Dendritic effects in catalysis by Pd complexes of bidentate phosphines on a dendronized support: Heck *vs.* carbonylation reactions†‡

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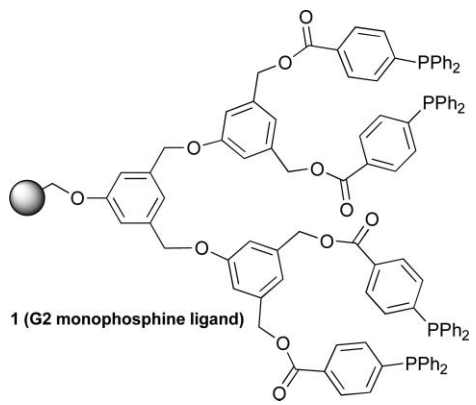
Bidentate phosphine ligands have been prepared on polystyrene beads modified with polyether dendron spacers. When complexed to Pd^0, these systems exhibited a negative dendritic effect on Heck catalysis (contrary to the analogous monodentate phosphine systems), but mostly a positive influence on carbonylation. This opposite influence of the dendronization falls into line with other differences in the optimal ligand structure for the two reactions. The negative effect on the Heck catalysis with bidentate phosphines may indicate that dendrimer-induced reduction in the cross-linking upon Pd complexation is responsible for the positive effect in the corresponding monodentate phosphine systems.

Introduction

In the past few years a few research groups have explored the issue of dendritic catalysts immobilized on solid supports.[1,2] In most cases positive dendritic effects, *i.e.* improved catalytic output of the dendritic catalysts as compared to their non-dendritic analogues, were observed.[3] Thus, we reported polymer-supported catalysts based on dendrons decorated with monodentate phosphines (*e.g.* structure **1**), revealing positive dendritic effects on the activity and chemoselectivity of Co complexes in the Pauson–Khand reaction and Pd complexes in the Heck and Suzuki reactions.[3a–c] While dendronization of the polystyrene matrix must influence the catalyst performance through a variety of different factors, only some of them will lead to an improvement in the catalyst action, while others are likely to negatively affect the catalysts.



1 (G2 monophosphine ligand)

The aforementioned experiments demonstrated that, in the case of the monodentate phosphine systems in the tested reactions, the superposition of all the factors affected by the dendronization results in a positive net outcome. During these experiments it was found that one of the most important factors, contributing to the positive effect, was reduced cross-linking of the polymer upon complexation, a property directly derived from the dendronization-induced proximity of the ligating groups. In this communication we demonstrate that for bidentate terminal ligands the contribution of this factor to the net result is of substantially reduced magnitude (if it exists at all), and accordingly the effect of dendronization can become negative.

Herein we report the preparation of dendrons decorated with chelating bidentate phosphine ligands on a support, their complexation with a Pd^0 precursor and catalysis of Heck and amidocarbonylation reactions with the obtained complexes.[4–6]

Results and discussion

In the past, our group communicated the preparation of polyether dendrons on polystyrene, and their use as spacers for the aforementioned catalytic systems.[3a,b,7] Although these dendrons were prepared in a highly efficient and selective way *via* a Mitsunobu–reduction reaction sequence (Scheme 1), the Mitsunobu reaction required the two-step synthesis of a special coupling agent **3**, which must be prepared from expensive starting materials and has a limited shelf-life.

In order to remove this obstacle, we reworked the synthesis, changing the monomer coupling step to the nucleophilic substitution of benzyl halide by the phenolate of **2**, and adding an additional monomer activation step – chlorodehydroxylation (Scheme 2).

Clean and efficient substitution reactions yielding **Gn(CO_2Me)** were carried out using LiH. The reduction step conditions are the same as those previously reported for the two-step assembly sequence, while excellent results were obtained for chlorodehydroxylation with a PPh_3/C_2Cl_6 reagent mixture, yielding **Gn(Cl)** quantitatively. All steps exhibited quantitative conversion. The purity of each step is excellent as confirmed by the cleavage analysis. Morever, gel phase ^{13}C NMR did not detect any impurities on the support. Thus, replacing the two-step sequence with the three-step one, we were able to reach approximately the same yield and purity of the dendrons, using only readily available commercial reagents.

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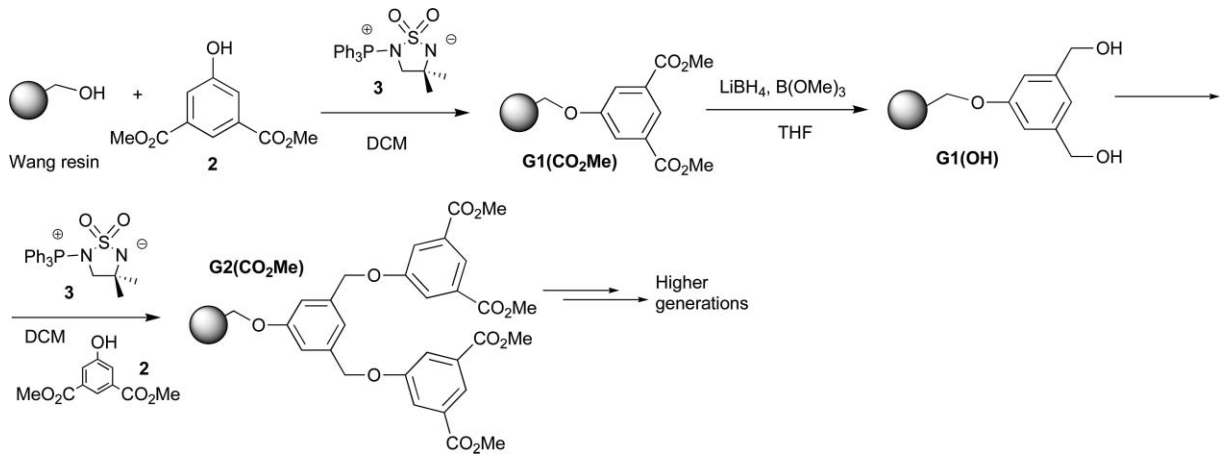
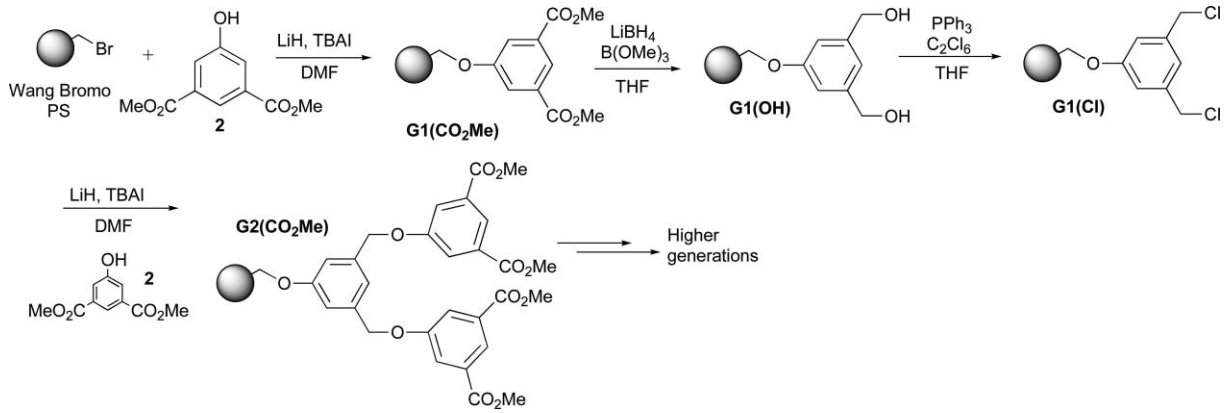
† This paper is dedicated to Prof. D. Milstein on the occasion of his 60th birthday.

‡ Electronic supplementary information (ESI) available: General experimental conditions and characterization data of intermediates **Gn(CO_2Me)**, **Gn(serinol-OH)** and **Gn(serinol-Cl)**. See DOI: 10.1039/b809715a



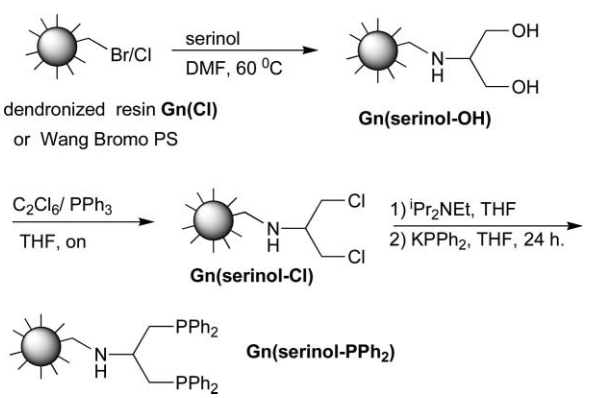
Scheme 1 The reported synthesis of polyether dendrons.[6]



Scheme 2 The modified synthesis of polyether dendrons.

This alternative sequence also directly provided the chloromethyl-terminated dendrons **Gn(Cl)** that were used as starting materials for the bidentate ligand synthesis.

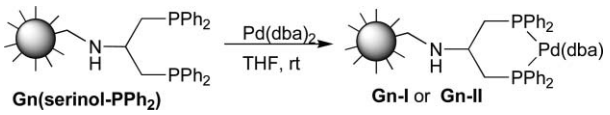
The synthesis of the diphosphine ligand followed the route previously reported for its assembly on the Wang Bromo polystyrene, and was initiated from immobilization of serinol on the **Gn(Cl)** *via* a nucleophilic substitution reaction (Scheme 3).[8] Although for the synthesis of the first two generation ligands, serinol itself is used in this step as an HCl-sequestering base, diisopropylethylamine must be added for the immobilization of serinol on **G3(Cl)**, to prevent dendron cleavage. It is possible that a higher local concentration of HCl is temporarily generated in this reaction with **G3(Cl)** and is responsible for the cleavage. The next step, chlorodehydroxylation, followed under the conditions previously described. The synthesis was accomplished *via* phosphinodechlorination with $KPPh_2$.



Scheme 3 Synthesis of the bidentate phosphines.

For most steps *en route* from **Gn(Cl)** to **Gn(serinol-PPh$_2$)** the conversion and yield were close to quantitative, and only for the last two steps of the **G3(serinol-PPh$_2$)** synthesis was a lower yield observed. The synthesis of the ligands was monitored by the cleavage analysis (first two steps) and gel-phase NMR (the last step). The yield of the phosphination in the last step was determined using a ^{31}P NMR-based quantification experiment with the commercial supported diphenylphosphino polystyrene reference.[9] The cleavage analysis and quantification, being in a very good agreement, demonstrated that the overall yield of the **G1(serinol-PPh$_2$)** is 71%. For the higher generations, the 9-step and 12-step reaction sequences yielded 45% and 11% of the second- and third-generation structures respectively.

The ligands **Gn(serinol-PPh$_2$)** were converted to catalytic resins, following their complexation with $Pd(dba)_2$ (Scheme 4).[10] Two series of catalysts were prepared. For the first series, the incubation procedure was based on a 1 : 1 ratio between the bisphosphine ligand and the soluble Pd precursor, thus leading to systems where each ligating site is complexed by the Pd(dba) fragment (**Gn-I**).



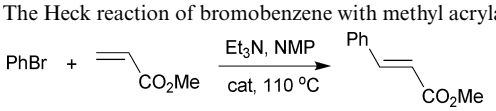
Scheme 4 The complexation with Pd^0.

The second series of the catalysts was generated using a 2 : 1 ratio between the bidentate ligand and the Pd precursor, thus leading to systems with only half of the ligating sites being occupied by Pd (**Gn-II**). In the synthesis of the second series, complete discoloration of the brown $Pd(dba)_2$ solution occurred during the incubation, while in the first series synthesis the discoloration was almost complete. This observation provides evidence for complete incorporation of the calculated amount of Pd into the ligating sites on the resin. Additional evidence for the generation of the planned catalytic series was obtained from gel-phase ^{31}P NMR. While the phosphorus signal of the free ligand appears at −23 ppm, that of the ligand complexed with Pd(dba) appears at +13 ppm. For the first series of dendritic catalysts the complete disappearance of the broad signal at −23 ppm was accompanied by the appearance of a new broad signal at +13 ppm. For the second series two signals in *ca.* 1 : 1 ratio appeared at −23 and +13 ppm.

The preliminary studies with the zeroth-generation ligand (**G0(serinol-PPh$_2$)**) prepared on the Wang resin through a sequence similar to that in Scheme 3 demonstrated that partial complexation with Pd (*versus* full complexation) somewhat improves the performance of the catalytic system in the Heck reaction. Therefore, the second series (**Gn-II**) was examined in the Heck arylation of methyl acrylate with bromobenzene (Table 1). The reaction was carried out at 110 °C for 14 h with the amount of catalytic resin normalized with respect to Pd equivalents, under conditions similar (though not equivalent) to those used in the dendritic effect study of the monodentate phosphine-based catalysts.[3b,c] The results in Table 1 demonstrate a negative effect of the dendronization on the catalytic performance of the complexes of the bisphosphine ligand. There is a notable decrease in the activity of **G1-II**, **G2-II** and **G3-II** compared with that of **G0-II**. The activity of the catalysis decreases steadily with the increase of dendron generation.

The striking difference with the monodentate phosphine system may point to the source of the dendritic effect in the monodentate ligand case. We have demonstrated that the catalytic systems are based on the $(phosphine)_2Pd$ complex fragments.[3c] Clearly in the monodentate phosphine case each formation of such fragment is a cross-linking event, unless the two phosphines are chemically connected to the same attachment point (*e.g.* dendronized support).

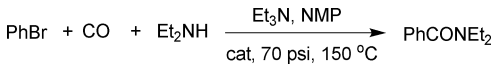
Table 1 The Heck reaction of bromobenzene with methyl acrylate[a]



Entry	Catalyst	Conversion (%)	Yield (%)[b]
1	**G0-II**	72	68
2	**G1-II**	56	52
3	**G2-II**	48	43
4	**G3-II**	16	12

[a] *Reagents and conditions*: 0.53 mmol bromobenzene, 0.64 mmol methyl acrylate, 0.7 mmol triethylamine and 3.75% catalyst (0.02 mmol Pd) in 1 ml NMP at 110 °C, 14 h. [b] HPLC yield.

Table 2 The amidocarbonylation reaction of bromobenzene with diethylamine[a]



Entry	Catalyst	Conversion (%)	Yield (%)[b]
1	**G0-I**	74	72
2	**G1-I**	43	42
3	**G2-I**	21	20
4	**G3-I**	100	99
5	**G0-II**	80	80
6	**G1-II**	97	97
7	**G2-II**	100	99
8	**G3-II**	100	99
9[c]	**G1-II**	44	40
10[c]	**G2-II**	79	78

[a] *Reagents and conditions*: 0.5 mmol bromobenzene, 2.0 mmol diethylamine, 0.7 mmol triethylamine and 1% catalyst (0.005 mmol Pd) in 2 ml NMP under 70 psi CO at 150 °C, 17 h. [b] HPLC yield. [c] Reaction time 6 h.

This is not the case with the strongly chelating bidentate ligands. Therefore, the dendronized resins do not gain a strong cross-linking related advantage, as compared to the non-dendronized one, when decorated with the bidentate ligands. Most likely other factors associated with the dendronization of the support, such as reduced pore volume and diminished swelling,[2a] are responsible for the differences between the dendritic and non-dendritic supported catalysts. These properties can definitely lead to the restricted access of reagents to the pores and, consequently, the decreased activity in the higher generations.

In the case of the amidocarbonylation reaction (Table 2), the zeroth generation ligand demonstrated an even stronger dependence on the degree of complexation than in the Heck reaction.[10,11] In this case we decided to examine both series of the catalyst, fully complexed **Gn-I** and partially complexed **Gn-II**. In the series **Gn-I** a negative dendritic effect was observed up to the second-generation **G2-I** catalyst (Table 2, entries 1–3). This trend was drastically altered for the **G3-I** catalyst, which led to quantitative conversion (entry 4). A substantially better performance was demonstrated by the second series of catalysts (entries 5–8). In this case a positive effect was observed, with the quantitative conversion for the second- and third-generation catalysts. At shorter reaction times the dendritic influence is even more dramatic, as a comparison between **G1-II** and **G2-II** in the 6 hour reaction demonstrated (entries 9 and 10).

Usually, Pd leaching, revealed by black Pd particle precipitation, is observed in both catalytic processes. However, this phenomenon was minimal for **G3-II** in the carbonylation reaction and, upon recycling, the second run yielded 97% of the product. It is even plausible that high ligand density of the third-generation dendrons prevented complete precipitation of Pd from the **G3-I** system, converting it into a **G3-II**-like catalyst and, thus, eventually leading to its high activity in the amidocarbonylation reaction.[12] On the other hand, **G0-II** recycled from the Heck reaction (the most active catalyst in the first run) led to substantially lower conversion and yield in the second run (*ca.* 10%).

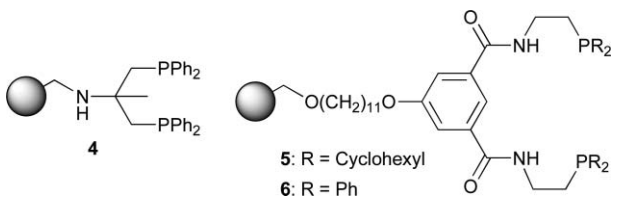
The considerable differences between the Heck and carbonylation reactions, in regard to the dendritic influence, fall into line with the differences in the preferred ligand architecture that we observed for the two reactions catalyzed by the supported

Table 3 Differences in the performance of bisphosphine ligands in the Heck and amidocarbonylation reactions[a]

		Heck reaction		Carbonylation	
Entry	Ligand	Conversion (%)	Yield (%)[b]	Conversion (%)	Yield (%)[b]
1	**G0-I**	65	61	74	72
2	**4**	91	72	18	16
3	**5**	41	37	74	73
4	**6**	100	96	56	54

[a] *Reagents and conditions*: Heck reaction: 0.53 mmol bromobenzene, 0.64 mmol methyl acrylate, 0.7 mmol triethylamine and 3.75% catalyst (0.02 mmol Pd, Pd:P ratio 1 : 2) in 1 ml NMP at 110 °C, 14 h. Carbonylation reaction: 0.5 mmol bromobenzene, 2.0 mmol diethylamine, 0.7 mmol triethylamine and 1% catalyst (0.005 mmol Pd, Pd:P ratio 1 : 2) in 2 ml NMP under 70 psi CO at 150 °C, 17 h. [b] HPLC yield.

non-dendritic phosphine–Pd complexes. Ligands **4–6** were prepared on Wang support, complexed with $Pd(dba)_2$, and used in catalysis of the two reactions. The results (Table 3) reveal dramatic differences between the influences of different structural features of the ligand on the outcome of the two reactions. Thus, carbonylation catalysis is strongly favored by complexes of six-membered chelates, while the Heck reaction can also proceed effectively with ligands forming larger chelate rings (if at all) (entries 1 and 4). Substituents on the bridge of the six-membered chelates improve the Heck catalysis, while negatively affecting the carbonylation reaction (entries 1 and 2). The replacement of diarylalkylphosphines by strongly electron-donating trialkylphosphines substantially improves the carbonylation catalysis, while it is disadvantageous in the case of the Heck reaction (entries 3 and 4).



The common factor of these findings is that strong chelates/high electron density on Pd are "good" for carbonylation, while they are not contributing as much, or are even disadvantageous, for Heck reaction. Plausibly, Pd with a single coordinated phosphine (likely Pd^{II}) is a necessary intermediate in the Heck reaction, though the ability to easily form the $(phosphine)_2Pd$ fragment is also crucial (probably for the stabilization of Pd^0). On the other hand, the stable bisphosphine chelate–Pd fragment can propagate without dissociation through the intermediates of the carbonylation cycle. Though it is difficult to supply direct experimental evidence for this hypothesis in supported catalysis, the mechanistic study of the related systems in solution revealed a similar explanation for the differences in the chelating strength requirement from the optimal ligand in the Heck and alkoxycarbonylation catalysis of chloroarenes.[13] It is possible that at some stage of the carbonylation reaction even three phosphine donors are required for stabilizing the catalytic intermediate (frequently, phosphine excess is used in homogeneous Pd-catalyzed carbonylation processes[14]).

For all these reasons we believe that, in the case of bidentate phosphine ligands, the high local density of phosphines dictated by the dendritic architecture is an advantage for the carbonylation process, while it does not contribute to (or even inhibits) the Heck catalytic reaction.

Experimental

General synthesis of Gn(CO_2Me)

A mixture of dimethyl 5-hydroxyisophthalate (10 equiv.) and LiH (5 equiv.) was stirred in the minimal volume of dry DMF at room temperature for 5 minutes, and added to a suspension of the appropriate halomethyl-functionalized resin (1 equiv. of halomethyl group.) in the minimal volume of dry DMF. TBAI (3 equiv.) was added and the mixture was stirred at 60 °C overnight. The resin was filtered off and washed with DMF, DMF–water, THF, THF–water, THF and DCM and dried in vacuum.

Synthesis of Gn(OH)

G1(OH), **G2(OH)** and **G3(OH)** were prepared *via* the reported procedures.[6]

General synthesis of Gn(Cl)

Hexachloroethane (5.5 equiv.) and triphenylphosphine (5.5 equiv.) were added to a suspension of the resin-bound alcohol (1 equiv. of OH groups) in dry THF (10 ml g^{-1} resin). The suspension was mixed at room temperature overnight. The resin was washed with THF (× 3) and dichloromethane and dried under vacuum.

G1(Cl). Prepared from **G1(OH)** (0.54 mmol g^{-1}). Yield 96%, purity >99%, loading 0.50 mmol g^{-1}. Gel-phase ^{13}C NMR (100.8 MHz, C_6D_6): δ 158.5, 144.6, 138.7, 120.8, 114.5, 69.2, 45.0. Following TFA-induced cleavage: ^1H NMR (200 MHz, $CDCl_3$–TFA 1 : 1): δ 7.11 (s, 1H), 6.94 (s, 2H), 4.56 (s, 4H). ^{13}C NMR (100.8 MHz, $CDCl_3$–TFA 1 : 1): δ 154.1, 140.0 122.1, 115.4, 45.0.

G2(Cl). Prepared from **G2(OH)** (0.31 mmol g^{-1}). Yield >99%, purity >95%, loading 0.30 mmol g^{-1}. Following TFA-induced cleavage: ^1H NMR (200 MHz, $CDCl_3$–TFA 1 : 1): δ 7.01–6.82 (m, 9H), 5.28 (s, 4H), 4.56 (s, 8H). ^{13}C NMR (100.8 MHz, $CDCl_3$–TFA 1 : 1): δ 160.9, 139.7, 138.7, 122.0, 121.9, 115.3, 114.4, 70.2, 54.3.

G3(Cl). Prepared from **G3(OH)** (0.28 mmol g^{-1}). Yield 95%, purity >90%, loading 0.26 mmol g^{-1}. Gel-phase ^{13}C NMR (100.8 MHz, C_6D_6): δ 158.7, 144.9, 120.8, 118.5, 114.4, 113.0, 69.1, 45.0. Following TFA-induced cleavage: ^1H NMR (200 MHz, $CDCl_3$–TFA 1 : 1): δ 7.07–6.91 (m, 21H), 5.13 (broad s, 12H), 4.55 (s, 16H). ^{13}C NMR (100.8 MHz, $CDCl_3$–TFA 1 : 1): δ 158.4, 158.5, 139.6, 138.9, 138.5, 121.8, 119.9, 115.3, 114.3, 114.2, 70.2, 70.1, 45.4.

General synthesis of Gn(serinol-OH)

Serinol (10 equiv.) was added to a suspension of the Gn(Cl) resin (1 equiv. of Cl groups) in a minimal volume of dry DMF. The suspension was stirred for 17 hours at 50 °C, filtered, the resin washed with ethanol (× 2) and DCM (× 2) and dried *in vacuo*.

General synthesis of Gn(serinol-Cl)

The synthesis followed the procedure for preparation of **Gn(Cl)**.

General synthesis of Gn(serinol-PPh_2)

N,*N*-Diisopropylethylamine (20 equiv.) was added to a suspension of the Gn(serinol-Cl) resin (1 equiv. of NH groups) in the minimal volume of dry THF. After 1 hour of stirring of the suspension at room temperature, the resin was washed with THF. For better results the procedure was performed twice. The resin was re-suspended in a minimal volume of THF, in a glove box, and potassium diphenylphosphide (0.5 M in THF, 20 equiv.) was added to the suspension of resin. The suspension was stirred for 24 hours. The resin was filtered off and washed with water, acetone, chloroform and ether and dried in vacuum.

G1(serinol-PPh_2). Prepared from **G1(serinol-Cl)** (0.44 mmol g^{-1}). Yield >99%, purity >99%, loading 0.36 mmol g^{-1}. Partial gel-phase ^{13}C NMR (100.8 MHz, C_6D_6): δ 139.2, 133.0, 114.2, 69.6, 52.6, 50.8, 36.2. Gel-phase ^{31}P NMR (162 MHz, C_6D_6): δ −23.3.

G2(serinol-PPh_2). Prepared from **G2(serinol-Cl)** (0.23 mmol g^{-1}). Yield >99%, purity >95%, loading 0.19 mmol g^{-1}. Gel-phase ^{31}P NMR (162 MHz, C_6D_6): δ −23.4.

G3(serinol-PPh_2). Prepared from **G3(serinol-PPh_2)** (0.11 mmol g^{-1}). Yield 50%, loading 0.043 mmol g^{-1}. Gel-phase ^{31}P NMR (162 MHz, C_6D_6): δ −23.4. TFA-induced cleavage: ^1H NMR (200 MHz, $CDCl_3$–TFA 1 : 1): δ 7.87–7.67 (m, 160H, Ph), 7.00–6.70 (m, 28H), 4.90–3.90 (m, 68H).

Synthesis of 4

The synthesis followed the route reported earlier for **G0(serinol-PPh_2)**.[8] Yield >99%. Partial gel-phase ^{13}C NMR (100.8 MHz, C_6D_6): δ 139.8, 132.7, 56.2, 27.6, 26.0, 16.1. Gel-phase ^{31}P NMR (162 MHz, C_6D_6): δ −24.5.

Synthesis of 5

In a glove box, a solution of *tert*-butyllithium (10% in pentane, 3.2 ml, 4.9 mmol, 10 equiv.), was added slowly to a solution of dicyclohexylphosphine (7.4 mmol, 15 equiv.) in dry THF. The mixture was stirred for 3 hours, the solvent was evaporated and the resulting salt was dissolved in a minimal amount of dry THF. This solution was added to the suspension of Wang PS-bound 11-(4-(2,6-bis(2-chloroethyl)carboxamide)phenyloxy)undec-1-yl (1.0 g, 0.49 mmol g^{-1}, 0.98 mmol of Cl groups, 4 equiv.) in 2 ml THF and stirred overnight.[15] The resin was filtered off (in the hood), washed with water, acetone, chloroform and ether, and dried in vacuum. Yield 95%, purity >95%, loading 0.40 mmol g^{-1}. Partial gel-phase ^{13}C NMR (100.8 MHz, C_6D_6): δ 167.3, 114.6, 69.8, 56.8, 40.6, 33.2, 29.4, 28.9, 27.2 26.4, 22.2. Gel-phase ^{31}P NMR (162 MHz, C_6D_6): δ −10.1. Following TFA-induced cleavage: ^1H NMR (200 MHz, $CDCl_3$–TFA 1 : 1): δ 8.03 (br, 1H), 7.53 (s, 2H), 5.70 (d, J_{HP} = 460 Hz, 4H), 4.39 (t, J = 6.5 Hz, 2H), 4.02 (m, 2H), 3.90 (m, 4H), 2.55 (m, 4H), 1.6 (m, 98H). ^{13}C NMR (100.8 MHz, $CDCl_3$–TFA 1 : 1): δ 170.0, 159.7, 134.2, 118.6, 117.5, 69.3, 69.0, 42.8, 29.2, 29.0, 28.8, 28.7, 27.8, 25.7, 25.2. ^{31}P NMR (162 MHz, C_6D_6): δ 22.5.

Synthesis of 6

The general procedure for synthesis of **Gn(serinol-PPh_2)** was applied on Wang PS-bound 11-(4-(2,6-bis(2-chloroethyl)-carboxamide)phenyloxy)undec-1-yl (0.49 mmol g^{-1}).[15] Yield 90%, purity >95%, loading 0.38 mmol g^{-1}. Partial gel-phase ^{13}C NMR (100.8 MHz, C_6D_6): δ 138.2, 136.4, 132.5, 116.0, 115.1, 69.9, 29.4, 25.9. Gel-phase ^{31}P NMR (162 MHz, C_6D_6): δ −23.4.

The complexation with $Pd(dba)_2$ and the carbonylation reaction procedures were reported elsewhere.[10]

General procedure for the Heck reaction

Bromobenzene (0.056 ml, 0.53 mmol, 1 equiv.), methyl acrylate (0.057 ml, 0.64 mmol, 1.2 equiv.) and triethylamine (0.1 ml, 0.73 mmol, 1.3 equiv.) were added to the suspension of the supported complex (0.02 mmol Pd) in 1 ml NMP. The mixture was stirred for 14 h at 110 °C. The suspension was filtered and washed with acetonitrile. The filtrate was diluted with acetonitrile and analyzed by HPLC.

Conclusions

In conclusion, we have demonstrated synthesis of and catalysis with a new type of supported dendritic ligand. The dendritic influence in this case reflects its multifactor nature. The delicate balance between the factors depends on the chosen catalytic process and even on the conditions of the particular reaction. For the carbonylation reaction it was demonstrated that an overall negative dendritic effect could be turned into a positive one. The Heck reaction catalysis with the bidentate ligands displayed an overall negative dendritic effect. This finding supports the hypothesis of the reduced cross-linking as the main factor responsible for the positive dendritic effect, observed previously for supported dendritic monodentate phosphine-based catalysts.

Acknowledgements

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