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Dendron-Functionalized Core–Shell Superparamagnetic Nanoparticles: Magnetically Recoverable and Reusable Catalysts for Suzuki C−C Cross-Coupling Reactions

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Abstract: A metallodendron functionalized with dicyclohexyldiphosphino palladium complex was synthesized. The metallodendron was grafted onto core–shell superparamagnetic nanoparticles (γ-Fe_2O_3/polymer, 200–500 nm) to give optimal catalytic reactivity in cross-coupling reactions. The grafted nanoparticles were used as recoverable and reusable catalysts for Suzuki C−C cross-coupling reactions. They showed remarkable reactivity towards iodo- and bromoarenes under mild conditions, and unprecedented reactivity towards chloroarenes. On completion of the catalytic reaction, the catalysts were readily recovered by using a simple magnet to attract the superparamagnetic grafted nanoparticles. Catalysts were recovered more than 25 times with almost no discernable loss of reactivity.

Keywords: cross-coupling • dendrons • heterogeneous catalysis • nanoparticles • supported catalysts

Introduction

Over the past few decades, supported catalysts have become powerful tools for transition metal catalysis, since environmental concerns are favorable to green methodologies compatible with the recovery and reuse of the catalyst and the removal of toxic metals from the reaction medium.[1] In this context, many efforts have been made to design and synthesize recoverable catalysts. Various inorganic and organic supports have been explored, such as mesoporous silica and polymers.[2] The grafting of such supports with homogeneous catalysts often provides good catalytic activity together with possible recovery of the catalyst system by filtration or liquid/liquid extraction.[3] More recently, new smart supports, such as superparamagnetic nanoparticles (MNPs), usually known as ferrofluids, have emerged and have great potential for catalyst recovery, as the recovery step requires a simple external magnet. The first example, reported by Lee et al.,[4] involved magnetic ferrite nanoparticles ($CoFe_2O_4$) coated with a rhodium-based complex catalyst that showed catalytic activity in hydroformylation of olefins. MNPs[5] have been widely used in the last few decades in various magnetic devices[6] and in biomedical applications[7] such as magnetic carriers for bioseparation, enzyme and protein immobilization, and contrast-enhancing media. They can be used neat or coated with a silica or polymer shell to avoid toxic effects on biological media.

Catalytic functionalization of the MNPs was mainly achieved by a direct alloying approach (impregnation of transition metal nanoparticles and superparamagnetic Fe_3O_4)[8] or by functionalization of neat MNPs with silane,[9] phosphonic acid,[10] or carboxylic acid ligands.[11] Another functionalization strategy is immobilization of homogeneous catalysts on core–shell γ-Fe_2O_3 MNPs based on an oxide/polymer[12] or oxide/silica[13] structure. These nanoparticles are made up of a magnetic iron oxide core coated by a layer of cross-linked polymer or silica shell. The organic or inorganic layer stabil-

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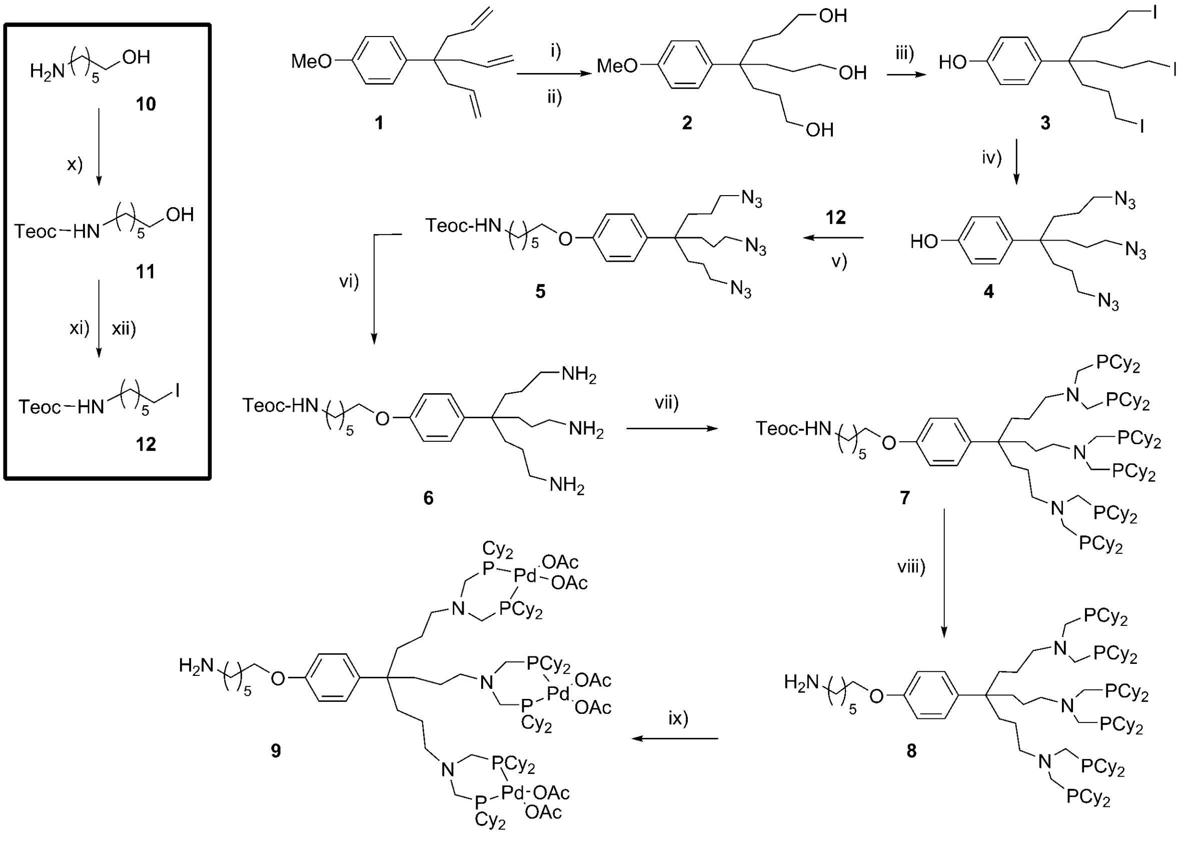
izes nanoparticles by preventing aggregation of oxide cores and offers a surface for immobilization of catalysts.

Dendrimers[14] are macromolecules developed since the 1990s with a highly branched three-dimensional architecture. Recently, dendrons or dendrimers have been used as coatings to stabilize MNPs,[15] to investigate protein interactions,[16] and for catalytic applications.[17,18] Previously, we explored the ability of dendronized molecules to increase the surface functionalization of MNPs through fluorescent dendrons grafted onto core–shell γ-Fe_2O_3/polymer 300 nm MNPs.[19] The dendron-functionalized core–shell MNPs were generally synthesized by a divergent route wherein the dendron was built step by step on the MNP surface. Surprisingly, only few examples of convergent routes using well-defined dendrons synthesized and characterized before their grafting onto the MNP surface have been reported in the literature.[16,20] Here we report the synthesis of a dendron bearing catalytic groups (diphosphino palladium(II)-based complexes) on one side and a primary amino group at the focal point for grafting onto core–shell γ-Fe_2O_3/polymer MNPs. Grafting of the metallodendrons onto core–shell γ-Fe_2O_3/polymer 300 nm MNPs was performed and optimized by a convergent approach. These functionalized MNPs were used as magnetically recoverable and reusable catalysts in Suzuki coupling of halogenoarenes and boronic acid compounds. We demonstrated that it is possible to recover and reuse these grafted catalysts at least 25 times without significant loss of reactivity.

Results and Discussion

Synthesis of Pd-complex-functionalized dendron 9: We prepared tris[N(PCy_2)$_2$Pd^{II}] dendron **9** with a primary amino group at the focal point necessary for grafting onto core–shell MNPs as described in Scheme 1. The first step was to prepare methoxyphenyl triol **2** by oxidative hydroboration of the terminal olefin groups of triallyl compound **1**.[21] Hydroboration/oxidation of the allyl groups of **1** gave triol **2**, treatment of which with NaI in the presence of Me_3SiCl gave tris(iodoalkyl) phenol dendron **3**. Treatment of **3** with NaN_3 yielded triazido phenol dendron **4**, which was coupled with iodo compound **12** to generate **5**. Spacer group **12** was obtained from Teoc-protected amino alcohol **11**, prepared from commercially available 6-aminohexanol (**10**). Catalytic reduction of **5** gave triamine **6**. Aminophosphine dendron **7** was then obtained by phosphinomethylation of **6**, as reported for dendrimer analogues.[22] Deprotection of the terminal



Scheme 1. Synthesis of dendron **9**. Reagents and conditions: i) HB(sia)$_2$, THF, 24 h, −15 °C to RT; ii) H_2O_2, NaOH, H_2O, 24 h, 50 °C; iii) Me_3SiCl, NaI, MeCN, 72 h, 80 °C; iv) NaN_3, DMF, 15 h, 40 °C; v) KOH, DMF, 4 h, RT; vi) H_2, Pd/C, MeOH, 5 h, RT; vii) HCHO, $HPCy_2$, MeOH, toluene, 12 h, 70 °C to RT; viii) Bu_4NF, THF, 5 h, 60 °C; ix) Pd(OAc)$_2$, CH_2Cl_2, 2 h, RT; x) Teoc-OC_6H_4-NO_2, Et_3N, CH_2Cl_2, 2 h, RT; xi) $MeSO_2Cl$, Et_3N, CH_2Cl_2, 2 h, RT; xii) NaI, MeCN, 24 h, RT. sia = 3-methyl-2-butyl, Teoc = 2-(trimethylsilyl)ethoxycarbonyl.

amino group with Bu_4NF gave dendron **8**. Complexation of the phosphine groups of **8** with Pd^{II} led to metallodendron **9** bearing three $N(PCy_2)_2Pd^{II}$ catalytic groups. Completion of the reaction was followed by ^{31}P NMR spectroscopy by monitoring disappearance of the free phosphine signal at $\delta = -18.3$ ppm and appearance of that of the coordinated phosphine at $\delta = 26.7$ ppm. Dendron **9** is stable towards moisture, but was stored under nitrogen to avoid degradation of the Pd complex.

Grafting of dendrons onto MNPs: Dendron **9** was covalently grafted onto MNPs. Core–shell γ-Fe_2O_3/polymer 300 nm superparamagnetic nanoparticles (Carboxyl-Adembeads 300 nm, Ademtech, France, 300 μmol COOH/g of particles) were used as MNPs.[23] The grafting method was reported previously.[19] However, in the present work we optimized the grafting conditions (solvent, dilution, etc.) by taking into account the solubility of metallodendron **9** bearing pallado phosphine groups.

Grafting of **9** onto core–shell γ-Fe_2O_3/polymer was based on the peptide reaction between the terminal primary amino group of **9** and the carboxyl groups of the MNP polymer shell. Coupling was carried out in the presence of coupling agents at room temperature overnight and usually in aqueous media. We have tested the grafting reaction in various solvents (Table 1). The grafting efficiency was estimated by means of a Suzuki catalytic reaction.[24] In DMF, we observed aggregation of MNPs and low catalytic activity (Table 1, entry 1). Similarly, in an aqueous medium with a nonionic surfactant such as Pluronic F127 (PF127)[25] or PF127/Mes[26] we observed macroscopic aggregation and notable precipitation of the dendron to give a heterogeneous medium and low catalytic activity (Table 1, entries 4 and 5). Nevertheless, optimal grafting steps were achieved in an aqueous medium in the presence of nonionic surfactant with a lower hydrophilic–lipophilic balance,[27] such as triton X405 (Tx;[28] Table 1, entry 3) or in an organic/aqueous medium with MeOH/Tx (1/2; Table 1, entry 2). In these cases, an optimal colloidal state and optimal catalytic activity of the resulting grafted MNPs were observed. However, in all cases preliminary dissolution of the dendrons in DMF (30 mM) was necessary in order to improve their solubility in the grafting medium. If the colloidal state of particles was better in a diluted medium,[29] the grafting reaction was improved in that medium.

Table 1. Grafting conditions:[a] influence of the solvent.

Entry	Grafting solvent	Catalytic reaction[b] reaction time [h]	Catalytic reaction[b] conversion [%]
1	DMF	2	16
2	MeOH/Tx[c] (1/2)	0.5	94
3	Tx[c]	0.5	93
4	PF127[d]	1	72
5	PF127/Mes[e]	2.5	59

[a] Grafting was carried out with Carboxyl-Adembeads 300 nm and dendron **9** (4 equiv) in DMF with CHMC as coupling agent at RT for 16 h. Then particles were washed with NaOH (10 mM), Tx, and THF/H_2O (2/1). [b] See ref. [24]. [c] Tx: triton X405 aqueous solution (0.21 wt %) obtained from triton X405 (70 wt %, Aldrich). [d] PF127: Pluronic F127 aqueous solution (0.3 wt %) obtained from Pluronic F127 (Aldrich). [e] 2-(*N*-Morpholino)ethanesulfonic acid (50 mM) in an aqueous solution of PF127.

We have also studied the effect of the coupling agent in the grafting efficiency. Carboxyl groups at the MNP surface are usually activated by an excess of carbodiimide along with *N*-hydroxysuccinimide (NHS) to avoid hydrolysis of *O*-acyl isourea intermediates. We tested two carbodiimides:[30] *N*-cyclohexyl-*N'*-(2-morpholinoethyl) carbodiimide methyl-*p*-toluenesulfonate (CHMC) and *N*-(3-dimethylaminopropyl)-*N*-ethylcarbodiimide hydrochloride (EDC), with or without NHS, in MeOH/Tx under the grafting conditions described in Table 1. Interestingly, CHMC and EDC gave basically the same result,[31] but the use of NHS[32] led to difficulties such as low magnetic susceptibility of the MNPs to an external magnet field during the washing step at the end of the grafting reaction, with a notable loss of particles. Therefore, we selected CHMC as coupling agent for the grafting reactions.

Afterwards, the surface functionalization of the MNPs was optimized with respect to increasing the dendron loading from 2 to 25 equiv, based on the accessible free carboxyl groups at the polymer shell.[33] The grafting efficiency was then estimated by means of a catalytic Suzuki reaction (Figure 1). Substrates and conditions were chosen to give appropriate reaction times to detect notable variations in catalytic activity. Inductively coupled plasma (ICP) analysis showed an effective degrees of grafting of 24 and 60 % for 2 and 10 equivalents of dendron **9**, respectively.[34] Therefore, 10 equivalents of dendron **9** were used to investigate the catalytic performance of this MNP grafted catalyst.

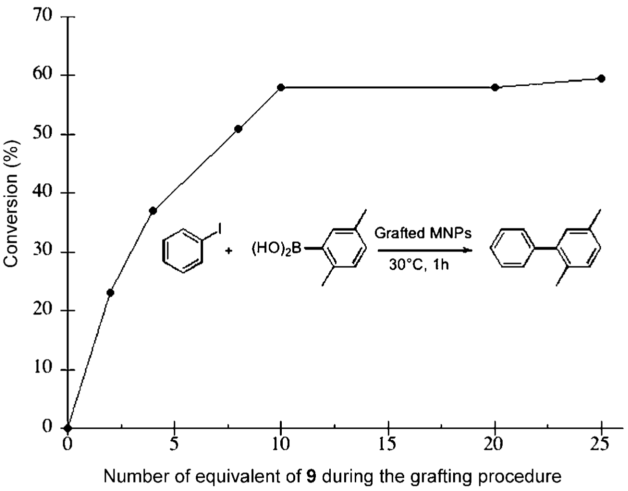


Figure 1. Catalytic activity of MNPs grafted with dendron **9** versus number of equivalents of dendron **9** used in the grafting reaction. Catalytic reactions were performed with 0.125 mg of MNP according to the general procedure (see Experimental Section).

Catalytic performances of dendron-grafted MNPs in C−C cross-coupling reactions: The catalytic activity of grafted MNPs was investigated in Suzuki C−C cross-coupling reaction between halo arenes and phenyl boronic acid compounds. Classic reaction conditions[35] were used, except for the solvent, since THF/H_2O was retained during the grafting procedures. A THF/Tx (1/9) mixture was used instead of THF/H_2O (2/1) to keep nanoparticles perfectly dispersed in the reaction medium. The MNP catalyst in THF/H_2O (2/1) gave good results up to the first four cycles using recovered catalyst. Then the reactivity decreased rapidly in terms of the reaction time needed to obtain total conversion (Table 2). Also, in THF/H_2O we observed progressive aggregation of the particles with increasing number of recovery steps. In the THF/Tx mixture, Tx preserves the colloidal state of the particles, and THF is necessary for solubility of the grafted dendron. Thus, in choosing the reaction solvent, we need to strike a fine balance between the solubility of the organic wedge of the particle and aggregation of the particles.

Table 2. Catalytic activity of grafted MNPs in the Suzuki reaction of iodobenzene and phenylboronic acid at 30 °C and 3 mol % Pd.

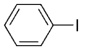
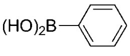
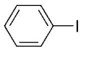
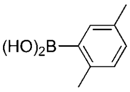
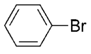
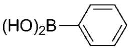
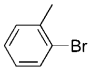
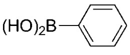
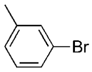
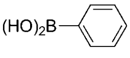
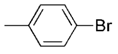
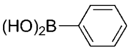
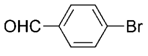
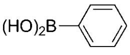
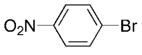
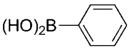
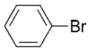
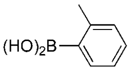
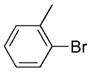
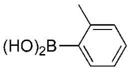
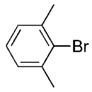
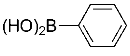
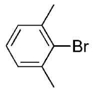
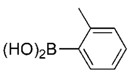
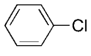
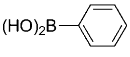
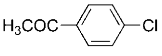
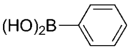
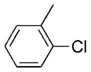
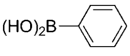
Cycle[a]	Solvent THF/H_2O (2/1) reaction time [h]	Solvent THF/H_2O (2/1) conversion [%]	Solvent THF/Tx (1/9) reaction time [h]	Solvent THF/Tx (1/9) conversion [%]
1	1.5	100	1	100
2	4.5	80	2.5	100
3	14	100	2	96
4	8.5	86	1.5	94
5	38.5	85	1.5	96
6	90	77	2	90

[a] Grafting was carried out with Carboxyl-Adembeads 300 nm and dendron **9** (see Experimental Section, and Table 4, entry 2). Then particles were washed with NaOH (10 mM), Tx, and THF/H_2O (2/1).

This result highlights the importance of the colloidal state of the MNPs during the catalytic processes. The catalytic activity of grafted MNPs was tested in the Suzuki coupling reaction between iodo-, bromo-, and chlorobenzene derivatives and phenyl boronic acids (Table 3). The catalytic activity of MNPs with iodobenzene (Table 3, entries 1 and 2) was quantitative, even with *ortho*-substituted phenylboronic acid and low catalyst loading (0.12 mol % Pd). In the case of bromo derivatives (Table 3, entries 3–12), high reactivity (quantitative yields) was also found, even with *ortho*-substituted substrates (Table 3, entries 11 and 12). In contrast to bromo- and iodobenzene derivatives, the reactivity of chlorinated substrates (Table 3, entries 13–15) was lower but still significant, since we obtained 79 % yield with *p*-chloroacetophenone (Table 3, entry 14). In fact, chlorinated derivatives seem to be adsorbed onto the MNP surfaces, so THF/Tx (2/1) was used instead of THF/Tx (1/9) to minimize the extent of this side phenomenon but with slight negative effect on the reactivity.

Furthermore, 200 and 500 nm MNPs[36] were grafted with dendron **9** by using the procedure described for 300 nm MNPs (see above). Grafting conditions were optimized by means of experimental curves of catalytic activity of MNPs grafted with dendron **9** versus number of equivalent of dendron **9** used in the grafting reaction (see Supporting Information, Figure S1). Similar to 300 nm MNPs, the best grafting of 200 nm MNPs was obtained with 10 equiv of dendrons,[37] in contrast to 500 nm MNPs, which aggregate above 8 equiv of dendron **9**. Catalytic activities of 200 and 300 nm MNPs were nearly the same (Figure 2).[38] Thus, no discernable effect of particle size was detected in the framework of the catalytic activity study.

Table 3. Catalytic activity of MNPs grafted with dendron **9** in Suzuki reactions.

Entry	Aryl halide	Aryl boronic acid	Cat. [mol % Pd][d]	Reaction time [h]	Conversion [%]
1			2.4	1	100[a]
2			0.12	5	95[a]
3			2.4	4	>99[b]
4			2.4	4	92[b]
5			2.4	4	94[b]
6			2.4	4	>99[b]
7			2.4	1	100[b]
8			2.4	1	100[b]
9			2.4	1	93[b]
10			2.4	4	92[b]
11			2.4	12	79[b]
12			2.4	12	88[b]
13			4.8	24	50[c]
14			4.8	6	79[c]
15			4.8	24	29[c]

[a] Reaction conditions: see Experimental Section, $T = 30$ °C. [b] Reaction conditions: see Experimental Section, $T = 65$ °C. [c] Reaction conditions: see Experimental Section, $T = 65$ °C, solvent THF/Tx (2/1). [d] Grafted MNPs with 10 equiv of dendron **9** were used (see Experimental Section and Table 4, entry 4).

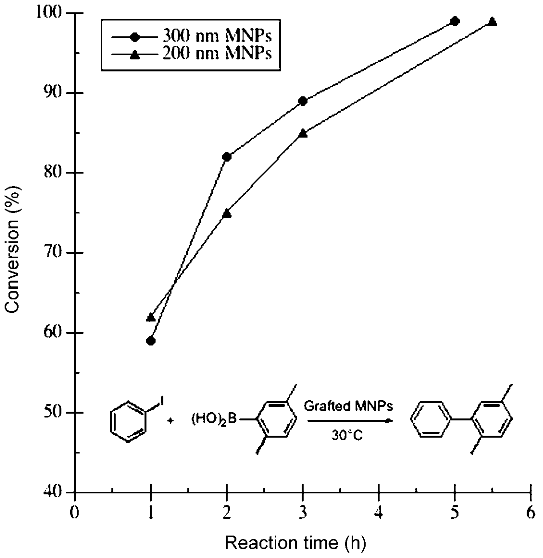


Figure 2. Catalytic reactions were performed with 0.125 mg of 200 or 300 nm grafted MNPs.

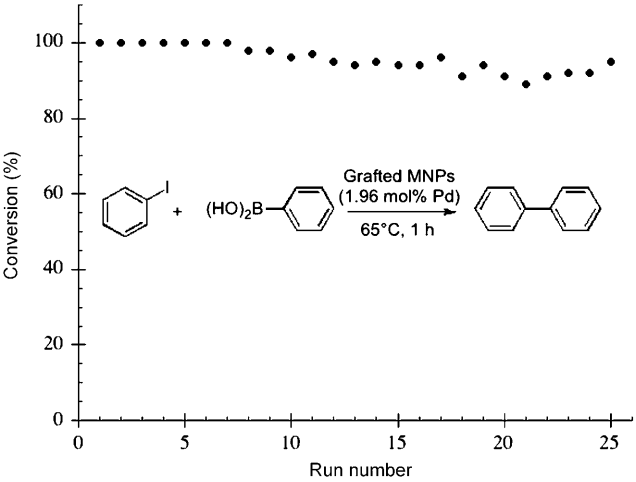


Figure 4. Recovery experiments on grafted MNPs. Grafting conditions: see Experimental Section and Table 4, entry 1. Reaction conditions: see Experimental Section for grafted MNP materials (5 mg, 1.96 mol% Pd), phenylboronic acid, and iodobenzene. The mixture was stirred for 1 h at 65 °C.

Recovery of dendron-grafted MNPs: Using surface-modified magnetic nanoparticles as catalyst support ensures minimal loss, easy and soft separation, and reusability of the catalyst at the end of each reaction cycle. Indeed, after each cycle, the metallodendritic catalyst was separated from the reactant by magnetic separation. Then the catalyst was washed several times with THF/Tx and reused in the next catalytic cycle (Figure 3). Recovery experiments were performed for the coupling reaction between iodobenzene and phenyl boronic acid in the presence of 300 nm MNPs grafted with dendron **9** (Figure 4).[39] They revealed almost no significant loss of activity even after 25 cycles of recovery. These results indicate good stability of the catalyst, in contrast to the precipitation technique used in previous work.[22b–e] The slight decrease (<5%) of reactivity observed after 25 cycles was probably due to the recovery technique (slight loss of particles during the magnetic separation process) and the leaching of Pd often observed in such catalytic species, and this was confirmed by ICP analysis of the supernatent after the catalytic reaction (0.36% loss of Pd/cycle, i.e., 14 ppm of Pd in the crude product).

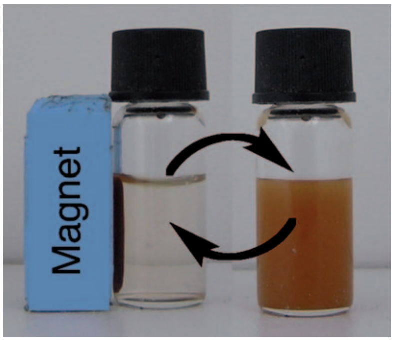


Figure 3. Magnetic separation of a grafted MNP catalyst in solution (THF/Tx 1/9) by an external magnet. Particles come close to the vial wall and supernatant can be removed.

Conclusions

We have synthesized an AB_3 metallodendron funtionalized by catalytic groups (diphosphino palladium(II) complexes) on one side and a primary amino group at the focal point. Grafting of this dendron onto core–shell γ-Fe_2O_3/polymer 300, 200, and 500 nm MNPs was studied and optimized by a convergent approach. The catalytic activity of this supported catalyst towards Suzuki C–C cross-coupling reactions between halogenoarenes and boronic acid compounds was investigated. The presence of the chelating diphosphines on the dendron is necessary for the stability and a key feature for their efficiency. Indeed, we obtained highly active catalysts for a range of iodo- and bromobenzene derivatives and an unprecedented reactivity towards chloroarenes by using core–shell γ-Fe_2O_3 grafted MNP catalysts. Finally, we showed that it is easy to recover and reuse this grafted catalyst at least 25 times without any significant loss of reactivity. In addition, the grafted catalyst is environmentally friendly because of its low extent of Pd leaching 0.36% (14 ppm of Pd in crude product) after each catalytic reaction.

Experimental Section

All reactions were performed under a nitrogen atmosphere in standard glassware (Schlenk use for **7**, **8**, and **9**). The starting materials were obtained commercially and used without further purification. The solvents were dried according to standard procedures and saturated with nitrogen. The ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded on the following spectrometers: Bruker DPX 200 FT NMR spectrometer (^{1}H: 200.16, ^{13}C:

50.33, ^{31}P: 81.02 MHz), Bruker AC 250 FT NMR spectrometer (^{1}H: 250.13, ^{13}C: 62.90 MHz), and Bruker Avance 300 FT NMR spectrometer (^{1}H: 300.13, ^{13}C: 75.46, ^{31}P: 121.49 MHz). Chemicals shifts are reported in parts per million (δ) against referenced solvent signals. Mass spectra were performed by CESAMO (Bordeaux, France) on a QStar Elite mass spectrometer (Applied Biosystems). The instrument is equipped with an ESI source and spectra were recorded in negative or positive mode. MALDI-TOF spectra were performed by CESAMO (Bordeaux, France) on a Voyager mass spectrometer (Applied Biosystems). The instrument is equipped with a pulsed N_2 laser (337 nm) and a time-delayed extracted-ion source. Spectra were recorded in positive-ion mode by using a reflectron and with an accelerating voltage of 20 kV. Elemental analyses were carried out in elemental analysis department at CNRS-Vernaison, France. GC spectra were recorded with a Varian star 3900 gas chromatograph equipped with a fused-silica capillary column heated gradually to 250 °C (from 40 °C, rate $10\,^{\circ}\mathrm{C\,min^{-1}}$) with He as vector gas at a column head pressure of 10 psi, or with a Varian star 3400 gas chromatograph equipped with a fused-silica column heated gradually to 220 °C (from 40 °C, rate $10\,^{\circ}\mathrm{C\,min^{-1}}$) with N_2 as vector gas and a column head pressure of 5 or 10 psi An FID detector was used. Yields were calculated by an integration of product peaks (Star chromatography workstation 5.50) after determination of the response coefficient of each product versus each chloroarene reagent. For column chromatography, Merck silica gel 60 (230–400 mesh) was used. Compound **9** was synthesized in ten steps from known methoxyphenyl triallyl compound **1** and spacer compound **12**. Synthesis of **2** and **3** has been previously described.[21]

***p*-OH(C$_6$H$_4$)CH(CH$_2$CH$_2$CH$_2$N$_3$)$_3$ (4)**: A mixture of **3** (4.95 g, 8.1 mmol) and $\mathrm{NaN_3}$ (7.89 g, 121 mmol) was stirred in DMF (11 mL) at 40 °C for 24 h under nitrogen atmosphere. Water (15 mL) was then added and the mixture extracted with $\mathrm{Et_2O}$ (3×20 mL). Organic layers were gathered, washed with water (10×20 mL), and dried over anhydrous $\mathrm{Na_2SO_4}$. Solvent was removed under reduced pressure to afford **4** as a brown oil (2.67 g, 92% yield). ^{1}H NMR ($\mathrm{CDCl_3}$): $\delta=7.14$ (d, 2H, $\mathrm{CH_{(Ar)}}$), 6.80 (d, 2H, $\mathrm{CH_{(Ar)}}$), 4.93 (br, 1H, OH), 3.23 (t, 6H, $\mathrm{CH_2N_3}$), 1.66 (m, 6H, $\mathrm{CH_2}$), 1.35 ppm (m, 6H, $\mathrm{CH_2}$); ^{13}C NMR ($\mathrm{CDCl_3}$): $\delta=153.9$ (s, 1C, $\mathrm{C_{(Ar)}O}$), 138.0 (s, 1C, $\mathrm{C_{q(Ar)}}$), 127.4 (s, 2C, $\mathrm{CH_{(Ar)}}$), 115.3 (s, 2C, $\mathrm{CH_{(Ar)}}$), 52.0 (s, 3C, $\mathrm{CH_2N_3}$), 42.5 (s, 1C, $\mathit{C}_\mathrm{q}\mathrm{C_{(Ar)}}$), 34.4 (s, 3C, $\mathit{C}\mathrm{H_2C_q}$), 23.3 ppm (s, 3C, $\mathit{C}\mathrm{H_2CH_2N_3}$); elemental analysis calcd (%) for $\mathrm{C_{16}H_{23}N_9O}$ (357.41): C 53.8, H 6.5; found: C 54.5, H 6.6.

***p*-teocNH(CH$_2$)$_6$O(C$_6$H$_4$)CH(CH$_2$CH$_2$CH$_2$N$_3$)$_3$ (5)**: Triazo dendron **4** (590 mg, 1.65 mmol) and KOH (280 mg, 4.96 mmol) were dissolved in dry DMF (2 mL) in a Schlenk tube and stirred for 20 min. A solution of Teoc-protected 6-iodo-1-aminohexane **12** (613 mg, 1.65 mmol) in DMF (1 mL) was added to the reaction mixture, which was stirred at room temperature for 4 h. Water was added and the product extracted with $\mathrm{Et_2O}$. The organic layer was washed several times with water, dried over $\mathrm{MgSO_4}$, and evaporated under reduced pressure to give **5** as a brown oil (0.91 g, 92%). ^{1}H NMR ($\mathrm{CDCl_3}$): $\delta=7.17$ (d, 2H, $\mathrm{CH_{(Ar)}}$), 6.84 (d, 2H, $\mathrm{CH_{(Ar)}}$), 4.61 (br, 1H, NH), 4.14 (t, 2H, $\mathrm{C}\mathit{H}_2\mathrm{OCO}$) 3.93 (t, 2H, $\mathrm{CH_2O}$), 3.22 (t+q, 8H, $\mathrm{C}\mathit{H}_2\mathrm{NH}+\mathrm{C}\mathit{H}_2\mathrm{NH_2}$), 1.74–1.26 (m, 20H, $\mathrm{CH_2}$), 0.97 (t, 2H, $\mathrm{CH_2Si}$), 0.03 ppm (s, 9H, $\mathrm{CH_3Si}$); ^{13}C NMR ($\mathrm{CDCl_3}$): $\delta=157.2$ (s, 1C, $\mathit{C}\mathrm{{=}O}$), 156.9 (s, 1C, $\mathrm{CO_{Ar}}$), 137.4 (s, 1C, $\mathrm{C_{q(Ar)}}$), 127.2 (s, 2C, $\mathrm{CH_{(Ar)}}$), 114,3 (s, 2C, $\mathrm{CH_{(Ar)}}$), 67.7 (s, 1C, $\mathrm{CH_2O}$), 62.9 (s, 1C, $\mathit{C}\mathrm{H_2OCO}$), 52.0 (s, 3C, $\mathrm{CH_2N_3}$), 42.0 (s, 1C, $\mathit{C}_\mathrm{q}\mathrm{C_{Ar}}$), 40.9 (s, 1C, $\mathit{C}\mathrm{H_2NH}$), 34.5 (s, 3C, $\mathit{C}\mathrm{H_2C_q}$), 30.1 (s, 1C, $\mathit{C}\mathrm{H_2CH_2NH}$), 29.3 (s, 1C, $\mathit{C}\mathrm{H_2CH_2O}$), 26.6 (s, 1C, $\mathrm{CH_2}$), 25.9 (s, 1C, $\mathrm{CH_2}$), 23.3 (s, 3C, $\mathrm{CH_2}$), 17.8 (s, 1C, $\mathrm{CH_2Si}$), −1.4 ppm (s, 3C, $\mathrm{CH_3Si}$); MS (ESI): *m/z* (%): [*M*+Na] (100) calcd 623.36; found: 623.36.

***p*-TeocNH(CH$_2$)$_6$O(C$_6$H$_4$)CH(CH$_2$CH$_2$CH$_2$NH$_2$)$_3$ (6)**: A mixture of **5** (900 mg, 1.49 mmol) and Pd/C (330 mg, 0.31 mmol) in dry MeOH (10 mL) under $\mathrm{H_2}$ atmosphere (1.5–2 bars) was stirred at room temperature for 5 h. The mixture was filtered through Celite and the solvent was removed under reduced pressure. The product was dried under vacuum to afford **6** as alight yellow oil (678 mg, 87%). ^{1}H NMR ($\mathrm{CDCl_3}$): $\delta=7.13$ (d, 2H, $\mathrm{CH_{(Ar)}}$), 6.75 (d, 2H, $\mathrm{CH_{(Ar)}}$), 4.84 (br, 1H, NH), 4.11 (t, 2H, $\mathrm{C}\mathit{H}_2\mathrm{OCO}$), 3.86 (t, 2H, $\mathrm{CH_2O}$), 3.10 (q, 2H, $\mathrm{C}\mathit{H}_2\mathrm{NH}$), 2.56 (t, 6H, $\mathrm{C}\mathit{H}_2\mathrm{NH_2}$), 1.71 (q, 2H, $\mathrm{C}\mathit{H}_2\mathrm{CH_2O}$), 1.56 (m, 6H, $\mathrm{CH_2}$), 1.5–1.20 (m, 6H, $\mathrm{CH_2C}\mathit{H}_2\mathrm{CH_2}$), 1.14 (m, 6H,$\mathrm{CH_2}$), 0.91 (t, 2H, $\mathrm{CH_2Si}$), −0.02 ppm (s, 9H, $\mathrm{CH_3Si}$); ^{13}C NMR ($\mathrm{CDCl_3}$): $\delta=156.8$ (d, 2C, $\mathit{C}\mathrm{O_{Ar}}+\mathit{C}\mathrm{{=}O}$), 138.9 (s,1C, $\mathrm{C_{q(Ar)}}$), 127.3 (s, 2C, $\mathrm{CH_{(Ar)}}$), 113.9 (s, 2C, $\mathrm{CH_{(Ar)}}$), 67.6 (s, 1C, $\mathrm{CH_2O}$), 62.8 (s, 1C, $\mathit{C}\mathrm{H_2OCO}$), 42.8 (s, 3C, $\mathrm{CH_2NH_2}$), 42.0 (s, 1C, $\mathit{C}_\mathrm{q}\mathrm{C_{Ar}}$), 40.8 (s, 1C, $\mathrm{CH_2NH}$), 34.8 (s, 3C, $\mathit{C}\mathrm{H_2C_q}$), 30.0 (s, 1C, $\mathit{C}\mathrm{H_2CH_2NH}$), 29.3 (s, 1C, $\mathit{C}\mathrm{H_2CH_2O}$), 27.7 (s, 3C, $\mathrm{CH_2}$), 26.5 (s, 1C, $\mathrm{CH_2}$), 25.8 (s, 1C, $\mathrm{CH_2}$), 17.8 (s, 1C, $\mathrm{CH_2Si}$), −1.4 ppm (s, 3C, $\mathrm{CH_3Si}$); MS (ESI): *m/z*: [*M*+H] calcd 523.40, found 523.40.

***p*-TeocNH(CH$_2$)$_6$O(C$_6$H$_4$)CH{CH$_2$CH$_2$CH$_2$N(CH$_2$PCy$_2$)$_2$}$_3$ (7)**: A solution of 10% dicyclohexylphosphine (22.7 mL, 11.2 mmol) in hexane was introduced into a Schlenk tube and evaporated under reduced pressure. A solution of paraformaldehyde (1.8 g, 60.0 mmol) in MeOH/toluene (2/1, 10 mL) was added under inert atmosphere, and the reaction mixture heated at 70 °C for 10 min. A solution of **6** (0.8 g, 1.54 mmol) in MeOH/toluene (2/1, 10 mL) was added, and the mixture stirred at 70 °C for 10 min and then at room temperature for 12 h. The volume of the reaction mixture was reduced and MeOH (20 mL) added. The residue was isolated from the medium, washed several times with MeOH, and dried under vacuum to yield **7** as a glassy colorless solid (2.1 g, 78%). ^{1}H NMR ($\mathrm{CDCl_3}$): $\delta=7.13$ (d, 2H, $\mathrm{CH_{(Ar)}}$), 6.75 (d, 2H, $\mathrm{CH_{(Ar)}}$), 4.58 (br, 1H, NH), 4.13 (t, 2H, $\mathrm{C}\mathit{H}_2\mathrm{OCO}$), 3.86 (t, 2H, $\mathrm{CH_2O}$), 3.15 (q, 2H, $\mathrm{C}\mathit{H}_2\mathrm{NH}$), 2.67 (s, 12H, $\mathrm{NCH_2P}$) 2.59 (t, 6H, $\mathrm{C}\mathit{H}_2\mathrm{NCH_2P}$), 1.7–1.1 (m, 152H), 0.95 (t, 2H, $\mathrm{CH_2Si}$), 0.02 ppm (s, 9H, $\mathrm{CH_3Si}$); ^{13}C NMR ($\mathrm{CDCl_3}$): $\delta=156.9$ (d, 2C, $\mathrm{CO_{(Ar)}+C{=}O}$), 139.3 (s, 1C, $\mathrm{C_{q(Ar)}}$), 127.6 (s, 2C, $\mathrm{CH_{(Ar)}}$), 113.7 (s, 2C, $\mathrm{CH_{(Ar)}}$), 67.6 (s, 1C, $\mathrm{CH_2O}$), 62.9 (s, 1C, $\mathit{C}\mathrm{H_2OCO}$), 56.7 (s, 3C, $\mathit{C}\mathrm{H_2NCH_2P}$), 52.4 (s, 6C, $\mathrm{CH_2P}$) 42.6 (s, 1C, $\mathrm{C_{Ar}}\mathit{C}_\mathrm{q}$), 41.0 (s, 1C, $\mathit{C}\mathrm{H_2NH}$), 35.6 (s, 3C,$\mathit{C}\mathrm{H_2C_q}$), 32.9 (d, 12C, $\mathrm{PCH_{(Cy)}}$), 29.8 (dd, 24C, $\mathrm{CH_{2(Cy)}}$), 27.5 (s, 24C, $\mathrm{CH_{2(Cy)}}$), 26.7 (s, 12H,$\mathrm{CH_{2(Cy)}}$), 26.0 (s, 1C, $\mathrm{CH_2}$), 17.9 (s, 1C, $\mathrm{CH_2Si}$), −1.3 ppm (s, 3C, $\mathrm{CH_3Si}$); ^{31}P NMR ($\mathrm{CDCl_3}$): $\delta=-18.2$ ppm; MS (MALDI-TOF): *m/z* (%): product also appeared in oxidized forms (

1–6O) due to the matrix and experimental conditions: [*M*+Na] (17) calcd: 1807.31, found: 1807.29; [*M*+O+Na] (45) calcd: 1822.30, found: 1822.28; [*M*+2O+Na] (100) calcd: 1838.30, found: 1838.28; [*M*+3O+Na] (61) calcd: 1854.29, found: 1854.27; [*M*+4O+Na] (35) calcd: 1870.29, found: 1870.27; [*M*+5O+Na] (14) calcd: 1886.28, found: 1886.28; [*M*+6O+Na] (10) calcd: 1902.28, found: 1902.27.

***p*-NH$_2$(CH$_2$)$_6$O(C$_6$H$_4$)CH{CH$_2$CH$_2$CH$_2$N(CH$_2$PCy$_2$)$_2$}$_3$ (8)**: A mixture of **7** (1.79 g, 1.0 mmol), tetrabutylammonium fluoride 1 M in THF (10 mL, 10.0 mmol), and THF (3 mL) was stirred under inert atmosphere at 60 °C for 5 h. Then the solvent was removed under reduced pressure and the residue washed several time with iced methanol. The product was dried under vacuum to give **8** as a white powder (1.3 g, 82%). ^{1}H NMR ($\mathrm{CDCl_3}$): $\delta=7.13$ (d, 2H, $\mathrm{CH_{(Ar)}}$), 6.76 (d, 2H, $\mathrm{CH_{(Ar)}}$), 3.87 (t, 2H, $\mathrm{CH_2O}$), 2.68 (s, 12H, $\mathrm{NCH_2P}$) 2.59 (t, 8H, $\mathrm{C}\mathit{H}_2\mathrm{NCH_2P}+\mathrm{C}\mathit{H}_2\mathrm{NH_2}$), 1.7–1.1 ppm (m, 152H); ^{13}C NMR ($\mathrm{CDCl_3}$): $\delta=156.65$ (s, 1C, $\mathit{C}\mathrm{O_{Ar}}$), 139.3 (s, 1C, $\mathrm{C_{q(Ar)}}$), 127.5 (s, 2C, $\mathrm{CH_{(Ar)}}$), 113,6 (s, 2C, $\mathrm{CH_{(Ar)}}$), 67.7 (s, 1C, $\mathrm{CH_2O}$), 56.8 (s, 3C, $\mathit{C}\mathrm{H_2NCH_2P}$), 52.3 (s, 6C, $\mathrm{CH_2P}$) 42.5 (s, 2C, $\mathrm{C_{Ar}}\mathit{C}_\mathrm{q}+\mathit{C}\mathrm{H_2NH_2}$), 35.5 (s, 3C, $\mathit{C}\mathrm{H_2C_q}$), 33.0 (d, 12C, $\mathrm{PCH_{(Cy)}}$), 29.8(dd, 24C, $\mathrm{CH_{2(Cy)}}$), 27.5 (s, 24C, $\mathrm{CH_{2(Cy)}}$), 26.7 (s, 12H, $\mathrm{CH_{2(Cy)}}$), 20.3 ppm (s, 6C, $\mathrm{CH_2}$); ^{31}P NMR ($\mathrm{CDCl_3}$): $\delta=-18.3$ ppm ($\mathrm{PCy_2}$); MS (MALDI-TOF): *m/z*: product appeared in oxidized form due to the matrix and experimental conditions: [*M*+6O+Na] calcd: 1758.22, found: 1758.15.

***p*-NH$_2$(CH$_2$)$_6$O(C$_6$H$_4$)CH{CH$_2$CH$_2$CH$_2$N(CH$_2$ PCy$_2$)$_2$Pd(OAc)$_2$}$_3$ (9)**: A mixture of **8** (1.0 g, 0.61 mmol) and palladium diacetate (411 mg, 1.83 mmol) was stirred in $\mathrm{CH_2Cl_2}$ (15 mL) at room temperature under inert atmosphere for 2 h. Then the mixture reaction was evaporated and the product dried under vacuum to give **9** as a dark brown powder (1.4 g, quant.). ^{1}H NMR ($\mathrm{CDCl_3}$, 25 °C): $\delta=7.13$ (d, 2H, $\mathrm{CH_{(Ar)}}$), 6.80 (d, 2H, $\mathrm{CH_{(Ar)}}$), 3.84 (t, 2H, $\mathrm{CH_2O}$), 2.48–2.2 (m, 20H, $\mathrm{NCH_2P}+\mathrm{C}\mathit{H}_2\mathrm{NCH_2P}+\mathrm{C}\mathit{H}_2\mathrm{NH_2}$), 1.94 (s, 12H, $\mathrm{CH_3COO}$), 1.7–1.1 (m, 152H, $\mathrm{CH_2}$); ^{13}C NMR ($\mathrm{CD_2Cl_2}$): $\delta=177.6$ (m, 6C, $\mathrm{CO_{(Ac)}}$), 157.2 (s, 1C, $\mathrm{CO_{Ar}}$),139.0 (s, 1C, $\mathrm{C_{q(Ar)}}$), 127.1 ppm (s, 2C, $\mathrm{CH_{(Ar)}}$), 114.0 (s, 2C, $\mathrm{CH_{(Ar)}}$), 67.6 (s, 1C, $\mathrm{CH_2O}$), 63.3 (s, 3C, $\mathit{C}\mathrm{H_2NCH_2P}$), 48.7 (s, 6C, $\mathrm{CH_2P}$) 42.7 (s, 2C, $\mathrm{C_{Ar}}\mathit{C}_\mathrm{q}+\mathit{C}\mathrm{H_2NH_2}$), 36.0 (m, 9C, $\mathit{C}\mathrm{H_2C_q+CH_{3(Ac)}}$), 29.7(m, 12C, $\mathrm{PCH_{(Cy)}}$), 29.8 (s, 24C, $\mathrm{CH_{2(Cy)}}$), 26.9 (s, 24C, $\mathrm{CH_{2(Cy)}}$), 25.9 (s, 12H,$\mathrm{CH_{2(Cy)}}$), 19.7 ppm (s, 6C, $\mathrm{CH_2}$); ^{31}P NMR ($\mathrm{CDCl_3}$): $\delta=26.7$ ppm; MS (MALDI-TOF): *m/z* (%): product appeared in oxidized form due to the matrix and experimental conditions [M+4O+H] (95%): calcd: 2376.04, found: 2377.04; [M+5O+H] (100%): calcd: 2392.03, found: 2392.97.

Teoc-NH(CH$_2$)$_6$OH (11): Triethylamine (2.9 mL, 21.1 mmol) was added to a solution of 6-aminohexan-1-ol (**10**, 1.25 g, 10.66 mmol) in CH_2Cl_2 (5 mL) under inert and dry atmosphere. The mixture was stirred at room temperature for 10 min and a solution of 4-nitrophenyl 2-(trimethylsilyl)-ethyl carbonate (3 g, 10.59 mmol) in CH_2Cl_2 (5 mL) was then added. The reaction mixture was stirred at room temperature for 2 h and dried to remove triethylamine. The crude product was extracted with CH_2Cl_2 (40 mL) and the organic layer washed several times with brine and $NaHCO_3$, and with an aqueous solution of NaOH (2 N) until the organic layer became colorless. The organic layer was dried over anhydrous Na_2SO_4, and the solvent removed under reduced pressure to give a light yellow oil (2.40 g, 86.7%). ^{1}H NMR ($CDCl_3$): $\delta=4.67$ (br, 1H, NH), 4.12 (t, 2H, 8.4 Hz, CH_2OCO), 3.61 (t, 2H, 6.4 Hz, CH_2OH), 3,14 (q, 2H, CH_2NH), 1.78 (br, 1H, OH/NH), −1.33 (m, 8H, $CH_2\times4$), 0.95 (t, 8.5 Hz, 2H, CH_2Si), 0.01 ppm (s, 9H, CH_3Si); ^{13}C NMR ($CDCl_3$): $\delta=157.01$ (s, 1C, C=O), 62.57 (s, 2C, $CH_2OCO+CH_2OH$), 40.75 (s, 1C, CH_2NH), 32.58 (s, 1C, CH_2), 30.03 (s, 1C, CH_2), 26.42 (s, 1C, CH_2), 25.38 (s, 1C, CH_2), 17.8 (s, 1C, CH_2Si), 6.9 (s, 1C, CH_2I), −1.43 ppm (s, 3C, CH_3Si); MS (ESI): m/z (%): calcd 284.166, found 284.166 (93) [M+Na], 545.342 (100) [2M+Na].

Teoc-NH(CH$_2$)$_6$I (12): A mixture of **11** (0.5 g, 1.9 mmol) in CH_2Cl_2 (5 mL) and NEt_3 (400 µL, 2.86 mmol) was cooled with an ice bath, and methanesulfonyl chloride (200 µL, 2.57 mmol) was added slowly to the mixture. The solution was stirred for one hour at room temperature. The reaction medium was washed with brine and with water. The organic layer was then dried over anhydrous Na_2SO_4 and solvent was removed to afford a brown oil, which was dissolved in CH_3CN (10 mL). Then NaI (1.42 g, 9.5 mmol) was added and the reaction medium was stirred at room temperature for 48 h. The solvent was removed and the crude product dissolved in water (10 mL) and extracted with CH_2Cl_2 (4× 10 mL). Organic layers were gathered, washed with a saturated aqueous solution of $Na_2S_2O_3$, and dried over Na_2SO_4. Solvent was removed under reduced pressure to give a brown oil, which was purified on a silica gel chromatography column (petroleum ether/Et_2O 70/30) to yield a colorless oil (0.58 g, 82.2%). ^{1}H NMR ($CDCl_3$): $\delta=4.61$ (br, 1H, NH), 4.12 (t, 2H, CH_2OCO), 3.15 (m, 4H, CH_2I+CH_2NH), 1.81 (q, 2H, CH_2CH_2I), 1.52–1.32 (m, 6H, $CH_2\times3$), 0.95 (t, 2H, CH_2Si), 0.02 ppm (s, 9H, CH_3Si); ^{13}C NMR ($CDCl_3$): $\delta=156.8$ (s, 1C, C=O), 62.8 (s, 2C, CH_2OCO), 40.8 (s, 1C, CH_2NH), 33.3 (s, 1C, CH_2), 30.1 (d, 2C, CH_2), 25.6 (s, 1C, CH_2), 17.78 (s, 1C, CH_2Si), −1.43 ppm (s, 3C, CH_3Si); MS (ESI): m/z (%): calcd 394.068, found 394.068 (93) [M+Na], 765.145 (100) [2M+Na].

General procedure for the grafting of dendron 9 onto core–shell MNPs: Carboxyl-Adembeads 300 nm nanoparticles[40] (250 µL, 2.5 mg, 0.75 µmol CO_2H), dendron **9** in DMF solution (see table below), and CHMC[41] (12 mg mL^{-1}, 200 µL, 5.66 µmol) were mixed and MeOH/Tx (1/2) was added to adjust the reaction mixture to 1 mL (see Table 4). The reaction flask was shaken on a rotator for 16 h at room temperature. Then particles were gathered close to the flask wall with an external magnet and washed several times with NaOH (10 mM), Tx, and THF/Tx (2/1) solution (1 mL).

General procedure for catalytic reactions and recovery of catalysts: Grafted MNPs (0.05–5 mg), NaOH (168 µmol), aryl boronic acid (84.37 µmol), and halo arene (56.25 µmol) were mixed in THF/Tx (1 mL, 1/9). The mixture was stirred at 30–65 °C. Then grafted MNPs were separated from the mixture by attraction with an external magnet and washed with THF/Tx (1/9, 2×500 µL). Then they were introduced into a freshly made reaction mixture.

Table 4. Grafting of dendron **9** onto MNPs.

Entry	Dendron **9** (equiv)	DMF [µL]	MeOH/Tx (1/2) [µL]
1	1.5 µmol, 3.5 mg (2)	100	450
2	3 µmol, 7 mg (4)	200	350
3	6 µmol, 14 mg (8)	200	350
4	7.5 µmol, 17.5 mg (10)	200	350
5	15 µmol, 35 mg (20)	250	300
6	18.75 µmol, 43.7 mg (25)	312.5	237.5

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[24] See general procedure for catalytic reactions and recovery of catalysts with 5 mg of grafted MNPs, iodobenzene, and phenylboronic acid in THF/Tx (2/1) at RT. Conversions were determined by GC analysis.

[25] PF127: Pluronic F127 aqueous solution (0.3 wt %) obtained from Pluronic F127 (Aldrich).

[26] 2-(*N*-Morpholino)ethanesulfonic acid (50 mM) in an aqueous solution of PF127 (see ref. [25]).

[27] HLB: hydrophilic/lipophilic balance. HLB(Pluronic F127) = 22, HLB(triton X405) = 17.9.

[28] Tx: triton X405 aqueous solution (0.21 %) obtained from triton X405 (70 %) purchased from Aldrich.

[29] Ten times more dilute medium. Total reaction volume was 10 mL.

[30] We used 200 μL of EDC in aqueous solution (12 mgmL^{-1}) or 200 μL of CHMC in aqueous solution (6 mgmL^{-1}). Total reaction volume was 1 mL.

[31] See general procedure for catalytic reactions and recovery of catalysts with 2.5 mg of grafted MNPs, iodobenzene, and phenylboronic acid at RT in THF/Tx (2/1). After 1.5 h, we obtained 100 % conversion with CHMC or EDC in the first cycle and 100 % conversion (with CHMC, in 14 h) and 98 % conversion (with EDC, in 16 h) in the second cycle.

[32] 200 μL of NHS water solution (12 mgmL^{-1}).

[33] Accessible free carboxyl groups amount to 300–355 μmol per gram of particles, determined by conductimetric measurements.

[34] Pd ICP analyses of grafted MNPs were 1.83 and 3.8 %, respectively, for 2 and 10 equivalents of **9** in the grafting reaction.

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[36] Core–shell γ-Fe_2O_3/polymer 200 nm superparamagnetic nanoparticles (Carboxyl-Adembeads 200 nm, Ademtech, France, 300 μmol COOH per gram of particles) and core–shell γ-Fe_2O_3/polymer 500 nm superparamagnetic nanoparticles (Carboxyl-Adembeads 500 nm, Ademtech, France, 250 μmol COOH per gram of particles).

[37] Catalytic tests were performed with 0.125 mg of grafted MNP materials according to the general procedure (see Experimental Section).

[38] For coupling of bromobenzene and phenylboronic acid with NaOH in Tx/THF (9/1), at 65 °C for 4 h, with 2.5 mg of catalyst (2.4 mol % Pd) we obtained 99 and 97 % yield for 300 and 200 nm MNPs, respectively.

[39] See general procedure: Grafted MNPs with 2 equiv of dendron **9** (5 mg, 1.96 mol % Pd), NaOH (168 μmol), phenylboronic acid (84.37 μmol), and iodobenzene (56.25 μmol) were mixed in 1 mL of Tx/THF (9/1). The mixture was stirred at 65 °C for 1 h. Then grafted MNPs were separated from the mixture by an external magnet and were washed with Tx/THF (9/1, (2 × 500 μL). Particles were washed twice with Tx/THF (9/1) between each run.

[40] Suspension of Carboxyl-Adembeads 300 nm nanoparticles 1 wt % MeOH/Tx (1:2).

[41] Solution of carbodiimide CHMC 12 mgmL^{-1} in MeOH/Tx (1:2).

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