Copper-Free Monomeric and Dendritic Palladium Catalysts for the Sonogashira Reaction: Substituent Effects, Synthetic Applications, and the Recovery and Re-Use of the Catalysts

Karine Heuzé,*[a] Denise Méry,[a] Dominique Gauss,[a] Jean-Claude Blais,[b] and Didier Astruc*[a]

Abstract: A series of bis(*tert*-butylphosphine)- and bis(cyclohexylphosphine)-functionalized Pd^{II} monomers and polyamino (DAB) dendritic catalysts were synthesized and investigated for Sonogashira carbon–carbon coupling reactions in a copper-free procedure. The influence of phosphine substituents (*t*Bu versus Cy) on the reaction kinetics was investigated by a GPC technique to monitor the reactions. The dendritic catalysts containing the cyclohexylphosphine ligands could be recovered and reused without loss of efficiency until the fifth cycle. The dendritic Pd^{II} catalysts show a negative dendritic effect, that is, the catalyst efficiency decreases as the dendrimer generation increases.

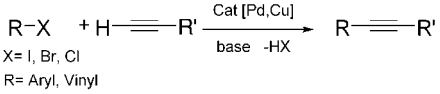
Keywords: catalysis · C–C coupling · dendrimers · P ligands · palladium · star-shaped molecules

Introduction

One of the most promising applications of dendrimers[1] is their use as recoverable and reusable homogeneous catalysts.[2] Indeed, they combine the potential kinetic information available for monomeric homogeneous catalysts and the possibility of insolubilization as for heterogeneous catalysts. The considerable richness and perfection of their molecular definition makes them superior to supported catalysts. The use of metallodendrimers in catalysis has been known for a decade, and reusable dendritic catalysts have started to appear more recently.[3,4]

A large body of work along this line has been achieved by the van Leeuwen and van Koten groups with particular emphasis on membrane filtration for catalyst recovery. Recently, we published a preliminary report on a family of recoverable pallado-dendritic catalysts for the Sonogashira coupling in a copper-free procedure.[4] These catalysts exhibited tremendous differences in their reactivities and recoverabilities that were dependent on the phosphine substituents (*t*Bu versus Cy).

The Sonogashira cross-coupling reaction has become a standard method for the synthesis of functionalized acetylides (Scheme 1). Its popularity is based on its wide tolerance to functional groups, the availability of common aryl halides and access to pharmacologically important compounds.[5] The Sonogashira cross-coupling reaction usually proceeds with Pd^{0}/Cu^{I} catalysts and a base as the solvent,[6] if necessary starting from the more convenient Pd^{II}/Cu^{I} system. Active 14-electron Pd^{0} species are generated in situ by a bis-alkynylation of the Pd complex followed by reductive elimination of diacetylene. Nevertheless, only a few examples of efficient copper-free procedures have been described with aryl bromides or aryl chlorides.[7] Recently, we reported a Pd^{II} complex based on a bulky, electron-rich chelating bis(*tert*-butylphosphine) ligand coordinated to a Pd^{II} center that allowed very high turnover numbers (TONs).[8] The absence of Cu^{I} in the reaction medium allowed avoidance of the oxidative Glaser homo-coupling of the acetylenic reagent.[9]



Scheme 1. Sonogashira coupling of aryl or vinyl halides with alkynes.

Herein, we report an advanced study of the reactivity, kinetics and recoverability of monomeric and dendritic bis-

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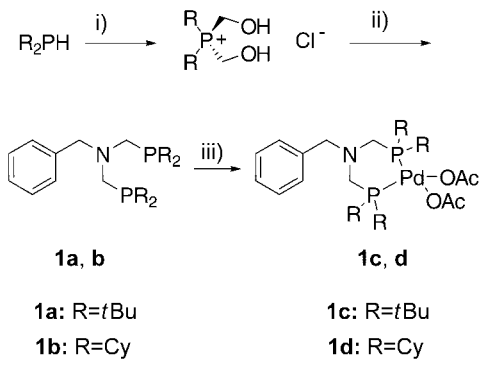
(*tert*-butylphosphine) and bis(cyclohexylphosphine)palladium(II) complexes and an example of their application to the synthesis of star-shaped organoiron-centered and organic molecules.

Results and Discussion

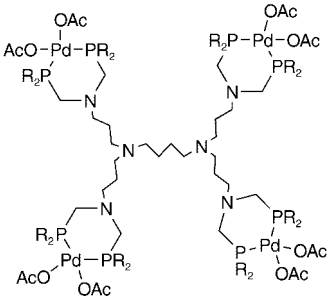
Synthesis and characterization of monomeric and dendritic bis{alkylaminomethylphosphine}palladium(II) complexes: We have synthesized monomeric and dendritic Pd^{II}-based catalysts in which bulky and electron-rich chelating bisphosphine ligands (bis(*tert*-butylphosphines) and bis(cyclohexylphosphines)) are coordinated to a Pd^{II} center. The six dendritic complexes are derived from the commercial polyamino dendrimers DAB-dendr-$(NH_2)_x$ ($x = 4$, 8, or 16 for generation 1, 2, or 3, respectively).

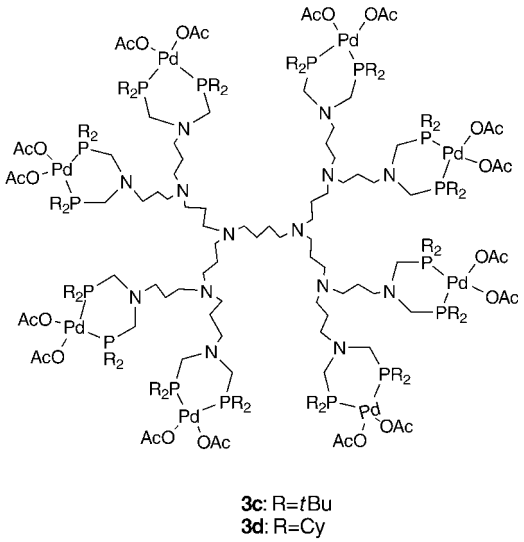
The bis(*tert*-butyl)aminomethylphosphine (**1a**) and bis(cyclohexyl)aminomethylphosphine (**1b**) were obtained from the corresponding phosphines by addition of benzylamine to the bis(*tert*-butyl)- or bis(cyclohexyl)hydroxymethylphosphonium salts according to a known procedure (Scheme 2).[10] The Pd^{II} complexes **1c** and **1d** (Scheme 2) were then readily obtained by treatment of **1a** and **1b**, respectively, with $[Pd(OAc)_2]$.

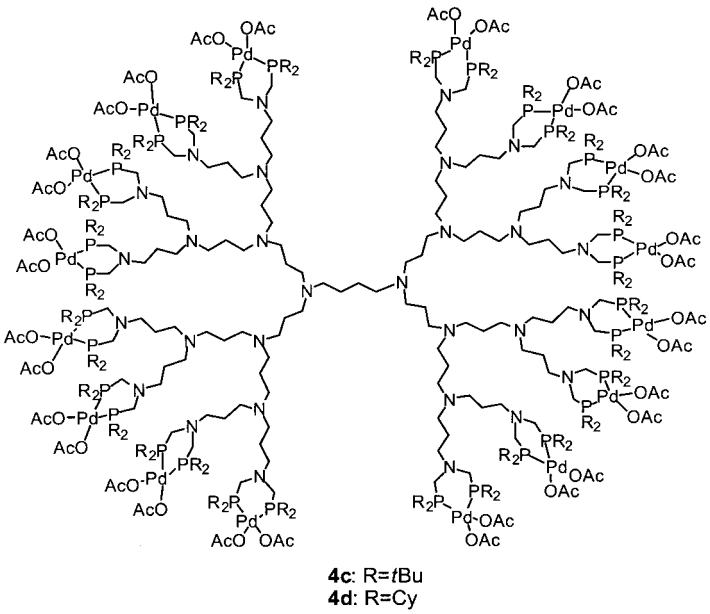


Scheme 2. Synthesis of **1a**–**d**. Reagents and conditions: i) HCHO, HCl; ii) Et_3N, $MeOH/H_2O$, $PhCH_2NH_2$; iii) $[Pd(OAc)_2]$, CH_2Cl_2.

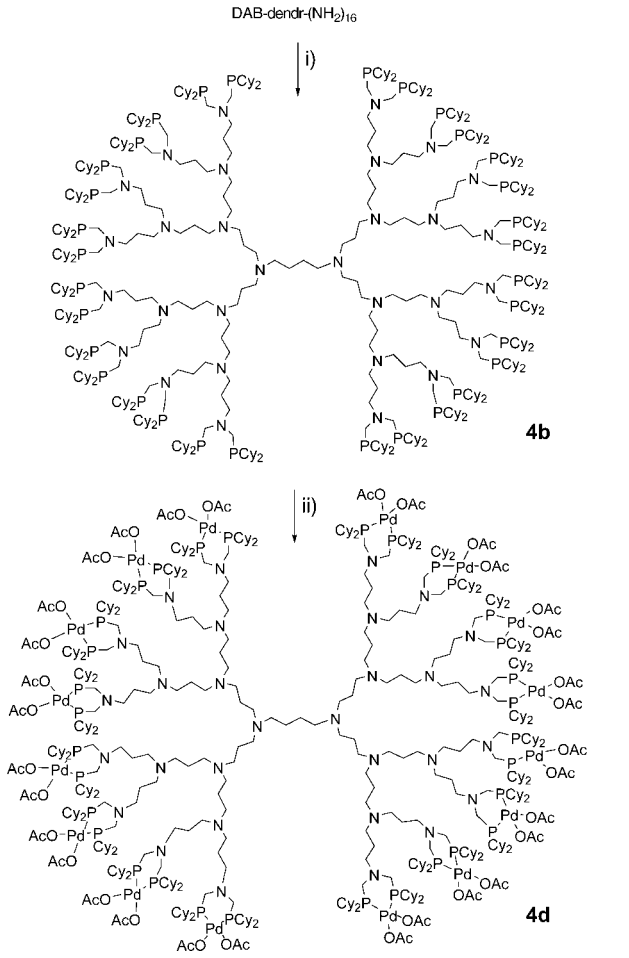
The monomers, the Pd^{II} dendrimers of the first, second, and third generation, **2c**,**d**, **3c**,**d**, and **4c**,**d**, respectively, were readily prepared by treatment of the corresponding aminophosphines **2a**,**b**, **3a**,**b**, **4a**,**b** with $[Pd(OAc)_2]$ (Schemes 3 and 4). All the compounds were characterized by ^1H, ^{13}C, and ^{31}P NMR spectroscopy and by elemental analysis of the Pd^{II} complexes. Chemical shifts of the inner CH_2 of the dendrimers were determined in accordance with the literature.[11]







Complete metallation was established by ^{31}P NMR spectroscopy. Thus, the ^{31}P NMR spectra clearly demonstrate the absence of unreacted phosphine units after complete conversion, which occurs within a few hours at most. The corresponding Pd^{II} complexes **1c**–**4c** (with *tert*-butylphosphine substituents) were very soluble in various solvents (including even pentane) and were stable towards moisture. However, they were stored under nitrogen because since some degradation occurred after a few days in air. Conversely, the Pd^{II} complexes **1d**–**4d** (with cyclohexylphophine substituents) were stable towards air and moisture for at least one year.



Scheme 3. Synthesis of **4b** and **4d**.Reagents and conditions: i) HCHO, HCl, $HPCy_2$; ii) $[Pd(OAc)_2]$, CH_2Cl_2.

DAB-dendr-$[N(CH_2PR_2)_2]_x$ ⟶ DAB-dendr-$[N(CH_2PR_2)_2Pd(OAc)_2]_x$

x= 4 : R=*t*Bu (**2a**); Cy (**2b**)	x= 4 : R=*t*Bu (**2c**); Cy (**2d**)
x= 8 : R=*t*Bu (**3a**); Cy (**3b**)	x= 8 : R=*t*Bu (**3c**); Cy (**3d**)
x= 16 : R=*t*Bu (**4a**); Cy (**4b**)	x= 16 : R=*t*Bu (**4c**); Cy (**4d**)

Scheme 4.

Catalytic C–C cross-coupling between acetylenes and aryl halides: In previous work,[8] the reactivity of **1c** towards aryl iodides, bromides and chlorides was investigated in a Sonogashira copper-free procedure (Table 1). Excellent activity was observed towards aryl iodides with TONs as high as 71000. Good activity was also obtained for aryl bromides and a substantial reactivity was found with aryl chlorides, thus demonstrating the efficiency of bis(*tert*-butylphosphine) ligands in such C–C cross-coupling. Nevertheless, **1d** showed a lower, albeit good, activity towards aryl iodides and bromides in copper-free Sonogashira procedures (Table 2). The conversion observed for aryl iodides and bromides with the dendritic series of catalysts **2c**,**d**, **3c**,**d**, **4c**,**d** revealed the same distinction in the reactivity between the phosphine substituents (*tert*-butyl versus cyclohexyl)(Table 3). Also, a negative dendritic effect was demonstrated for metallodendrimers of the third generation (**4c** and **4d**) for which a lower reactivity was observed (Figure 1).[4]

In all the experiments, triethylamine was chosen both as a base and as a solvent. The functional group tolerance inherent to the Sonogashira reaction, however, means that any co-solvent may be used when required to help solubilize the reagents or to improve the reactivity by increasing the reaction temperature. Thus, solvents other than triethylamine were tested (Table 4). No significant improvement in reactivity with these solvents was observed, however, because a degradation of the catalyst occurred rapidly at such high temperatures as a result of the P–C bond degradation in the phosphine ligands.[12]

Application to the construction of organoiron and organic stars: Recently, we were able to extend the $CpFe^+$-induced hexabenzylation of hexamethylbenzene[5d] to *p*-$BrCH_2$-C_6H_4Br in excellent yields under mild conditions.[13] The hexabenzylated stars bearing bromo substituents in the *para* position of the arene rings are excellent candidates for the Sonogashira reaction.

The cross-coupling of phenylacetylene with the iron complex $[FeCp\{C_6(CH_2CH_2C_6H_4Br_6)_6\}][PF_6]$[13] was investigated (Scheme 5). The good activity (one-step six C–C coupling) and the good tolerance toward functional groups of the Pd catalyst **1c** was demonstrated because the hoped-for iron complex product was obtained. In addition, cross-coupling of phenylacetylene with the iron-free star $C_6(CH_2CH_2C_6H_4Br)_6$ allowed the isolation of the product resulting from cross-coupling (Scheme 5). This original one-step multiple C–C cross-coupling reaction provides a valuable strategy for the synthesis of stars and dendrimers.

Kinetics of the reactions with *t*Bu and Cy ligand-based catalysts: We carried out kinetic investigations in order to obtain a better quantification of the differences in reactivity between the *tert*-butylphosphine- and cyclohexylphosphine-functionalized catalysts. Mechanistic and kinetic studies of Pd^{II} catalytic systems have often been reported in detail and have highlighted the intermediacy of catalytic species in the cross-coupling reactions.[14] Different techniques may be used, such as NMR spectroscopy,[15] analytical techniques (conductivity measurements)[16] or electrochemical techniques (cyclic voltammetry).[17] This study was based on the overall reaction, that is, only the final product was isolated. The *tert*-butyl– and cyclohexylpalladium(II) catalysts **1c** (1 mol%) and **1d** (1 mol%) were used in a typical Sonogashira reaction procedure involving iodobenzene (4 mmol) and phenylacetylene (6 mmol) in Et_3N (10 mL). A GPC technique was used to monitor the appearance of diphenylacetylene and the disappearance of iodobenzene from which the rate constants were determined. To study the kinetics with **1c**, the GPC samples were frozen in liquid nitrogen as soon as they were taken from the reaction because the kinetics were too fast compared to the retention times for each GPC experiment. The variation of $\ln x$ versus time ($x = c/c_0$) was linear for both plots (Figure 2a and b). This establishes an overall reaction order of +1. The observed apparent rate constants k_{obs} for the overall reactions were then

Table 1. Sonogashira coupling of aryl halide substrates with phenylacetylene and the monomeric catalyst **1c**.[a]

Entry	X	R	R′	T[°C]	Catalyst [mol %]	Reaction time	Conversion [%][b]	TON
1	I	C_6H_5	C_6H_5	80	1	15 min	100	100
2	I	C_6H_5	C_6H_5	25	1	30 min	100	100
3	I	C_6H_5	C_6H_5	−20	1	1 day	70	70
4	I	C_6H_5	C_6H_5	−40	1	2 days	51	51
5	I	C_6H_5	$Si(CH_3)_3$	25	1	8 h	76	76
6	I	C_6H_5	C_6H_5	80	0.5	15 min	100	200
7	I	C_6H_5	C_6H_5	80	0.1	2 h	100	1000
8	I	C_6H_5	C_6H_5	80	0.01	1 day	87	8700
9	I	C_6H_5	C_6H_5	80	0.001	7 days	71	71 000
10	Br	C_6H_5	C_6H_5	80	1	20 min	100	100
11	Br	C_6H_5	C_6H_5	25	1	1 h	100	100
12	Br	(*p*-Me)C_6H_5	C_6H_5	80	1	3 h	96	96
13	Br	C_6H_5	$Si(CH_3)_3$	25	1	15 h	54	54
14	Cl	C_6H_5	C_6H_5	80	1	50 min	4	4
15	Cl	C_6H_5	C_6H_5	25	1	3 h	9	9
16	Cl	C_6H_5	$Si(CH_3)_3$	25	1	2 days	5	5
17	Cl	(*p*-CN)C_6H_5	C_6H_5	80	1	5 days	13	13
18	Cl	(*p*-F)C_6H_5	C_6H_5	80	1	5 days	14	14
19	Cl	(*p*-$COOCH_3$)C_6H_5	C_6H_5	25	1	3 days	15	15
20	Cl	(*p*-$COOCH_3$)C_6H_5	C_6H_5	80	2	3 days	30	30
21	Cl	(*p*-$COOCH_3$)C_6H_5	C_6H_5	40	1	3 days	22	22

[a] Reaction conditions: aryl halide (2 mmol), acetylene (3 mmol), Et_3N (6 mL). [b] Yield of isolated product.

Table 2. Sonogashira coupling of aryl halide substrates with phenylacetylene and the monomeric catalyst **1d**.[a]

Entry	X	R	R′	T[°C]	Reaction time	Conversion [%][b]	TON
1	I	C_6H_5	C_6H_5	80	5 h	76	76
2	I	C_6H_5	C_6H_5	45	3 days	100	100
3	Br	C_6H_5	C_6H_5	80	4 h	71	71
4	Cl	C_6H_5	C_6H_5	80	5 h	traces	–

[a] Reaction conditions: aryl halide (2 mmol), phenylacetylene (3 mmol), catalyst **1d** (1 mol %), Et_3N (6 mL). [b] Yield of isolated product.

Table 3. Sonogashira coupling of aryl halide substrates with phenylacetylene and dendrimeric catalysts **2c**,**d**, **3c**,**d** and **4c**,**d**.[a]

Entry	Aryl halide	Solvent	Catalyst [1 mol %]	T[°C]	Reaction time [h][b]	Conversion [%][c]
1	iodobenzene	Et_3N	**2d**	80	24	79
2	iodobenzene	Et_3N	**3d**	80	24	72
3	iodobenzene	Et_3N	**4d**	80	24	46
4	iodobenzene	Et_3N	**2c**	25	15	97
5	iodobenzene	Et_3N	**3c**	25	40	100
6	iodobenzene	Et_3N	**4c**	25	48	100
7	bromobenzene	Et_3N	**2d**	80	48	17
8	bromobenzene	Et_3N	**3d**	80	48	15
9	bromobenzene	Bu_2NH	**3d**	120	20	20
10	bromobenzene	Et_3N	**4d**	80	48	6
11	bromobenzene	Et_3N	**2c**	25	17	100
12	bromobenzene	Et_3N	**3c**	25	48	93
13	bromobenzene	Et_3N	**4c**	25	48	96

[a] Reaction conditions: aryl halide (2 mmol), phenylacetylene (3 mmol), Et_3N (6 mL). [b] The reaction was monitored by TLC. [c] Yield of isolated product.

determined from the slopes of the regression for each plot. The calculated rate constants were 0.925 mol L^{-1} h^{-1} at 25 °C for **1c** and 0.028 mol L^{-1} h^{-1} 27 °C for **1d**. This gives a k(**1c**)/k(**1d**) ratio of ≈33.

Recovery of metallodendritic catalysts: Various techniques can be used to recycle the metallodendritic catalysts.[3a] The most recent one required CFMR devices based on nanofiltration through membranes. Very often, however, the catalyst was recovered by precipitation from the product solution once the reaction was complete.[3b,18]

We have processed a set of recycling experiments based on the precipitation of the metallodendritic catalyst. In a typical procedure, iodobenzene (2 mmol) in Et_3N (8 mL) with catalyst **2d**, **3d** or **4d** (2 mol % based on the catalytic sites) was treated with phenylacetylene (3 mmol) at 80 °C for 48 h. The reaction time was chosen in order to complete all the reactions, even with the dendritic catalyst of third generation whose reactivity is lower than that of the first and second ones (see above). Subsequently, pentane (30 mL) was added to the reaction mixture to precipitate the catalyst and extract the product. The pentane extraction was carried out five times to optimize product recovery. The reactants and solvents were then re-added to the dried catalyst under nitrogen to proceed to the next cycles. The results are summarized in Table 5 and Figure 3. The catalytic activity for all the generations of dendrimers remained the same up to the fifth cycle. However, a significant drop in the activity was observed from the fifth cycle for all the generations of dendrimers. This behavior mostly resulted from a decomposition of the dendritic ligand because no leaching was observed. The subsequent decomposition was confirmed

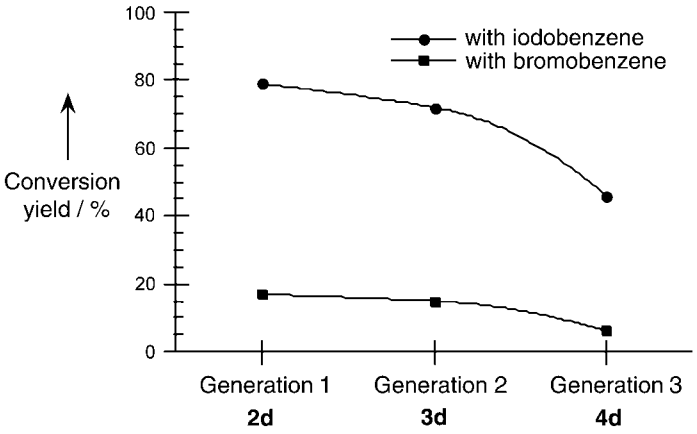


Figure 1. Conversion of aryl halides with phenylacetylene catalyzed by **2d**, **3d**, and **4d** at 80 °C.

Table 4. Solvent effect in the Sonogashira coupling between iodobenzene and phenylacetylene with the dendritic catalyst **3d**.[a]

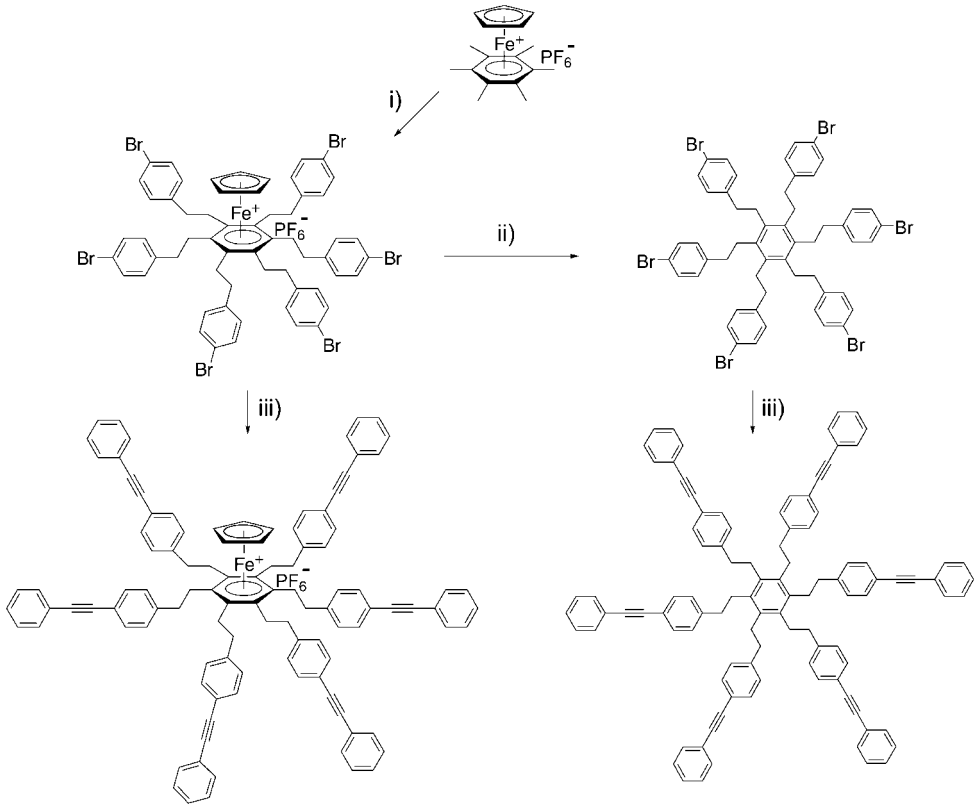
Entry	Solvent	T [°C]	Reaction time [h]	Conversion [%][b]
1	Et_3N	80	5	72
2	Et_3N/DMF	140	3	34
3	Bu_3N	140	8	16
4	Bu_2NH	120	8	31

[a] Reaction conditions: iodobenzene (2 mmol), phenylacetylene (3 mmol), solvent (6 mL). [b] Yield of isolated product.

by ^{31}P NMR analysis of the catalyst after the cycles. Indeed, the appearance of several peaks at $\delta \approx 50$ ppm confirmed the presence of oxidation and decomposition species. However, the signal for the active catalytic species was still observed at $\delta = 25$ ppm (with a slight shift of 2 ppm in comparison with the initial signal of the Pd^{II} catalyst). This decomposition has also been reported with a variety of other dendritic systems that employ either precipitation or other recovery techniques. Interestingly, the fifth cycle often seems to be of crucial importance in the reactivity drop.[18a,19]

Conclusion

New copper-free Sonogashira Pd catalysts were synthesized. that exhibit very good reactivity under mild conditions with aryl iodides, bromides, and even some reactivity with activated aryl chlorides. The catalytic activity was much higher with *t*Bu substituents on the phosphines than with Cy substituents. The monomeric Pd catalyst bearing *t*Bu substituents on the phosphines was applied to the synthesis of organoiron and organic stars whereby six Sonogashira C–C coupling reactions occur. Dendritic versions of these copper-free catalysts were designed, synthesised and used with a reactivity that showed a negative dendritic effect, the largest dendritic catalysts being the less active ones. This negative dendritic effect is attributed to the increasing steric bulk around the active metal centres as the dendrimer generation increases, and this finding confirms similar observations made previously.[20] The kinetics of the reaction, monitored by GPC, are much faster with *t*Bu substituents on the phosphine ligands than with Cy substituents. The dendritic cata-



Scheme 5. Reagents and conditions: i) *p*-Br-$C_6H_5CH_2Br$, KOH, DME, 40 °C, 6 days; ii) PPh_3, MeCN, 24 h, (Xe lamp); iii) phenylacetylene, Et_3N, catalyst **1c**.

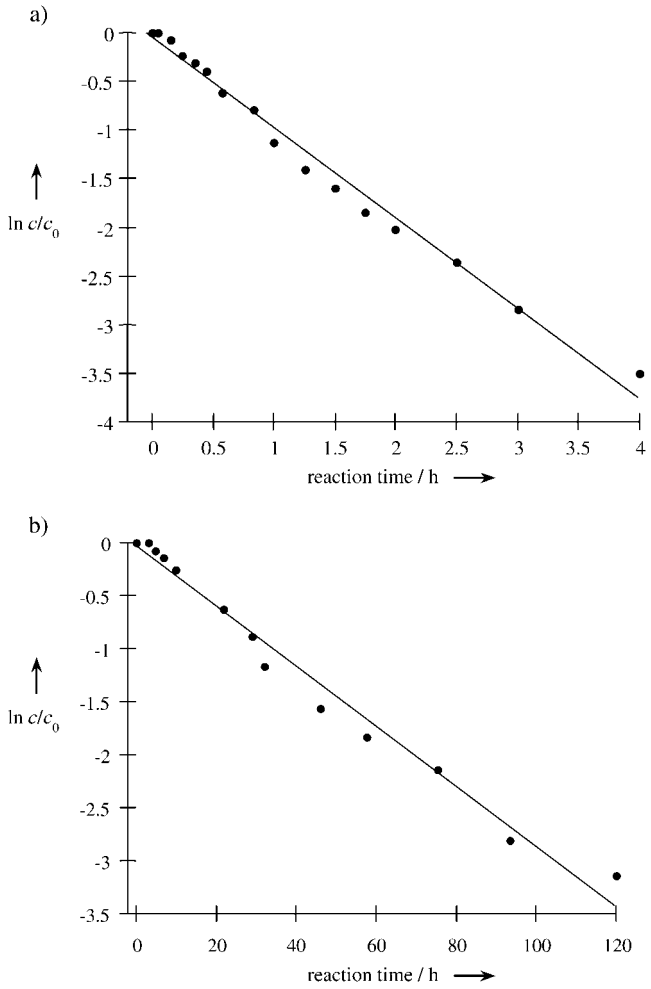


Figure 2. Kinetics of the disappearance of iodobenzene in a Sonogashira reaction with a) **1c** at 25 °C, and b) **1d** at 27 °C. Variation of $\ln(c/c_0)$ versus time (c: concentration of iodobenzene at t, c_0: initial concentration of iodobenzene).

Table 5. Coupling of iodobenzene with phenylacetylene and the dendritic catalysts **2d**, **3d** and **4d**.[a]

Catalyst	Cycle	Conversion [%][b]
2d	first	92
	second	74
	third	61
	fourth	56
	fifth	26
	sixth	26
3d	first	83
	second	66
	third	66
	fourth	71
	fifth	21
	sixth	26
	seventh	16
4d	first	78
	second	70
	third	78
	fourth	76
	fifth	51
	sixth	46
	seventh	39

[a] Reaction conditions: iodobenzene (2 mmol), phenylacetylene (3 mmol), Et_3N (8 mL), catalyst (2 mol %), N_2. [b] Yield of isolated product.

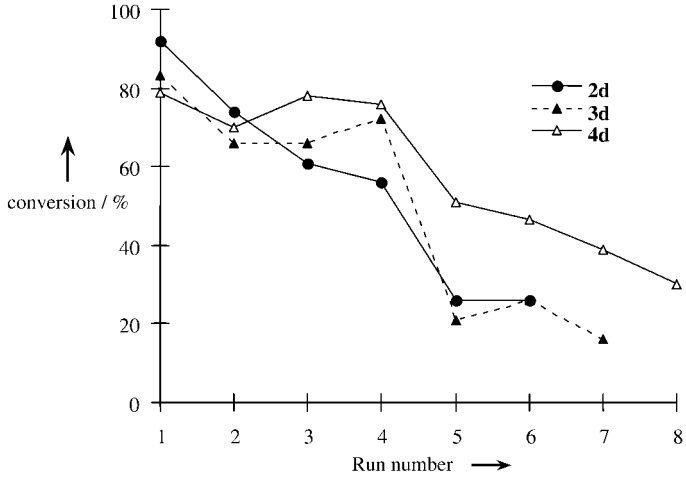


Figure 3. Reaction conditions: iodobenzene (4 mmol), phenylacetylene (6 mmol), catalyst (1 mol %), Et_3N (10 mL), 80 °C, 48 h. The product was extracted and purified by silica gel column chromatography.

lysts with R = Cy are recoverable by precipitation with pentane and can be reused up to five times with a good activity level. However, the dendritic catalysts with R = *t*Bu could not be easily recovered by this method on account of their high solubility in pentane. Ongoing studies are underway in our laboratory in order to investigate catalysts for Pd-catalyzed C–C coupling that are both extremely reactive and recoverable.

Experimental Section

All reactions were performed under a nitrogen atmosphere in standard (Schlenk) glassware. The solvents were dried according to standard procedures and saturated with nitrogen. The ^1H, ^{13}C and ^{31}P NMR spectra were recorded with the following spectrometers: Brucker DPX200 FT NMR spectrometer (^1H: 200.16, ^{13}C: 50.33, ^{31}P: 81.02 MHz), Brucker AC250 FT NMR spectrometer (^1H: 250.13, ^{13}C: 62.90 MHz) and Avance 300 FT NMR spectrometer (^1H: 300.13, ^{13}C: 75.46, ^{31}P: 121.49 MHz). Mass spectroscopic measurements (MALDI-TOF) were performed at the LCSOB, University of Paris 6. The elemental analyses were carried out in the analysis laboratory of the elemental analysis department at CNRS-Vernaison. The starting materials were obtained commercially and were used without further purification.

General procedure for the syntheses of aminophosphine 1a and 1b monomers:

Bis(*tert*-butylaminophosphine) (1a): Triethylamine (0.29 mL, 2.1 mmol) was added to a stirred solution of the phosphonium salt (0.5 g, 2.1 mmol) in water/methanol (2:1, 3 mL). On addition of benzylamine (0.11 mL, 1 mmol) the mixture became viscous, thus toluene (3 mL) was added. The solution was refluxed for 1 h. On cooling, two layers separated, and the organic layer was extracted and dried over sodium sulfate. Methanol was added to precipitate a white gummy solid. The solvents were removed, and the solid was dried under a high vacuum to yield the product as a white solid (385 mg, 91 %). ^1H NMR (200.16 MHz, $CDCl_3$, 300 K): δ = 7.24 (m, 5H, CH_{arom}), 3.79 (s, 2H, CH_2N), 2.73 (s, 4H, PCH_2N), 1.09 (s, 18H, *t*Bu), 1.04 ppm (s, 18H, *t*Bu); $\{^1H\}^{13}C$ NMR (62.90 MHz, $CDCl_3$, 300 K): δ = 130.14 (C_{arom}), 129.1 (C_{arom}), 128.2 (C_{arom}), 127.6 (C_{arom}), 61.0 (CH_2N), 60.7 (PCH_2N), 33.4 (*t*Bu), 27.3 (*t*Bu), 26.9 ppm (*t*Bu); $\{^1H\}^{31}P$ NMR (81.02 MHz, $CDCl_3$, 300 K): δ = 12.9 ppm.

Bis(cyclohexylaminophosphine) (1b): The same procedure as for **1a** was used. Phosphonium salt (1.466 g, 5 mmol), triethylamine (0.68 mL, 5 mmol), benzylamine (0.27 mL, 2.5 mmol). Yield: 1.07 g (82 %) of a

white solid. ^{1}H NMR (200.16 MHz, $CDCl_3$, 300 K): δ = 7.25 (m, 5H, CH_{arom}), 3.77 (s, 2H, CH_2N), 2.82 (s, 4H, PCH_2N), 2.45 (s, 4H, PCH_{Cy}), 2.37 (s, 4H, CH_{Cy}), 1.73–1.21 ppm (m, 40H, $CH_{2,Cy}$); $\{^1H\}^{13}$C NMR (62.90 MHz, $CDCl_3$, 300 K): δ = 129.7 (C_{arom}), 129.1 (C_{arom}), 128.2 (C_{arom}), 127.8 (C_{arom}), 61.4 (CH_2N), 60.7 (PCH_2N), 32.9 (Cy), 29.7 (Cy), 27.3 (Cy), 26.6 ppm (Cy); $\{^1H\}^{31}$P NMR (81.02 MHz, $CDCl_3$, 300 K): δ = −17.4 ppm; elemental analysis calcd (%) for $C_{33}H_{55}P_2N$ (527.75): C 75.10, H 10.50; found: C 73.87, H 10.37.

General procedure for the syntheses of aminophosphine dendrimers 2a, 3a, 4a and monomers 2b, 3b, 4b:

G1-DAB-*dendr*-[bis(*tert*-butylaminophosphine)]$_4$ (2a): Di-*tert*-butylphosphine (1.05 mL, 6 mmol) and paraformaldehyde (0.17 g, 6 mmol) in methanol (5 mL) were heated at 65 °C for 10 min. Upon cooling, DAB-*dendr*-$(NH_2)_4$ (0.2 g, 0.7 mmol) in methanol (3 mL) was added, and the mixture was stirred at room temperature for 30 min. Toluene (15 mL) was added, and the mixture was heated at 65 °C for 30 min. The reaction medium was stirred at room temperature for another 12 h. The solvent was removed under vacuum, and the solid was recrystallised (cold pentane) and dried to yield the aminophosphine dendrimer as a white solid (830 mg, 75 %). ^{1}H NMR (250.13 MHz, $CDCl_3$, 300 K): δ = 2.74 (m, 16H, NCH_2P), 2.39 (m, 20H, NCH_2), 1.24 (m, 12H, CH_2-CH_2), 1.16 (s, 72H, *t*Bu), 1.11 ppm (s, 72H, *t*Bu); $\{^1H\}^{13}$C NMR (62.90 MHz, $CDCl_3$, 300 K): δ = 54.8 (NCH_2), 53.2 (NCH_2), 52.4 (NCH_2), 29.6 (*t*Bu), 29.5 (*t*Bu), 24.7 ($CH_{2,dendr}$), 23.4 ppm ($CH_{2,dendr}$); $\{^1H\}^{31}$P NMR (81.03 MHz, $CDCl_3$, 300 K): δ = 12.2 ppm; elemental analysis calcd (%) for $C_{88}H_{192}P_8N_6$ (1579.792): C 66.80, H 12.23; found: C 66.76, H 12.17.

G2-DAB-*dendr*-[bis(*tert*-butylaminophosphine)]$_8$ (3a): The same procedure as for **2a** was used with di-*tert*-butylphosphine (0.86 mL, 4.6 mmol), paraformaldehyde (0.14 g, 4.6 mmol) and DAB-*dendr*-$(NH_2)_8$ (0.2 g, 0.26 mmol). Yield: 1.05 g (91 %) of a white solid. ^{1}H NMR (250.13 MHz, $CDCl_3$, 300 K): δ = 2.73 (m, 32H, NCH_2P), 2.39 (m, 52H, NCH_2), 1.24 (m, 28H, CH_2-CH_2), 1.16 (s, 144H, *t*Bu), 1.11 (s, 144H, *t*Bu); $\{^1H\}^{13}$C NMR (62.90 MHz, $CDCl_3$, 300 K): δ = 54.7(NCH_2), 53.6 (NCH_2), 52.4 (NCH_2), 29.7 (*t*Bu), 29.6 (*t*Bu), 24.9 ($CH_{2,dendr}$), 23.6 ($CH_{2,dendr}$); $\{^1H\}^{31}$P NMR (81.03 MHz, $CDCl_3$, 300 K): δ = 12.2; elemental analysis calcd (%) for $C_{184}H_{400}P_{16}N_{14}$ (4434.974): C 66.87, H 12.20; found: C 66.45, H 11.98.

G3-DAB-*dendr*-[bis(*tert*-butylaminophosphine)]$_{16}$ (4a): The same procedure as for **2a** was used with di-*tert*-butylphosphine (0.79 mL, 4.2 mmol), paraformaldehyde (126 mg, 4.2 mmol), and DAB-*dendr*-$(NH_2)_{16}$ (0.2 g, 0.12 mmol). Yield: 0.727 g (90 %) of a white solid. ^{1}H NMR (250.13 MHz, $CDCl_3$, 300 K): δ = 2.73 (m, 64H, NCH_2P), 2.39 (m, 116H, NCH_2), 1.28 (m, 60H, CH_2-CH_2), 1.16 (s, 288H, *t*Bu), 1.11 ppm (s, 288H, *t*Bu); $\{^1H\}^{13}$C NMR (62.90 MHz, $CDCl_3$, 300 K): δ = 54.7(NCH_2), 53.3 (NCH_2), 52.2 (NCH_2), 30.0 (*t*Bu), 29.7 (*t*Bu), 24.6 ($CH_{2,dendr}$), 23.5 ppm ($CH_{2,dendr}$); $\{^1H\}^{31}$P NMR (81.03 MHz, $CDCl_3$, 300 K): δ = 12.2 ppm; elemental analysis calcd (%) for $C_{376}H_{816}P_{32}N_{30}$ (6739.168): C 66.91, H 12.18; found: C 66.22, H 11.53.

G1-DAB-*dendr*-[bis(cyclohexylaminophosphine)]$_4$ (2b): The same procedure as for **2a** was used with dicyclohexylphosphine (2.82 mL, 13.98 mmol), paraformaldehyde (0.46 g, 13.98 mmol), and DAB-*dendr*-$(NH_2)_4$ (500 mg, 1.58 mmol). Yield: 2.29 g (73 %) of a white solid. ^{1}H NMR (200.16 MHz, $CDCl_3$, 300 K): δ = 2.72 (m, 16H, PCH_2N), 2.65 (m, 16H, PCH_{Cy}), 2.37 (m, 20H, CH_2N), 1.72 (m, 80H, $CH_{2,Cy}$), 1.53 (m, 12H, $CH_2CH_{2,dendr}$), 1.20 ppm (m, 80H, $CH_{2,Cy}$); $\{^1H\}^{13}$C NMR (50.33 MHz, $CDCl_3$, 300 K): δ = 55.35 ($CH_2N_{central}$), 52.48 (CH_2N + PCH_2N), 32.7 ($d_{,Cy}$), 29.7 ($t_{,Cy}$), 28.89 (CH_2-$CH_{2,dendr}$) 27.16 (d, Cy), 27.35 (s, Cy), 25.24 ppm ($CH_{2,dendr}$); $\{^1H\}^{31}$P NMR (81.02 MHz, $CDCl_3$, 300 K): δ = −17.8 ppm.

G2-DAB-*dendr*-[bis(cyclohexylaminophosphine)]$_8$ (3b): The same procedure as for **2a** was used with dicyclohexylphosphine (2.54 mL, 12.56 mmol), paraformaldehyde (342 mg, 11.44 mmol), and DAB-*dendr*-$(NH_2)_8$ (500 mg, 0.64 mmol). Yield: 1.64 g (64 %) of a white solid. ^{1}H NMR (200.16 MHz, $CDCl_3$, 300 K): δ = 2.73 (m, 32H, PCH_2N), 2.63 (m, 32H, PCH_{Cy}), 2.34 (m, 52H, CH_2N), 1.74 (m, 160H, $CH_{2,Cy}$), 1.54 (m, 28H, $CH_2CH_{2,dendr}$), 1.21 ppm (m, 160H, $CH_{2,Cy}$); $\{^1H\}^{31}$P NMR (81.02 MHz, $CDCl_3$, 300 K): δ = −17.8 ppm.

G3-DAB-*dendr*-[bis(cyclohexylaminophosphine)]$_{16}$ (4b): The same procedure as for **2a** was used with dicyclohexylphosphine (3.35 mL, 16.5 mmol), paraformaldehyde (454 mg, 15.1 mmol), and DAB-*dendr*-$(NH_2)_{16}$ (720 mg, 42.7 mmol). Yield: 2.5 g (70 %) of a white solid. ^{1}H NMR (200.16 MHz, $CDCl_3$, 300 K): δ = 2.69 (m, 64H, PCH_2N), 2.58 (m, 64H, PCH_{Cy}), 2.33 (m, 116H, CH_2N), 1.70 (m, 320H, $CH_{2,Cy}$), 1.50 (m, 60H, $CH_2CH_{2,dendr}$), 1.17 ppm (m, 320H, $CH_{2,Cy}$); $\{^1H\}^{13}$C NMR (75.47 MHz, $CDCl_3$, 300 K): δ = 53.86 ($CH_2N_{central}$), 51.72 (CH_2N + PCH_2N + PCH), 31.9 ($d_{,Cy}$), 29.05 (dd, Cy), 28.75 (CH_2-$CH_{2,dendr}$) 26.4 ($d_{,Cy}$), 25.7 (Cy), 22.66 ppm ($CH_{2,dendr}$); $\{^1H\}^{31}$P NMR (81.02 MHz, $CDCl_3$, 300 K): δ = −18.1 ppm.

General procedure for the syntheses of (*tert*-butylaminophosphine)palladium(II) monomer 1c and dendrimers 2c, 3c, 4c:

Bis(*tert*-butylaminophosphine)palladium(II) complex 1c: $[Pd(OAc)_2]$ (70 mg, 0.32 mmol) was added to a solution of aminophosphine **1a** (132 mg, 0.32 mmol) in CH_2Cl_2 (5 mL). The solution was stirred for 2 h at room temperature. The solvent was removed under vacuum to give a solid that was washed with cold pentane and dried under vacuum to yield complex **1c** as a yellowish solid (190 mg, 94 %). ^{1}H NMR (300.13 MHz, $CDCl_3$, 300 K): δ = 7.25 (m, 5H, CH_{arom}), 3.58 (s, 2H, CH_2N), 2.66 (s, 4H, PCH_2N), 1.89 (s, 6H, CH_3), 1.39 (s, 18H, *t*Bu), 1.32 ppm (s, 18H, *t*Bu); $\{^1H\}^{13}$C NMR (62.90 MHz, $CDCl_3$, 300 K): δ = 176.0 (CO), 135.1–128.6 (C_{arom}), 67.5 (CH_2N), 54.6 (PCH_2N), 36.3 (CH_3), 33.2 (Bu), 31.8 ppm (*t*Bu); $\{^1H\}^{31}$P NMR (81.02 MHz, $CDCl_3$, 300 K): δ = 35.9 ppm. elemental analysis calcd (%) for $C_{29}H_{53}P_2NO_4Pd$ (648.10): C 53.74, H 8.24, P 9.56; found: C 53.23, H 8.02, P 9.44.

G1-DAB-*dendr*-[bis(*tert*-butylaminophosphine)]$_4$palladium(II) complex 2c: The same procedure as for **1c** was used with $[Pd(OAc)_2]$ (100 mg, 0.44 mmol) and aminophosphine **2a** (170 mg, 0.11 mmol). Yield: 204 mg (75 %) of a yellow solid; ^{1}H NMR (250.13 MHz, $CDCl_3$, 300 K): δ = 2.75 (m, 16H, NCH_2P), 2.40 (m, 20H, NCH_2), 1.89, (s, 24H, CH_3), 1.46 (s, 72H, *t*Bu), 1.39 (s, 72H, *t*Bu), 1.26 ppm (m, 12H, CH_2-CH_2); $\{^1H\}^{13}$C NMR (62.90 MHz, $CDCl_3$, 300 K): δ = 176.2 (CO), 54.4(NCH_2), 53.5 (NCH_2), 52.9 (NCH_2), 30.1 ($CH_{3,OAc}$), 29.7 (*t*Bu), 29.5 (*t*Bu), 24.9 ($CH_{2,dendr}$), 23.5 ppm ($CH_{2,dendr}$); $\{^1H\}^{31}$P NMR (81.03 MHz, $CDCl_3$, 300 K): δ = 35.20 ppm; elemental analysis calcd (%) for $C_{104}H_{216}P_8N_6O_{16}Pd_4$ (2480.360): C 50.36, H 8.78; found: C 50.11, H 8.53.

G2-DAB-*dendr*-[bis(*tert*-butylaminophosphine)]$_8$palladium(II) complex 3c: The same procedure as for **1c** was used with $[Pd(OAc)_2]$ (100 mg, 0.44 mmol) and aminophosphine **3a** (184 mg, 0.056 mmol). Yield: 182 mg (64 %) of a yellow solid; ^{1}H NMR (200.16 MHz, $CDCl_3$, 300 K): δ = 2.71 (m, 32H, NCH_2P), 2.34 (m, 52H, NCH_2), 1.89, (s, 48H, CH_3), 1.47 (s, 144H, *t*Bu), 1.40 (s, 144H, *t*Bu), 1.28 ppm (m, 28H, CH_2-CH_2); $\{^1H\}^{13}$C NMR (62.90 MHz, $CDCl_3$, 300 K): δ = 177.0 (CO), 54.8(NCH_2), 53.6 (NCH_2), 52.5 (NCH_2), 30.5 ($CH_{3,OAc}$), 30.0 (*t*Bu), 29.9 (*t*Bu), 24.6 ($CH_{2,dendr}$), 23.3 ppm ($CH_{2,dendr}$); $\{^1H\}^{31}$P NMR (81.03 MHz, $CDCl_3$, 300 K): δ = 35.22 ppm; elemental analysis calcd (%) for $C_{216}H_{448}P_{16}N_{14}O_{32}Pd_8$ (5094.944): C 50.86, H 8.85; found: C 50.53, H 8.45.

G3-DAB-*dendr*-[bis(*tert*-butylaminophosphine)]$_{16}$palladium(II) complex 4c: The same procedure as for **1c** was used with $[Pd(OAc)_2]$ (100 mg, 0.44 mmol) and aminophosphine **4a** (188 mg, 0.028 mmol). Yield: 199 mg (69 %) of a yellow solid; ^{1}H NMR (200.16 MHz, $CDCl_3$, 300 K): δ = 2.73 (m, 64H, NCH_2P), 2.39 (m, 116H, NCH_2), 1.90, (s, 96H, CH_3), 1.47 (s, 288H, *t*Bu), 1.40 (s, 288H, *t*Bu), 1.26 ppm (m, 60H, CH_2-CH_2); $\{^1H\}^{13}$C NMR (62.9 MHz, $CDCl_3$, 300 K): δ = 176.9 (CO), 54.7(NCH_2), 53.7 (NCH_2), 52.6 (NCH_2), 30.8 ($CH_{3,OAc}$), 30.5 (*t*Bu), 30.2 (*t*Bu), 24.6 ($CH_{2,dendr}$), 23.6 ppm ($CH_{2,dendr}$); $\{^1H\}^{31}$P NMR (81.03 MHz, $CDCl_3$, 300 K): δ = 35.30 ppm; elemental analysis calcd (%) for $C_{440}H_{912}P_{32}N_{30}O_{64}Pd_{16}$ (10329.888): C 51.10, H 8.89; found: C 50.79, H 8.61.

General procedure for the syntheses of (cyclohexylaminophosphine)palladium(II) monomer 1d and dendrimers 2d, 3d, 4d:

Bis(cyclohexylaminophosphine)palladium(II) complex 1d: $[Pd(OAc)_2]$ (326 mg, 1.45 mmol) was added to a solution of aminophosphine **1b** (765 mg, 1.45 mmol) in CH_2Cl_2 (50 mL). The solution was stirred for 2 h at room temperature. The volume was reduced to 10 mL, and pentane was added to precipitate complex **1d** that was dried under vacuum to yield a yellow solid (803 mg, 87 %). ^{1}H NMR (200.16 MHz, $CDCl_3$, 300 K): δ = 7.37–7.25 (m, 5H, CH_{arom}), 3.58 (s, 2H, CH_2N), 2.58 (s, 4H, PCH_2N), 2.26 (s, 4H, PCH_{Cy}), 1.95 (s, 6H, CH_3), 1.65–1.19 ppm (m, 40H, $CH_{2,Cy}$); $\{^1H\}^{13}$C NMR (75.47 MHz, $CDCl_3$, 300 K): δ = 177.1 (CO), 135.74 (CH_{arom}),130.23 (CH_{arom}), 128.81 (CH_{arom}), 128.40 (CH_{arom}), 67.5 (PCH_{Cyclo}), 47.73 (CH_2N + PCH_2N), 35.3 (dt, $CH_{2,Cy}$), 28.7 ($CH_{2,Cy}$),

27.24 (dt, $CH_{2,Cy}$), 25.78 (CH_3), 24.19 ppm ($CH_{2,Cy}$); $\{^1H\}^{31}P$ NMR (81.02 MHz, $CDCl_3$, 300 K): δ = 26.5 ppm; elemental analysis calcd (%) for $C_{37}H_{61}P_2NO_4Pd$ (752.263): C 59.08, H 8.17, N 1.86; found: C 58.34, H 8.24 N 1.96.

G1-DAB-*dendr*-[bis(cyclohexylaminophosphine)]$_4$palladium(II) complex 2d: The same procedure as for **1d** was used with $[Pd(OAc)_2]$ (900 mg, 4 mmol) and aminophosphine **2b** (2 g, 1 mmol). Yield: 2.175 g (75%) of a yellow solid; ^1H NMR (300.13 MHz, $CDCl_3$, 300 K): δ = 2.55 (m, 32H, PCH_2N + PCH_{Cy}), 2.33 (m, 20H, CH_2N), 1.89 (s, 24H, CH_3), 1.70 (m, 80H, $CH_{2,Cy}$), 1.59 (m, 12H, $CH_2CH_{2,dendr}$), 1.16 ppm (m, 80H, $CH_{2,Cy}$); $\{^1H\}^{13}C$ NMR (62.90 MHz, $CDCl_3$, 300 K): δ = 175.9 (CO), 61.0 (CHP), 52.0 ($CH_2N_{central}$), 48.94 (CH_2N + PCH_2N), 30.5 (CH_3), 29.79–26.25 ($CH_{2,Cy}$), 23.52 ppm ($CH_{2,dendr}$); $\{^1H\}^{31}P$ NMR (121.49 MHz, $CDCl_3$, 300 K): δ = 27 ppm; elemental analysis calcd (%) for $C_{136}H_{248}P_8N_6O_{16}Pd_4$ (2896.966): C 56.39, H 8.63; found: C 55.65, H 8.71.

G2-DAB-*dendr*-[bis(cyclohexylaminophosphine)]$_8$palladium(II) complex 3d: The same procedure as for **1d** was used with $[Pd(OAc)_2]$ (736 mg, 3.3 mmol) and aminophosphine **3b** (1.64 g, 0.41 mmol). Yield: 2.3 g (96%) of a yellow solid; ^1H NMR (300.13 MHz, $CDCl_3$, 300 K): δ = 2.61 (m, 64H, PCH_2N + PCH_{Cy}), 2.42 (m, 52H, CH_2N), 1.96 (s, 48H, CH_3), 1.79 (m, 160H, $CH_{2,Cy}$), 1.66 (m, 12H, CH_2CH_2), 1.24 ppm (m, 160H, $CH_{2,Cy}$); $\{^1H\}^{31}P$ NMR (121.49 MHz, $CDCl_3$, 300 K): δ = 27.2 ppm; elemental analysis calcd (%) for $C_{280}H_{512}P_{16}N_{14}O_{32}Pd_8$ (5934.161): C 56.67, H 8.63; found: C 54.98, H 8.79.

G3-DAB-*dendr*-[bis(cyclohexylaminophosphine)]$_{16}$palladium(II) complex 4d: The same procedure as for **1d** was used with $[Pd(OAc)_2]$ (592 mg, 2.64 mmol) and aminophosphine **4b** (1.39 g, 0.17 mmol). Yield: 1.6 g (81%) of a yellow solid; ^1H NMR (300.13 MHz, $CDCl_3$, 300 K): δ = 2.57 (m, 128H, PCH_2N + PCH_{Cy}), 2.29 (m, 104H, CH_2N), 1.91 (s, 96H, CH_3), 1.77 (m, 320H, $CH_{2,Cy}$), 1.63 (m, 12H, $CH_2CH_{2,dendr}$) 1.23 ppm (m, 320H, $CH_{2,Cy}$); $\{^1H\}^{13}C$ NMR (75.47 MHz, $CDCl_3$, 300 K): δ = 175.1 (CO), 59.35 (CHP), 50.2 ($CH_2N_{central}$), 47.1 (CH_2N + PCH_2N), 32.4 (CH_3), 27.1–24.29 ($CH_{2,Cy}$), 22.32 ppm ($CH_{2,dendr}$); $\{^1H\}^{31}P$ NMR (121.49 MHz, $CDCl_3$, 300 K): δ = 27.3 ppm.

Synthesis of $[FeCp\{C_6(CH_2CH_2C_6H_4CCC_6H_5)_6\}][PF_6]$: To a solution of $[FeCp\{C_6(CH_2CH_2C_6H_4Br)_6\}][PF_6]$ (1 g, 0.7 mmol) and catalyst **1c** (27 mg, 6 mol%) in dry Et_3N (3 mL) was added dropwise a solution of phenylacetylene (0.7 mL, 6 mmol) in dry Et_3N (3 mL).The mixture was heated to 80°C for three days. Et_3N was then removed, and the product was extracted with ether (5×20 mL). The organic layer was dried over Na_2SO_4, and flash silica gel chromatography with petroleum ether yielded a light brown solid (291 mg, 27%); ^1H NMR (300.13 MHz, $CDCl_3$, 300 K): δ = 7.02–7.59 (m, 54H, H_{ar}), 5.35 (s, 5H, Cp), 2.78 and 2.88 ppm (m, 12H, CH_2); $\{^1H\}^{13}C$ NMR (62.90 MHz, $CDCl_3$, 300 K): δ = 120.82–140.93 (C_{ar}), 80.11 (Cp), 37.12 (CH_2), 33.05 ppm (CH_2); MS (MALDI-TOF, *m*/*z*): calcd: 1424.68; found: 1425.38 $[M-PF_6]^+$.

Synthesis of $C_6(CH_2CH_2C_6H_4CCC_6H_5)_6$: To a solution of $C_6(CH_2CH_2C_6H_4Br)_6$ (0.2 g, 0.17 mmol) and catalyst **1c** (7 mg, 6 mol%) in dry Et_3N (3 mL) was added dropwise a solution of phenylacetylene (0.16 mL, 1.5 mmol) in dry Et_3N (3 mL). The mixture was heated at 80°C for 8 h. Et_3N then was removed, and the product was extracted with ether (3×20 mL). The organic layer was dried over Na_2SO_4, and flash silica gel chromatography with petroleum ether yielded a light brown solid (141 mg, 59%). ^1H NMR (300.13 MHz, $CDCl_3$, 300 K): δ = 7.03–7.45 (m, 54H, H_{ar}), 2.79 and 2.89 ppm (m, 12H, CH_2); $\{^1H\}^{13}C$ NMR (62.90 MHz, $CDCl_3$, 300 K): δ = 122.24–139.59 (C_{ar}), 37.02 (CH_2), 33.15 ppm (CH_2); elemental analysis calcd (%) for $C_{102}H_{78}$ (1403.741): C 93.97, H 6.03; found: C 93.28, H 5.59; MS (MALDI-TOF): *m*/*z* (%):calcd: 1411.61; found: 1411.54 (100) $[M+Ag]^+$.

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