Homogeneous Catalysis

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A Recyclable Nanoparticle-Supported Palladium Catalyst for the Hydroxycarbonylation of Aryl Halides in Water**

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Separation and recycling of homogeneous catalysts is considered a main objective in the area of green chemistry.[1] One approach to such an environmentally benign process is based on the development of solid-supported catalysts exhibiting high activity even in aqueous media.[2] Palladium complexes have received tremendous interest as powerful catalysts for coupling reactions of aryl halides[3] with great industrial potential. Hence, efforts have been made to immobilize them on diverse soluble and insoluble supports, such as inorganic solids,[4] polymers,[5] dendrimers,[6] perfluorinated tags,[7] and nanoparticles.[8]

Heterogeneous supports allow efficient recycling by filtration, albeit a substantial decrease in the activity of the immobilized catalysts is frequently observed. Soluble supports usually require a second solvent for the selective precipitation of the supported catalyst out of the reaction mixture (e.g. JandaJel, ROMP-gel, MeOPEG) or for extraction into the orthogonal liquid phase (e.g. into a fluorinated solvent).

Nanoparticles are considered a semi-heterogeneous support since they are readily dispersed and exhibit an intrinsically high surface area, which is combined with excellent accessibility of the surface-bound catalytic sites. Some particles are even amenable to magnetic separation, thus, avoiding the need for catalyst separation by filtration. However, examples for nanoparticle-grafted catalysts showing equal or even superior activity when compared to their homogeneous counterparts are still scarce.[9]

Ultimately, a catch–release system for a homogeneous catalyst would be a remedy for rate limitations caused by solid supports provided that a low contaminant level of the catalyst in solution is maintained. Herein we describe a palladium complex, noncovalently grafted on Co/C nanoparticles that dissociates from the nanoparticles for the course of the hydroxycarbonylation of aryl halides in water (100 °C) and is then recaptured on the graphene-layer of the magnetic nanoparticles (room temperature).[10] The high magnetic remanence of the nanoparticle powder permits its efficient separation and recycling.

Grass et al. have reported the preparation of cobalt nanoparticles coated with multiple graphene layers that are produced by a scalable one-step flame spray synthesis process.[11] We could demonstrate that the carbon shell of these particles can be suitably functionalized to allow the covalent attachment of catalysts,[12] however, multiple synthetic steps are required. Pyrene moieties interact with graphene layers through π–π stacking,[13] and some examples exploiting this were recently published showing the noncovalent modification of carbon nanotubes, for example, with biomolecules[13c] or olefin metathesis initiators and catalysts.[14] We envisaged that carbon-encapsulated Co/C nanomagnets are equally suited for such a reversible functionalization with pyrene units, which would greatly facilitate the immobilization of catalysts. In addition, the remarkable stability of the Co/C particles along with the exceptionally high saturation magnetization (158 emu g^{-1}) fulfills all the requirements for catalysis in aqueous media under basic conditions,[12] in sharp contrast to most nanoparticles frequently used as catalyst support, for example, magnetite@silica.[8]

To test the feasibility of our catch–release concept, we synthesized nitrophenyl pyrene derivative **1**,[15] which allows a facile quantification of the adsorption of **1** on the Co/C particles at room temperature and the level of desorption from the surface at reaction temperature (100 °C). Briefly, a dispersion of Co/C nanoparticles in water was sonicated in the presence of an excess of **1** (Scheme 1). The loading typically obtained by the noncovalent grafting was assessed by means of UV/Vis spectroscopy.[13] To this end, the nitrophenyl-functionalized particles **2** were subjected to basic hydrolysis (1 M $NaOH_{(aq)}$, 12 h) upon which the concentration of the generated nitrophenolate was determined against a likewise hydrolyzed standard solution of **1** (Figure 1, top). Thus, it was found that a loading of 0.2 mmol g^{-1} was established, a value being almost twice as high as that obtained by covalent modification.[13]

To estimate the degree of desorption of **1** from the carbon surface at elevated temperatures, the nitrophenyl-tagged nanoparticles **2** in boiling water were filtered through a sinter funnel, as a result 49 % of the nitrophenyl moieties dissociated from the surface of the nanobeads (Figure 1, bottom). In an alternative procedure, repeated (four or eight times) magnetic decantation of nanomagnets **2** from the hot supernatant solution caused desorption of 60 % and 76 % of **1**, respectively. Importantly, under the same treatment with

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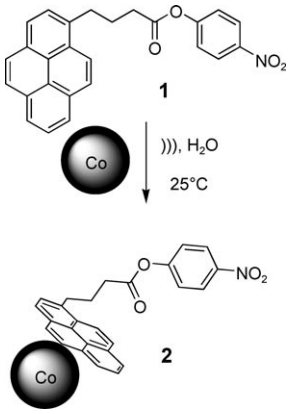


Scheme 1. Noncovalent grafting of **1** on carbon-coated cobalt-nanoparticles.)))) = ultrasound.

water at ambient temperature no removal of pyrene-moieties from the support occurred.

These results indicate that the π–π-stacking interaction between pyrene units and the graphene layer is strongly temperature dependent. Therefore, such a noncovalent immobilization is reversible under appropriate reaction conditions, and is in line with a similar, temperature-controlled desorption of a pyrene-tagged ruthenium complex from single-walled nanotubes (SWNTs) in organic solvents that was published during our studies.[14b] Moving to palladium-complexes tagged with pyrenes, we next fused 4-(4-bromobutyl) pyrene[17] (**3**) with 1-methylimidazole (**4**) to yield ligand precursor **5** and finally complex **6** (Scheme 2). N-heterocyclic carbenes (NHCs) proved to be a excellent class of ligands, because NHC–Pd bonds are generally inert towards cleavage.[18]

The immobilization of **6** on the cobalt nanoparticles to give **7** was carried out successfully in an analogous manner to the synthesis of **2**. The catalyst-loading (0.1 mmol g^{-1}) and the dissociation behavior of **6** was measured by inductively coupled plasma atomic emission spectroscopy (ICP-AES) and found to be in accord with the observations made for **2**, for example, 63 % of **6** was desorbed from **7** after filtration in boiling water. The supported catalyst **7** was used in the hydroxycarbonylation[19] of aryl halides in water under an atmospheric pressure of CO. In total, 16 reaction cycles were carried out on each of six different substrates at 100 °C. After each cycle **6** was recovered in the form of immobilized catalyst **7**, at ambient temperature, by magnetic decantation (Figure 2).

Therefore, the catalyst was quantitatively recycled after each run and leaching of palladium into product phase was negligible as determined by ICP-AES (0.7 ppm) in a representative run. Complementary measurements of the palladium content of catalyst **7** before (0.1 mmol g^{-1}) and after (0.08 mmol g^{-1}) the first run showed a rather pronounced decrease, which is probably due to residual non-immobilized compounds inherited from catalyst preparation. However, the loading

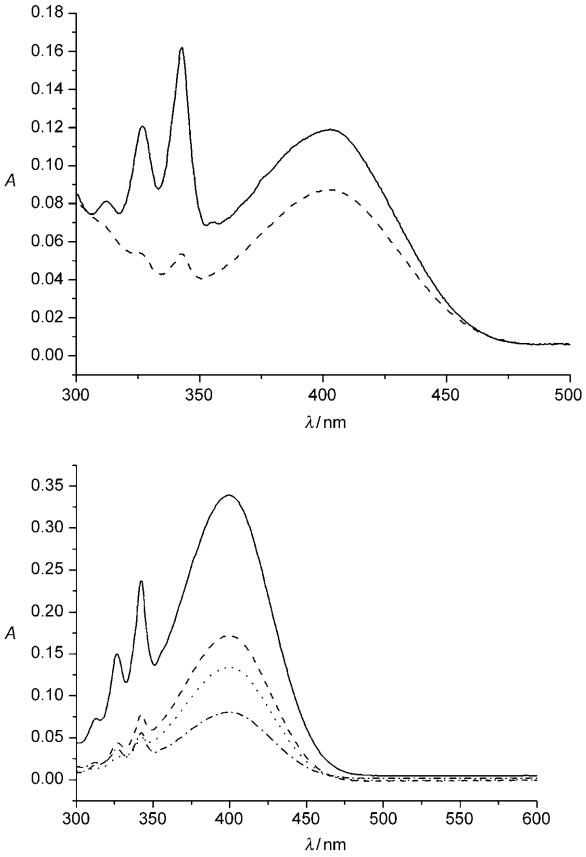
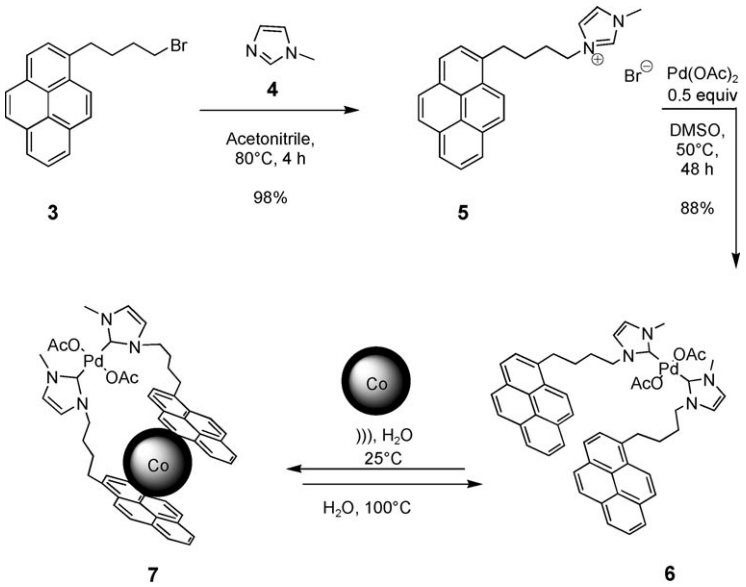


Figure 1. Top: UV/Vis spectra of reference **1** after basic hydrolysis (——) and nitrophenolate cleaved from **2** (-----) in water. Signals at 400 nm are assigned to the nitrophenolate. Signals below 350 nm correspond to the pyrene unit.[16] Bottom: Desorption experiments by treating **2** with boiling water followed by filtration (-----) or repeated magnetic decantation (••••• four times, –•–• eight times); (——) reference.



Scheme 2. Synthesis of pyrene-tagged palladium NHC complex **6** and reversible immobilization on Co/C-nanomagnets.

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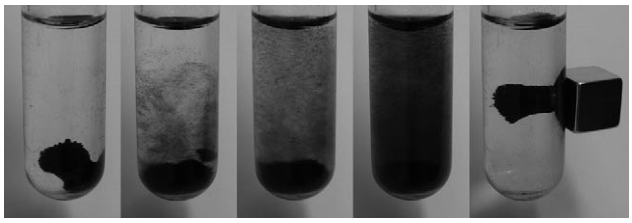
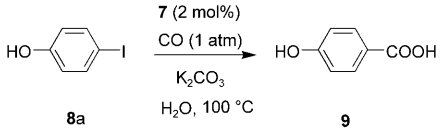


Figure 2. Co/C-nanomagnets reversibly tagged with homogeneous palladium complex **6** in water at ambient temperature at different levels of dispersion (left) and separation of the immobilized catalyst **7** with the aid of an external neodymium-based magnet (right).[20]

remained constant after the subsequent cycles with only a small decrease after the 10th run (0.07 mmol g^{-1}), thus verifying that virtually no leaching occurred during the catalyses. These findings are in agreement with the excellent activity of the recycled material, albeit it was necessary to increase reaction times after the seventh run to ensure quantitative conversion (Table 1, entries 7 and 8). Moreover, TEM micrographs recorded before and after the reactions showed no evidence of palladium precipitates being formed from the NHC complexes (Figure 3).

Table 1: Hydroxycarbonylation of 4-iodophenol with CO in water using immobilized catalyst **7**: Recycling experiments.[a]



8a **9**

Entry	Run	*t* [h]	Yield [%][b]
1	1	10	95
2	2	10	94
3	3	10	87
4	4	10	93
5	5	10	92
6	6	10	94
7	7	10	90
8	8	14	93
9	9	14	93
10	10	14	91

[a] 4-Iodophenol (0.5 mmol) in Millipore water (5 mL), K_2CO_3 (0.375 mmol), catalyst **7** (2.0 mol%), CO (1 atm), 100°C. [b] Yields of isolated products.

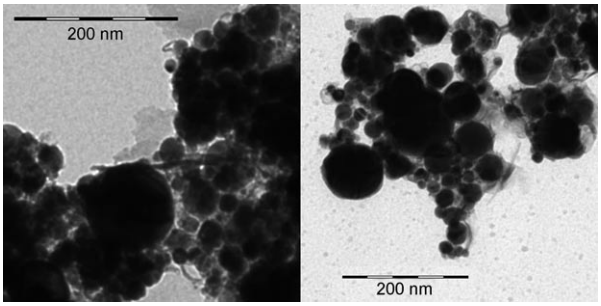
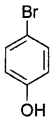
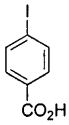
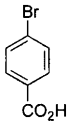
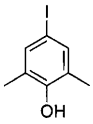
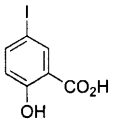


Figure 3. TEM-images of Co/C-nanoparticle grafted palladium complex **7** before (left) and after five catalytic cycles (right).

After 10 runs, the recovered nanoparticle powder **7** was still highly active in transforming diverse aryl halides into the corresponding benzoic acid derivatives (Table 2).Grafting of the desorbed complex **6** onto the glass surface of the vessel was negligible, since the amount of nanoparticle-bound palladium did not decrease significantly after 10 cycles, neither did the glassware exhibit notable catalytic activity, as was found in a control experiment without catalyst **7** (Table 2, entry 7).

Table 2: Hydroxycarbonylation of different aryl halides with CO in water using immobilized catalyst **7**.[a]

Entry	Run	Aryl halide	*t* [h]	Yield [%][b]
1	11	 **8b**	20	81
2	12	 **8c**	20	89
3	13	 **8d**	36	86
4	14	 **8e**	24	79
5	15	 **8f**	36	75
6	16	**8a**	16	88
7[c]	–	**8a**	48	1

[a] Aryl halide (0.5 mmol) in Millipore water (5 mL), K_2CO_3 (0.375 mmol), catalyst **7** (2.0 mol%), CO (1 atm), 100°C. [b] Yields of isolated products. [c] Catalyst **7** was removed from the reaction vessel prior to the addition of **8a**.

In conclusion, we have developed a method for the reversible immobilization of pyrene-tagged palladium NHC complexes on highly magnetic, graphene-coated cobalt nanoparticles through π–π stacking interactions. This noncovalent grafting is strongly temperature dependent in polar solvents, such as water, giving rise to a "boomerang"-type catalyst that dissociates from the heterogeneous support into the homogeneous phase at elevated temperatures. The feasibility of this concept was demonstrated in the hydroxycarbonylation of aryl halides in water under an atmospheric pressure of carbon monoxide. Palladium catalyst **6** was highly active in more than

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16 iterative runs and could be recycled as Co/C-nanoparticle-immobilized catalyst **7** by magnetic decantation.

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[20] A movie of this sequence is provided in the Supporting Information.

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