Cyclodextrin-Grafted Silica-Supported Pd Nanoparticles: An Efficient and Versatile Catalyst for Ligand-Free C–C Coupling and Hydrogenation

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Dedicated to Professor Bice Fubini on the occasion of her retirement

Silica is an extremely versatile support, which is capable of hosting metal nanoparticles (NPs) and enhancing their stability and reactivity. In this study, a novel cyclodextrin/silica support for Pd NPs, which we have denoted Pd/Si-CD, has been prepared. The highly efficient and homogeneous impregnation of small palladium nanoparticles on this support has been carried out under conventional conditions, and ultrasound irradiation

Introduction

The discovery, in the late 1980s by Haruta et al., that α -Fe₂O₃supported Au nanoparticles smaller than 5 nm are very active in CO oxidation caused the catalysis community to realize the significance that size has on catalytic properties.^[1,2] The high surface energy of these particles makes them extremely reactive, meaning that most systems undergo aggregation without protection or surface passivation.^[3] Although it is well known that nanosize in catalysis is important because of high surface area and reactivity, the mechanistic action of a nanocatalyst is not so clear. Several other key catalyst parameters need to be considered. These include nanoparticle shape and any synergic effects that may exist between metal and support.^[4] Nanoparticles (NPs) have so far been synthesized by using various chemical and physical methods.^[5] The preparation of NPs frequently involves the reduction of metal ions in solutions or in high temperature gaseous environments, meaning that not only has the search for new nanocatalysts been a focus of interest

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 Supporting Information and the ORCID identification number(s) for the author(s) of this article can be found under http://dx.doi.org/10.1002/ cctc.201501225. has been shown to have a beneficial effect on catalyst preparation. The catalyst exhibited excellent activity in ligand-free C–C Suzuki and Heck couplings with a large number of aryl iodide and bromides, in which microwave irradiation use cuts down reaction time. Pd/Si-CD have shown high activity and selectivity in the hydrogenation reaction, and the semihydrogenation of phenyl acetylene was also studied with excellent results.

but even the optimization of metallic NP green syntheses has attracted significant attention from the scientific community.^[6] Palladium catalysts have emerged as powerful and versatile tools in organic synthesis.^[7] A number of palladium catalysts are commercially available and, interestingly, their reactivity, stability and selectivity can be tuned by ligands^[8] (phosphines, carbenes, amines, etc.) and/or additives.^[9] Although ligand-containing molecular palladium catalysts have long proven to be efficient and very popular,^[10] continuous investigation into "green", so-called "ligand-less", palladium catalysts is ongoing.^[11] Phosphine-free C-C coupling reactions may involve the presence of nanosized Pd colloids as suggested by Reetz et al.^[12] In fact, Bönneman et al.^[13] observed in 1991 that these colloids are generated from Pd^{II} salts in polar solvents in the presence of tetraalkylammonium salts at high temperatures. PdNPs have now become a valuable alternative and provide several "green" chemistry benefits.^[14] One of the principle advantages that these systems present is the fact that they are catalytically active in low amounts, driving interest from industry in this field. Recent years have thus seen various syntheses being scaled up to the kilogram scale.^[15] De Vries^[16] has detailed the role of PdNPs as a source of Pd atoms that detach from the surface during oxidative addition and undergo highly efficient turnover in solution. At high temperature, PdNPs are stabilized by the presence of polar solvents or ammonium salts and ionic liquids, which influence PdNP dimensions and favor productive reactions.^[17] Heterogeneous supports also provide a valuable influence on reaction outcome. Many studies have validated the use of Pd colloids in Heck reactions, although reactions with less reactive aryl bromides have not been very successful in the absence of stabilizers, such as ammonium salts or ligands.



Silica is an extremely versatile support and one which is capable of hosting metal NPs, enhancing their stability and reactivity.^[18] Silica has found widespread use in the preparation of solid-supported PdNPs because of the benefits that it provides, which include excellent stability (chemical and thermal), mechanical robustness, good accessibility, and porosity. In fact, a number of organic-inorganic hybrid materials have seen extensive use in the design of novel catalytic systems.^[19] Our recent study into the efficient grafting of cyclodextrin (CD) into an inorganic silica framework provided a material that showed a hydrophilic/hydrophobic profile and surface reactivity, which were modified with respect to material bulk properties.^[20] To the best of our knowledge, only one manuscript has so far reported the use of a CD-silica derivative in the preparation of a heterogeneous PdNP catalyst and its subsequent Heck reaction.^[21] This work therefore aims to exploit our experience in CD synthesis to explore this field further.^[22]

We herein report the preparation of a new PdNP catalyst, which attempts to amalgamate the properties of an amino alcoholic branched spacer and a triazolyl- β -CD derivative to effectively immobilize and stabilize PdNPs. Our intention here is to produce an extremely versatile catalyst and explore its potential in a series of hydrogenation and coupling reactions, such as the Suzuki, Heck, and Sonogashira reactions, which are ranked among the most general transformations in organic synthesis.

Scientists have recently devoted a great deal of research to designing more environmentally sound and low impact protocols to operate under non-conventional conditions.^[23] Solventfree and aqueous media reactions, NPs, microwave-assisted and ultrasound-promoted syntheses are all key developments in the design of greener protocols. Sonochemistry has been very reliably employed in the synthesis of small, high production yield NPs, and the selective heating of catalytically active metal species under microwave irradiation is currently generating significant interest.^[24] The objective of this manuscript is to investigate the efficacy of ultrasound irradiation in the preparation of the Pd/Si-CD hybrid system, which supports PdNPs. Microwave (MW) irradiation has also been used to optimize the synthetic procedure for high reaction yields in short reaction times. All protocols were designed to operate without a stabilizer (ammonium salts or ionic liquid) and to be ligand free so as to fulfil green chemistry criteria.

Results and Discussion

The silica derivative consists of β -CD anchored to silica through an alkyl hydroxyl amino spacer (Scheme 1). The silica was derivatized with 3-glycidoxypropyltrimethoxysilane (GPMS), which was then reacted with 10-undecynil-1-amine (Und) to open the epoxide ring. The Si–CD derivative was finally obtained from a Cu-catalyzed azide–alkyne cycloaddition (CuAAC) with 6monoazido-6-deoxy- β -CD. The synthetic protocol can be performed either under MW irradiation or through mechanochemical activation as already described in a previous study.^[20] All samples were extensively characterized by thermogravimetric analysis (TGA), elemental analysis, IR, Brunauer–Emmett–Teller (BET) analysis, and HR-TEM. A highest final loading of 135 μ molg⁻¹ of β -CD was measured when all three steps were performed under MW irradiation.^[20]

PdNPs were immobilized on the Si–CD by reduction of the $Pd(OAc)_2$ precursor in ethanol or in water. The procedure was repeated at room temperature and with heating at reflux. The reaction was monitored by the color change of the silica support.

The reaction from Si–G–Und afforded a light-grey silica derivative, whereas all the other attempts with Si–CD furnished a dark-grey solid. Inductively coupled plasma (ICP) analyses confirmed that the Pd content was lower, 2.3 wt.% Pd, when CD was absent from the silica support (see Table 1, entries 1– 4). The Pd content in the Si–CD samples was in the range 4.7– 6 wt.% and the highest amount was achieved when the loading was performed in ethanol heated at reflux. Ultrasound irradiation of the Pd(OAc)₂ solution in ethanol with Si–CD afforded 4.7 wt.% Pd.

The XRD patterns of the catalysts show that PdNPs exist on the Pd/Si-CD substrates (Figure 1, curve c). The strongest peak in the XRD pattern (21.86°) is the typical diffused scattering of the amorphous SiO₂ support. The other weaker peaks are indexed as the (111), (200), (220), and (311) planes of the PdNPs (cubic phase, JCPDS 46-1043). A slight shift in the 2 θ values is observed, with respect to standard references, for all peaks, which suggests that a small increase in crystallite d spacing occurs as a consequence of particle nanosize. These peaks are absent in the sample that was prepared without CD (sample Pd/Si-Und, curve a). The average crystallite size, estimated by using the Scherrer formula, is 6.2 nm for



Scheme 1. Synthetic scheme for the preparation of Si-CD.



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Table 1. Preparation conditions and Pd wt.% content of the various supported Pd catalysts.							
Entry	Sample name	Starting silica derivative	Reaction conditions ^[a]	Pd content ^[b] [wt.%]	Particle size ^[c] [nm]		
1	Pd/Si-Und	Si–G–Und	EtOH, reflux, 2 h	2.30	n.d.		
2	Pd/Si-CD (A)	Si–CD	EtOH, RT, 48 h	4.75	14.7		
3	Pd/Si-CD (B)	Si–CD	EtOH, reflux, 2 h	6.00 (5.95) ^[d]	5.4 (6.2) ^[e]		
4	Pd/Si-CD (C)	Si–CD	H₂O, 80 °C, 2 h	4.88	14.1		
5	Pd/Si-CD (US)	Si–CD	EtOH, ultrasound (US), 2 h	4.70	4.0 ^[e]		

[a] All reactions were performed in the presence of $Pd(OAc)_2$ (400 μ molg⁻¹). [b] Determined by inductively coupled plasma analysis (ICP). [c] Average particle size of Pd particles measured on the basis of TEM images. [d] Data measured for the catalyst after first usage. [e] The particle size was measured by XRD.



Figure 1. XRD patterns measured for the samples listed in Table 1.

sample B and 4.0 nm for the sample prepared in the ultrasound bath.

TEM images of the catalysts are shown in Figure 2. Pd/Si-CD samples A and C, which were prepared in ethanol at room temperature and water at 80 °C, respectively, consist of nonuniform (mainly spheroidal) particles with a diameter range 6– 25 mm (Figure 1, examples A and C). Pd particle size distributions of the same materials are also reported in Figure 2. A larger number of particles were measured in sample A (135), whereas only a few (9) were detected in sample C, meaning that no statistical considerations can be made in this case. Sample A particles are found most abundantly at 9 and 13 nm. By contrast, Pd particles were present in larger amounts, were smaller and more uniformly distributed (distribution centered around 5 nm, Figure 2 sample B) when the sample was heated at reflux in ethanol for 1 h. The TEM and XRD data were in accordance.

The above-mentioned analyses show that the presence of CD plays a crucial role in influencing the Pd content and PdNP size distribution. The amino alcohol on the Si–G–Und intermediate can coordinate Pd species, but only on the Si–CD derivative were PdNPs loaded in reasonable amounts. Solvent choice and reaction temperature also influenced NP size distribution on the silica. The smallest NPs were produced under ultrasound irradiation.

The Suzuki–Miyaura reaction was tested first as the applicability of the new catalyst was investigated (Table 2). The study



Figure 2. TEM images of Pd/Si-CD catalysts (scale bars = 20 nm): A) Pd/Si-CD, sample was prepared in EtOH at RT; B) Pd/Si-CD, sample was prepared in EtOH heated at reflux; C) Pd/Si-CD, sample was prepared in water at 80 °C. Pd particle size distributions measured on the same samples are also reported.

initially focused on the optimization of a phenyl boronic acid and halobenzene model reaction. These reactions were performed in a $H_2O/dioxane$ 9:1 mixture with the aim of following green principles. The study aimed to optimize reaction conditions in terms of the lowest catalyst amount and shortest reaction time. As depicted in Table 2, we compared conventional



Table 2. Suzuki–Miyaura optimization. ^[a]							
$X = Br, I, CI$ $X = Br, I, CI$ $H_2O:Diox (9:1)$ $H_2O:Diox (9:1)$ TEA $H_2O:Diox (9:1)$							
Entry	Х	Reaction conditions ^[a]	Pd/Si-CD loading [mol%]	Yield [%] (conv. [%])			
1	I	o.b., 100 °C, 4 h	0.5	98 (>99)			
2	1	o.b., 100 °C, 4 h	0.2	98 (>99)			
3	I.	MW, 100 °C, 1 h	0.5	99 (>99)			
4	I.	MW, 100 °C, 1 h	0.2	98 (>99)			
5	1	MW, 100°C, 1 h	0.1	97 (>99)			
6	1	MW, 100 °C, 30 min	0.2	96 (>99)			
7	1	MW, 100 °C, 15 min	0.2	91 (92)			
8	1	MW, 100 °C, 30 min	0.1	98 (>99)			
9	I.	MW, 100 °C, 30 min	0.05	96 (>99)			
10	1	MW, 100 °C, 15 min	0.1	90 (91)			
11	Br	o.b., 100 °C, 4 h	0.5	98 (>99)			
12	Br	o.b., 100 °C, 4 h	0.2	98 (>99)			
13	Br	MW, 100 °C, 1 h	0.2	98 (>99)			
14	Br	MW, 100 °C, 1 h	0.1	100 (>99)			
15	Br	MW, 100 °C, 30 min	0.2	99 (>99)			
16	Br	MW, 100 °C, 30 min	0.1	99 (>99)			
17	Br	MW, 100 $^\circ$ C, 30 min	0.05	98 (>99)			
[a] All reactions were performed in $H_2O/dioxane 9:1$, with 1 equiv. aryl-X, 1.1 equiv. boronic acid, 2 equiv. TEA. o.b. = oil bath.							

conditions to MW irradiation as we maximized the catalytic performances of Pd/Si-CD.

Complete conversion was obtained with iodobenzene and bromobenzene under conventional conditions with 0.2 mol% Pd after 4 h heating at 100 °C. MW irradiation enabled the Pd amount to be decreased to 0.05 mol% and the reaction time to be reduced to 30 min; however, 8–9% of the starting material was unreacted when the reaction time was further reduced to 15 min.

An array of twelve aryl halides, both electron rich and electron deficient, was chosen as the Suzuki–Miyaura cross-coupling reaction substrates and phenyl boronic acid was used for further investigations of Pd/Si-CD catalytic performance (Table 3).

The reaction was performed with 0.1 mol% Pd at 100°C for 30 min and yields of 61–99% were achieved. The reaction outcomes showed good aryl iodide and bromide reactivity, and high yields were obtained even in presence of high steric hindrance (entries 4, 5, 7, and 9, Table 3). The high reaction rate enabled ethyl 4-iodo benzoate to be selectively converted to the diphenyl derivative in water without hydrolyzing the ester moiety (entry 1, Table 3).

The optimized protocol was used in screening a set of four boronic acids with iodo- and bromobenzene, giving yields of 88–99% (Table 4). 2,5-Dimethoxy fenil boronic acid surprisingly reacted in 30 min at 100 °C to give 97 and 88% yields with iodo- and bromobenzene, respectively.

The above-mentioned results prompted us to continue with a study of Pd/Si-CD catalytic activity in the Heck reaction. A series of reactions were performed by using varying conditions for the sake of optimizing the protocol.

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boronic acid, 2 equiv. TEA, 0.2 mol% Pd. [b] Reaction performed with 0.2 mol% Pd. [c] Reaction performed with 0.5 mol% Pd.

The model substrates for the initial screening were phenyl iodide and styrene, leading to stilbene. As summarized in Table 5, Pd/Si-CD quantitatively converted the starting material under conventional conditions in 4 h at reflux in dioxane/H₂O 1:1 (Table 5, entries 1–4). The reaction was successful with K₂CO₃ as a base and 0.5 mol% of Pd. MW irradiation sped up the reaction and full conversion was obtained after 1 h, while the catalyst amount was reduced to 0.2 mol% (Table 5, entries 11 and 12). Excellent results were also achieved in DMF with K₂CO₃ as a base (Table 5, entry 7). A slight decrease in yield was observed when the optimized protocol was performed with 4-iodoanisole.

To gauge the versatility of this protocol, a large number of substrates were screened in parallel by using the MW reactor (SynthWave by Milestone), which is well suited to parallel syntheses at any reaction temperature and gas pressure (up to 300 °C and 200 bar). Aryl bromides and iodides with electron-withdrawing and electron-donating substituents were reacted





Table 5. Heck optimization.							
R = H, OMe $Pd/Si-CD$ $R = H,$ $R = H,$ $H = H,$ $R = H,$ R							
Entry	R	Solvent	Reaction conditions ^[a]	Pd/Si-CD [mol %]	Yield [%] (conv. [%])		
1	Н	DMF	Et₃N o.b., 110°C, o.n.	1	52 (60)		
2	Н	H ₂ O/diox 1:1	K ₂ CO ₃ , o.b., 90 °C, o.n.	1	98 (>99)		
3	Н	H ₂ O/diox 1:1	K ₂ CO ₃ , o.b., 90 °C, 4 h.	1	98 (>99)		
4	Н	H ₂ O/diox 1:1	K₂CO₃, o.b., 90 °C, 4 h	0.5	98 (>99)		
5	Н	H ₂ O/diox 1:1	K ₂ CO ₃ , MW, 120 °C, 4 h	1	96 (>99)		
6	Н	DMF	Et₃N, MW, 120 °C, 4 h	1	87 (>99)		
7	Н	DMF	K ₂ CO ₃ , MW, 120 °C, 4 h	1	85 (98)		
8	Н	H ₂ O/diox 1:1	Et₃N, MW, 120 °C, 4 h	1	34 (56)		
9	Н	H ₂ O/diox 1:1	K ₂ CO ₃ , MW, 120 °C, 1 h	1	99 (>99)		
10	Н	H ₂ O/diox 1:1	K ₂ CO ₃ , MW, 120 °C, 30 min	1	87 (90)		
11	Н	H₂O/diox 1:1	K₂CO₃, MW, 120 °C, 1 h	0.5	97 (>99)		
12	Н	H ₂ O/diox 1:1	K ₂ CO ₃ , MW, 120 °C, 1 h	0.2	89 (95)		
13	OMe	H ₂ O/diox 1:1	K ₂ CO ₃ , MW, 120 °C, 1 h	1	66 (84)		
14	OMe	H ₂ O/diox 1:1	K ₂ CO ₃ , MW, 120 °C, 1 h	0.5	71 (76)		
15	OMe	H ₂ O/diox 1:1	K ₂ CO ₃ , MW, 120 °C, 1 h	0.2	62 (68)		
[a] Reactions performed with 1.25 equiv. styrene, 2 equiv. of base. o.n. = overnight.							

with styrene, *n*-butyl and *tert*-butyl acrylate. Excellent results were obtained in 1 h with 0.5 mol% Pd without the addition of ligands and the reactions almost always gave quantitative yields (see Tables 6 and 7). Triazolyl and thiazole iodo derivatives were included in the list of reagents, as representative heterocyclic compounds, and yielded the desired product in yields of 34–75%.

The regiochemical outcome of the Heck reaction with unsymmetrical olefins is of utmost importance and so Tables 6 and 7 not only indicate conversion, but also selectivity. Although acrylates showed >99% selectivity, styrene gave a slight decrease. Regiochemistry was influenced by steric and electronic factors: sterically hindered and electron-rich halides showed selectivities in the 98–95% range, whereas all the other experiments only furnished the desired regioisomer. As depicted in Figure 3, the α -substituted regioisomer was the main side product when a mixture of isomers was observed. α -Substitution products were present in the 1–3% range, whereas the β -*cis* regioisomer was detected at 0.5% when the reaction was performed with halo anisoles, iodophenol, 2methyl iodobenzene, 2,5 dimethyl halobenzenes, and 2-amino iodobenzene.



Figure 3. Observed range of selectivity for the ligand-free Heck reaction.

An example of the intramolecular ligand-free Heck reaction^[25] was also successfully performed to display the high reactivity of this catalyst. The carbazole derivative was obtained in 85% after 1 h at 100°C with 0.5 mol % Pd (see Scheme 2). Pd/Si-CD recycling was also investigated (see Figure 4). The cross-coupling reaction was carried out with phenyl iodide and phenyl boronic acid in the presence of 0.1 mol% catalyst to better understand catalyst performance. The supported nanocatalyst was separated by filtration, washed with water, CH₂Cl₂, dioxane, and then reused. As depicted in Figure 2, no significant loss in catalytic activity was observed after five cycles. The ICP analysis of the catalyst after first usage showed constant Pd loading^[14d] from 6.0 wt.% to 5.95 wt.% Pd after usage (Table 1, entry 3). An XRD analysis carried out on a sample after usage only showed a slight increase in particle size, from 6.2 to 7.1 nm (Figure 1, curve d). With the aim to confirm the catalytic effect of Pd/Si-CD rather than the leached homogeneous Pd species, the model Suzuki and Heck reactions with iodobenzene and phenyl boronic acid or styrene, respectively, were performed in two steps (see the Supporting Information). The reaction was carried

out in an oil bath and the hot reaction mixtures were filtered to remove the Pd/Si-CD. Without solid catalyst, the reaction



Scheme 2. Intramolecular Heck reaction.





Figure 4. Pd/Si-CD catalyst reusability. Reaction conditions: 1 equiv. bromobenzene, 1.1 equiv. boronic acid, 2 equiv. triethylamine (TEA), 0.1 mol% (Pd/Si-CD), H₂O/dioxane 9:1, 100 $^{\circ}$ C, 30 min.





Table 7. Scope of the Heck reaction with different aryl iodides and bromides and butyl acrylate.^[a] K₂CO₃,Pd/Si-CD R 6 Arl 1 ArBr 0.5 mol % ò R 'n. Conversion 120°C. 1h R = nBu, (Selectivity) R = *n*Bu, *t*Bu *t*Bu 37-46 но



[[]a] Reactions performed with 1.25 equiv. acrylate, 2 equiv. K₂CO₃, 0.5 mol% Pd, 120 °C, 1 h. The solvent was H₂O/dioxane 1:1 for the reaction with *tert*-butyl acrylate, whereas DMF was chosen for *n*-butyl acrylate.

monitored by GC-MS did not proceed (only 1–5% of further conversion), confirming the central role of Pd/Si-CD. $^{\rm [26]}$

Finally, we explored the hydrogenation of a range of unsaturated hydrocarbons under 1 bar initial hydrogen pressure at room temperature (Table 8). Pd/Si-CD (0.15 mol% Pd) showed excellent catalytic activity in the reduction of substrates with double and triple bonds to the corresponding alkane with excellent yields (>99%). Reduction of azido and nitro groups fur-



tion was performed at 50 °C. [c] The reaction was performed in methanol.

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nished the corresponding amines in 2 h. Benzaldehyde gave the corresponding alcohol in 1 h at 50 °C in a >99% yield and the *p*-nitrobenzaldehyde was selectively reduced to *p*-amino benzaldehyde overnight at room temperature.

Conscious of the importance of alkyne semihydrogenation in providing the alkene derivative and of conventional monometallic Pd catalysts not giving high selectivity in these processes,^[27] we proceeded to evaluate the kinetics of the catalytic hydrogenation of phenyl acetylene. Five experiments were performed at room temperature under 1 bar initial hydrogen pressure and the reactions underwent workup and analysis after 15, 30, 45, 60, 90, 120, and 150 min. As depicted in Figure 5, full conversion of the alkyne was obtained in 60 min and the highest selectivity (alkene/alkane) achieved was > 95%.



Figure 5. Profile of the hydrogenation of phenyl acetylene with Pd/Si-CD.

Conclusions

We report the preparation of a new hybrid CD silica derivative supported PdNP catalyst. As the presence of a coordinating group is considered the key factor in the formation of small sized, homogeneously dispersed Pd nanoparticles, we herein demonstrated that CD-grafted silica is an optimal support for this task. The amino alcohol groups and triazole on the spacer can also coordinate Pd species and influence PdNP content, size, and distribution on the silica surface. An extensive study of the catalytic performances of this catalyst in ligand-free C-C Suzuki and Heck couplings with a large number of aryl iodides and bromides has been reported. The catalyst exhibited excellent results and MW irradiation cut down reaction times. Pd/Si-CD showed high activity and selectivity in the hydrogenation reaction, and the semihydrogenation of phenyl acetylene was studied, giving excellent alkene/alkane selectivity. All protocols were designed to be ligand free and carried out without the addition of a stabilizer, in accordance with green chemistry criteria, and catalyst reuse was also evaluated. The Suzuki-Miyaura reaction was repeated five times and no significant loss in catalytic activity was observed. ICP analysis of the catalyst after recycling confirmed negligible Pd leakage, moreover, XRD showed that the NP dimensions only increased slightly after usage.

Experimental Section

Materials and method

All commercially available reagents and solvents were used without further purification. SIPERNAT 320 amorphous silica was supplied by Evonik Degussa. Reactions were carried out in a professional MW reactor, SynthWave (MLS GmbH, Milestone S.r.l.). Mechanochemistry was performed in a planetary ball mill, PM100 (Retsch GmbH). Si-G-Und-CD was fully characterized as described in one of our previous studies. The cations were determined with a Perkin-Elmer Optima 7000 (PerkinElmer, Norwalk, Connecticut, USA) inductively coupled plasma-optical emission spectrometer (ICP-OES). NMR spectra were recorded with a Bruker 300 Avance (300 MHz and 75 MHz for 1 H and 13 C, respectively) at 25 °C. Chemical shifts were calibrated to the residual proton and carbon resonances of the solvent; CDCl₃ (δ H=7.26, δ C=77.16 ppm) and DMSO (δ H= 2.54, $\delta C\!=\!40.45$ ppm). GC-MS analyses were performed in a GC Agilent 6850 (Agilent Technologies, Palo Alto, CA, USA) that was fitted with a mass detector Agilent Network 5973.

Preparation of Si-CD

(3-Glycidoxypropyl)methyltriethoxysilane (0.934 mL, 0.420 mol) was dissolved in toluene (10 mL) and silica SIPERNAT 320 (1 g) was added. The suspension was either heated under stirring in an oil bath (80 $^\circ\text{C}$ for 5 h) or in a MW reactor (80 $^\circ\text{C}$ for 1 h, average power 53 W). The modified silica was then filtered, washed thoroughly, and dried under vacuum. Si-GPMS (1 g) and 10-undecynil-1-amine (0.275 g, 1.64 mmol) were dissolved in DMF (3 mL). The solution was either heated to 80 °C and stirred for 24 h or the reaction was performed in a MW reactor (100 °C for 2 h, average power approximately 20 W). The silica was finally filtered and washed with DMF, water, and toluene, and dried under vacuum. Si-G-Und (1 g), 6-monoazido-β-CD (1.95 g, 1.68 mmol), CuSO₄·4H₂O (0.100 g, 0.4 mmol), and ascorbic acid (0.148 g, 0.84 mmol) were dissolved in H_2O (30 mL). The reaction was heated under MW at 80 $^\circ$ C for 2 h (average power approximately 12 W). The silica was filtered, washed with water, and dried under high vacuum. The silica was purified of copper salts by the addition of Na₂H₂EDTA (3.14 g) and dissolved in H₂O (5 mL). The suspension was left under magnetic stirring overnight. The silica was then filtered, washed with water, and dried under high vacuum.

Preparation of the Pd/Si-CD catalyst

 $Pd(OAc)_2$ (0.0024 g, 1.09 mmol) was dissolved in ethanol (5 mL) and Si-CD (0.250 g) was added. The suspension was heated under reflux with an oil bath and stirred for 2 h.

When the preparation of the catalyst was performed under ultrasound irradiation the reaction was sonicated (cup-horn, 90–100 W, 20.4 kHz), for 1 h and the temperature was maintained at 35-37 °C.

Characterization

Powder X-ray diffraction (XRD) patterns were measured with a PW3050/60 X'Pert PRO MPD diffractometer (Panalytical) working in Bragg–Brentano geometry using CuK_a radiation ($\lambda = 1.5406$ Å) and operated at 45 kV, 40 mA, with a step size of 0.0170° and time per step of 90 s. Crystallite size, D = 4/3L was calculated by applying the Scherrer equation to the (111) peak at 39.33°:



$L = k\lambda/(\beta \cos\theta)$

where λ is the X-ray wavelength, k is the dimensionless shape factor (0.9), β the measured broadening of the diffraction peak, and θ the diffraction angle. The measured β value was corrected by subtracting instrumental line broadening, estimated at 0.02°.

Transmission electron microscopy (HRTEM) measurements were performed on a JEM 3010-UHR microscope (JEOL Ltd.) operating at 300 kV. The sample powder was dispersed on a copper grid coated with a perforated carbon film for measurements.

Suzuki-Miyaura reaction

Aryl halide (0.5 mmol), boronic acid (0.55 mmol), and TEA (1 mmol) were dissolved in H₂O/dioxane (9:1, 5 mL) and Pd/Si-CD (0.2–0.5 mol%) was added. The reaction was carried out under magnetic stirring in a MW reactor (SynthWave) at 100 °C for 1 h. The crude product was filtered through a Büchner funnel with a sintered glass disc using CH_2CI_2 and dioxane to wash the catalyst. After concentration to half volume under vacuum, the mixture was extracted with a HCl solution and CH_2CI_2 , washed with H₂O three times, and finally dried (Na_2SO_4). The crude product was analyzed by GC-MS and purified by flash chromatography on silica gel to afford the desired product.

Heck reaction

The aryl halide (0.16 mmol), alkene or acrylate (0.2 mmol), K_2CO_3 (1 mmol), and Pd/Si-CD catalyst (1 mol%) were dissolved in a solution of $H_2O/1,4$ -dioxane (1:1) or DMF (2 mL). The reaction was heated under MW irradiation at 120 °C for 30 min (average power approximately 25 W). The crude mixture was filtered and washed with CH_2Cl_2 . The desired product was extracted with CH_2Cl_2 . The organic layer was washed three times with acid and H_2O and finally dried (Na_2SO_4 and under high vacuum).

Hydrogenation reaction

The substrate (1 equiv) was dissolved in 3 mL of hexane (or MeOH) and Pd/Si-CD (0.156 mol %) was added to the mixture. The reaction was carried out under magnetic stirring at RT or in an oil bath 50 °C for 1–2 h. The solution was filtered through a 0.45 μ m syringe filter and dried. The desired product was obtained without further purification.

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