# Recyclable Tridentate Stable Palladium(II) PCP-Type Catalysts Supported on Silica for the Selective Synthesis of Lactones

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**Abstract:** Five- or seven-membered ring lactones are synthesized, in good selectivity and high yields, by the cyclocarbonylation reaction of 2-allylphenols, using a tridentate diphosphinoaryl ligand (PCP-type) palladium(II) catalyst immobilized on silica (**A**) and silica supported dendrimers (**B**, **C** and **D**). These immobilized catalysts, which are highly active and can be recycled by simple filtration in air, and reused with only moderate loss of activity, combine the advantages of heterogeneous and homogeneous catalysts. These complexes are also stable towards oxygen and moisture.

**Keywords:** carbonylation; dendrimers; heterogeneous catalysts; immobilization; lactones; palladium

## Introduction

Carbonylation involves the direct insertion of carbon monoxide into an organic substrate. This reaction usually occurs in the presence of a transition metal complex as the catalyst. Palladium catalysts are especially useful for carbonylation reactions leading to amides,[1–4] acids,[5,6] ketones,[7] esters,[8–10] lactones,[11–14] and other compounds.[15,16] One of the most interesting applications of the carbonylation reaction is for intramolecular cyclocarbonylation to give heterocyclic compounds such as five-, six- and seven-membered lactones in moderate to high yields.[11,12,14] Some of these products are pharmacologically active, or are used as intermediates to synthesize biologically active compounds[17] or polyesters,[18,19] and are often less readily accessible by conventional synthetic methods.

It has been shown that a dendrimer–palladium complex immobilized on silica is catalytically active for several reactions,[20–22] including carbonylation reactions.[10] Immobilization of the homogeneous catalyst by means of a heterogeneous support can, in principle, retain the properties observed for the homogeneous system and allow simple separation from the reaction mixture. It is known that palladium complexes with pincer ligands (e.g., PCP, this ligand comprises an anionic aryl ring which is *ortho, ortho*-disubstituted with $CH_2PR_2$. The latter groups coordinate to the palladium centre resulting in two metallacycles which share the Pd–C bond) display extraordinary thermal stability (up to 180 °C) and are not sensitive to oxygen or moisture. Recently, the generation zero dendrimer (**G-0**), (**A**), obtained by the immobilization of a PCP-type palladium(II) complex onto silica, was described in the literature (Figure 1).[23]

In this paper, we report the cyclocarbonylation reaction of 2-allylphenols to form five- or seven-membered ring lactones in good selectivity and in high yields by generation zero dendrimer (**G-0**) (**A**). Subsequently, generation one dendrimer (**G-1**) (**B**) and generation two dendrimer (**G-2**) (**C**) polyaminoamido (PAMAM) dendrimers were synthesized (Figures 2 and 3). A similar dendrimer, but with a 6-carbon spacer group, was also synthesized as another generation one complex (**G-1**) (**D**) to compare the reactivity with that of (**G-1**) (**B**) (Figure 4). These complexes were found to be effective catalysts for the cyclocarbonylation reaction. In addition, the catalysts can be recycled by simple filtration in air and reused with only moderate loss of activity.

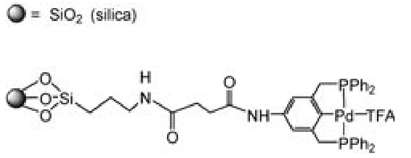

**Figure 1.** Generation zero silica-supported dendrimer (**G-0**) (**A**).

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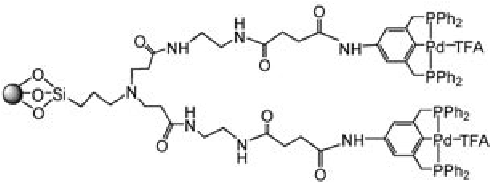


**Figure 2.** Generation one silica supported dendrimer (**G-1**) (**B**).

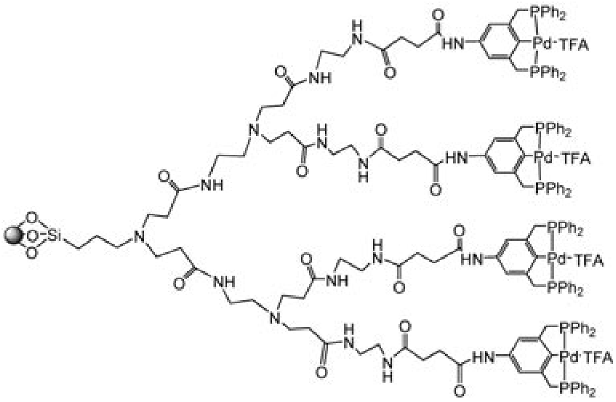


**Figure 3.** Generation two silica supported dendrimer (**G-2**) (**C**).

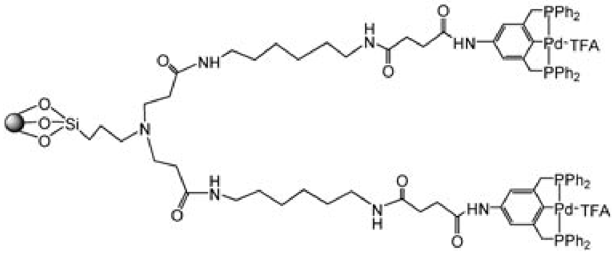


**Figure 4.** Generation one silica supported dendrimer (**G-1**) (**D**).

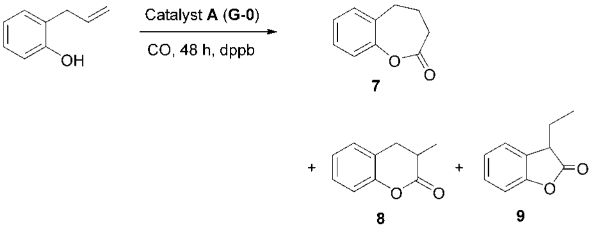
## Results and Discussion

### Synthesis and Characterization of Generation One Dendrimer (G-1) (B), Generation Two Dendrimer (G-2) (C) and Generation One Dendrimer (G-1) (D) Silica Supported PCP-Type Palladium(II) Complexes

Compounds **1**, **2** and **5** were prepared according to literature methods.[23,24] Generation one dendrimer (**G-1**) (**B**), generation two dendrimer (**G-2**) (**C**) and generation one dendrimer (**G-1**) (**D**) were prepared by a strategy similar to that described the for generation zero dendrimer (**G-0**) (**A**),[23] (Schemes 1 and 2). The CP/MAS $^{31}$P NMR and $^{13}$C NMR spectra of compounds **B**, **C**, and **D** were similar to those of **A** reported previously. The percentages of palladium, determined by ICP analyses, were 3.22%, 4.29 and 2.84%, respectively.

### The Catalytic Properties of A (G-0), B (G-1), C (G-2) and D (G-1) for the Intramolecular Cyclocarbonylation Reaction

The catalytic reactivity of **A (G-0)** was investigated for the intramolecular cyclocarbonylation of 2-allylphenol. First, 2-allylphenol was treated with a 1/1 mixture of CO/$H_2$ (total pressure 600 psi) and dppb in toluene at 120 °C for 48 h to form the corresponding lactone in 93% yield and in 78% selectivity for the seven-membered ring lactone (7) (entry 1, Table 1). Small amounts of the six- and five-membered ring lactones (8 and 9) were also formed. Various conditions were used to obtain a better yield and increased selectivity, including changing the relative pressures of carbon monoxide and hydrogen, temperature, and solvent [Eq. (1)]. The results are summarized in Table 1.



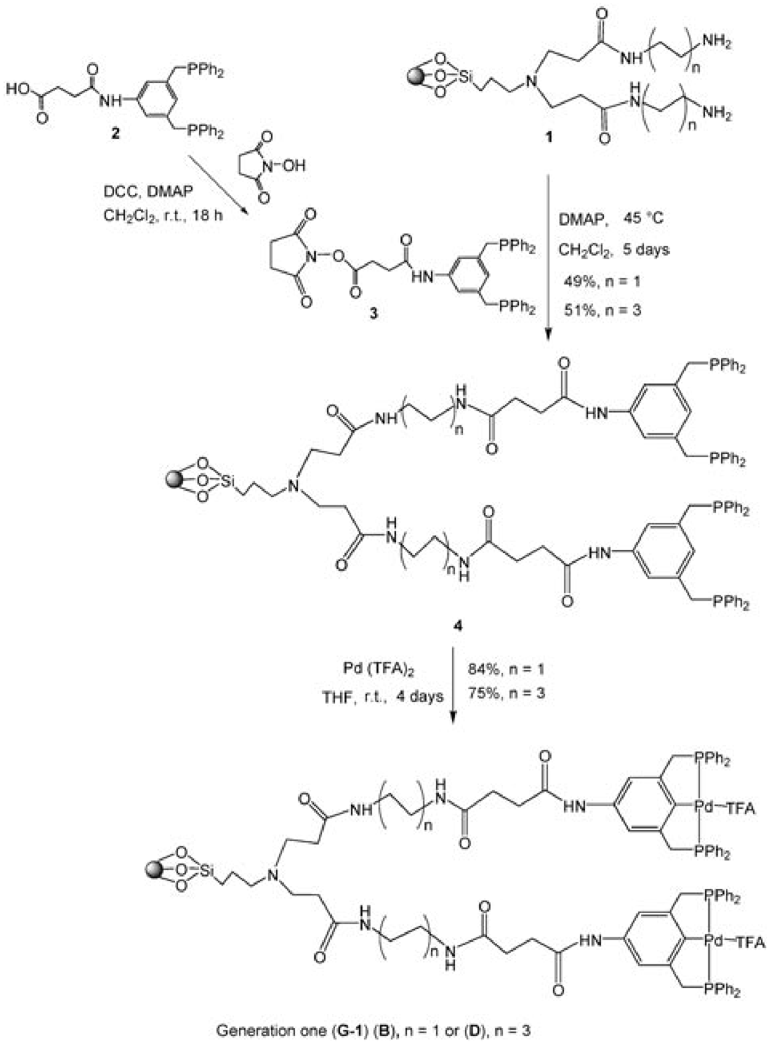
(1)

The reaction yields increased by increasing the temperature to 140 °C or by using $CH_2Cl_2$ instead of toluene, but there was only moderate selectivity for the five-membered ring lactone (entries 2 and 3, Table 1). The five-membered ring lactone was formed in good yield and in high selectivity using a 1/5 mixture of CO/$H_2$ (total pressure 600 psi) in $CH_2Cl_2$, at 140 °C (entry 5, Table 1). The selectivity for the seven-membered ring lactone increased in the absence of hydrogen. The best yield and selectivity for the 7-membered ring lactone was obtained when the pressure of CO was 400 psi in toluene at 140 °C (entry 9, Table 1). The seven-membered ring lactone was also obtained in good yield, and in high selectivity, with a 5/1 mixture of CO/$H_2$ (total pressure 600 psi) in toluene at 120 °C (entry 13, Table 1). Traces of lactones were obtained at lower temperature (100 °C) or at lower pressure (200 psi) (entries 6 and 8, Table 1). Substitution of bidentate (dppb) by monodentate ($PPh_3$) ligands afforded moderate selectivity for the seven-membered ring lactone in 54% yield (entry 14, Table 1).

The recyclability of the catalyst was studied, using several of the best conditions (entries 5, 9 and 13 in Table 1). It was found that under the conditions of entry 5, Table 1, the catalyst **A** (**G-0**) decomposed in the third run (Table 2).

Using the conditions of entry 9, Table 1, the catalyst **A** (**G-0**) also decomposed in the third run (Table 3).

Nevertheless, these conditions are still of interest since the homogeneous hydridoaquopalladium complex



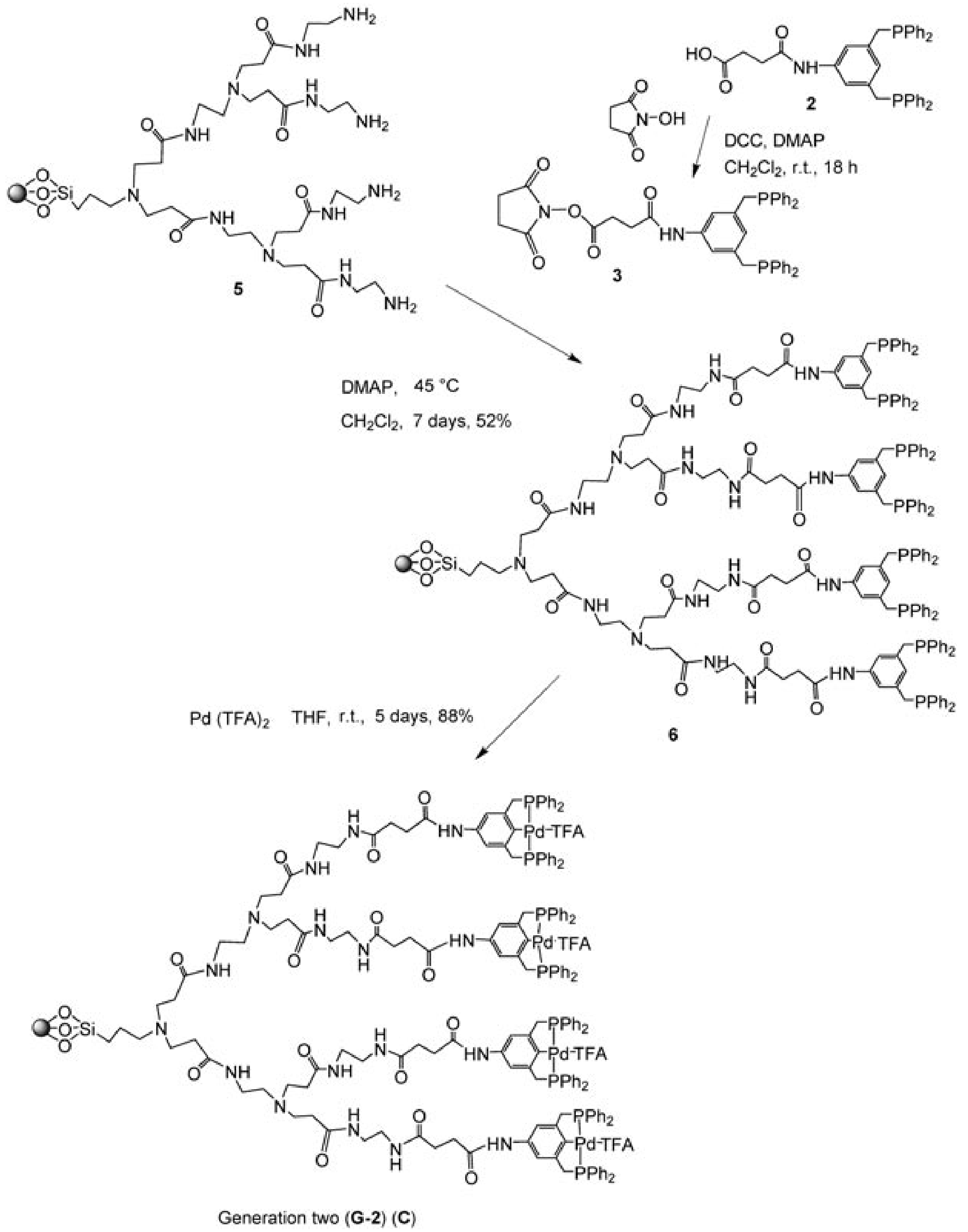
**Scheme 1.** Preparation of generation one (**G-1**) (**B**), n = 1 and (**D**), n = 3.

*trans*-[$(Cy_3P)_2Pd(H)(H_2O)$]$BF_4$, in the absence of hydrogen, gave only traces of lactones.[11] In addition, heterogeneous Pd-clay, in the absence of hydrogen, afforded only 37% lactones with high selectivity for the seven-membered ring product.[12] Therefore, the catalytic reactivities of **B** (**G-1**), **C** (**G-2**), and **D** (**G-1**) were also investigated under these conditions. We found similar results to those obtained for catalyst **A** (**G-O**): the reactions worked well for the first and second runs but the catalyst decomposed after that (Tables 4 and 5). The catalyst containing a 6-carbon spacer group, (**G-1**) (**D**), was more reactive than **B** (**G-1**), and **C** (**G-2**) was more reactive than either **B** (**G-1**) or **D** (**G-1**).

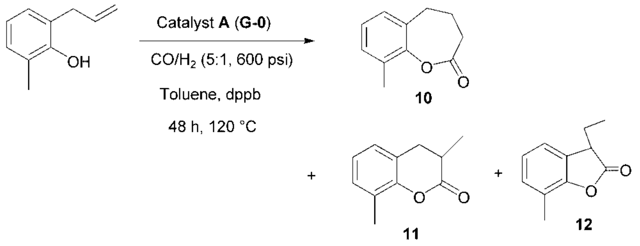
It was found that catalyst **A** (**G-O**) could be recycled five times, under the conditions of entry 13, Table 1 (5/1 mixture of $CO/H_2$, total pressure 600 psi, in toluene at 120 °C) (Table 6).

When catalyst **A** (**G-0**) was replaced by **B** (**G-1**), **C** (**G-2**), or **D** (**G-1**) under the same conditions, similar yields and selectivities were obtained. The reactivities of **B** (**G-1**), **C** (**G-2**), and **D** (**G-1**) correspond to those mentioned previously (Tables 7 and 8).

We also investigated the effect of changing the substrate for the cyclocarbonylation reaction by replacing 2-allylphenol with 2-allyl-6-methylphenol and using **A** (**G-0**) as the catalyst. The yield was similar to 2-allylphenol, and the catalyst could be recycled three times [Eq. (2), Table 9]. It was also noticed that the selectivities were slightly better and the five-membered ring lactone was formed only in traces, if at all. This might be due to the steric and/or electronic effects of the methyl group, which is ortho to the hydroxy group.



**Scheme 2.** Preparation of generation two (**G-2**) (**C**).



(2)

We continued the investigation of the effect of different substrates by replacing 2-allyl-6-methylphenol with 2-allyl-4-chlorophenol. Under the same conditions, the selectivity was similar to 2-allylphenol but different from that of 2-allyl-6-methylphenol [Eq. (3), Table 10]. Clearly, these results show that the cyclocarbonylation is not sensitive to electronic effects but principally steric hindrance affects the selectivity of this reaction.

**Table 1.** Catalytic cyclocarbonylation of 2-allylphenol by **A (G-0)**.[a]

| Entry | Temperature [°C] | $P_{CO}$ [psi] | $P_{H2}$, [psi] | Solvent | Total Yield [%][b] | Product Distribution,[c] % | | | TON [mol of product/ mol of Pd] |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | | **7** | **8** | **9** | |
| 1 | 120 | 300 | 300 | Toluene | 93 | 78 | 11 | 11 | 118 |
| 2 | 140 | 300 | 300 | Toluene | >99 | 24 | 24 | 52 | 127 |
| 3 | 120 | 300 | 300 | $CH_2Cl_2$ | >99 | 28 | 25 | 47 | 127 |
| 4 | 120 | 100 | 500 | Toluene | >99 | 77 | 8 | 15 | 127 |
| 5 | 140 | 100 | 500 | $CH_2Cl_2$ | >99 | 5 | 13 | 82 | 127 |
| 6 | 120 | 200 | 0 | Toluene | 11 | 91 | 5 | 4 | 14 |
| 7 | 120 | 400 | 0 | Toluene | 63 | 86 | 13 | 1 | 83 |
| 8 | 100 | 400 | 0 | Toluene | 3 | 86 | 7 | 7 | 4 |
| 9 | 140 | 400 | 0 | Toluene | 98 | 86 | 11 | 5 | 125 |
| 10 | 130 | 400 | 0 | Toluene | 92 | 83 | 14 | 3 | 117 |
| 11 | 120 | 600 | 0 | Toluene | 90 | 82 | 15 | 3 | 115 |
| 12 | 140 | 600 | 0 | Toluene | 96 | 78 | 16 | 6 | 123 |
| 13 | 120 | 500 | 100 | Toluene | >99 | 83 | 10 | 7 | 127 |
| 14 | 120 | 500 | 100 | Toluene | 54[d] | 63 | 28 | 9 | 69 |

[a] Reactions were conducted using 50 mg ($0.8 \times 10^{-2}$ mmol) of **A** and 1 mmol of 2-allylphenol for 48 h.

[b, c] Determined by NMR and GC.

[d] Using $PPh_3$ instead of dppb.

**Table 2.** Catalytic cyclocarbonylation of 2-allylphenol by **A (G-0)**;[a] a recycling study using 1:5 CO/$H_2$.

| Run No | Yield [%][b] | Product Distribution,[c] % | | |
|---|---|---|---|---|
| | | **7** | **8** | **9** |
| 2 | 97 | 7 | 21 | 72 |
| 3 | 38 | 54 | 36 | 10 |

[a] Reactions were conducted using 50 mg of **A** ($0.8 \times 10^{-2}$ mmol), 0.04 mmol of dppb and 1 mmol of 2-allylphenol for 48 h in $CH_2Cl_2$ at 600 psi and 140 °C.

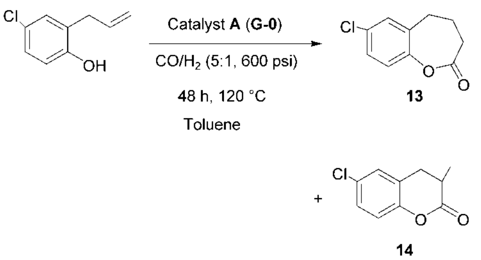
[b, c] Determined by NMR and GC.

**Table 3.** Catalytic cyclocarbonylation of 2-allylphenol by **A (G-0)**;[a] a recycling study using only CO.

| Run No | Yield [%][b] | Product Distribution,[c] % | | |
|---|---|---|---|---|
| | | **7** | **8** | **9** |
| 2 | 96 | 88 | 9 | 3 |
| 3 | 11 | 86 | 14 | 0 |

[a] Reactions were conducted using 50 mg of **A** ($0.8 \times 10^{-2}$ mmol), 0.04 mmol of dppb and 1 mmol of 2-allylphenol for 48 h in toluene at 400 psi and 140 °C.

[b, c] Determined by NMR and GC.



(3)

The homogeneous complex, **16** (Figure 5), was also examined as a catalyst for the cyclocarbonylation reaction of 2-allylphenol so as to compare the results with those obtained using catalyst **A (G-0)** (Table 11).

It was found that in the absence of dppb, lactones were formed in low yield (entry 1, Table 11). Similar results were obtained for the heterogeneous catalyst **A (G-0)**. Lactones were synthesized in high yields when dppb was added but only with moderate selectivity for the seven-membered ring lactone (entry 2, Table 11). This is significantly different from the case of **A (G-0)**, **B (G-1)**, **C (G-2)**, or **D (G-1)**. Aminopropyl silica gel (Figure 6) or *N*-[3,5-bis(diphenylphosphinoylmethyl)phenyl]succinamic acid (**17**) (Figure 7) were added to the reaction but no significant change in the selectivity was noticed.

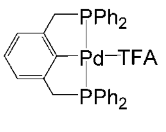


**Figure 5.** Complex **16**.

**Table 4.** Catalytic cyclocarbonylation of 2-allylphenol by **B** (**G-1**), **C** (**G-2**) or **D** (**G-1**);[a] using only CO.

| Catalyst | Yield [%][b] | Product Distribution,[c] % | | | TON [mol of product/mol of Pd] |
|---|---|---|---|---|---|
| | | **7** | **8** | **9** | |
| **B** | 97 | 89 | 9 | 2 | 128 |
| **C** | 91 | 84 | 11 | 5 | 180 |
| **D** | 98 | 82 | 8 | 10 | 147 |

[a] Reactions were conducted using 25 mg of catalyst **B** ($0.8 \times 10^{-2}$ mmol) or **D** ($0.7 \times 10^{-2}$ mmol), or 25 mg of catalyst **C** ($1.0 \times 10^{-2}$ mmol), 0.04 mmol of dppb, and 1 mmol of 2-allylphenol for **B** or **D**, or 2 mmol of 2-allylphenol for **C** for 48 h in toluene at 400 psi and 140 °C.

[b, c] Determined by NMR.

**Table 5.** Catalytic cyclocarbonylation of 2-allylphenol by **B** (**G-1**), **C** (**G-2**) or **D** (**G-1**);[a] a recycling study using only CO.

| Catalyst | Run No | Yield [%][b] | Product Distribution,[c] % | | |
|---|---|---|---|---|---|
| | | | **7** | **8** | **9** |
| **B** | 2 | 96 | 87 | 9 | 4 |
| | 3 | 75 | 90 | 8 | 2 |
| **C** | 2 | 91 | 84 | 11 | 5 |
| | 3 | 69 | 86 | 11 | 3 |
| **D** | 2 | 88 | 89 | 6 | 5 |
| | 3 | 46 | 86 | 11 | 3 |

[a] Reactions were conducted using 25 mg of catalyst **B** ($0.8 \times 10^{-2}$ mmol) or **D** ($0.7 \times 10^{-2}$ mmol), or 25 mg of catalyst **C** ($1.0 \times 10^{-2}$ mmol), 0.04 mmol of dppb, and 1 mmol of 2-allylphenol for **B** or **D**, or 2 mmol of 2-allylphenol for **C** for 48 h in toluene at 400 psi and 140 °C.

[b, c] Determined by NMR.

**Table 6.** Catalytic cyclocarbonylation of 2-allylphenol by **A** (**G-0**);[a] a recycling study using 5:1 CO/$H_2$.

| Run No | Yield [%][b] | Product Distribution,[c] % | | |
|---|---|---|---|---|
| | | **7** | **8** | **9** |
| 2 | 93 | 80 | 13 | 7 |
| 3 | >99 | 87 | 9 | 4 |
| 4 | 91 | 81 | 14 | 5 |
| 5 | 98 | 80 | 11 | 9 |

[a] Reactions were conducted using 50 mg of **A** ($0.8 \times 10^{-2}$ mmol), 0.04 mmol of dppb and 1 mmol of 2-allylphenol for 48 h in toluene at 600 psi and 120 °C.

[b, c] Determined by NMR and GC.

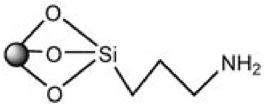


**Figure 6.** Aminopropyl silica gel.

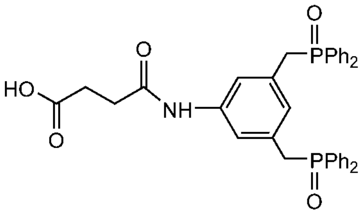


**Figure 7.** *N*-[3,5-Bis(diphenylphosphinoylmethyl)phenyl]succinamic acid (**17**).

Running the reaction in the absence of hydrogen for **16** gave lactones in high yield, comparable to the case when catalysts **A** (**G-0**), **B** (**G-1**), **C** (**G-2**), or **D** (**G-1**) were used but the selectivity for the seven-membered ring lactone was moderate.

The cyclocarbonylation reactions of 2-allylphenol in the presence of complexes **16**, **A** (**G-0**), **B** (**G-1**), **C** (**G-2**) and **D** (**G-1**) gave appreciably different yields and selectivities under the same conditions when compared with the work by El Ali and coworkers using the hydridoaquopalladium complex trans-[$(Cy_3P)_2Pd(H)(H_2O)]BF_4$ or $Pd(OAc)_2$ as homogeneous catalysts.[11] Therefore, the mechanism for the cyclocarbonylation reaction might be different from that which was previously proposed. Typically, temperatures of 120 °C, and addition of diphosphine ligands (dppb), are required, which suggest the possibility of diphosphine ligand exchange between dppb and PCP complexes to palladium. The observed different selectivities between **A** (**G-0**), **B** (**G-1**), **C** (**G-2**), or **D** (**G-1**) and compound **16** might be due to the substantial difference in size between heterogeneous catalysts **A** (**G-0**), **B** (**G-1**), **C** (**G-2**) or **D** (**G-1**) and compound **16**. The effect of substituents on the phenyl ring could also be investigated to determine the influence of electron-donating/withdrawing substituents on the ring as well as the steric effect.

## Conclusions

We have shown that the catalysts obtained by immobilization of a PCP-type palladium(II) complex onto silica

**Table 7.** Catalytic cyclocarbonylation of 2-allylphenol by **B** (**G-1**), **C** (**G-2**) or **D** (**G-1**);[a] using 5:1 CO/$H_2$.

| Catalyst | Yield [%][b] | Product Distribution,[c] % | | | TON [mol of product/mol of Pd] |
|---|---|---|---|---|---|
| | | **7** | **8** | **9** | |
| **B** | 97 | 85 | 10 | 5 | 128 |
| **C** | 98 | 89 | 10 | 1 | 194 |
| **D** | 98 | 80 | 12 | 8 | 147 |

[a] Reactions were conducted using 25 mg of catalyst **B** ($0.8 \times 10^{-2}$ mmol) or **D** ($0.7 \times 10^{-2}$ mmol), or 25 mg of catalyst **C** ($1.0 \times 10^{-2}$ mmol), 0.04 mmol of dppb, and 1 mmol of 2-allylphenol for **B** or **D**, or 2 mmol of 2-allylphenol for **C** for 48 h in toluene at 600 psi and 120 °C.

[b, c] Determined by NMR.

**Table 8.** Catalytic cyclocarbonylation of 2-allylphenol by **B** (**G-1**), **C** (**G-2**) or **D** (**G-1**);[a] a recycling study using 5:1 CO/$H_2$.

| Catalyst | Run No | Yield [%][b] | Product Distribution,[c] % | | |
|---|---|---|---|---|---|
| | | | **7** | **8** | **9** |
| **B** | 2 | 85 | 89 | 10 | 1 |
| | 3 | 97 | 85 | 11 | 4 |
| **C** | 2 | 97 | 82 | 11 | 7 |
| | 3 | 92 | 88 | 10 | 2 |
| **D** | 2 | 87 | 86 | 11 | 3 |
| | 3 | $>99$ | 86 | 8 | 6 |

[a] Reactions were conducted using 25 mg of catalyst **B** ($0.8 \times 10^{-2}$ mmol) or **D** ($0.7 \times 10^{-2}$ mmol), or 25 mg of catalyst **C** ($1.0 \times 10^{-2}$ mmol), 0.04 mmol of dppb, and 1 mmol of 2-allylphenol for **B** or **D**, or 2 mmol of 2-allylphenol for **C** for 48 h in toluene at 600 psi and 120 °C.

[b, c] Determined by NMR.

and silica supported dendrimers are effective catalysts for the cyclocarbonylation reaction of 2-allylphenol yielding five- or seven-membered ring lactones in good selectivity and in high yields. These complexes, which are stable towards oxygen and moisture, can be recycled effectively. The dendritic systems show higher activity compared to the non-dendritic systems.

## Experimental Section

### General

Chemicals were purchased from Aldrich, Strem and Lancaster Chemical companies were used without further purification. Generation zero dendrimer (**G-0**) (**A**), PAMAM-$SiO_2$ dendrimer compounds **1**, **5** and *N*-[3,5-bis(diphenylphosphanylmethyl)phenyl]succinamic acid (**2**) were prepared by literature

**Table 9.** Catalytic cyclocarbonylation of 2-allyl-6-methylphenol by **A** (**G-0**);[a] using 5:1 CO/$H_2$.

| Run No | Yield [%][b] | Product Distribution,[c] % | | | TON [mol of product/mol of Pd] |
|---|---|---|---|---|---|
| | | **10** | **11** | **12** | |
| 1 | $>99$ | 88 | 11 | 1 | 127 |
| 2 | 96 | 91 | 9 | 0 | –[d] |
| 3 | $>99$ | 88 | 11 | 1 | –[d] |

[a] Reactions were conducted using 50 mg ($0.8 \times 10^{-2}$ mmol) of **A**, 0.04 mmol of dppb and 1 mmol of 2-allyl-6-methylphenol for 48 hours in toluene at 600 psi and 120 °C.

[b, c] Determined by NMR and GC.

[d] Palladium loading was not measured.

**Table 10.** Catalytic cyclocarbonylation of 2-allyl-4-chlorophenol by **A** (**G-0**);[a] using 5:1 CO/$H_2$.

| Run No | Yield [%][b] | Product Distribution,[c] % | | | TON [mol of product/mol of Pd] |
|---|---|---|---|---|---|
| | | **13** | **14** | **15** | |
| 1 | 98 | 81 | 9 | 10 | 125 |
| 2 | 90 | 88 | 9 | 3 | –[d] |
| 3 | 97 | 84 | 11 | 5 | –[d] |

[a] Reactions were conducted using 50 mg ($0.8 \times 10^{-2}$ mmol) of **A**, 0.04 mmol of dppb and 1 mmol of 2-allyl-4-chlorophenol for 48 hours in toluene at 600 psi and 120 °C.

[b, c] Determined by NMR and GC.

[d] Palladium loading was not measured.

**Table 11.** Catalytic cyclocarbonylation of 2-allylphenol by **16**;[a] using 5:1 $CO/H_2$.

| Entry | dppb [mmol] | **17** [mmol] | Silica [mg] | Yield [%][b] | Product Distribution,[c] % | | |
|---|---|---|---|---|---|---|---|
| | | | | | **7** | **8** | **9** |
| 1 | – | – | – | 25 | 48 | 26 | 26 |
| 2 | 0.04 | – | – | 99 | 48 | 20 | 32 |
| 3 | 0.04 | 0.03 | – | 95 | 59 | 21 | 20 |
| 4 | 0.04 | – | 50 | 99 | 54 | 18 | 28 |

[a] Reactions were conducted using 7 mg ($1.5 \times 10^{-2}$ mmol) of catalyst **16** and 1 mmol of 2-allylphenol for 48 h in toluene at 600 psi and 120 °C.

[b, c] Determined by NMR and GC.

procedures.[23,24] All the reaction products are known compounds and have spectral data in accord with that in the literature.[25–28]

All reactions were carried out under an atmosphere of nitrogen. All manipulations of air-sensitive materials were carried out using standard Schlenk techniques. Solvents were purified and dried following standard procedures.[29]

Solution NMR spectra were recorded at 20.5 °C, unless otherwise indicated, on a Varian Gemini-200 ($^1$H at 199.97 MHz and $^{13}$C{$^1$H} at 50.28 MHz) or a Bruker 300 NMR spectrometer ($^1$H at 300.13 MHz, $^{13}$C{$^1$H} at 75.48 MHz and $^{31}$P{$^1$H} at 121.49 MHz). $^1$H and $^{13}$C NMR spectra are reported in ppm, with the residual non-deuterated solvent in the deuterated solvents served as a reference. $^{31}$P chemical shifts are reported in ppm relative to the external standard, 85% $H_3PO_4$. The $^{13}$C and $^{31}$P CP/MAS (cross polarization/magic angle spinning) NMR spectra, frequency 50.32 MHz and 81.00 MHz respectively, were recorded on a Bruker ASX-200 spectrometer. Solid samples were prepared by transfer of the relevant material to a 5 mm o.d. pyrex NMR tube and connected to a high vacuum stopcock in an M. Braun GmbH glovebox. The sample was then removed from the drybox, placed under high vacuum and, without breaking vacuum, sealed off at 30 mm lengths. The tubes were then placed in zirconia rotors used in the Bruker ASX-200 instrument.

High-pressure reactions were conducted in stainless steel autoclaves fitted with a screw cap from Parr Instruments. The reactions with carbon monoxide were carried out in a fume hood with CO detectors installed nearby.

ICP analyses were carried out by Galbraith Laboratories, Knoxville, TN. or by the Institute for National Measurement Standards Chemical Metrology at the National Research Council, Ottawa. Gas chromatography was carried out using a Hewlett Packard HP 5890 Series II chromatograph.

## Synthesis of Compound 4 (n = 1)

To a solution of **2** (1.7 g, 2.9 mmol) and 4-(dimethylamino)pyridine (DMAP; 0.35 g, 2.9 mmol) in dichloromethane (30 mL) was added 1, 3-dicyclohexylcarbodiimide (DCC; 0.59 g, 2.9 mmol) in dichloromethane (2 mL) and *N*-hydroxysuccinimide (0.33 g, 2.9 mmol) at 0 °C. The mixture was stirred at room temperature for 18 h. The white solid was filtered and the solvent was evaporated under reduced pressure, affording compound **3** as a yellow solid. DMAP (0.35 g, 2.9 mmol) in dichloromethane (80 mL) and PAMAM-$SiO_2$ dendrimer compound **1** **(**n = 1; 0.5 g, 0.37 mmol) were added, the reaction mixture was stirred at room temperature for 1 day and then heated at 45 °C for 5 days. The suspension was filtered, washed with dichloromethane several times, and dried under vacuum to afford **4**, n = 1 as a pale yellow solid; yield: 0.7 g (49%); $^{31}$P CP/MAS NMR: $d = -8.6$ and 27.9 (phosphine oxide); $^{13}$C CP/MAS NMR: $\delta = 171.4$, 157.3, 142.4, 107.7, 40.8, 20.3, 9.6; ICP analysis: mass % P 2.37.

## Synthesis of the Generation One Dendrimer, (G-1) (B)

A suspension of compound **4** (n = 1; 0.6 g, 0.24 mmol), and $Pd(TFA)_2$ (0.08 g, 0.24 mmol) in THF (50 mL) was stirred at room temperature for 4 days. The suspension was filtered, washed with THF several times, and dried under vacuum to afford generation one dendrimer (**G-1**) (**B**) as a dark yellow solid; yield: 0.6 g (84%); $^{31}$P CP/MAS NMR: $\delta = 38.7$ and 29.3 (phosphine oxide); $^{13}$C CP/MAS NMR: $\delta = 172.1$, 157.5, 141.8, 130.1, 108.4, 50.4, 40.5, 31.0, 20.4, 10.0; ICP analysis: mass % Pd 3.22.

## Synthesis of Compound 6

To a solution of **2** (2.9 g, 4.9 mmol) and 4-(dimethylamino)pyridine (DMAP; 0.6 g, 4.9 mmol) in dichloromethane (70 mL) was added 1,3-dicyclohexylcarbodiimide (DCC; 1.01 g, 4.9 mmol) in dichloromethane (5 mL) and *N*-hydroxysuccinimide (0.6 g, 4.9 mmol) at 0 °C. The mixture was stirred at room temperature for 18 h. The white solid was filtered and the solvent was evaporated under reduced pressure, affording compound **3** as a yellow solid. DMAP (0.6 g, 4.9 mmol) in dichloromethane (50 mL) and PAMAM-$SiO_2$ dendrimer compound **5** (0.5 g, 0.28 mmol) were added, the reaction mixture was stirred at room temperature for 1 day and then heated at 45 °C for 7 days. The suspension was filtered, washed with dichloromethane several times, and dried under vacuum to afford **6** as a pale yellow solid; yield: 0.8 g (52%). $^{31}$P CP/MAS NMR: $d = -11.3$ and 27.1 (phosphine oxide); $^{13}$C CP/MAS NMR: $\delta = 172.7$, 157.7, 143.3, 108.5, 40.2, 26.0, 10.6; ICP analysis: mass % P 3.0.

## Synthesis of a Generation Two Dendrimer, (G-2) (C)

A suspension of compound **6** (0.7 g, 0.17 mmol), and $Pd(TFA)_2$ (0.11 g, 0.34 mmol) in THF (50 mL) was stirred at room temperature for 5 days. The suspension was filtered, washed with

THF several times, and dried under vacuum to afford generation two dendrimer (**G-2**) (**C**) as a dark yellow solid; yield: 0.7 g (88%). $^{31}$P CP/MAS NMR: $\delta = 36.3$ and 28.7 (phosphine oxide); $^{13}$C CP/MAS NMR: $\delta = 172.5$, 156.3, 142.3, 131.4, 108.4, 48.1, 40.9, 31.0, 26.0, 10.3: ICP analysis mass: % Pd 4.29.

### Synthesis of Compound 4 (n = 3)

To a solution of **2** (1.7 g, 2.9 mmol) and 4-(dimethylamino)pyridine (DMAP; 0.35 g, 2.9 mmol) in dichloromethane (30 mL) was added 1, 3-dicyclohexylcarbodiimide (DCC; 0.59 g, 2.9 mmol) in dichloromethane (2 mL) and *N*-hydroxysuccinimide (0.33 g, 2.9 mmol) at 0 °C. The mixture was stirred at room temperature for 18 h. The white solid was filtered and the solvent was evaporated under reduced pressure, affording compound **3** as a yellow solid. DMAP (0.35 g, 2.9 mmol) in dichloromethane (80 mL) and PAMAM-$SiO_2$ dendrimers, compound **1** (n = 3; 0.5 g, 0.34 mmol) were added, the reaction mixture was stirred at room temperature for 1 day and then heated at 45 °C for 5 days. The suspension was filtered, washed with dichloromethane several times, and dried under vacuum to afford **4**, n = 3 as a pale yellow solid; yield: 0.7 g (51%); $^{31}$P CP/MAS NMR: d = −11.2; $^{13}$C CP/MAS NMR: $\delta = 172.9$, 158.9, 129.1, 107.8, 39.9, 27.9, 10.6; ICP analysis: mass % P 2.33.

### Synthesis of the Generation One Dendrimer, (G-1) (D)

A suspension of compound **4** (n = 3; 0.6 g, 0.22 mmol), and $Pd(TFA)_2$ (0.07 g, 0.22 mmol) in THF (50 mL) was stirred at room temperature for 4 days. The suspension was filtered, washed with THF several times, and dried under vacuum to afford generation one dendrimer (**G-1**) (**D**) as a dark yellow solid; yield: 0.6 g (75%); $^{31}$P CP/MAS NMR; $\delta = 35.6$; $^{13}$C CP/MAS NMR: $\delta = 172.8$, 157.5, 143.3, 131.3, 106.8, 51.9, 40.5, 28.6, 22.7, 10.6; ICP analysis: mass % Pd 2.84.

### General Procedure for the Cyclocarbonylation Reactions

A mixture of the 2-allylphenol (1 mmol), catalyst **A** (50 mg) and 1,4-bis(diphenylphosphino)butane (dppb; 0.04 mmol) in dry solvent (5 mL) was placed in a 45 mL autoclave equipped with a magnetic stirring bar. The autoclave was flushed three times with CO and then was pressured using a predetermined ratio of carbon monoxide and hydrogen gases (see Tables). The autoclave was placed in an oil bath preheated to the appropriate temperature. The reaction mixture was magnetically stirred for 48 h, cooled to room temperature, and the unreacted carbon monoxide was slowly released. The mixture was filtered to separate the catalyst from the liquid phase. The catalyst was washed several times with $CH_2Cl_2$ and dried under reduced pressure before being recycled. The organic layer was concentrated by rotary evaporation affording an oil.

Analogous procedures were used for catalysts **B**, **C**, and **D** except for different amounts of catalysts and the amount of the 2-allylphenol.

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