Palladium complexes of phosphine functionalised carbosilane dendrimers as catalysts in a continuous flow membrane reactor†

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Received (in Cambridge, UK) 4th June 1999, Accepted 15th July 1999

Phosphine functionalised carbosilane dendrimers have been synthesised and their palladium complexes used as catalysts in the allylic alkylation reaction performed in a continuous flow membrane reactor.

Since Vögtle and co-workers synthesised branched structures in 1978,[1] much research has been devoted to the synthesis and investigation of dendrimeric molecules.[2] One of the main applications of dendrimers[2h,i] is in catalysis,[3] allowing easy recycling of the homogeneous catalyst by means of nanofiltration.[4] Here we report the synthesis of phosphine functionalised carbosilane dendrimers and their use as catalysts in a continuous process.

We have chosen carbosilane dendrimers[5] as a backbone for our catalytic system because of their catalytic inertness. A previous report describes the synthesis of these dendrimers.[6] The second generation dendrimer is a white solid and crystals suitable for X-ray analysis were grown from a diethyl ether–methanol solution.‡ The structure (Fig. 1a) shows that the molecule crystallised with all the bonds in a zigzag conformation. This dendrimer has a calculated molecular volume of 2414 Å^3, which is anticipated to be large enough for separation from a reaction mixture by nanofiltration.

The phosphine functionalised carbosilane dendrimers were synthesised by hydrosilylation of the double bonds of the various generations (G_0, G_1, G_2) with chlorodimethylsilane or dichloromethylsilane followed by reaction with lithium methyldiphenylphosphine–TMEDA[7] (Scheme 1).§ All the phosphine functionalised dendrimers were obtained as wax-like solids. Characterisation by ^{1}H and ^{31}P-{^{1}H} NMR and MALDI-TOF MS shows that the P-functionalised dendrimers were obtained in at least 95% purity. The dendrimer with seventy-two phosphine groups could not be prepared, probably because of surface congestion.

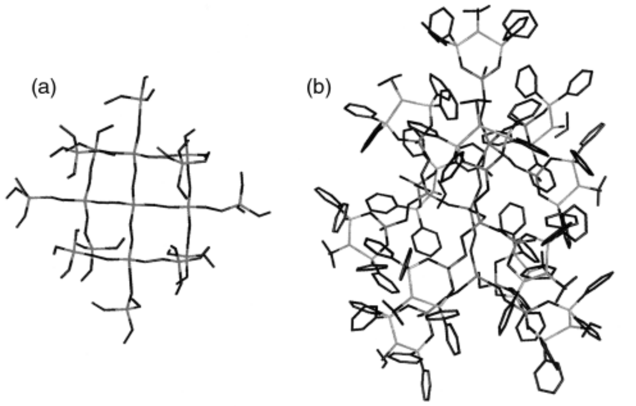
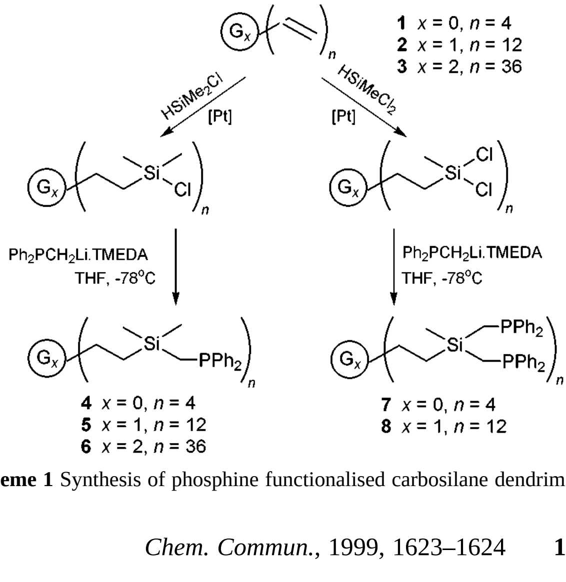


Fig. 1 Crystal structure of the second generation dendrimer (a) and a modelled structure of the Pd(allyl) complex of **8** (b). Hydrogens and counterions have been omitted for clarity. [See Electronic Supplementary Information (ESI) for a colour version of this figure (Si in red, C in dark blue, Pd in green, P in yellow)].

Dendrimers **7** and **8** have four and twelve endgroups, respectively, each containing a chelating bidentate phosphine ligand. The endgroups of dendrimers **4**, **5** and **6** contain monodentate phosphine ligands. Allylpalladium complexes of these dendrimers were synthesised by reaction with [(η^3-C_3H_7)PdCl]$_2$. According to ^{1}H and ^{31}P-{^{1}H} NMR the phosphine dendrimers **7** and **8** co-ordinate in a bidentate way resulting in well defined Pd complexes, while the monodentate phosphine dendrimers give rise to a mixture of products.

All the Pd(allyl) dendrimer complexes were used as catalysts in the allylic alkylation reaction of allyl trifluoroacetate and sodium diethyl methylmalonate yielding diethyl allylmethylmalonate. The reaction was first carried out *via* a batch process. All the dendrimeric catalysts showed a very high activity. Using a substrate–Pd ratio of 2000 the yield after 30 min was over 80%, and only small differences in reaction rates were observed for the different catalysts.¶ The fact that the activity did not decrease with increasing generation indicates that all active sites act as independent catalysts. From molecular modelling (Fig. 1b) it was clear that indeed all the Pd(allyl) groups reside at the outer surface of the dendrimer and should be easily accessible to



Scheme 1 Synthesis of phosphine functionalised carbosilane dendrimers.

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† Electronic supplementary information (ESI) available: full colour version of Fig. 1. See http://www.rsc.org/suppdata/cc/1999/1623/

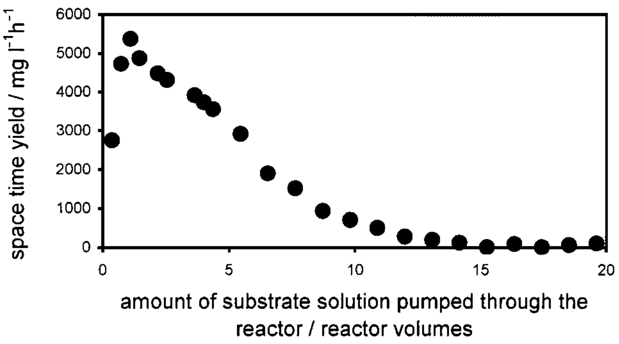

Fig. 2 Space time yield *versus* amount of solvent pumped through the reactor of the continuous allylic alkylation reaction in a membrane reactor.‡‡

the nucleophile. Addition of a second portion of substrate after nearly full consumption of the sodium diethyl methylmalonate (over 90%) showed that the catalyst remained active.

These novel dendrimeric catalysts were studied in a continuous process using a membrane reactor.‖ A solution of allyl trifluoroacetate and sodium diethyl methylmalonate in THF (including *n*-decane as an internal standard) was pumped through the reactor. The allylpalladium complex of the largest dendrimer with bidentate phosphines (**8**) was used as a catalyst.**

In Fig. 2 the space time yield is plotted as a function of the amount of solvent (expressed in reactor volumes) pumped through the reactor. The reaction started immediately after addition of the catalyst and reached its maximum space time yield after one reactor volume. The space time yield slowly dropped to zero after *ca.* 15× the reactor volume of substrate solution had been pumped through the reactor. Regarding the size of the catalyst, this decrease was unexpectedly rapid. The retention in the membrane reactor of the second generation dendrimer (molecular volume: 2414 Å^3), which is much smaller than the Pd catalyst (calculated molecular volume: $\approx$7600 Å^3 (Fig. 1)), was determined to be 98.1%. Using this number the decrease in catalyst activity is calculated to be only 25% after flushing the reactor fifteen times. The observed decrease in catalyst activity is therefore ascribed to decomposition†† of the palladium compound and not to loss of the dendrimeric catalyst. This is in agreement with the observation that samples taken from the product flow were not catalytically active, indicating that no active catalyst had gone through the membrane.

In conclusion, carbosilane dendrimers functionalised with diphenylphosphine groups at the periphery have been synthesised and characterised. Palladium complexes of these dendrimers have been used as catalysts in the allylic alkylation reaction. It has been shown that these dendrimeric catalysts can be used in a continuous process using a membrane reactor. Current work is aiming at the enhancement of the stability of these catalysts, and the exploration of these systems in other reactions.

This work was supported in part (A. L. S.) by the Council for Chemical Sciences of the Netherlands Organisation for Scientific Research (CW-NWO).

Notes and references

‡ *Crystal data* for **3**: $C_{104}H_{172}Si_{17}$, M_r = 1899.96, triclinic, space group $P\bar{1}$, a = 17.2970(4), b = 19.5782(4), c = 22.2298(5) Å, α = 106.1813(15), β = 108.1431(15), γ = 106.6735(14)°, V = 6268.0(2) Å^3, Z = 2, μ(Mo-Kα) = 0.2 mm^{-1}, 80242 reflections measured, 14833 independent, R_{int} = 0.1352, (1.6° < θ < 24.1°, T = 150 K). Only Si atoms were refined with anisotropic displacement parameters. The outside of the molecule shows considerable dynamic disorder, which gives rise to high displacement parameters and unrealistic geometries. No satisfactory disorder models could be obtained. Mild distance restraints were introduced for the most unrealistic parameters. $wR2$ = 0.2949, $R1$ = 0.1369, S = 0.886, $-0.38 < \Delta\rho < 0.78$ e Å^{-3}. CCDC 182/1331. See http://www.rsc.org/suppdata/cc/1999/1623/ for crystallographic files in .cif format.

§ *Selected data* for **4**: ^{1}H NMR (CDCl$_3$): δ 7.5 (m, 16H, ArH), 7.3 (m, 24H, ArH), 1.40 (s, 8H, SiCH_2P), 0.26 (s, 16H, SiCH_2CH_2Si), -0.10 (s, 24H, SiCH_3). ^{31}P-{^{1}H} NMR (CDCl$_3$): δ -20.8. Dendrimers **5** and **6** have similar NMR spectra. For **7**: ^{1}H NMR (CDCl$_3$): δ 7.5–7.1 (m, 80H, ArH), 1.26 (s br, 16H, SiCH_2P), 0.19 (m, 16H, SiCH_2CH_2Si), -0.29 (s br, 12H, SiCH_3). ^{31}P-{^{1}H} NMR (CDCl$_3$): δ -22.5. Dendrimer **8** has similar NMR spectra.

¶ Room temperature, solvent: THF, [allyl trifluoroacetate] = 50 mM, [diethyl methylmalonate] = 25 mM, [Pd] = 12.5 μM.

‖ Koch/SelRO MPF-60 NF membrane, Koch Membrane Systems, Düsseldorf, Germany, molecular weight cut-off (MWCO) = 400 Daltons.

** Room temperature, reactor volume: 20 ml, solvent: THF, [allyl trifluoroacetate] = 50 mM, [diethyl methylmalonate] = 25 mM, [Pd] = 12.5 μM, flow rate: 44 ml h^{-1}.

†† Much higher turnover numbers can be reached in a batch reactor compared to the membrane reactor, showing that in the membrane reactor new problems are introduced that are not related to the dendrimeric catalyst.

‡‡ The space time yield has been corrected for the background reaction.

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Communication 9/04455H