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Carbonylation Reactions of Iodoarenes with PAMAM Dendrimer-Palladium Catalysts Immobilized on Silica

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Palladium complexes immobilized onto generation 0−3 PAMAM dendrimers supported on silica were used as catalysts for the carbonylation of iodobenzene in methanol to form methyl benzoate. High yields were obtained and the catalyst was recycled 4−5 times without significant loss of activity. The carbonylation reaction was found to be applicable to a variety of iodoarenes regardless of the nature of the substituent.

Introduction

The carbonylation of haloarenes has been extensively investigated in the liquid phase.[1] Most of the work reported in this area has involved bromo- and iodoarenes as starting materials, and metal complexes as catalysts which are capable of oxidative addition to a C−X bond (e.g. Pd or Rh). Phosphine-modified palladium complexes such as dichlorobis(triphenylphosphine)palladium(II) or bromoarylbis(triphenylphosphine)palladium(II) are catalytically active for the carbonylation of iodobenzene or bromobenzene to produce benzoic acid derivatives.[2] The carbonylation of haloarenes with Pd catalysts and phase transfer systems, (e.g., poly(ethylene glycol) and water-soluble catalysts[3]) gave satisfactory yields of benzoic acids. The carbonylation reaction can proceed in a different manner if the intermediate is intercepted by another species. An example is the novel approach for the one-pot preparation of α-amino amides by Pd-catalyzed double carbohydroamination of haloarenes.[4] The preparation of polyesters and polyamides by palladium-catalyzed alkoxycarbonylation of haloarenes[5] is also noteworthy.

Different strategies have been successfully pursued to overcome the low reactivity of chloroarenes toward oxidative addition. Milstein et al.[6] described the use of Pd complexes containing electron-rich and bulky chelating diphosphines. Also, Osborn et al.[7] and Alper and Grushin[8] demonstrated that Pd complexes with phosphines possessing both high basicity (pK_a > 6.5) and substantial steric hindrance are useful catalysts (e.g. $(Cy_3P)_2PdCl_2$) for the carbonylation of chlorobenzene under mild conditions. Other methods of functionalizing chloroaromatics include photochemical activation[9] or the use of tricarbonyl(chloroarene)chromium complexes which react in a stoichiometric fashion.[10]

Heterogeneous catalysts have advantages of heat stability and ease of separation from the product when compared with homogeneous catalysts. Application of solid catalysts for the carbonylation of haloarenes has been examined by the use of $NiCl_2$ on pumice[11] or on SiO_2.[12] A study on the use of solid catalysts for the carbonylation of haloarenes concluded that Pd supported on charcoal was the most active system.[13]

Transition metal catalysis based on functionalized dendrimers has become an interesting and promising way of using a heterogeneous catalytic system. From a catalytic point of view the ideal catalyst should be highly active and selective under mild conditions, stable and easy to separate from the product by using a simple

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(1) (a) Beller, M.; Cornils, B.; Frohning, C. D.; Kohlpaintner, C. W. *J. Mol. Catal.* **1995**, *104*, 17. (b) Beller, M. In *Applied Homogeneous Catalysis with Organometallic Compounds*; Cornils, B., Herrmann, W. A., Eds.; VCH: New York, 1996; Vol. 1.

(2) (a) Stille, J. K.; Wong, P. K. *J. Org. Chem.* **1975**, *40*, 532. (b). Ozawa, F.; Kawasaki, N.; Okamoto, H.; Yamamoto, T.; Yamamoto, A. *Organometallics* **1987**, *6*, 1640. (c). Schoenberg, A.; Heck, R. F. *J. Org. Chem.* **1974**, *39*, 3318. (d) Hidai, M.; Hikita, T.; Wada, Y.; Fujikura, Y.; Uchida, Y. *Bull. Chem. Soc. Jpn.* **1975**, *48*, 2075.

(3) (a) Huang, X.; Wu, J. L. *Chem. Ind.* **1990**, 548. (b) Monteil, F.; Kalck, P. *J. Organomet. Chem.* **1994**, *482*, 45.

(4) Lin, Y. S.; Alper, H. *Angew. Chem., Int. Ed.* **2001**, *40*, 779 and references therein.

(5) (a) Yoneyama, M.; Kakimoto, M.; Imai, Y. *Macromolecules* **1989**, *22*, 2593. (b). Perry, R. J.; Turner, S. R.; Blevins, R. W. *Macromolecules* **1993**, *26*, 1509. (c) Kubota, Y.; Takeuchi, K.; Hanaoka, T.; Sugi, Y. *Bull. Chem. Soc. Jpn.* **1994**, *67*, 563.

(6) Ben David, Y.; Portnoy, M.; Milstein, D. *J. Am. Chem Soc.* **1989**, *111*, 8742.

(7) Huser, M.; Youinou, M. T.; Osborn, J. A. *Angew. Chem., Int. Ed.* **1989**, *28*, 1427.

(8) (a) Grushin, V. V.; Alper, H. *J. Chem. Soc., Chem. Commun.* **1992**, 611. (b) Grushin, V. V.; Alper H. *Chem. Rev.* **1994**, *94*, 1047.

(9) Kashimura, T.; Kudo, K.; Mori, S.; Sugita, N. *Chem. Lett.* **1986**, 851.

(10) Mutin, R.; Lucas, C.; Thivolle-Cazat, J.; Dufaud, V.; Dany, F.; Basset, J. M. *J. Chem. Soc., Chem. Commun.* **1988**, 896.

(11) Dieterle H.; Eschenbasch, W. *Arch. Pharm.* **1927**, *265*, 187.

(12) Palit, S. K.; Tripathy, N. *J. Appl. Chem.* **1969**, *19*, 301.

(13) Maeda, K.; Yagita, H.; Omata, K.; Fujioto, K. *J. Mol. Catal.* **1992**, *71*, 347.

10.1021/jo020271n CCC: $22.00

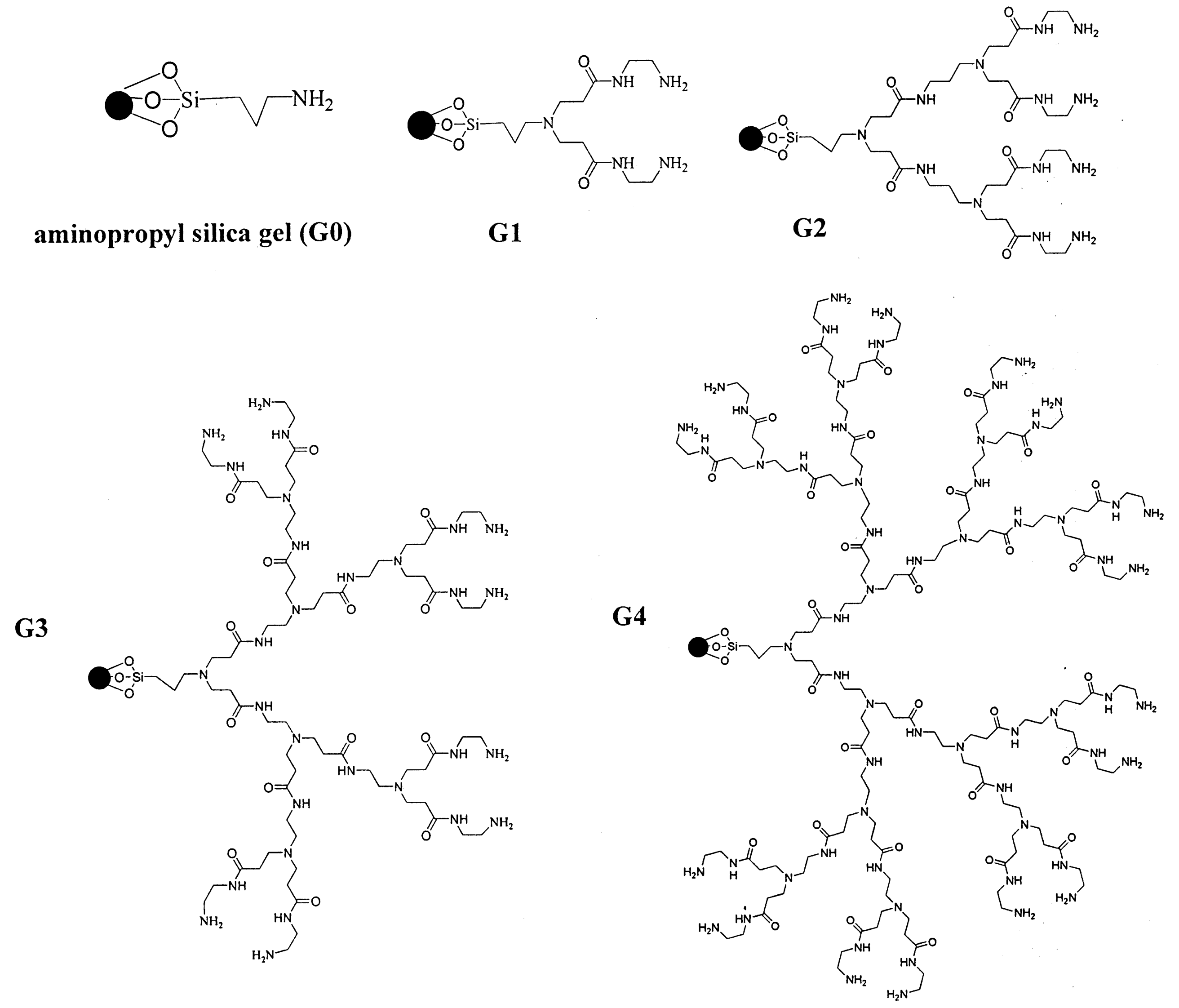

FIGURE 1. Structures of generation 0−4 of PAMAM-SiO$_2$ dendrimers.

process such as filtration.[14] Dendrimer metal catalysts can, in principle, fill the gap between homogeneous and heterogeneous systems, due to their monodisperse structure and multiarm topology that give the peripheral catalytic sites the ability to act as soluble supported catalysts.

PAMAM (polyaminoamido) dendrimers supported on silica, with their globular shape, make them more suitable for recycling than other soluble polymer-supported catalysts. They can be easily removed from the reaction mixture by membrane or nanofiltration techniques because of their large size compared to the products. Several groups prepared systems that were functionalized with phosphine ligands at the periphery of the dendrimers. Reetz et al.[15] used commercially available DAB-dendr(NH$_2$)$_2$ dendrimer as a source of dendrimer-N(CH$_2$PPh$_2$)$_2$ groups. The latter function as bidentate ligands when complexed with Pd(tmeda)Me$_2$. The dendrimer catalyst was used for the coupling of bromobenzene and styrene to form stilbene. The Heck reaction of bromoarenes and styrene was also investigated by using a Pd catalyst in which the metal was complexed to phosphines of a PAMAM dendrimer supported on silica gel.[16b]

The hydroformylation of styrene was realized by using a bis-diphenylphosphine terminated PAMAM dendrimer supported on SiO$_2$, complexed to Rh[(CO)$_2$Cl]$_2$.[16a,c] A solid phase and biomimetic approach to obtain catalytic dendrimer ligands attached to polystyrene beads was employed by Alper and co-workers.[16d] The rhodium complexes of these dendrimers were excellent catalysts for the hydroformylation of several olefins.

We now describe the carbonylation of haloarenes using catalytic quantities of Pd-PPh$_2$-PAMAM dendrimer on

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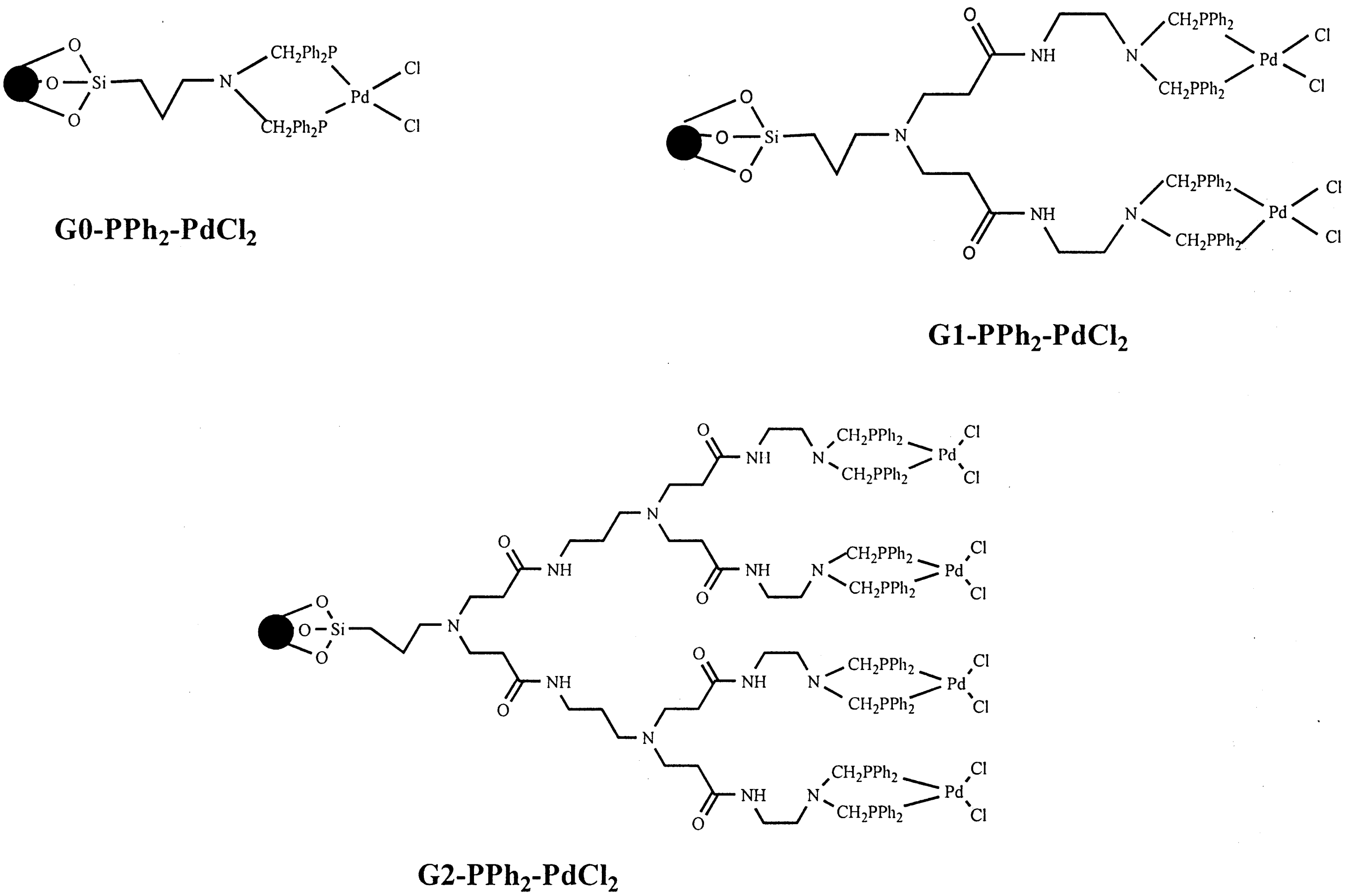
(14) Oosterom, G. E.; Reek, J. N. H.; Kamer, P. C. J.; van Leeuven, P. W. N. M. *Angew. Chem., Int. Ed.* **2001**, *40*, 1828.

(15) Reetz, M. T.; Lohmer, G.; Schwickardi, R. *Angew. Chem., Int. Ed.* **1997**, *36*, 1526.

(16) (a) Bourque, S. C.; Maltais, F.; Xiao, W. J.; Tardif, O.; Alper, H.; Arya, P.; Manzer, L. E. *J. Am. Chem. Soc.* **1999**, *121*, 3035 and references therein. (b) Alper, H.; Arya, P.; Bourque, S. C.; Jefferson, G. R.; Manzer, L. E. *J. Can. Chem.* **2000**, *78*, 920. (c) Arya, P.; Panda, G.; Rao, N. V.; Alper, H.; Bourque, S. C.; Manzer, L. E. *J. Am. Chem. Soc.* **2001**, *123*, 2889. (d) Arya, P.; Rao, N. V.; Singkhonrat, J.; Alper, H.; Bourque S. C.; Manzer, L. E. *J. Org. Chem.* **2000**, *65*, 1881.


G0-PPh$_2$-PdCl$_2$

G1-PPh$_2$-PdCl$_2$

G2-PPh$_2$-PdCl$_2$

FIGURE 2. Proposed structures of generation 0−2 of PdCl$_2$-PPh$_2$-PAMAM-SiO$_2$ dendrimers.

silica. It was of interest to compare these results with other heterogeneous methods for the carbonylation reaction.

Results and Discussion

Preparation of PAMAM-SiO$_2$ Dendrimers. Commercial aminopropylsilica gel with aminopropyl groups (0.9 mmol/g ± 0.1) was used to prepare generations 0−3 of polyaminoamido (PAMAM) dendrimers (Figure 1), using a previously described method.[16a]

Preparation of Phosphonated PAMAM-SiO$_2$ Dendrimers. The dendrimers on silica were phosphonated with PPh$_2$H to provide a coordination site for palladium. Double phosphinomethylation of each terminal amine was carried out with diphenyphosphinomethanol prepared in situ from paraformaldehyde and diphenylphosphine. The detailed preparation was described before[16a] and based on the procedure by Reetz.[15] The resulting phosphonylated dendrimers (Figure 2) were characterized by ^{31}P solid-state NMR. A chemical shift of −27 ppm for the various generations compared well with the published value of −28 ppm for the homogeneous polyaminophosphonated dendrimer.[15,16a] When dicyclohexylphosphine was used for the phosphinomethylation reaction, the chemical shift of the free phosphine groups on the dendrimer was observed at −28.3 ppm.[16a]

Complexation of the Phosphino-PAMAM Dendrimer Supported on SiO$_2$ with Pd. The phosphonated dendrimers (i.e. with PPh$_2$) were complexed to Pd with either Pd(RCN)$_2$Cl$_2$ (R = Me, Ph) or Pd(tmeda)Me$_2$ according to literature procedures.[16c,17] The complexation was usually carried out in toluene, after mixing the dendrimer and the palladium compound for 1 h to overnight, at room temperature. The Pd dendrimer complexes generally showed three types of chemical ^{31}P shifts (Table 1): (a) at 9.0−9.4 ppm for the PdMe$_2$ complexes (comparing well with the previously published value of 9.7 ppm);[16c] (b) at 12.2−13.8 ppm for the PdCl$_2$ complexes; and (c) and at 28.0−28.5 for the PPh$_3$ or dba complexes.

When the reaction time was reduced to 1.0−2.5 h (entries 1, 13) with Pd(PhCN)$_2$Cl$_2$ as the Pd reactant, chemical shifts at 13.2 and 13.8 ppm were observed in the ^{31}P NMR spectrum (in accord with literature for non-oxidized, complexed PPh$_2$ groups). When the ratio between the phosphinated dendrimer and the palladium compound was 4:1 (entry 10 in Table 1), after a reaction time of 2.5 h, the chemical shift in the ^{31}P NMR was at 8.6 ppm (with some oxide formed). In the preparation of the G3 dendrimer, using Pd(PhCN)$_2$Cl$_2$ and a reaction time of 1.5 h, there was little complexation as indicated by the ^{31}P solid-state NMR spectrum. The major signal was at −28 ppm, accompanied by one at 13.8 ppm. These observations are in accordance with the low (0.8%) Pd loading, which is 6.5% of the expected theoretical value (ICP, Table 1, entry 12). When the reaction was repeated

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(17) Mizugaki, T.; Ooe, M.; Ebitani, K.; Kaneda, K. *J. Mol. Catal.* **1999**, *145*, 329.

TABLE 1. Solid-State ^{31}P NMR and ICP Results in the Preparation of Palladium Catalysts on PAMAM Supported on SiO_2

			conditions for preparation (rt; argon)						
catalyst no.	dendrimer catalyst[a]	complexing agent A	B[b]	solvent	time, h	^{31}P-solid NMR δ (ppm)[c]	ICP results % Pd	theoretical amounts % Pd	yield % Pd
1	G1-C2-PPh_2-$PdCl_2$	$Pd(PhCN)_2Cl_2$	2:1	toluene	1	13.2	5.6	8.7	65
2	G1-C2-$PCycl_2$-$PdCl_2$	$Pd(PhCN)_2Cl_2$	2:1	toluene	1	13.7	6.7	8.7	77
3	G1-C2-PPh_2-$PdCl_2$	$Pd(MeCN)_2Cl_2$	2:1	toluene	19	12.2	8.8	8.7	100
4	G0-C2-PPh_2-$PdMe_2$	$Pd(tmeda)Me_2$	2:1	benzene	19	9.0	5.5	6.5	85
5	G1-C2-PPh_2-$PdMe_2$	$Pd(tmeda)Me_2$	2:1	toluene	19	9.4	2.0	8.9	22
6	G1-C2-PPh_2-$Pd(PPh_3)_2$	$Pd(PPh_3)_4$	2:1	toluene	19	28	1.1	6.3	17
7	"G1-C2-PPh_2-$Pd(dba)_2$"	$Pd(dba)_3{\cdot}CHCl_3$	2.5:1	toluene	19	28.5	6.5	9.1	71
8	G1-C2-PPh_2-$PdCl_2$	$Pd(MeCN)_2Cl_2$	2:1	benzene	19	12.4	8.3	8.7	96
9	G1-C2-PPh_2-$PdCl_2$	$Pd(MeCN)_2Cl_2$	4:1	toluene	19	12.8	5.0	4.9	102
10	G2-C2-PPh_2-$PdCl_2$	$Pd(PhCN)_2Cl_2$	4:1	toluene	2.5	8.6	2.7	5.2	46
11	G2-C2-PPh_2-$PdCl_2$	$Pd(PhCN)_2Cl_2$	2:1	toluene	2.5	8.9	4.0	10.4	38.5
12	G3-C2-PPh_2-$PdCl_2$	$Pd(PhCN)_2Cl_2$	2:1	toluene	1.5	13.8	0.8	11.7	6.5
13	G3-C2-PPh_2-$PdCl_2$	$Pd(PhCN)_2Cl_2$	2:1	toluene	19	13.8	3.1	11.7	26.5

[a] G*n*: *n* designates the generation number. C*m*: *m* designates the number of carbons in the diamino linker, i.e., $m - 2$ in $NH_2(CH_2)_2NH_2$. PPh_2, $Pcycl_2$ (cyclohexyl) are the phosphine groups to which the Pd is complexed. [b] *B* is the molar ratio between the no. of equivalents of PPh_2 in PPh_2-PAMAM-dendrimer on SiO_2 to the no. of moles of Pd (A) used. [c] Signals for oxidized phosphorus were sometimes observed in the ^{31}P spectra. [d] Mixture of recycled catalysts from entries 8 and 10 from the carbonylation reactions of PhI.

TABLE 2. Comparison of Theoretical Percent Pd Loading in $PdCl_2$-PPh_2-PAMAM-SiO_2 in Generations 0, 1, 2, 3, and 4

	theoretical % Pd loading	% growth of Pd loading		
		G*n*/G0[a]	G*n*/G1[b]	G(*n*+1)/G*n*[c]
G0	6.3			
G1	8.6	136		136
G2	10.4	165	121	121
G3	11.7	185	136	112
G4	12.4	196	144	106

[a] The ratio indicates the increase of % Pd loading for each generation with reference to the 0 generation of $PdCl_2$-PPh_2 APS (aminopropylsilica). [b] The ratio indicates the increase of % Pd loading with reference to the first generation of the $PdCl_2$-PPh_2-PAMAM on SiO_2. [c] The ratio indicates the % Pd loading between two subsequent generations of G*n*-PPh_2-$PdCl_2$.

overnight at rt, there was a slight increase of the signal at 13.8 ppm in the ^{31}P NMR spectrum (assigned to the coordinated phosphine−Pd bond). In this case, 3.1% Pd loading occurred, which is 26% of the expected theoretical value (as determined by ICP Table 1, entry 13).

The structure of the dendrimer complex plays a role in the catalytic system of the PAMAM dendrimers. As one proceeds to higher generations of dendrimer, the percentage of Pd loading does not increase by the same factor compared to the growth of the number of equivalents of the amine and phosphine. Thus when going to a higher generation the number of equivalents is multiplied by a factor of 2 for the amine equivalents, and by a factor of 4 for the phosphine equivalents (Figures 1 and 2). However, the calculated percentage of the Pd loading increases insignificantly (only 6%) between generation 3 and generation 4 (for a $PdCl_2$ dendrimer complex; Table 2). In terms of actual loading, while 100% Pd loading was observed for generations 0 and 1, the loading was 26−40% (Table 1) for generations 2 and 3.

Based on these findings, the fourth generation of the dendrimer and its Pd complex were not prepared.

ICP Analysis of the Complexes. Samples of the catalyst complexes were digested in aqua-regia (HCl−HNO_3; 3:1) and boiled for 30 min. The samples were diluted to 25 mL with H_2O and were examined for Pd content. A Perkin-Elmer Optima 3000 Radial View ICP-AES (Inductively Coupled Plasma-Atomic Emission Spectrometer) was used for ICP analysis. Measurements were performed at 340.458 nm with Pd standard in 1 M HCl, using external calibration.

The ICP results for Pd shed some light on the Pd loading in the various dendritic catalysts, prepared under different conditions (Table 1). When the complexation process was effected overnight with $Pd(RCN)_2Cl_2$ (R = Me, Ph) as the Pd source, Pd immobilization was near quantitative (entries 3, 4, 8, and 9). Exceptions occurred with either $Pd(tmeda)Me_2$ or $Pd(PPh_3)_4$ (entries 5 and 6).

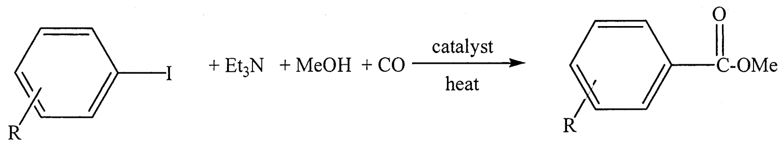
Use of short reaction times (between 1 and 2.5 h) did not give full complexation of the metal to the dendrimer. However, these conditions allow the isolation of the complexed Pd-PPh_2 with little if any oxidation at the phosphorus.

Catalytic Carbonylation of Iodobenzene with $PdCl_2$ Complexed to PPh_2-PAMAM Dendrimers Supported on Silica. The carbonylation of iodoarenes compounds **1** to the corresponding methyl esters, **2**, was studied initially with iodobenzene (R = H) as the model reactant (Scheme 1).

The reactions were monitored by ^1H NMR (tetrachloroethane (TCE) used as reference) and by GC (area %) analyses. Isolation of the reaction products by liquid chromatography showed good correlation between the two methods. This allowed us to monitor the reactions using GC (area %).

The Pd-dendrimer catalyst (entry 8, Table 2)-G1-PPh_2-$PdCl_2$ (2:1) was used for the first series of carbonylation reactions of iodobenzene. The reaction in MeOH was completed overnight, when a pressure of 600 psi of CO was applied and in the presence of an excess of Et_3N as the HI acceptor (Table 3, entry 1). This result was comparable with the reaction where $PdCl_2(MeCN)_2$ was used alone (entry 3) or with the precursor of catalyst 8 (entry 2). When K_2CO_3 was used as the base (entries 4 and 5), the reaction was complete only at the higher temperature of 105 °C. The time required for the completion of the reaction was 6 h even at lower CO pressure (100 psi; entries 6−8).

SCHEME 1. Carbonylation of Iodoarenes to Their Methyl Esters



1 2

R= H; 4-NO_2, 4-Me, 2-MeO; 4-MeO, 4-CF_3; 4-I; 4-Br; 4-OH; 4-CH_3CO; 4-I-C_6H_4-

TABLE 3. Screening Experiments with G1-PPh_2-$PdCl_2$ (catalyst entry 8, Table 1)[a]

	base								yield[b]	
	Et_3N, mmol	K_2CO_3	temp, °C	CO, psi	time, h	dendrimer-$PdCl_2$, mg (G1) 2:1	$PdCl_2(MeCN)_2$, mg	dendrimer-CH_2PPh_2, mg	Ph-I, %	PhCOOMe, %
1	21.5		95	600	22	25			17	73
2	21.5		105	600	23		7.4	25		87
3	21.5		105	600	23		7.4			100
4		2.2	60	300	22.5	25			29	42
5		2.2	105	300	22.5	25				94
6	4.3		105	100	2	25			22	72
7	4.3		105	100	5	25			12	80
8	4.3		105	100	6	25				90

[a] Conditions: PhI (2 mmol); MeOH (6 mL); catalyst (entry 8, Table 1; based on 2:1 G1-PPh_2:Pd); [b] ^{1}H NMR yields.

TABLE 4. Screening Experiments with G1-PPh_2-$PdCl_2$ (catalyst entry 9, Table 1)[a,c,d]

	temp, °C	CO, psi	time, h	dendrimer-$PdCl_2$, mg (G1-PPh_2) (4:1)	% Ph-I	% PhCOOMe[b]	remarks
1	105	100	16	25	28	50	
2	105	85	16	25	n.d.	72	
3	100	50	19	25	n.d.	95	
4	85	50	19	25	n.d.	100	
5	70	50	23	25	38	38	
6	105	50	23	25	64	36	toluene:MeOH 10:1[d]
7	105	50	23	Pd/C; 70 mg		100	
8	105	600	23	no catalyst	94	6	
9	95	*d*	8			92	

[a] Conditions: PhI (2 mmol); MeOH (6 mL); Et_3N (4.3 mmol); catalyst (from entry 10, Table 1; based on 4:1 G1-PPh_2:Pd). [b] ^{1}H NMR yields. [c] Use of *n*-propanol instead of MeOH. [d] By volume.

One other catalyst system (system 10, Table 1), having more vacant PPh_2 sites (4:1), gave similar results to those obtained with the catalyst having fully occupied PPh_2 site (Table 3), and the results are presented in Table 4. The data compared well even with a theoretically lower loading of Pd, and with lower CO pressures. Carbonylation was complete after 8 h when CO was bubbled into refluxing *n*-propanol (Table 4; entry 9). The carbonylation reaction did not proceed without any catalyst (entry 8).

The reaction depends on the temperature. Low conversion of iodobenzene occurred at 60 °C, while temperatures higher than 85 °C afforded good conversions and yields. Two molar equivalents of Et_3N or K_2CO_3 was sufficient to attain complete conversion of iodobenzene to the ester. Although carbonylation was accomplished under atmospheric pressure (CO bubbling), for ease of handling, subsequent experiments were carried out in an autoclave with use of 100 psi of CO.

Generality of the Pd-PPh_2-Dendritic System for the Carbomethoxylation of Iodoarenes. The scope of the catalytic system for the carbomethoxylation of iodoarenes was examined by overnight reactions with use of 1.5 mmol of ArI, 0.4 mL of Et_3N, 100 psi of CO, and 5 mL of MeOH, at 100 °C. All reactions went to completion under these conditions, and there was no significant effect by substituents on the phenyl ring (Table 5). It was also found that there was no difference between electron-withdrawing substituents (nitro, ester) and electron-donating groups (methoxy, methyl).

To determine the difference in the activities of iodoarenes with an electron-donating and with an electron-withdrawing group, reactions were effected for 5 instead of 19 h. With the electron-withdrawing *p*-CF_3 substituent, a 73% yield (entry 6; GC, area %) of the ester was obtained, whereas for the *p*-OMe analogue, the product yield was 90% (entry 13). With *o*-MeO-C_6H_4I, only 63% of the ester was obtained, probably because of steric interactions (entry 5).

When bromobenzene was used as the starting material the reaction did not take place at 105 °C, nor at higher temperatures (e.g. 150 °C, KI), The addition of dppp [1,3-bis(diphenyphospino)propane] or dppb (1,4-bis(diphenylphosphino)butane) to the reaction mixture did not result in the activation of the C−Br bond toward the carbonylation reaction. Nonetheless, this lack of activity can be used to advantage for the preparation of derivatives of methylbenzoate esters, by employing bromoiodoarenes as starting materials.

Influence of the Nature of the Phosphine on the Catalytic Process. Two $PdCl_2$-phosphinated dendrimers

TABLE 5. Carbonylation of Iodoarenes (R-PhI) with G1-PR$^1_2$-PdCl$_2$ (R^1 = Ph or Cycl)[a]

	R	catalyst; R^1=/mg	recovered catalyst /mg	spectral data[i] IR vis; MS *m/e*	% ArI	% ArCOOMe[b]
1	H	2; cycl[f]/17.7	14.4	1724 cm^{-1} 136 *m/e*		100
2	H	3; Ph[g]/16.1	11.3	1724 cm^{-1} 136 *m/e*		100
3	4-NO$_2$	3; Ph[g]/16.9	13.3	1719 cm^{-1} 181 *m/e*		81[c]
4	Me	3; Ph[g]/16.1	11.3	1721 cm^{-1} 150 *m/e*		100
5	2-OMe	3; Ph[g]/17.1	10	1727 cm^{-1} 166 *m/e*		100 (63[k])
6	4-CF$_3$	3; Ph[g]/16.8	10.2	1730 cm^{-1} 204 *m/e*		100 (73[k])
7	4-I	3; Ph[g]/22.7	*e*	1723 cm^{-1} 194 *m/e*		100
8	3-OMe	1; Ph[h]/16.6	11.2	1722 cm^{-1} 166 *m/e*	14	86
9	4′-I-Ph[d]	1; Ph[h]/17.7	*e*	1722 cm^{-1} 270 *m/e*		100
10	4-OH	1; Ph[h]/16.9	8.9	1711 cm^{-1} 152 *m/e*		100
11	4-Br	1; Ph[h]/16.5	10.4	1719 cm^{-1} 214 *m/e*	2	98
12	CH$_3$CO−	1; Ph[h]/16.4	7.5	1679, 1722 cm^{-1} 178 *m/e*		100
13	4-MeO−	1; Ph[h]/18	12		10	90[k]

[a] ArI (1.5 mmol); Et$_3$N (0.4 mL), MeOH (5 mL); CO (100 psi); 100 °C; overnight (~19 h), unless stated otherwise. [b] ^{1}H NMR yields and GC (area %). [c] 19% methyl *p*-aminobenzoate; as a result of the reduction of the NO$_2$ function. [d] 4,4′-Diiodobiphenyl (0.75 mmol), Et$_3$N (0.4 mL); MeOH (5 mL). [e] The product was insoluble in MeOH. [f] R^1 = cyclohexyl (catalyst 2 from entry 2, Table 1). [g] R^1= phenyl (catalyst 3 from entry 3 Table 1). [h] R^1= phenyl (catalyst 3 from entry 4 Table 1). [i] ^{1}H NMR spectra were in accordance with the structure of the compounds. [k] Reaction time 5 h.

TABLE 6. Recycling of G1-PR$_2$1-PdCl$_2$-(R^1 = Ph or Cycl) in the Carbonylation of Iodobenzene[a]

A. G1-PCycl$_2$-PdCl$_2$[b]

entry	catalyst/ mg	recovered catalyst/mg	recycle no.	% PhI	% PhCOOM
1	16.8[b]	12.9	0		100
2	17.7[b]	14.4	0		100
3	25[c];	21.4	1	5	95
4	21.4[d]	16.2	2	2	98
5	16.2[d]	13.2	3	29	71
6	13.2[d]	8.3	4	27	73
7[e]	7.2[d]		5	24	76

B. G1-PPh$_2$-PdCl$_2$[f]

entry	catalyst/ mg	recovered atalyst /mg	recycle no.	% ArI	% ArCOOM
1	16.9[f]	9.4	0		100
2	16.1[f]	11.3	0		100
3	16.7[f]	10.4	0		100
4	25[g]	22.8	1	8	92
5	22[h]	16.8	2	23	77
6	16.8[h]	15.4	3	29	71
7	15.4[h]		4	24	76

[a] All reactions were run for 19 h with 1.5 mmol of PhI, 5 mL of MeOH, 0.4 mL of Et$_3$N, and 100 psi of CO at 100 °C. [b] Catalyst no. 2, entry 2 in Table 1. [c] Isolated catalysts from previous cycle (entries 1 + 2). [d] Isolated catalysts from previous cycle. [e] 1 mmol of PhI was used. [f] Catalyst no. 3, entry 3 in Table 1. [g] Isolated catalysts from previous cycle (entries 1 + 2 + 3). [d] Isolated catalysts from previous cycle.

on silica, **2** [based on P(cyclohexyl)$_2$] and **3** (based on PPh$_2$), were compared for their activities for the carbonylation of iodobenzene (Table 6). Despite the more basic character, and larger steric bulk, of the dicyclohexylphosphine group as compared with that of diphenylphosphine, there was actually no significant difference in behavior of the two catalytic systems. Both catalysts gave complete conversion of iodobenzene to its ester and we were pleased that both catalysts are capable of being recycled at least 4−5 times. The reduction in the yield in the last cycles can be attributed to the decreasing amount of recycled catalyst.

Comparison of Activities of Pd-Phosphinated Dendrimers of Different Generations, and from Different Pd Sources. The activity of different Pd-dendritic complexes was compared for the methoxycarbonylation of iodobenzenes. To examine relative catalytic activities, the reaction time was decreased to 5 h (Table 7).

(a) Comparison of G0 and G1 complexed with Pd(tmeda)Me$_2$ shows that G0 gave a higher yield of the ester (89%) than G1 (74% yield; Table 7; entries , and 2). However, it must be noted that in G1 the actual Pd loading in catalyst 5 was only 3.2 μmol of Pd compared to 8.8 μmol in catalyst 4.

(b) G1 complexed to PdCl$_2$ gave a 91% yield of the ester after 5 h (entry 3). The catalyst was isolated as a black solid. However, when the reaction was repeated with dppb (entry 4), a yellow catalyst was isolated and 100% of the ester was formed. Recycling this yellow catalyst without dppb (entry 5) gave 60% of the ester. It was thus suspected that the recycled catalyst did not contain Pd because dppb extracted the Pd into the solution. Nevertheless, recycling (entry 6) the catalyst again (entry 5) in the presence of dppb increased the yield to 83%.

(c) There was no significant change in the activity within the same generation for dendrimer catalysts prepared with different complexation ratios between the phosphinated dendrimer and the Pd compound, i.e., 2:1

TABLE 7. Yields of Methyl Benzoate from Iodobenzene with Different Dendritic Palladium Catalysts[a]

	cat.	type	time, h	% PhCOOMe	% PhI
1	4	G0-C2-PPh$_2$-PdMe$_2$	5	89	11
2	5	G1-C2-PPh$_2$-PdMe$_2$	5	74	26
3	8	G1-C2-PPh$_2$-PdCl$_2$ no dppb	5	91	9
4	8	G1-C2-PPh$_2$-PdCl$_2$ +dppb	5	100	
5		1st recycled, 23 mg of 4, no dppb	5	60	40
6		2nd recycle 18 mg of 5 + 20 mg dppb	5	83	17
7	1	G1-C2-PPh$_2$-PdCl$_2$	5	86	14
8	3	G1-C2-PPh$_2$-PdCl$_2$	19	100	
9	2	G1-C2-PCy$_2$-PdCl$_2$	5	87	13
10	2	G1-C2-PCy$_2$-PdCl$_2$	19	100	
11	8	G1-C2-PPh$_2$-PdCl$_2$ (2:1)	5	88	12
12	9	G1-C2-PPh$_2$-PdCl$_2$ (4:1)	5	91	9
13	10	G2-C2-PPh$_2$-PdCl$_2$ (4:1)	5	67	33
14	11	G2-C2-PPh$_2$-PdCl$_2$ (2:1)	5	73	27
15[b]	11	G2-C2-PPh$_2$-PdCl$_2$ (2:1)	5	92	8
16	10	G2-C2-PPh$_2$-PdCl$_2$ (4:1)	19	93	7
17	12	G3-C2-PPh$_2$-PdCl$_2$ (2:1)	19	89	11
18	12	G3-C2-PPh$_2$-PdCl$_2$ (2:1)	5	53	47
19		G3-C2-PPh$_2$-PdCl$_2$ (2:1)[c]	5	78	22
20	7	“G1-C2-PPh$_2$-Pd-dba$_2$”	5	76	24
21	6	“G1-C2-PPh$_2$-Pd-(PPh$_3$)$_2$”	5	36	64

[a] Conditions: PhI (1.5 mmol), MeOH (5 mL), Et$_3$N (0.4 mL), CO (100 psi); 105 °C and 17 mg of the dendritic catalyst; product yields were determined by GC. [b] Pretreatment of catalyst (no. 11 from entry 11 in Table 1) in MeOH; Et$_3$N; 105 °C; 100 psi of CO without PhI, which formed a black catalyst, then PhI was introduced and the reaction mixture was heated again for 5 h. [c] Retaining 3.1% Pd loading.

and 4:1. For the G1 catalyst 88% and 91% yield of the ester were observed for 2:1 and 4:1 complexes, respectively (entries 11 and 12). Quite similar results were observed for the G2 catalyst, where 73% and 67% yields of the ester were obtained for 2:1 and 4:1 complexes, respectively (entries 14 and 13). It is clear though that the activity of the catalyst decreases when going to the higher generation 2 compared to generation 1.

(d) The yield of ester increases by pretreatment of the catalyst before the carbonylation reaction. Thus, the ester yield was 92% when PhI was added to a mixture of all the components heated beforehand (entry 15) compared to 73% yield obtained without the pretreatment (entry 14).

It is probable that under the reducing reaction conditions, the PdCl$_2$, immobilized on the dendrimer, is reduced to Pd(0), which is immobilized on the periphery of the dendrimer, serving as the activated species.

(e) With the G3 dendrimer catalyst, the results were surprising due to the low Pd loading (catalyst 15; 0.8% Pd by ICP analysis, Table 1). The reaction (Table 7, entry 18) gave 53% of the ester after 5 h. However, 89% of methyl benzoate was obtained when the reaction was effected overnight (entry 17). When the Pd loading on the third generation Pd catalyst was increased to 3.1% (catalyst 13, Table 1), the yield increased to 78% after 5 h (entry 19).

(f) In comparison with the G1-PdCl$_2$ catalyst, lower yields were observed for G1 catalysts obtained with other Pd complexes (entries 20 and 21), e.g. a catalyst prepared from Pd-dba$_2$·CHCl$_3$ gave 76% ester (the loading of Pd was 71%, entry 20), while the yield of ester was 36% for a G1 catalyst obtained from Pd(PPh$_3$)$_4$ (17% of the theoretical Pd, entry 21).

In conclusion, when dendrimers of higher generations (2 and 3) are used, a lower yield is observed, probably because of lower Pd loading obtained in the higher generations.

(g) The TONs obtained are usually around 100 (Table 8) and were comparable to other nondendrimeric Pd catalysts (120 for Pd/C and 99 for Pd(PhCN)$_2$Cl$_2$ (entries 17 and 18)).

A TON of 176 (and 89% yield) resulted for the dendritic G0 complexed to “PdMe$_2$” (entry 12), with nearly identical data obtained for a G1 catalyst (entry 2) when the ratio between the phosphonated dendrimer and the Pd compound was 4:1 (leaving vacant PPh$_2$ coordination sites). Catalyst 9 (entry 2) gave 91% yield versus 88% yield for catalyst 8 (entry 1), despite the fact that the Pd loading was less (50%). A similar case is observed for G2 catalysts where 67% of the ester was obtained for catalyst no. 10 with a TON of 236 (entry 7) compared to 73% yield and a TON of 179 (entry 8).

A notable TON of 358 was obtained for catalyst no. 5 with a good yield of 74% (entry 13) despite the very low Pd loading (0.2 mol % Pd, where the ratio substrate/Pd was 500:1). Another catalyst, no. 6 (entry 14), seemed to be of comparable activity to catalyst no. 5. It showed a TON of 318 (with 0.1 mol % of Pd, or substrate/Pd 1000:1). However, repeating a second reaction with 3.6 times the amount of catalyst increased the yield from 36% to 60%, whereas the TON dropped to 145.

The highest TON values are obtained for the carbonylation reaction when a G3 catalyst was used. Thus for a substrate-to-Pd ratio of 300 a TON of 234 is obtained. An interesting result is reported in entry 10, where the substrate-to-Pd ratio was as high as 1226, with a TON value of 652. These high values can be attributed to the low loading, but still they compare well with other examples (entries 2, 12, and 13) for lower generation catalysts.

There are several other observations made which merit attention:

(a) The catalyst changes in color from brown-maroon to black by the end of the reaction. When isolated from the reaction mixture, ca. 30% of the original weight was lost. This black catalyst (from Table 1, entry 8) retained 6.4% Pd by ICP analysis, allowing for the recycling of the dendritic Pd catalyst as shown above. It was found that pretreatment of the catalyst under the reaction conditions, without the substrate (PhI), gave a higher product yield when PhI was introduced (Table 7, entry 15). It is reasonable to assume that, under CO pressure, reducing conditions exist, and the Pd(II) immobilized onto the phosphinated dendritic sites was transformed to Pd(0), which was stabilized by the dendrimer. Kaneda et al.[20] used dendrimer-bound PdCl$_2$ complexes prepared

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(18) (a) Onoda, T. *Chemtech* **1993**, *23*, 34. (b) Sato, K.; Miyazawa, C.; Wada, K.; Onoda, T. *Nippon Kagaku Kaishi* **1994**, 681; *Chem. Abstr.* **1994**, *121*, 136524.

(19) (a) Abu-Gnim, C.; Amer, I. *J. Chem Soc., Chem. Commun.* **1994**, 115. (b) Basoli, C.; Botteghi, C.; Cabras, M. A.; Chelucci, G.; Marchetti, M. *J. Organomet. Chem* **1995**, *C20*, 488.

(20) Mizugaki, T.; Murata, M.; Ooe, M.; Ebitani, K.; Kaneda, K. *J. Chem. Soc., Chem. Commun.* **2002**, 52.

TABLE 8. TON and TON/h for Different Palladium Catalysts Supported on PAMAM Dendrimers on SiO_2 for the Carbonylation of PhI[a]

	reaction no.[b]	ratio subst/Pd	mol % Pd	μmol of Pd/ 25 mg of catalyst	actual μmol of Pd	catalyst no.	type of catalyst	% yield of ester	TON	TON/hr
1	11	96	1	20.4	16.2	8	G1-C2-PPh_2-$PdCl_2$ (2:1)	88	87	18
2	12	194	0.5	11.7	8	9	G1-C2-PPh_2-$PdCl_2$ (4:1)	91	176	35
3	3	116	0.9	19	13.2	8	G1-C2-PPh_2-$PdCl_2$	91	105	21
4	4[c]	91	1.1	19	16.4	8	G1-C2-PPh_2-$PdCl_2$ + dppb	100	91	18
5	7	166	0.6	13.2	9.3	1	G1-C2-PPh_2-$PdCl_2$	86	138	28
6	9	133	0.75	15.8	11.3	2	G1-C2-$PCycl_2$-$PdCl_2$	87	119	24
7	13	333	0.3	6.3	4.3	10	G2-C2-PPh_2-$PdCl_2$ (4:1)	67	236	47
8	14	245	0.4	9.3	6.4	11	G2-C2-PPh_2-$PdCl_2$ (2:1)	73	179	36
9	15[d]	240	0.4	9.3	6.3	11	G2-C2-PPh_2-$PdCl_2$ (2:1)	92	220	44
10	18	1226	0.08	1.8	1.25	12	G3-C2-PPh_2-$PdCl_2$ (2:1)	53	652	130
11	19	300	0.33	7.2	5	13	G3-C2-PPh_2-$PdCl_2$ (2:1)	78	234	47
12	1	167	0.6	13	8.8	4	G0-C2-PPh_2-$PdMe_2$	89	176	35
13	2	500	0.2	4.7	3.2	5	G1-C2-PPh_2-$PdMe_2$	74	358	72
14	21	1000	0.1	2.5	1.7	6	G1-C2-PPh_2-$Pd(PPh_3)_2$	36	318	64
15		250	0.4	2.5	6.2	6	G1-C2-PPh_2-$Pd(PPh_3)_2$	60	145	29
16	20	143	0.7	15.2	10.7	7	"G1-C2-PPh_2-$Pd(dba)_2$"	76	144	29
17		156	0.60		10		10% Pd/C	78	121	24
18		132	0.8		11.5		$Pd(PhCN)_2Cl_2$	75	99	20

[a] General conditions: PhI (1.5 mmol), MeOH (5 mL), Et_3N (0.4 mL), and the catalyst with 100 psi of CO at 105 °C over 5 h. Catalyst was a palladium complex of a phosphinated PAMAM supported on SiO_2. [b] Entry from Table 7. [c] 20.5 mg of dppb (excess) added 3:1 over Pd; the recycled isolated catalyst is yellow. [d] The same catalyst 11 (entry 11 in Table 1) was used. However, the reaction was carried out in two stages: first, the catalyst was heated for 5 h under the same conditions with MeOH and Et_3N, but without PhI. The catalyst turned black. In stage 2, PhI was introduced and the reaction was run under the same conditions for 5 h.

TABLE 9. Evaluation of Palladium Leaching from Different Dendrimer Catalysts in the Carbonylation of Iodobenzene[a]

	reaction[b]	catalyst	catalyst no.[c]	% Pd loading[d]	ratio[d]	reaction time, h	% yield of ester	% Pd leaching
1	7	G1-PPh_2-$PdCl_2$	1	65	2:1	5	86	10.2
2	8	G1-PPh_2-$PdCl_2$	3	100	2:1	19	100	10.4
3	11	G2-PPh_2-$PdCl_2$	10	46	4:1	5	67	6.3
4	14	G2-PPh_2-$PdCl_2$	10	46	4:1	19	100	7.2
5	12	G1-PPh_2-$PdCl_2$	11	38	2:1	5	73	7.5

[a] Based on ICP analysis. [b] The numbering of the reactions (entries) as they appear in Table 7. [c] The number of the catalysts as they appear in Table 1. [d] Ratio of the phosphinic dendrimer to the Pd agent;

by the reaction of diphenylphosphino-methylated dendrimers with $PdCl_2(PhCN)_2$, after their reduction with hydrazine to Pd(0) complexes immobilized at the periphery of the dendrimers. These Pd(0) dendrimers showed high catalytic activity for the stereoselective allylic substitution of allylic acetates with amines. Although not practical, the addition of dppb to the reaction mixture stabilizes the Pd(0) formed under the reducing conditions, and the catalyst is usually isolated as a yellow solid (Table 7, entry 4).

(b) The Pd complexes immobilized on the phosphonated PAMAM dendrimers on SiO_2 often gave a signal in the ^{31}P solid-state NMR at +27 ppm, which is assigned to the oxidized phosphorus in the complex dendrimer (Table 1). Despite the presence of some phosphine oxide, the reactions went to completion in all cases.

Several authors have described triphenylphosphine oxide, long considered as being inactive in oxo synthesis, to be an efficient ligand despite its weak coordination to metal centers. In 1987 Mitsubishi Kasei launched a 30 000 t/year plant for the production of isononyl alcohol by reductive hydroformylation of octenes.[18] The basic catalyst was a rhodium-triphenylphosphine oxide (TPPO). The beneficial effect of phosphine oxides in P−N bidentate ligands for the Rh-catalyzed hydroformylation of styrene was reported by several groups.[19a,b] The ligand $Ph_2PCH_2NMe_2$, used with $[RhCl(cod)]_2$ (cod = 1,5-cyclooctadiene), gave 59% olefin conversion, with aldehydes formed in a 96:4 i/n ratio, whereas with the corresponding oxide $Ph_2P(O)CH_2NMe_2$ conversions of 100% (80% after 1 h) and selectivities of 91:9 were observed under identical conditions.

(c) Residual solids obtained from five separate reactions (Table 9) after removal of the solvent and after the nanofiltration of the catalyst were digested with aqua-regia and analyzed by ICP. Leaching of palladium ranged from 6 to 10%. The extent of leaching for the first generation of the Pd-dendrimer catalyst was higher (ca. 10% entries 1 and 2) than that observed for the second generation (6−7%; entries 3−5). The loading level of the Pd and the time for the reaction (5 or 19 h) did not play a role in the leaching process. The same pattern was noted for the second-generation Pd dendrimer catalysts, where the leaching level of Pd was 6.3−7.5% regardless of the time of reaction, Pd loading level, and the ratio between the phosphine-substituted dendrimer and the palladium compound (either 2:1 or 4:1). It is possible that a longer reaction time had a small effect on the leaching, where 7.2% leaching was obtained after 19 h of reaction compared to 6.3% after 5 h. The presence of Pd metal in the solution is a result of partial dissolution of the solid silica based catalyst in methanol. The higher the generation of the dendrimer the less the catalyst dissolved.

TABLE 10. Carbonylation of Iodobenzene with Different Pd Sources[a]

reaction	catalyst/mg	μmol of Pd used	recovered catalyst/mg	recycle no.	% PhI	% PhCOOMe
1	Pd black/4.7	44.2		0	76	24
2	G1-C2-Pcycl$_2$-PdCl$_2$ + Pd metal	47	16.9; gray	0	35	65
3	recycle from 2/16.9		13.4; gray	1	18	82
4	10% Pd/C (dry) (50% H$_2$O); 70 mg	32.9		0		100
5	APS[b] + Pd black/17.4 + 5.7	53.3	18.6	0	53	47
6	SiO$_2$ + Pd black/16.6 + 5.5	51.7	18.1	0	57	43
7	recycle from 6/18 mg		15	1	22	78

[a] Conditions: PhI (1.5 mmol); Et$_3$N (0,4 mL), MeOH (5 mL), at 105 °C with 100 psi of CO, 19 h. [b] APS is aminopropylsilica (0.9 mmol/g amino groups).

TABLE 11. Carbonylation of Iodobenzene with Different Heterogeneous Pd Supports[a]

reaction	catalyst	% selectivity of PhCOOMe	% conversion of PhI
1	10%Pd/C	93.8	98.9
2	5%Pd/C	97.0	99.0
3	5%Pd/C	98.6	99.5
4	5%Pd/Al$_2$O$_3$	97.0	98.9
5	5%Pd/Al$_2$O$_3$	98.8	98.3
6	5%Pd/BaSO$_4$	97.0	99.7
7	5%Pd/CaCO$_3$	98.5	99.5

[a] Conditions: 10% PhI/10% TEA. [b] /MeOH, 105 °C, 600 psi of CO, 1 h. [b] TEA = triethylamine.

(d) The yields obtained for the carbonylation of iodobenzene decrease when going to higher generations. Thus, 91% yield was obtained for G1 (and G0), 73% for G2, and 53% for G3 (after 5 h and a 2:1 ratio of the phosphinated dendrimer and the Pd reactant; Table 7). This trend could be attributed to the extent of immobilization of the Pd compound on higher generations of the dendrimer.

Miscellaneous Issues. Different nondendrimeric Pd sources were examined for the carbonylation of PhI under 100 psi of CO at 105 °C with Et$_3$N (Table 10). When Pd metal was used (entry 1) the yield of the ester was only 24%. Interestingly, when the same amount of Pd metal was mixed with G1-C2-P(cyclohexyl)$_2$ the yield of the ester rose to 65%. Recycling the isolated gray catalyst from the reaction, under the same conditions, afforded an even higher yield of product (82%). This can be explained by the formation of finely divided Pd particles stabilized on the phosphonated dendritic surface. The mixing of Pd metal with the starting aminopropysilica (APS; used for the building of the dendrimer) or with SiO$_2$ resulted in similar yields (47% and 43% yield respectively). These results are lower than the 65% yield obtained with the phosphonated dendrimer (entry 2), which suggests that the phosphines act as better coordination sites for the fine precipitating Pd particles. When 10% Pd/C was used the yield was quantitative, which could explain the role of a high surface factor in the promotion of the carbonylation with Pd(0). This is further confirmed with the recycling of the isolated catalyst mixture of Pd/SiO$_2$ (entry 6) and the increase of the yield to 78% (entry 7).

In another set of reactions Pd on different supports such as 10% Pd/C, 5% Pd/C, 5% Pd/Al$_2$O$_3$, 5%Pd/BaSO$_4$, and 5% Pd/CaCO$_3$ was examined for the carbonylation of PhI. When the reaction was carried out in MeOH at 105 °C, at 600 psi of CO with Et$_3$N acting as the base, it was complete in 1 h in high selectivity (Table 11). In comparison, Yagita et al.[13] used water in the reaction, claiming it enhanced the activity for the Pd/C, for the carbonylation of bromobenzene. Thus, PhI was carbonylated in MeOH/H$_2$O at 160 °C and 154 psi of CO, giving a mixture of PhCOOMe/PhCOOH in a 77:20 ratio.

Conclusions. The dendrimer-bound Pd complexes of PAMAM dendrimers supported on SiO$_2$ show high catalytic activity for the carbonylation of iodoarenes to the methyl esters. The reaction can be carried out in MeOH as the solvent, at low pressure of CO and at 100 °C, using Et$_3$N as a base. The catalysts are active even with an oxidized phosphorus in the coordination site. The catalysts could be recycled 4−5 times under the same reaction conditions. The scope of the carbonylation reaction with Pd-bound dendrimers was good, as the reaction proceeded with electron-withdrawing and -donating groups.

Experimental Section

General Experimental Procedure for the Carbonylation of Iodoarenes. To a 50- mL stainless steel autoclave, equipped with a glass liner and a magnetic stirring bar, were charged ArI (1.5 mmol), MeOH (5 mL), Et$_3$N (0.4 mL), and 17 mg of the Pd-dendritic catalyst.[16a,c] The autoclave was flushed several times with CO, and then CO was introduced until a pressure of 100 psi was obtained. The reaction mixture was heated in an oil bath to 105 °C for a period of 5 h (or overnight, ca. 19 h). After cooling, the reaction mixture was filtered through a 0.45 μm membrane and washed with dichoromethane. The ratio of ester to starting material was determined by GC analysis.

For quantitative ^{1}H NMR experiments, the solvent was removed carefully under vacuum at 40 °C. The ratio between the methyl group in the ester and the two hydrogens in 1,2-tetraachloroethane (δ 5.9 ppm), used as the reference, gave a reliable determination of the yield of the formed ester.

The isolation of several products by liquid chromatography demonstrated good correlation between the GC results and the ^{1}H NMR experiments (i.e. the isolated yield was 4−6% lower than determined by GC). Consequently, it was decided to monitor the reaction with GC (area %).

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