*, 2899.

[60] M. Gaborieau, L. Nebhani, R. Graf, L. Barner, C. Barner-Kowollik, *Macromolecules* **2010**, *43*, 3868.

[61] N. Z. Shang, S. T. Gao, C. Feng, H. Y. Zhang, C. Wang, Z. Wang, *RSC Adv.* **2013**, *3*, 21863.

[62] S. Men, K. R. J. Lovelock, P. Licence, *RSC Adv.* **2015**, *5*, 35958.

[63] R. Arrigo, M. E. Schuster, Z. Xie, Y. Yi, G. Wowsnick, L. L. Sun, K. E. Hermann, M. Friedrich, P. Kast, M. Hävecker, A. Knop-Gericke, R. Schlögl, *ACS Catal.* **2015**, *5*, 2740.

[64] R. Arrigo, M. E. Schuster, S. Abate, S. Wrabetz, K. Amakawa, D. Teschner, M. Freni, G. Centi, S. Perathoner, M. Hävecker, R. Schlögl, *ChemSusChem* **2014**, *7*, 179.

[65] M. C. Militello, S. J. Smiko, *Surf. Sci. Spect.* **1994**, *3*, 387.

[66] G. Kumar, J. R. Blackburn, R. G. Aldridge, W. E. Moddeman, M. M. Jones, *Inorg. Chem.* **1972**, *11*, 296.

[67] J. Gao, A. V. Teplyakov, *Catal. Today* **2014**, *238*, 111.

[68] E. T. Kang, H. C. Ti, K. G. Neoh, T. C. Tan, *Polym. J.* **1988**, *20*, 399.

[69] D. T. Clark, D. K., D. B. Adams, W. K. R. Musgrave, *J. Electron Spectrosc. Rel. Phen.* **1975**, *6*, 117.

[70] J. P. Mathew, M. Srinivasan, *Eur. Polym. J.* **1995**, *31*, 835.

[71] J. R. Pels, F. Kapteijn, J. A. Moulijn, Q. Zhu, K. M. Thomas, *Carbon* **1995**, *33*, 1641.

[72] S. Maldonado, S. Morin, K. J. Stevenson, *Carbon* **2006**, *44*, 1429.

[73] Y. Zhang, J. Zhang, C. Sheng, J. Chen, Y. Liu, L. Zhao, F. Xie, *Energy Fuels* **2011**, *25*, 240.

[74] D. Kalyani, M. S. Sanford, *Org. Lett.* **2005**, *7*, 4149.

[75] L. V. Desai, H. A. Malik, M. S. Sanford, *Org. Lett.* **2006**, *8*, 1141.

[76] L. V. Desai, K. J. Stowers, M. S. Sanford, *J. Am. Chem. Soc.* **2008**, *130*, 13285.

[77] K. J. Stowers, M. S. Sanford, *Org. Lett.* **2009**, *11*, 4584.

[78] M. H. Emmert, A. K. Cook, Y. J. Xie, M. Sanford, *Angew. Chem. Int. Ed.* **2011**, *50*, 9409.

[79] A. K. Cook, M. H. Emmert, M. S. Sanford, *Org. Lett.* **2013**, *15*, 5428.

[80] C. Valderas, K. Naksomboon, M. Á. Fernández-Ibáñez, *Chem. Cat. Chem.* **2016**, *8*, 3213.

[81] F. Glorius, In *Topics in Organometallic Chemistry*; Springer: Berlin, 2007; vol. *21*, pp 1.

[82] J. L. Farmer, M. Pompeo, M. G. Organ, In *Ligand Design in Metal Chemistry: Reactivity and Catalysis*; Wiley: United Kingdom, 2016; pp 134.

[83] J. E. Leffler, L. J. Story, *J. Am. Chem. Soc.* **1967**, *89*, 2333.

[84] L. Y. Wang, P. F. Fang, C. H. Ye, J. W. Feng, *J. Polym. Sci. Pol. Phys.* **2006**, *44*, 2864.

[85] C. M. G. De Souza, M. I. B. Tavares, *J. Appl. Polym. Sci.* **2002**, *86*, 116.

[86] G. C. Stael, M. I. B. Tavares, *Polym. Test.* **1997**, *16*, 193.

[87] D. L. Trumbo, *Polym. Bull.* **1996**, *37*, 617.