Metallodendritic Grafted Core–Shell γ-Fe₂O₃ Nanoparticles Used as Recoverable Catalysts in Suzuki C–C Coupling Reactions

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Abstract: The use of dendritic structures for the grafting of core–shell γ -Fe₂O₃/polymer 300 nm superparamagnetic nanoparticles (MNPs) has been performed with four metallodendrons that were functionalized with diphosphinopalladium complexes. The catalytic performance of these nanocatalysts was optimized for the Suzuki C–C

Introduction

Nowadays, chemistry appears to be a stakeholder in economic issues that need to be addressed by means of sustainable and compliant science. Over the last few years, "green" methodologies in accordance with economic and environmental issues have been widely investigated in many research areas, including catalysis in the pursuit of sustainable catalysts. Indeed, the recovery and the reuse of catalysts and the eviction of toxic metal waste from reaction media are the two predominant current research axes of the scientific community, encouraged by the strong demand from industri-

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cross-coupling reaction. These results demonstrated the importance of optimizing the catalytic efficiency of graft-

Keywords: catalyst recovery • coreshell magnetic nanoparticles • crosscoupling • dendrimers • magnetic properties • nanoparticles ed MNPs by optimizing the dendritic structures and the nature of the peripheral phosphine ligands. All of these nanocatalysts showed remarkable reactivity towards bromoarenes and they were recovered and efficiently reused by magnetic separation with almost no loss of reactivity, even after 25 cycles.

al partners.^[1] In this area, "smart" supports, such as superparamagnetic nanoparticles^[2] (MNPs), have come to the fore, opening up great potential for catalyst recovery because the recovery step requires only a simple and cheap external magnet unlike conventional techniques (such as filtration), which are difficult to carry out owing to the nanometer size of the catalyst particles. In general, these nanoparticles (usually nanometer to submicrometer in size) have enhanced surface areas relative to bulk materials and provide better access to substrate molecules and higher reactivities than conventional supports.^[3] Furthermore, their magnetic behavior ensures that their flocculation or dispersion is reversibly controlled by a static magnetic field. As a result, in the absence of an external magnetic field, superparamagnetic nanoparticles can be well-dispersed in the reaction medium for their reuse. Indeed, the recent development of MNP-supported catalysts has emerged because of significant advances in the synthesis of size-controlled and monodisperse MNPs^[4] as well as in their surface stabilization by simple organic compounds, such as silanes,^[5] carboxylic acids,^[6] and phosphonic acids.^[7] This surface modification is often performed through a process that involves the exchange of stabilizing ligands or the coating of the magnetic core with an organic/inorganic polymer shell.^[8,9] In those cases, the polymer or the silica shell allows the formation of core-shell nanostructures, which are used as supports for the immobilization of homogeneous catalysts. These shells ensure the confinement of the magnetic core and prevent the aggregation of the nanoparticles in suspension. Moreover, they provide chemical stability and a wide range of anchoring sites for catalytic species. Many applications of theses catalysts have been explored, mainly in C-C coupling reactions (such as Suzuki, Heck, Sonogashira, and Stille coupling), as well as for hydroformylation, hydrogenation, and olefin metathesis.^[10] All of these reported reactions involved

Chem. Eur. J. 2012, 18, 3305-3315

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the immobilization of metal-based catalysts (Pd, Pt, Rh, or Ru). It is noteworthy that recent applications and perspectives have dealt with the development of organocatalysis and biocatalysis for the entrapment of enzymes into MNPs.^[11]

Dendrimer-^[12] or dendron-functionalized MNPs have received great attention over the past decade owing to the ability to tune their properties by functionalization.^[13–15] Each dendron is made of an anchoring site (focal point) and branches that are terminated by catalytic sites. The synthesis of dendron-grafted MNPs has been typically carried out by using similar procedures to the synthesis of NPs by ligand exchange or by direct functionalization of the nanoparticle core or shell.^[16] We have previously demonstrated^[17] that the grafting of dendritic architectures onto MNPs afforded an enhancement of the surface functionalization with respect to their grafting with linear ligands.

Herein, we studied the effect of modulation of the catalyst structure on the reactivity and recovery of 300 nm coreshell y-Fe₂O₃/polymer MNP-grafted catalysts.^[18] In particular, we evaluated the effect of the dendritic structure and/or the nature of the catalytic site toward the reactivity and recovery of the MNP-grafted catalysts. Previously, we studied the efficiency of these supported catalysts in Suzuki and Sonogashira cross-coupling reactions.^[19,20] The grafting conditions (solvent, dendron loading, coupling reagent, nanoparticle size) were optimized using dendron 1 and its corresponding supported catalyst, MNP-1. The remarkable efficiency and recoverability of MNP-1 in Suzuki C-C cross-coupling reactions was emphasized. Indeed, this catalyst was able to catalyze the cross-coupling reaction between bromoarenes (and even chloroarenes) and phenylboronic acid with high conversions in a few hours and a catalyst loading of below 5 mol% at 65 °C. The recovery of the catalyst using an external magnet was studied and complete conversion was maintained until at least the 25th recovery cycle. To extend this study, herein, we report the synthesis of various supported nanoparticles that have been grafted with related tri- or nona-branched dendritic structures that contain diphosphinopalladium complexes with cyclohexyl or tert-butyl ligands at their periphery. Thus, four dendron-grafted nanoparticles (MNP-1 to MNP-4) were synthesized from tri- or nonabranched dendrons 1 to 4 (Scheme 1). These dendrons were composed of a primary amine group at their focal point, which was necessary for anchoring onto the core-shell MNPs, and catalytic sites at their periphery. The structure of their inner dendritic part was modulated, either by dendritic generation or by the addition of a spacer group. Their active catalytic sites were either composed of bis(cyclohexylaminomethylphosphine)palladium(II), N(CH₂PCy₂)₂-[Pd^{II}], or bis-(di-tert-butylaminomethylphosphine)palladium(II), N(CH₂- $PtBu_2)_2$ - $[Pd^{II}]$ ($[Pd^{II}] = Pd(OAc)_2$). These dendrons were grafted onto a core-shell y-Fe₂O₃/polymer (Carboxyl-Adembeads 300 nm, Ademtech, France, COOH: $300 \,\mu\text{mol}\,\text{g}^{-1}$). Indeed, the dendritic structure of dendron 1 involved a three-branched dendron, ended by $N(CH_2PCy_2)_2$ -[Pd^{II}] whilst dendron 2 had the same dendritic frame with a different catalytic part. Indeed, dicyclohexylphophine palladium complex $N(CH_2PCy_2)_2$ -[Pd^{II}] was replaced by its *tert*-butyl counterpart $N(CH_2PtBu_2)_2$ -[Pd^{II}]. In the case of dendron **3**, spacer groups were introduced into the dendritic structure of compound **1** to minimize the steric hindrance between the catalytic sites at the dendron periphery. As for dendron **4**, it represents the second generation of dendron **1**, with the same catalytic site $N(CH_2PCy_2)_2$ -[Pd^{II}]. These structural studies of two generations of dendron-grafted catalysts will help us to evaluate the dendritic effect on catalytic performance.

Results and Discussion

Synthesis of [Pd]-functionalized dendrons 1 and 2: First, we prepared the Pd^{II} catalyst tri-N(CH₂PCy₂)₂-[Pd^{II}] dendron 1 as described in our previous work^[19] from 4-methoxytriallylmethylbenzene. Tri-N(CH₂PtBu₂)₂-[Pd^{II}] dendron 2 was also prepared by following by a slightly modified procedure (Scheme 2), as reported previously.^[20] Thus, aminophosphine dendrons 6a and 6b were obtained by double phosphinomethylation^[19-21] of compound **5**. The deprotection of the terminal amino groups was carried out with Bu₄NF, thereby leading to dendrons 7a and 7b, respectively. Complexation of the phosphine groups of compound 7 with [Pd^{II}] led to the corresponding metallodendrons 1 and 2, respectively, which contained three N(CH₂PCy₂)₂-[Pd^{II}] or N(CH₂PtBu₂)₂-[Pd^{II}] catalytic groups. The completion of the reaction was confirmed by the disappearance of the signals in the ³¹P NMR spectra at $\delta = -18.3$ (for **7a**) and $\delta = 12.8$ ppm (for **7b**), which were attributed to the free phosphines, and the appearance of signals at $\delta = 26.7$ ppm (for 1) and $\delta = 36.5$ ppm (for 2), which were attributed to the coordinated phosphines. All of these dendritic palladium complexes were stable towards moisture; however, they were stored under nitrogen to avoid slow degradation.

Synthesis of [Pd]-functionalized dendron 3: Dendritic compound 3 was a three-branched dendron that was functionalized by a bis(dicyclohexylaminomethylphosphine)palladium(II) N(CH₂PCy₂)₂-[Pd^{II}] catalyst. Compound **3** was synthesized as described in Scheme 3. The first step was the preparation of spacer group 9 from tyrosol by substitution of the alcohol group by treatment with NaI in the presence of trimethylsilylchloride (TMSCl) at 70°C to give iodoalcohol 8; treatment of compound 8 with NaN₃ yielded azidoalcohol 9. Then, tri-iodo dendron $10^{[22]}$ was coupled with compound 9 in the presence of K_2CO_3 to afford triazide dendron 11. The latter was treated with KOH and then coupled with 2-(trimethylsilyl)ethoxycarbonyl (Teoc)-protected 1-iodoaminohexane^[23] to generate dendron **12**. The Staudinger reduction of compound 12 in the presence of PPh₃ and water gave triamine dendron 13. Aminophosphine dendron 14 was then obtained by the phosphinomethylation of compound 13. Deprotection of the terminal amino group was carried out with Bu₄NF at 60 °C to give dendron 15. Complexation of the

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Cy2 P-Pd-OAc Cy₂ .OAc ṔCy₂ ṔCy₂ MNPs -PCy₂.OAc PCy2,OAc γ-Fe₂O₃ -P-^{Pd}OAc Cy₂ -8_́₽ R_{Cy₂} RCy2 Pd-OAc Pd-OAc E_{y_2} \vec{c}_{y_2} MNP-1 1 -tBu₂ tBu₂ ^{Bu}2 ,OAc ⁻Pd-OAc ⁻Pd-OAc / -tBu₂ ∕ -tBu₂ MNPs P-tBu₂ OAc P-tBu₂ OAc γ-Fe₂O₃ H₂N Pd. OAc Pd. OAc -P^{_Pa} -tBu₂ -P -tBu₂ R-tBu₂ ?-tBu₂ P^{-Pd-OAc} -tBu₂ OAc Pd-OAc 2 MNP-2 ·P^{_PC} -tBu₂ Cy₂ OAc OAc OAc OAc MNPs Ćy₂ γ-Fe₂O₃ Cy₂ H_{5} Pd OAc Pd^{OAc} Fe₂C Ey2 OAc Ey₂ Cy₂ P∖ Pd OAc OAc Pd^{.OAc} MNP-3 3 €y₂ €y₂ OAc .Pd·OAc OAc Pd-OAc OAc OAc . 1-OAc , d-OAc Cy₂ Cy₂ OAc OAc Cy₂ C. P Pd-OAc P Pd-OAc PCy₂ PĆy₂ Cy₂ OAc P Pd OAc Cy2 .OAc P Pd OAc .PĊy₂ .PĆy₂ **MNPs** Cy₂ Cy₂ y₂ ,Pd∙OAc γ-Fe₂O₃ OAc Pd-OAc - E^{, P(} -B'_{P0} `RCy₂ `₽Cy₂ Cy2P-Pd-OAc OAc Cy₂P-Pd-OAc PCy₂ -PCy₂ MNP-4 P Pd-OAc Cy₂ OAc P Pd-OAc Cy2 OAc 4 PCy₂ Pd-OAc y₂ OAc PC_{V2} Pd-OAc PCy2 PCy2 Pd-OAc Cval Cy; Pd-OAc

Scheme 1. Synthesis of grafted core–shell γ -Fe₂O₃-polymer MNPs (Carboxyl-Adembeads, 300 nm) **MNP-1–MNP-4** from metallodendritic catalysts 1–4, respectively.

phosphine groups of compound **15** with Pd^{II} gave metallodendron **3**, which contained three N(CH₂PCy₂)₂-[Pd^{II}] catalytic groups. The completion of the reaction was determined by ³¹P NMR spectroscopy with the disappearance of a signal at $\delta = -17.7$ ppm, which was assigned to the free phosphine, and the appearance of a signal at $\delta = 27.7$ ppm, which was assigned to the coordinated phosphine. Synthesis of [Pd]-functionalized dendron 4: The nonabranched dendron 4 was functionalized at its periphery by bis(dicyclohexylaminomethylphosphine)palladium(II), N-(CH₂PCy₂)₂-[Pd^{II}]. This metallodendron was synthesized as shown in Scheme 4. Coupling of triazido phenol dendron 16 with compound 10^[22] in the presence of K₂CO₃ in DMF yielded dendron 17, which contained nine peripheral azide groups. Nona-azido dendron 17 was treated with KOH and then coupled with Teoc-protected 1-iodoaminohexane^[23] to

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Scheme 2. Synthesis of dendrons 1 and 2. Reagents and conditions: i) HCHO, HPR₂, MeOH/toluene 2:1?, 12 h, 70 °C \rightarrow RT; ii) Bu₄NF, THF, 5 h, 60 °C; iii) Pd(OAc)₂, CH₂Cl₂, 2 h, RT.

with [Pd^{II}] led to metallodendron 4, which contained nine N(CH₂PCy₂)₂-[Pd^{II}] catalytic groups. Completion of this final step was confirmed by the disappearance of the freephosphine signal in the ³¹P NMR spectrum at $\delta =$ -18.4 ppm and the appearance of the coordinated-phosphine signal at $\delta = 27.3$ ppm.

The optimization of the grafting of 1 versus 2 versus 3 versus 4 onto core–shell γ -Fe₂O₃/polymer nanoparticles was evaluated through the catalytic efficiencies of their corresponding MNPs, (**MNP-1**–accupling reactions

generate dendron 18. Azido groups of compound 18 were reduced into primary amine groups by using the Staudinger reduction described previously, thereby leading to nonaamine dendron 19. Aminophosphine dendron 20 was then obtained by the phosphinomethylation of compound 19 in the presence of HPCy₂ and paraformaldehyde. The deprotection of the terminal amino group of compound 20 was carried out with Bu_4NF at 60 °C, thereby leading to dendron 21. Complexation of the phosphine groups of compound 21 MNP-4) in Suzuki C–C cross-coupling reactions.

Grafting of the dendrons onto MNPs: Core–shell γ -Fe₂O₃/ polymer 300 nm superparamagnetic nanoparticles (Carboxyl-Adembeads 300 nm, Ademtech, France, COOH: 300 µmol g⁻¹ of particles) were used as MNP supports.^[24] The grafting of dendrons **2–4** were performed and optimized as reported previously for dendron **1**.^[19] By using covalent interactions, the terminal amine groups at the focal point of



Scheme 3. Synthesis of dendron 3. Reagents and conditions: i) TMSCl, NaI, MeCN, 70 °C, 24 h; ii) NaN₃, DMF, RT, 12 h; iii) 9, K_2CO_3 , DMF, RT, 48 h; iv) K_2CO_3 , H_2O , DMF, 40 °C, 48 h; v) KOH, DMF, RT, 20 min; vi) DMF, RT, 4 h; vii) PPh₃, H_2O , THF, 40 °C, 12 h; viii) HCHO, HPCy₂, MeOH/toluene 2:1, 12 h, 70 °C \rightarrow RT; ix) Bu_4NF , THF, 60 °C, 5 h; x) Pd(OAc)₂, CH₂Cl₂, RT, 20 min.

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Scheme 4. Synthesis of dendron 4. Reagents and conditions: i) 10, K_2CO_3 , DMF, RT, 72 h; ii) K_2CO_3 , H_2O , DMF, 40°C, 48 h; iii) KOH, Teoc-protected 6-iodo-aminohexane, DMF, RT, 3 h; iv) PPh₃, H_2O , THF, 40°C, 12 h; v) HCHO, HPCy₂, MeOH/toluene 2:1, 12 h, 70°C \rightarrow RT; vi) Bu₄NF, THF, 60°C, 5 h; vii) Pd(OAc)₂, CH₂Cl₂, RT, 2 h.

dendrons 1-4 were coupled with COOH groups on the MNP polymer shells. The grafting solvents and the coupling agents were chosen to obtain optimal colloidal states of both the starting MNPs and of the resulting grafted MNPs. This parameter could be directly evaluated by the catalytic activity of the grafted MNPs, because it had a direct effect on the catalytic activity. For all of the dendrons studied, the grafting was performed in organic/aqueous media with MeOH/Tx^[25] (1:2) in the presence of carbodiimide CHMC (CHMC = N-cyclohexyl-N'-(2-morpholinoethyl)carbodiimide metho-p-toluenesulfonate) as a coupling agent, with 10 equivalents of dendron for compounds 1-3 and 4 equivalents of dendron for compound 4, overnight at room temperature. Indeed, in our previous work, the optimized dendron loading during the grafting procedure was found to be 10 equivalents for three branched dendrons.^[19] For comparison, this parameter needed to be re-evaluated in the case of nona-branched dendrons. The loading of dendron 4 was increased from 2 to 8 equivalents, based on the number of accessible free carboxylic acid groups on the polymer shell.^[26] The grafting efficiency was then estimated by performing a Suzuki reaction (Figure 1). However, to perform these experiments, a preliminary dissolution of the dendron in DMF (30 mm) was necessary to improve its solubility in the grafting reaction medium. ICP-MS (inductively coupled plasma mass spectroscopy) measurements showed an effective grafting of 60% for three branched dendrons 1-3, which corresponded to 544-552 µmol of catalytic sites per gram of particles and an effective grafting of 19.5% for nona-branched dendron 4,^[27] which corresponded to 526 μ mol g⁻¹. It is noteworthy that this number of catalytic sites was about twice the initial amount of free COOH group available on the



Figure 1. Catalytic activity of **MNP-4** versus the number of equivalents of dendron **4** used during the grafting reaction. Catalytic reactions were performed with 0.125 mg MNP, according to the general procedure (see the Experimental Section).

MNP surface $(300 \,\mu\text{mol}\,g^{-1})$. We should also note that the amount of catalytic sites at the MNPs surface was approximately the same whichever dendron was used. We suggested that, under these conditions, we had reached the best grafting as possible.

Catalytic performance of dendron-grafted MNPs in Suzuki C–C cross-coupling reactions: First, the effect of the ligand on the catalytic performance of the grafted catalysts was studied. Thus, the catalytic activity of MNP-1, which contained PCy_2 ligands, was compared to the reactivity of

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MNP-2, which contained $PtBu_2$ ligands. Compounds **MNP-1** and **MNP-2** had the same tridentate dendritic structures and only the nature of the phosphine ligand at the catalytic sites was different. Their reactivities were studied for a range of aryl iodide and bromide substrates and for phenylboronic acid (Table 1).

Table 1. Ligand effect: comparison of the catalytic activities of **MNP-1** and **MNP-2** in the Suzuki cross-coupling reaction.^[a]

	Aryl	Aryl boronic	MNP-1		MNP-2	
	halide	acid	t	Conv.	t	Conv.
			[h]	[%]	[h]	[%]
1		(HO) ₂ B	1	100	1	100
2	Br	(HO) ₂ B	2	89	1	99
3	Br	(HO) ₂ B	2	76	2	99
4	—————Br	(HO) ₂ B	4	99	2	100
5	OHC — Br	(HO) ₂ B	1	100	0.5	100
6	O ₂ N-Br	(HO) ₂ B	1	100	0.5	92
7	Br	(HO) ₂ B	4	68	3	96

[a] Reaction conditions: see the Experimental Section. T=65 °C, THF/Tx (1:9), 2.4 mol% [Pd]. Conversions were determined by GC analysis.

Catalyst **MNP-2**, which contained di-*tert*-butyl phosphine ligands, appeared to be much more efficient than its dicyclo-hexylphosphine counterpart, **MNP-1**: complete conversion of bromobenzene was obtained within 1 h with **MNP-2** whilst 2 h was necessary to afford 89% conversion with **MNP-1** (Table 1, entry 2). This difference in reactivity was more pronounced for activated and sterically hindered aryl bromide substrates (Table 1, entries 3–7): for example, with 2,6-dimethylbenzene (Table 1, entry 7) 96% conversion was reached in 3 h with **MNP-2** whereas 4 h was required to afford 68% conversion with **MNP-1**.

To investigate the dendritic effect, we compared the catalytic performances of MNP-1 and MNP-3 to those of MNP-4. These three MNPs all contained the same catalytic groups and PCy₂ ligands. Thus, tri-branched MNP-3, which contained a spacer group, was compared to MNP-1, and to MNP-4, which was the nona-branched analogue of MNP-1. These structural modifications had a dramatic effect on the catalytic performance of these catalysts (Table 2). The results clearly indicated an increase in the catalytic reactivities for MNP-3 and MNP-4 with respect to MNP-1: for MNP-3 (with spacer groups), a decrease in the steric hindrance between catalytic sites, owing to lengthening of the branches, improved its catalytic performance compared to MNP-1. This improvement was noted for activated (Table 2, entries 5 and 6) and deactivated aryl bromide substrates (Table 2, entries 3, 4, 8, and 10) and in the presence of sterically hin-

Table 2. Dendritic structural effect: comparison of the catalytic efficient	n-
cies of MNP-1, MNP-3, and MNP-4 in the Suzuki cross-coupling re-	e-
action. ^[a]	

	Aryl	Aryl boronic	MNP-1		MNP-3		MNP-4	
	halide	acid	<i>t</i> [h]	Conv. [%]	<i>t</i> [h]	Conv. [%]	<i>t</i> [h]	Conv. [%]
1		(HO) ₂ B	1	100	1	100	1	100
2	Br	(HO) ₂ B	2	89	0.5	100	1	100
3	Бr	(HO) ₂ B	2	76	1	98	2	91
4	————Br	(HO) ₂ B	4	>99	1	100	2	94
5	OHCBr	(HO) ₂ B	1	100	0.5	100	0.5	100
6	O ₂ N-Br	(HO) ₂ B	1	100	0.5	100	0.5	100
7	⟨Br	(HO) ₂ B	1	93	1	100	1	100
8	Br	(HO) ₂ B	4	92	1	92	2	91
9	Br	(HO) ₂ B	4	68	2	100	3	98
10	Br	(HO) ₂ B	4	43	_	-	3	88

[a] Reaction conditions: see the Experimental Section. T=65 °C, THF/Tx (1:9), 2.4 mol % [Pd]. Conversions were determined by GC analysis.

dered aryl boronic acid (Table 2, entries 7–9). The secondgeneration catalyst **MNP-4** (nona-branched analogue of **MNP-1**) also showed improved reactivity, but to a lesser extent. Indeed, the increased number of catalytic sites at the dendron periphery allowed the complete conversion of sterically hindered substrates in 1–2 h (Table 2, entries 7–9). However, the most-significant improvement was with **MNP-3**, in which the dendritic branches were lengthened by spacer groups.

Recovery of dendron-grafted MNPs: The recovery procedure of MNP-1-MNP-4 was optimized by using an external permanent magnet.^[28] Thus, once the reaction had been completed, a magnet was used to separate the MNPs from the supernatant. After the separation was complete, and when the particles were held against the walls of the vial, the supernatant was removed. This procedure was repeated after each catalytic cycle. An interesting feature of this softseparation technique was that it ensured minimal loss and easy separation of the grafted MNPs as well as the reusability of the catalyst. Thus, the recovery of MNP-1-MNP-4 from the coupling reaction between iodobenzene and phenyl boronic acid (Figure 2) was investigated.^[29] In the same way as for MNP-1,^[19] almost no significant loss of activity was observed for all of the catalysts, even after 25 cycles. Remarkably, the conversions remained between 95 and 100% up to the 25th cycle. The slight decrease in reactivity was probably due a progressive aggregation of the par-

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Figure 2. Recovery of grafted **MNP-1–MNP-4**. Reaction conditions: see the Experimental Section, with grafted MNP materials (5 mg, 4.8 mol % [Pd]). The mixture was stirred for 1 h at 65 °C in THF/Tx (1:9).

ticles in the reaction medium as the number of recovery cycles increased. This aggregation mostly resulted from slight alterations in the polymer shells of the particles. Indeed, in the case of **MNP-1**, the amount of particles lost between each cycle was negligible: ICP-MS analysis showed 4 ppm of Fe in the crude product (0.006% loss of Fe per cycle).

Also, the leaching or decomposition, as often observed in these catalytic systems,^[29] was weak: 14 ppm of [Pd] in the crude product by ICP-MS (0.36 % loss of [Pd] per cycle).

Conclusion

This work has highlighted the widespread use of dendritic structures for the grafting of core-shell y-Fe₂O₃/polymer 300 nm superparamagnetic nanoparticles. We have synthesized highly active catalysts for a range of arylbromo derivatives. The presence of chelating diphosphine groups on the dendron ensured their stability and was a key feature in their efficiency. The catalytic performance of the nanocatalysts was optimized for the Suzuki C-C cross-coupling reaction, and we found that compound MNP-3, which had long dendritic branches, was the most-suitable catalyst. Indeed, its catalytic sites were kept apart from each other, thereby preventing the steric hindrance that is often responsible for lower catalytic efficiency. Furthermore, we have demonstrated the remarkable importance of adjusting the dendritic structures and the nature of the phosphine to optimize the catalytic efficiency of the grafted MNPs. Interestingly, all of these grafted catalysts could be recovered-and efficiently reused-by magnetic separation with no significant loss of reactivity, even after 25 cycles. These results indicated a good stability of these MNP catalysts towards the reaction medium, which was converse to the precipitation techniques we have previously experienced.^[31] In fact, these grafted catalysts were stable and environmentally friendly, as shown by

the low amount of Pd leaching (0.36% loss of [Pd] per cycle; 14 ppm [Pd] in thr crude product) and their efficient recovery (0.006% loss of Fe per cycle; 4 ppm Fe in the crude product). Therefore, nanocatalysts appear to be promising tools both economically and environmentally for the development of sustainable catalysts in accordance with green methodologies.

Experimental Section

All reactions were performed under a nitrogen atmosphere using standard glassware. The starting materials were obtained commercially and used without further purification. The solvents were dried according to standard procedures and saturated with nitrogen. ¹H, ¹³C, and ³¹P NMR spectra were recorded on the following spectrometers: Bruker DPX 200 FT NMR spectrometer (1H: 200.16, 13C: 50.33, 31P: 81.02 MHz), Bruker AC 250 FT NMR spectrometer (¹H: 250.13, ¹³C: 62.90 MHz), Bruker Avance 300 FT NMR spectrometer (1H: 300.13, 13C: 75.46, 31P: 121.49 MHz), Bruker Avance II 400 FT NMR spectrometer (1H: 400.13, ¹³C: 100.62, ³¹P: 161.97 MHz). Chemicals shifts are reported in parts per million (δ) against referenced solvent signals. MALDI-TOF spectra were performed by CESAMO (Université Bordeaux 1, France) on a Voyager mass spectrometer (Applied Biosystems). The instrument was equipped with a pulsed N₂ 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 at the CNRS-Vernaison, France. GC spectra were recorded on a Varian star 3900 gas chromatograph equipped with a fused-silica capillary column heated gradually from 40 °C to 250 °C (rate 10 °C min⁻¹) with He as a vector gas at a column head pressure of 10 psi. An FID detector was used. Yields were calculated by integration of the product peaks (Star chromatography workstation 5.50) after determination of the response coefficient of each product versus each bromoarene reagent. For column chromatography, Merck silica gel 60 (230-400 mesh) was used.

Compound 1, 5, 6a, and 7a: Compounds **1**, **5**, **6a**, and **7a** were synthesized according to a literature procedure, see Ref. [19].

Compound 2, 6b and 7b: Compounds **2, 6b**, and **7b** were synthesized according to a literature procedure, see Ref. [20].

Compound 3: A mixture of compound 15 (1.14 g, 0.57 mmol) and Pd-(OAc)₂ (384 g, 1.71 mmol) was stirred in CH₂Cl₂ (15 mL) at RT under an inert atmosphere for 20 min. Then, the mixture was evaporated and the product dried under vacuum to give compound 3 as a brown powder (1.5 g, 100%). ¹H NMR (200 MHz, CD₂Cl₂, 25°C): $\delta = 7.09$ (d, ³J(H,H) = 8 Hz, 8H; CH_{ar}), 6.80 (d, ${}^{3}J(H,H) = 8$ Hz, 8H; CH_{ar}), 3.86 (m, 8H; 6H; CH_2CH_2N), $CH_2O)$ 2.78 (m. 2.7 - 2.5(m, 20H· NCH₂P+CH₂NCH₂P+CH₂NH₂), 1.94 (s, 18H; CH_{3(OAc)}), 1.7-1.1 ppm (m, 152H; $CH_{(Cy)}+CH_{2(Cy)}+CH_{2}$; ¹³C NMR (75.46 MHz, CD₂Cl₂, 25 °C): $\delta =$ 177.2 (Cq(OAc)), 158.2 (COar), 39.0 (Cq(ar)), 31.2 (Cq(ar)), 130.0 (CHar), 127.9 (CH_{ar}), 114.8 (CH_{ar}), 68.9 (CH₂O), 64.4 (CH₂NCH₂P), 48.6 (d; CH₂P), 35.8 (CH_2C_q) , 35.5 $(CH_{3(OAc)})$, 31.9 $(CH_2CH_2N),$ 29.1 (d. $CH_{2(Cy)}+PCH_{(Cy)})$, 27.5 ($CH_{2(Cy)}$), 26.3 ($CH_{2(Cy)}$), 24.1 ppm (CH_{2}); ³¹P NMR (81.02 MHz, CD₂Cl₂, 25 °C): $\delta = 26.4$ ppm; elemental analysis calcd (%) for $C_{136}H_{222}N_4O_{16}P_6Pd_3$: C 61.1, H 8.37, N 2.1, Pd 11.9; found: C 59.9, H 7.5, N 2.0, Pd 12.7.

Compound 4: A mixture of compound **22** (2.5 g, 0.5 mmol) and Pd(OAc)₂ (1.02 g, 4.5 mmol) was stirred in CH₂Cl₂ (10 mL) at RT under an inert at mosphere for 2 h. Then, the reaction mixture was evaporated and the product was dried under vacuum to give compound **4** as a brown powder (3.5 g, 100%). ¹H NMR (400 MHz, CD₂Cl₂, 25°C): δ =7.18 (m, 8H; CH_{ar}), 6.84 (m, 8H; CH_{ar}), 3.87 (m, 8H; CH₂O), 2.5–2.2 (m, 56H; NCH₂P+CH₂NCH₂P+CH₂NH₂), 1.90 (s, 54H; CH_{3(OAc)}), 1.8–1.1 ppm (m, 452 H; CH₂); ¹³C NMR (100 MHz, CD₂Cl₂, 25°C): δ =157.6 (CO_{ar}), 137.7 (C_{q(ar})), 127.5 (CH_{ar}), 114.2 (CH_{ar}), 68.4 (CH₂O), 63.5 (CH₂NCH₂P), 59.0 (C_{ar}C_q), 48.6 (CH₂P), 43.1 (CH₂C_q+CH₂NH₂), 35.5 (CH_{3(OAc)}), 30.2 (PCH_(Cy)), 29.6 (CH₂(_{Cy)}), 27.2 (CH₂(_{Cy)}), 26.2 ppm (s, CH₂(_{Cy})); ³¹P NMR

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(160 MHz, CD₂Cl₂, 25 °C): δ = 27.3 ppm; elemental analysis calcd (%) for C₃₄₀H₅₈₈N₁₀O₄₀P₁₈Pd₉: C 58.5, H 8.5, P 8.0, Pd 13.7; found: C 56.1, H 8.2, P 7.8, Pd 13.7.

Compound 8: A mixture of tyrosol (4 g, 28.9 mmol), NaI (21.6 g, 145 mmol), TMSCl (18.4 mL, 145 mmol), and CH₃CN (25 mL) was stirred at 70 °C in a sealed Schlenk tube for 24 h. The solvent was removed and the crude product was dissolved in water (20 mL) and extracted with EtO₂ (4×20 mL). The organic layers were collected, washed with a saturated aqueous solution of Na₂S₂O₃, and dried over MgSO₄. The solvent was removed under reduced pressure to give compound **8** as a white solid (6.8 g, 95%). ¹H NMR (250 MHz, CDCl₃, 25°C): δ =7.06 (d, ³*J*(H,H)=8 Hz, 2H: CH_{ar}), 6.79 (d, ³*J*(H,H)=8 Hz, 2H; CH_{ar}), 3.31 (t, ³*J*(H,H)=7 Hz, 2H; CH₂L), 3.10 ppm (t, ³*J*(H,H)=7 Hz, 2H; CH₂CH₂L); ¹³C NMR (62.90 MHz, CDCl₃, 25°C): δ =154.4 (CO_{ar}), 133.1 (C_{q(ar)}), 129.7 (CH_{ar}), 115.6 (CH_{ar}), 39.6 (CH₂), 6.6 ppm (CH₂I); MS (EI): *m/z* (%): 247.8 (12) [*M*]⁺, 120.8 (100) [*M*–I]⁺.

Compound 9: A mixture of compound **8** (1.6 g, 6.45 mmol) and NaN₃ (2.1 g, 32.2 mmol) was stirred in DMF (5 mL) at RT for 12 h under a nitrogen atmosphere. Water (15 mL) was added and the mixture was extracted with Et₂O (3×20 mL). The organic layers were collected, washed with water (10×20 mL), and dried over anhydrous MgSO₄. The solvent was removed under reduced pressure to afford compound **9** as a brown oil (1.0 g, 95%). ¹H NMR (250 MHz, CDCl₃, 25°C): δ =7.11 (d, ³*J*-(H,H)=8 Hz, 2H; CH_{ar}), 6.87 (d, ³*J*(H,H)=8 Hz, 2H; CH_{ar}), 3.48 (t, ³*J*-(H,H)=7 Hz, 2H; CH₂N₃), 2.85 ppm (t, ³*J*(H,H)=7 Hz, 2H; CH₂); ¹³C NMR (62.90 MHz, CDCl₃, 25°C) δ =154.1 (CO_{ar}), 130.0 (C_{q(ar)}), 129.8 (CH_{ar}), 115.4 (CH_{ar}), 52.4 (CH₂N₃), 34.1 ppm (CH₂CH₂N₃); MS (EI): *m*/z (%): 162.9 (16) [*M*]⁺, 106.8 (100) [*M*-CH₂N₃]⁺.

Compound 11: A mixture of azoture 9 (1.0 g, 6.13 mmol) and K₂CO₃ (1.69 g, 12.2 mmol) was stirred in dry DMF (3 mL) at RT for 20 min. A solution of tri-iodo dendron 10 (1.36 g, 2.04 mmol) in DMF (3 mL) was added under an inert atmosphere and the reaction mixture was stirred at RT for 48 h. Then, water (5 mL) and K₂CO₃ (2.5 g, 18.4 mmol) were added and the resulting mixture was stirred at 40 °C for 48 h. Water (20 mL) was added and the product was extracted with Et_2O . The organic layers were collected, washed with water $(10 \times 20 \text{ mL})$, and dried over anhydrous MgSO₄. Solvent was removed under reduced pressure to give a brown oil, which was purified by column chromatography on silica gel (petroleum ether/Et₂O 90:10, then Et₂O) to yield compound 11 as a brown oil (1.09 g, 74%). ¹H NMR (250 MHz, CDCl₃, 25°C): $\delta = 7.09$ (d, ${}^{3}J(H,H) = 8$ Hz, 8H; CH_{ar}), 6.79 (d, ${}^{3}J(H,H) = 8$ Hz, 8H; CH_{ar}), 3.86 (t, ${}^{3}J$ -(H,H) = 7 Hz, 6H; CH₂O), 3.45 (t, ${}^{3}J(H,H) = 7$ Hz, 6H; CH₂N₃), 2.81 (t, ${}^{3}J(H,H) = 7$ Hz, 6H; CH₂CH₂N₃) 1.85–1.5 ppm (m, 12H; CH₂); ${}^{13}C$ NMR (75.46 MHz, CDCl₃, 25 °C) $\delta = 157.8$ (CO_{ar}), 154.8 (CO_{ar}), 138.2 (C_{q(ar)}), 129.9($C_{q(ar)}$), 129.7 (CH_{ar}), 128.2 (CH_{ar}), 115,6 (CH_{ar}), 114.7 (CH_{ar}), 68.3 (CH₂O), 52.7 (CH₂N₃), 42.0 (CarCq), 34.5 (CH₂CH₂N₃), 33.7 (CqCH₂), 23.6 ppm (CH_2CH_2O); elemental analysis calcd (%) for $C_{40}H_{47}N_9O_4{:}$ C 66.9, H 6.6; found: C 66.8, H 6.9.

Compound 12: Triazo dendron 11 (1.44 g, 2 mmol) and KOH (337 mg, 6 mmol) were dissolved in dry DMF (4 mL) in a Schlenk tube and stirred for 20 min at RT. A solution of Teoc-protected 6-iodo-aminohexane (743 mg, 2 mmol) in DMF (2 mL) was added to the reaction mixture, which was then stirred at RT for 4 h. Water was added and the product was extracted with CH₂Cl₂. The organic layer was washed several times with water, dried over MgSO4, and evaporated under reduced pressure. The crude product was purified by column chromatography on silica gel (petroleum ether/Et₂O, 90:10 to 50:50) to give compound 12 as a lightyellow oil (1.4 g, 73%). ¹H NMR (250 MHz, CDCl₃, 25°C): $\delta = 7.12$ (m, 8H; CH_{ar}), 6.82 (m, 8H; CH_{ar}), 4.64 (brs, 1H; NH), 4.15 (t, ${}^{3}J(H,H) =$ 8.5 Hz, 2H; CH₂OCO), 3.93 (t, ³J(H,H)=6 Hz, 2H; CH₂O), 3.86 (t, ³J-(H,H) = 7 Hz, 6H; CH₂O), 3.44 (t, ³J(H,H) = 7 Hz, 6H; CH₂N₃), 3.17 (q, ${}^{3}J(H,H) = 6$ Hz, 2H; CH₂NH), 2.81 (t, ${}^{3}J(H,H) = 7$ Hz, 6H; CH₂CH₂N₃) 1.8–1.2 (m, 20 H; CH₂), 0.97 (t, ${}^{3}J(H,H) = 8.5$ Hz, 2H; CH₂Si), 0.04 ppm (s, 9H; CH₃Si); ¹³C NMR (75.46 MHz, CDCl₃, 25 °C) $\delta = 157.8$ (C= $O+CO_{ar}$), 156.8 (CO_{ar}), 138.6 ($C_{q(ar)}$), 130.0 ($C_{q(ar)}$), 129.8 (CH_{ar}), 127.5 (CH_{ar}), 114,7 (CH_{ar}), 114.1 (CH_{ar}) 68.4 (CH₂O), 67.9 (CH₂O), 63.0 (CH₂OCO), 52.8 (CH₂N₃), 42.1 (C_{ar}C_q), 41.0 (CH₂NH), 34.6 (CH₂CH₂N₃), 33.8 (CH₂C_q), 30.1 (CH₂), 29.3 (CH₂), 26.6 (CH₂), 26.0 (CH₂), 23.7 (CH₂), 17.9 (CH₂Si), -1.3 ppm (CH₃Si); MS (MALDI): *m/z* calcd for C₅₂H₇₂N₁₀O₆Si+Na⁺: 983.58 [*M*+Na]⁺; found: 983.53; elemental analysis calcd (%) for C₅₂H₇₂N₁₀O₆Si: C 65.0, H 7.6, N 14.5; found: C 65.3, H 8.0, N 13.2.

Compound 13: A mixture of triazo dendron 12 (990 mg, 1.03 mmol), PPh₃ (4.05 g, 15.4 mmol), and H₂O (20 µL, 15.5 mmol) in THF (5 mL) was heated to 40 °C for 12 h. Then, the solvent was removed under reduced pressure. The residue was dissolved in a minimum volume of CH₂Cl₂, and pentane was added to form a precipitate, which was washed several times with pentane to yield compound 13 as a light-yellow powder (630 mg, 69%). ¹H NMR (200 MHz, CDCl₃, 25°C): $\delta = 7.07$ (d, ${}^{3}J(H,H) = 8$ Hz, 8H; CH_{ar}), 6.78 (d, ${}^{3}J(H,H) = 8.5$ Hz, 8H; CH_{ar}), 4.14 (t, ${}^{3}J(H,H) = 8.5 \text{ Hz}, 2H; CH_{2}OCO) 3.95-3.87 \text{ (m, 8H; CH}_{2}O), 3.15 \text{ (q, }^{3}J-$ (H,H) = 6 Hz, 2H; CH₂NH), 2.91 (t, ³J(H,H) = 6 Hz, 6H; CH₂CH₂NH₂), 2.66 (t, ${}^{3}J(H,H) = 6.5$ Hz, 6H; CH₂NH₂), 1.9–1.4 (m, 20H; CH₂), 0.96 (t, ${}^{3}J(H,H) = 8.5 \text{ Hz}, 2 \text{ H}; CH_{2}\text{Si}, 0.03 \text{ ppm} (s, 9 \text{ H}; CH_{3}\text{Si}); {}^{13}\text{C NMR}$ (50.33 MHz, CDCl₃, 25°C) $\delta = 157.4$ (C=O+CO_{ar}), 156.8 (CO_{ar}), 138.1 (C_{q(ar)}), 131.5 (C_{q(ar)}), 129.6 (CH_{ar}), 127.3 (CH_{ar}), 114,4 (CH_{ar}), 113.9 (CH_{ar}), 68.2 (CH₂O), 67.6 (CH₂O), 62.7 (CH₂OCO), 43.5 (CH₂NH₂), 41.8 $(C_{ar}C_q)$, 40.8 (CH₂NH), 38.9 (CH₂CH₂NH₂), 33.6 (CH₂C_q), 29.9 (CH₂), 29.2 (CH₂CH₂O), 26.4 (CH₂), 25.7 (CH₂), 23.6 (CH₂), 17.7 (CH₂Si), -1.5 ppm (CH₃Si); MS (MALDI): m/z calcd for C₅₂H₇₈N₄O₆Si+2H⁺: 442.80 [*M*+2H]⁺; found: 442.79.

Compound 14: A mixture of dicyclohexylphosphine (1.56 g, 47.89 mmol) and paraformaldehyde (1.25 g, 41.6 mmol) in MeOH/toluene (2:1, 5 mL) was heated to 70°C for 10 min. A solution of triamino dendron 13 (900 mg, 1.02 mmol) in MeOH/toluene (2:1, 10 mL) was added, and the mixture was stirred at 70 °C for 10 min and then at RT for 12 h. The volume of the reaction mixture was reduced under vacuum and MeOH was added. The residue was isolated from the medium, washed several times with MeOH, and dried under vacuum to yield compound 14 as a light-gray powder (1.6 g, 73 %). ¹H NMR (250 MHz, CDCl₃, 25 °C): $\delta =$ 7.06 (d, ${}^{3}J(H,H) = 7$ Hz, 8H; CH_{ar}), 6.73 (d, ${}^{3}J(H,H) = 7$ Hz, 8H; CH_{ar}), 4.11 (t, ³*J*(H,H)=7 Hz, 2H; CH₂OCO), 3.9–3.8 (m, 8H; CH₂O), 3.14 (q, 2H; CH₂NH), 2.90 (t, 6H; CH₂CH₂NH₂), 2.79 (s, 12H; NCH₂P) 2.63 (t, 6H; CH₂NCH₂P), 1.7–1.1 (m, 152H; CH_(Cy)+CH_{2(Cy)}+CH₂), 0.97 (t, 2H; CH₂Si), 0.00 ppm (s, 9H; CH₃Si); ¹³C NMR (75.46 MHz, CDCl₃, 25°C) $\delta = 157.3$ (C=O+CO_{ar}), 156.9 (CO_{ar}), (132.6 (C_{q(ar)}), 129.8 (CH_{ar}), 128.5 (CHar), 114,3 (CHar), 68.5 (CH2O), 62.8 (CH2OCO), 58.1 (CH2NCH2P), 52.6 (CH₂P), 41.8 (C_{ar}C_a), 40.7 (CH₂NH), 33.7 (3C; CH₂C_a), 33.0 (d, PCH_(Cy)), 31.3 (3C; CH₂CH₂N), 29.8 (dd; CH_{2(Cy)}), 27.6 (CH_{2(Cy)}), 26.7 (CH_{2(Cy)}), 25.9 (CH₂), 23.9 (CH₂), 17.8 (CH₂Si), -1.4 ppm (CH₃Si); ³¹P NMR (81.02 MHz, CDCl₃, 25 °C, H₃PO₄) $\delta = -17.7$ ppm; MS (MALDI): m/z calcd for $C_{130}H_{216}N_4O_6P_6Si+H^+$: 2144.49 [M+H]+; found: 2143.86; elemental analysis calcd (%) for C₁₃₀H₂₁₆N₄O₆P₆Si: C 72.8, H 10.1, N 2.6; found: C 70.9, H 10.0, N 2.6.

Compound 15: A mixture of compound 14 (1.58 g, 0.74 mmol), tetrabutylammonium fluoride (1 m in THF, 7.4 mL, 7.4 mmol), and THF (10 mL) was stirred under an inert atmosphere at 60 °C for 5 h. Then, the solvent was removed under reduced pressure and the residue was washed several times with ice-cold MeOH. The product was dried under vacuum to give compound 15 as a white powder (1.08 g, 73%). ¹H NMR (250 MHz, $CDCl_3$, 25°C): $\delta = 7.11$ (d, ${}^{3}J(H,H) = 8$ Hz, 8H; CH_{ar}), 6.78 (d, ${}^{3}J(H,H) =$ 8 Hz, 8 H; CH_{ar}), 3.9–3.8 (m, 8 H; CH₂O), 2.9 (m, 6 H; CH₂CH₂NH₂), 2.84 (s, 12H; NCH₂P), 2.7-2.6 (m, 8H; CH₂NCH₂P+CH₂NH₂), 1.8-1.1 ppm (m, 152 H; CH_(Cy)+CH_{2(Cy)}+CH₂); ¹³C NMR (50.33 MHz, CDCl₃, 25°C) $\delta = 157.4$ (CO_{ar}), 144.9 (C_{q(ar)}), 132.1 (C_{q(ar)}), 129.8 (CH_{ar}+C_{q(ar)}) 127.5 (CH_{ar}), 114,3 (CH_{ar}), 68.5 (CH₂O), 58.1 (CH₂NCH₂P), 52.6 (CH₂P), 42.1 (CH₂NH₂), 33.5 (CH₂C_q), 33.0 (d, PCH_{Cy}), 31.3 (CH₂CH₂N), 29.8 (dd; $CH_{2(Cy)}$), 27.4 ($CH_{2(Cy)}$), 26.7 (s; $CH_{2(Cy)}$), 23.9 ppm (CH_2); ³¹P NMR (81.02 MHz, CDCl₃, 25 °C, H₃PO₄) $\delta = -17.7$ ppm; elemental analysis calcd (%) for $C_{124}H_{204}N_4O_4P_6$: C 74.4, H 10.3, N 2.8; found: C 72.4, H 10.2, N 3.0.

Compound 17: A mixture of triazo dendron **16** (3.06 g, 8.42 mmol) and K_2CO_3 (1.75 g, 12.6 mmol) was stirred in dry DMF (2 mL) at RT for 20 min. A solution of triiodo dendron **10** (1.27 g, 1.87 mmol) in DMF (3.5 mL) was added under an inert atmosphere and the reaction mixture was stirred at RT for 72 h. Then water (6.5 mL) and K_2CO_3 (3.25 g,

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23.5 mmol) were added and the resulting mixture was heated to 40 °C for 48 h. Water (20 mL) was added and the product was extracted with Et₂O. The organic layers were collected, washed with water (10×20 mL), and dried over anhydrous Na₂SO₄. Solvent was removed under reduced pressure to give a brown oil, which was purified by column chromatography on silica gel (petroleum ether/Et₂O 70:30, then Et₂O/CH₂Cl₂ 95:5) to yield a light-brown oil (1.88 g, 77%). ¹H NMR (250 MHz, CDCl₃, 25 °C): δ =7.18–7.05 (m, 8H; CH_{ar}), 6.83 (m, 8H; CH_{ar}), 3.88 (t, 6H; CH₂O), 3.22 (t, 18H; CH₂N₃), 1.7–1.5 (m, 24H; CH₂), 1.5–1.2 ppm (m, 24H; CH₂); ¹³C NMR (50.33 MHz, CDCl₃, 25 °C) δ =157.1 (CO_{ar}), 137.4 (C_{q(ar)}), 127.2 (CH_{ar}), 114.3 (CH_{ar}), 68.3 (CH₂O), 52.0 (CH₂N₃), 42.1 (C_{ar}C_q), 34.5 (C_qCH₂), 23.3 ppm (CH₂); MS (MALDI): *m*/z calcd for C₆₄H₈₉N₂₇O₄+Na⁺: 1322.75 [*M*+Na]⁺; found: 1322.71.

Compound 18: Nona-azo dendron 17 (551 mg, 0.42 mmol) and KOH (120 mg, 2.14 mmol) were dissolved in dry DMF (3.5 mL) in a Schlenk tube and stirred for 15 min at RT. A solution of Teoc-protected 6-iodoaminohexane^[32] (157 mg, 0.42 mmol) in DMF (2 mL) was added to the reaction mixture, which was then stirred at RT for 3 h. Water was added and the product was extracted with CH2Cl2. The organic layer was washed several times with water, dried over MgSO4, and evaporated under reduced pressure to give compound 18 as a beige oil (531 mg, 81%). ¹H NMR (300 MHz, CDCl₃, 25°C): $\delta = 7.16$ (d, ³J(H,H) = 8 Hz, 8H; CH_{ar}), 6.82 (d, ${}^{3}J(H,H) = 8$ Hz, 8H; CH_{ar}), 4.67 (brs, 1H; NH), 4.14 $(t, {}^{3}J(H,H) = 8 Hz, 2H; CH_{2}OCO), 3.95-3.8 (m, 8H; CH_{2}O), 3.2-3.0 (m, 8H; CH_{2}O),$ 20H; CH₂NH+CH₂N₃), 1.84–1.66 (m, 8H; CH₂), 1.66–1.3 (m, 30H; CH_2), 1.3–1.1 (m, 18H; CH_2), 0.97 (t, ${}^{3}J(H,H) = 8$ Hz, 2H; CH_2 Si), 0.03 ppm (s, 9H; CH₃Si); ¹³C NMR (50.33 MHz, CDCl₃, 25 °C): $\delta = 157.2$ (CO_{ar}) , 157.0 (CO_{ar}) , 156.9 (C=O), 138.3 $(C_{q(ar)})$, 137.4 $(C_{q(ar)})$, 127.5 (CH_{ar}), 127.2 (CH_{ar}), 114.3 (CH_{ar}), 114.1 (CH_{ar}), 68.4 (CH₂O), 67.7 (CH₂O), 62.9 (CH₂OCO), 52.0 (CH₂N₃), 42.1 (C_qC_{ar}), 42.0 (C_qC_{ar}), 40.9 (CH₂NH), 34.45 (CH₂C_a), 33.9 (CH₂C_a), 30.1 (CH₂), 29.3 (CH₂), 26.6 (CH₂), 25.9 (CH₂), 23.8 (CH₂), 23.3 (CH₂), 17.8 (CH₂Si), -1.4 ppm (CH₃Si); MS (MALDI): m/z calcd for $C_{76}H_{114}N_{28}O_6Si+Na^+$: 1566.92 [*M*+Na]⁺; found: 1566.82.

Compound 19: A mixture of nona-azo dendron 18 (400 mg, 0.26 mmol), PPh₃ (920 mg, 3.5 mmol), and H₂O (140 μ L, 7,78 mmol) in THF (5 mL) was heated to 40 °C for 12 h. The solvent was removed under reduced pressure. Et2O was added and the product was extracted with water. The aqueous layer was washed several times with Et2O and evaporated under reduced pressure to yield compound 19 as a yellow powder (320 mg, 94%). ¹H NMR (250 MHz, $[D_4]$ MeOH, 25°C): $\delta = 7.23$ (d, ³J(H,H) = 8 Hz, 6 H; CH_{ar}), 7.02 (m, 2 H; CH_{ar}), 6.80 (d, ${}^{3}J(H,H) = 8$ Hz, 6 H; CH_{ar}), 6.67 (m, 2H; CH_{ar}), 4.11 (t, ${}^{3}J(H,H) = 8$ Hz, 2H; $CH_{2}OCO$), 3.86 (m, 8H; CH₂O), 3.07 (m, 2H; CH₂NH), 2.52 (m, 18H; CH₂NH₂), 1.9–1.7 (m, 8H; CH_2), 1.7–1.3 (m, 30H; CH_2), 1.22 (m, 18H; CH_2), 0.97 (t, ${}^{3}J(H,H) =$ 8 Hz, 2 H; CH₂Si), 0.04 ppm (s, 9 H; CH₃Si); ¹³C NMR (75.46 MHz, $[D_4]$ MeOH, 25°C): $\delta = 159.1$ (CO_{ar}), 158.2(C=O), 140.2 (C_{q(ar)}), 128.5 (CH_{ar}) , 115,1 (CH_{ar}) , 69.7 (CH_2O) , 63.5 (CH_2OCO) 43.4 (CH_2NH_2) , 43.0 (C_aC_{ar}), 41.6 (CH₂NH), 35.9 (CH₂C_a), 30.9 (CH₂CH₂NH), 30.5 (CH₂CH₂O), 28.2 (CH₂), 27.6 (CH₂), 26.8 (CH₂), 25.9 (CH₂), 25.0 (CH₂), 18.6 (CH₂Si), -1.34 ppm (CH₃Si); MS (MALDI): m/z calcd for $C_{76}H_{132}N_{10}O_6Si+H^+: 1310.02 [M+H]^+; found: 1309.98.$

Compound 20: A solution of 10% dicyclohexylphosphine (8.7 mL, 4.29 mmol) in n-hexane was added to a Schlenk tube and evaporated under reduced pressure. A solution of paraformaldehyde (690 g, 23.0 mmol) in MeOH/toluene (2:1, 10 mL) was added under an inert atmosphere and the reaction mixture was heated to 70 °C for 10 min. A solution of compound 19 (250 mg, 0.19 mmol) in MeOH/toluene (2:1, 5 mL) was added and the mixture was stirred at 70°C for 10 min and then at RT for 12 h. The volume of the reaction mixture was reduced and MeOH was added. The residue was isolated from the medium, washed several times with MeOH, and dried under vacuum to yield compound 20 as a fine yellow powder (810 mg, 83%). ¹H NMR (200 MHz, CDCl₃, 25°C): $\delta = 7.13$ (m, 8H; CH_{ar}), 6.74 (m, 8H; CH_{ar}), 4.12 (m, 2H; CH2OCO), 3.81 (m, 8H; CH2O), 3.19 (m, 2H; CH2NH), 2.67 (s, 36H; $NCH_{2}P$), 2.61 $(m, 18H; CH_2NCH_2P), 1.7-1.0 (m, 454H;$ $CH_{(Cy)}+CH_{2(Cy)}+CH_2$, 0.01 ppm (s, 9H; CH_3 Si); ¹³C NMR (50.33 MHz, CDCl₃, 25 °C): $\delta = 156.7$ (CO_{ar}+C=O), 139.4 (C_{q(ar)}), 127.5 (CH_{ar}), 113,5

 $\begin{array}{l} ({\rm CH}_{\rm ar}),\ 68.2\ ({\rm CH}_{2}{\rm O}),\ 67.7\ ({\rm CH}_{2}{\rm O}),\ 62.9\ ({\rm CH}_{2}{\rm OCO}),\ 56.8\ ({\rm CH}_{2}{\rm N}{\rm CH}_{2}{\rm P}), \\ 52.3\ ({\rm CH}_{2}{\rm P}),\ 42.5\ ({\rm C}_{\rm ar}C_{\rm q}),\ 41.0\ ({\rm CH}_{2}{\rm N}{\rm H})\ 35.5\ ({\rm CH}_{2}C_{\rm q}),\ 32.9\ (d;\ {\rm PCH}_{({\rm cy})}), \\ 29.8\ (dd;\ {\rm CH}_{2({\rm Cy})}),\ 27.5\ ({\rm CH}_{2({\rm cy})}),\ 26.7\ ({\rm CH}_{2({\rm cy})}),\ 24.0\ ({\rm CH}_{2}),\ 20.2\ ({\rm CH}_{2}), \\ 17.8\ ({\rm CH}_{2}{\rm Si}),\ -1.4\ ppm\ ({\rm CH}_{3}{\rm Si});\ ^{31}{\rm P}\ {\rm NMR}\ (81.02\ {\rm MHz},\ {\rm CDCl}_{3},\ 25\ {}^{\circ}{\rm C}, \\ {\rm H}_{3}{\rm PO}_{4})\ \delta=-18.2\ ppm;\ elemental\ analysis\ calcd\ (\%)\ for \\ {\rm C}_{310}{\rm H}_{546}{\rm N}_{10}{\rm O}_{6}{\rm P}_{18}{\rm Si}:\ C\ 73.0,\ {\rm H\ 10.8},\ {\rm N\ 2.75},\ {\rm P\ 10.3};\ found:\ C\ 71.9,\ {\rm H\ 10.8}, \\ {\rm N\ 2.6},\ {\rm P\ 10.5}. \end{array}$

Compound 21: A mixture of compound **20** (3.5 g, 0.69 mmol), tetrabutylammonium fluoride (1 м in THF, 6.9 mL, 6.9 mmol), and THF (10 mL) was heated under an inert atmosphere to 60 °C for 5 h. Then, the solvent was removed under reduced pressure and the residue was washed several times with ice-cold MeOH. The product was dried under vacuum to give compound **21** as a white powder (2.75 g, 81%). ¹H NMR (200 MHz, CDCl₃, 25 °C): δ =7.12 (m, 8H; *CH_a*), 6.73 (m, 8H; *CH_a*), 3.80 (m, 8H; *CH₂*O), 2.68 (s, 36H; NCH₂P), 2.61 (m, 20H; *CH*₂NCH₂P+*CH*₂NH₂), 1.7–1.0 ppm (m, 452H; *CH*_(Cy)+*CH*₂(Cy)+*CH*₂); ¹³C NMR (75.46 MHz, CDCl₃, 25 °C): δ =156.7 (*CO*_{ar}), 137.8 (*C*_{q(ar})), 127.5 (*CH*_{ar}), 133.6 (*CH*₂C_q), 3.0 (d; *PCH*_(Cy)), 30.1 (dd; 72 C, *CH*₂(Cy)), 2.7.5 (*CH*₂Cy), 26.7 (*CH*₂(Cy)), 24.3 (*CH*₂), 20.3 (*CH*₂), 19.9 ppm (*CH*₂); ³¹P NMR (81.02 MHz, CDCl₃, 25 °C, *H*₃PO₄) δ =-18.4 ppm; elemental analysis calcd (%) for C₃₀₄H₅₃₄N₁₀O₄P₁₈: C73.7, H 10.9, P 11.3; found: C 71.8, H 10.7, P 11.05.

General procedure for the grafting of dendrons 1–4 onto core-shell MNPs: Carboxyl-Adembeads 300 nm nanoparticles^[33] (250 μ L, 2.5 mg, 0.75 μ mol CO₂H), a solution of dendron in DMF (see Table 3), and CHMC^[34] (12 mgmL⁻¹, 200 μ L, 5.66 μ mol) were mixed and MeOH/Tx (1:2) was added to adjust the reaction mixture to 1 mL (Table 3). The reaction vessel was shaken in rotators for 16 h at RT. Then, the particles were collected by using an external magnet field and washed several times with NaOH (10 mM), Tx^[25], and THF/Tx (2:1) solutions (1 mL each).

Table 3. Grafting of dendrons 1-4 onto MNPs.

	Dendron	Conc. [µmol]	Weight (equiv) [mg]	DMF [µL]	MeOH/Tx (1:2) [μL]
1	1	7.5	17.5 (10)	200	350
2	2	7.5	15 (10)	200	350
3	3	7.5	20 (10)	200	350
4	4	3	20.9 (4)	200	350

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

Acknowledgements

Financial support from the Université Bordeaux 1, Centre National de la Recherche Scientifique (CNRS), the Region Aquitaine, the Ministère de l'Enseignement Supérieur et de la Recherche (DRA), and the Agence Nationale de la Recherche (ANR-05-JCJC-0245) is gratefully acknowledged.

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- [29] See the general procedure with: MNP-1, MNP-2, MNP-3, or MNP-4 (5 mg, 4.8 mol% [Pd]), NaOH (168 mmol), phenylboronic acid (84.37 mmol), and iodobenzene (56.25 mmol) were mixed in Tx/THF (9:1, 1 mL). The mixture was stirred at 65 °C for 1 h. Then, grafted MNPs were separated by a simple external magnet and were washed with Tx/THF (9:1, 2×500 mL). The particles were washed twice with Tx/THF (9:1) between each run.
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Received: October 6, 2011 Published online: February 6, 2012

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