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Phosphine-containing carbosilane dendrimers based on polyhedral silsesquioxane cores as ligands for hydroformylation reaction of oct-1-ene

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Abstract

Radical additions of diethyl- and diphenylphosphine have been used to prepare 1st and 2nd generation dendrimers based on polyhedral oligosilsesquioxane cores by a divergent synthetic method. The 1st generation dendrimer is built on either 16 and 24 vinyl or allyl arms formed by successive hydrosilation and vinylation or allylation of vinyl-functionalised polyhedral silsesquioxanes. Successive hydrosilation/allylation followed by hydrosilation/vinylation and addition of phosphine produce the 2nd generation dendrimer. The dendrimers have been used as ligands for the hydroformylation of oct-1-ene catalysed by $[Rh(acac)(CO)_2]$. Using the alkylphosphine-containing dendrimers as ligands, alcohols (nonan-1-ol and 2-methyloctanol) are obtained, whilst the diphenylphosphine counterparts lead to the formation of aldehydes (nonan-1-al and 2-methyloctanal). Linear to branched ratios of 3/1 are obtained for the diethylphosphine compounds while ratios of 12 to 14/1 are given by the diphenylphosphine dendritic molecules. © 2002 Published by Elsevier Science B.V.

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1. Introduction

In the last decade, dendritic molecules have stirred a lot of interest in chemistry and more particularly in the field of catalysis (for a recent review, see [1]). As they are well-defined macromolecules with potentially numerous functionalisable sites, they have the potential to bridge the gap between homogeneous and heterogeneous catalysis by acting as soluble macromolecular ligand(s). Numerous applications in catalysis, ranging from C–C coupling [2–4] to hydrogenation [5–7], have already demonstrated their ability to act as efficient ligand(s)/catalyst(s). Ultra-filtration techniques were successfully applied to this new catalytic system giving high expectations for future industrial applications [2,8,9]. In addition, their preparation allows the tuning of substituents and the diversity of branching patterns, size and crowding of the molecule, which may affect the activity or selectivity of the catalyst. These 'dendrimer effects' vary from total inhibition of the reaction [10] to enhanced reactivity [2,3,11,12] and selectivity [13].

The use of bidentate ligands in hydroformylation reactions is often useful in obtaining high selectivity catalysts [14,15]. The incorporation of phosphine moieties (possibly acting as bidentate ligands) into the structure of a dendrimer is therefore of great interest [16,17]. We have previously synthesised a dendrimer structure based on a polyhedral octaoligosilsesquiox-

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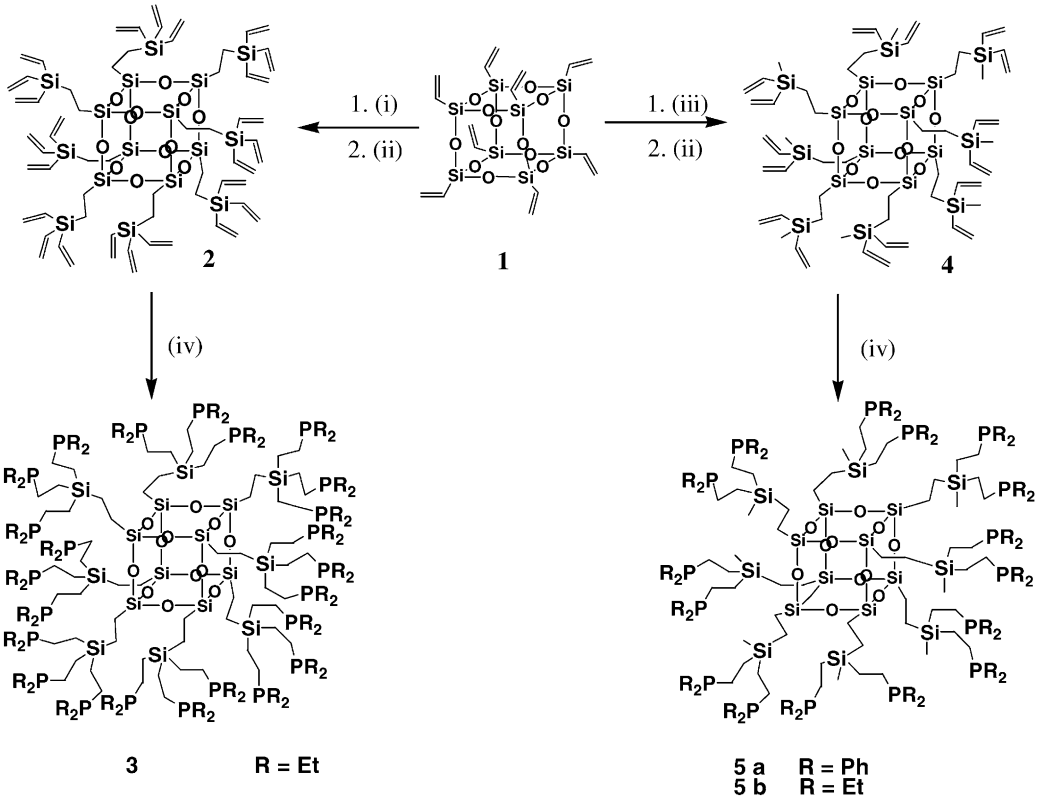

Fig. 1. Synthesis of 1st generation phosphine-containing POSS with a spacer of 5 atoms between the phosphine groups. (i) $HSiCl_3$ catalysed by H_2PtCl_6; (ii) $CH_2 = CHMgBr$; (iii) $HSiMeCl_2$ catalysed by H_2PtCl_6; (iv) HPR_2 (R = Et, Ph), AlBN, 50 °C; (v) $CH_2 = CHCH_2$ MgBr.

ane (POSS) core allowing the introduction of phosphine moieties on the periphery [13,18]. First generation alkyl and arylphosphine substituted dendrimers were shown to be excellent ligands for the hydroformylation of alkenes, in some cases leading to greatly increased selectivity compared with their parent monomers [13]. We report here a comparative study of the hydroformylation of oct-1-ene by rhodium complexes of different generation phosphine functionalised POSS cores.

2. Results and discussion

Diethyl- and diphenylphosphine functionalised dendrimers with 16, 24[1] or 48 arms were synthesised by radical addition of $HPEt_2$ and $HPPh_2$ to the vinyl substituted POSS. The number of phosphine arms was controlled by the dendrimer generation and the substitution pattern of the silicon (i.e. $–SiMe(vinyl)_2$ for the 16 and 48 arms, $–Si(vinyl)_3$ for the 24 arms). Good to high conversions and yields were obtained using this simple reaction for the vinyl compounds. We have previously reported the synthesis of compound **3** [18] and **5a** [13] (characterised by MALDI-TOF) and have now extended this synthesis to the 16 diethylphosphine branched dendrimer **5b** and to the 2nd generation dendrimers **11a** and **11b**. Compound **5b** was built upon the octavinyl oligosilsesquioxane **1** by subsequent hydrosilation with $HSiMeCl_2$ (catalysed by H_2PtCl_6), vinylation (vinyl magnesium bromide) and radical addition of $HPEt_2$ (AIBN as radical initiator) (Fig. 1). The 2nd generation dendrimer was prepared from the 24-allyl POSS (**7**) synthesised by hydrosilation with $HSiCl_3$ of **1**, followed by addition

[1] Compounds with 24 diphenyl groups could not be prepared [18].

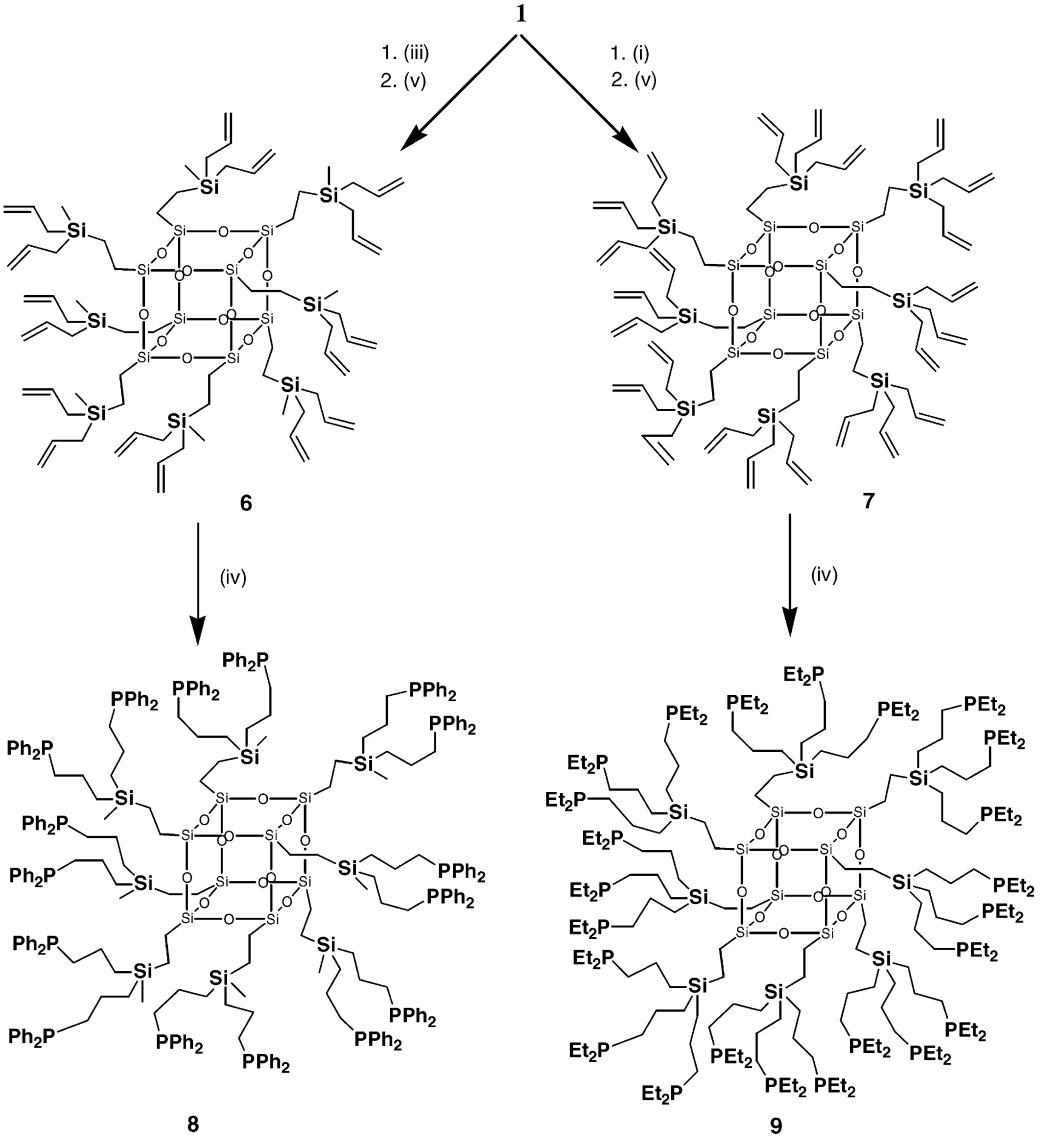

Fig. 2. Synthesis of 1st generation phosphine-containing POSS with a spacer of 7 atoms between the phosphine groups.

of allyl magnesium bromide (Fig. 2). Hydrosilation of **7** with $HSiMeCl_2$ yielded the 48-Cl POSS in >95% yield and finally addition of vinyl magnesium bromide led to the compound **10** (Fig. 3). Characterisation by ^1H, ^{13}C NMR and microanalysis indicates high conversion (>96%). The radical addition of phosphines to **10** gave the desired macromolecule ligands. Whist high conversion seems to occur for the 48-diethylphosphine compound **11b** (conversion of vinyl groups >90% determined by ^1H NMR, no trace of alkenyl protons in the ^1H NMR spectrum), complete loading of diphenylphosphine when preparing **11a** cannot, however, be obtained (conversion of vinyl groups 84% by ^1H NMR). The radical addition onto

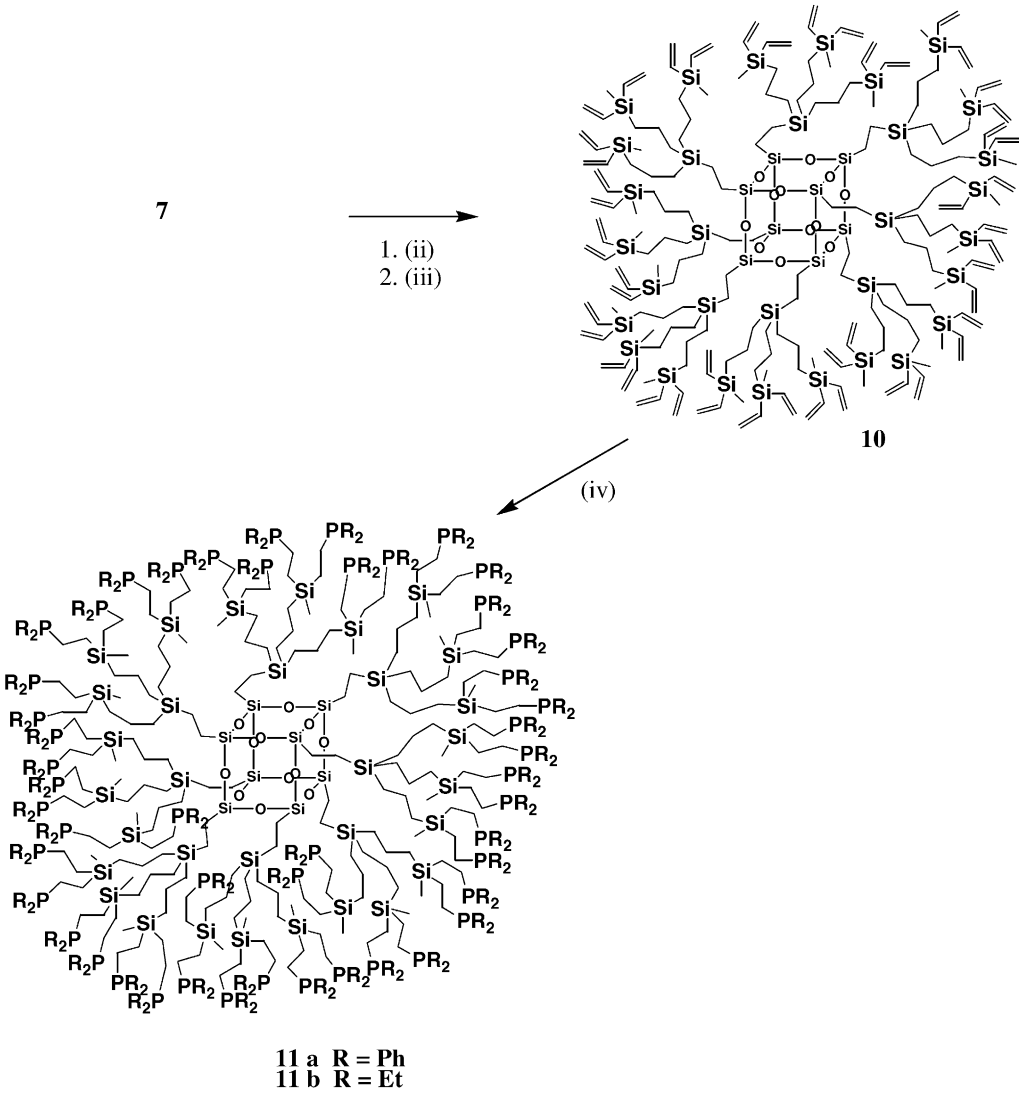

Fig. 3. Synthesis of 2nd generation phosphine-containing POSS with a spacer of 5 atoms between the phosphine groups: (i) $HSiCl_3$ catalysed by H_2PtCl_6; (ii) CH_2=CHMgBr; (iii) $HSiMeCl_2$ catalysed by H_2PtCl_6; (iv) HPR_2 (R = Et, Ph), AIBN, 50 °C; (v) CH_2=$CHCH_2MgBr$.

the 1st and 2nd generation dendrimers is extremely slow compared to smaller molecules[2] , it is believed that many arms are back-folded in the structure leading to mass transport limitations and steric hindrance. After partial conversion to the diphenylphosphine dendrimer, steric crowding on the periphery makes access to the back-folded arms even more difficult, perhaps explaining the lower conversion in this case.

The radical additions of diphenylphosphine and diethylphosphine respectively to the 16-allyl and 24-allyl compounds (**8** and **9**) were not so successful (Fig. 2). The addition of diethylphosphine to the allyl dendrimer is extremely slow but proceeds almost to completion since after 2 weeks of reaction and successive addition of radical initiator the conversion

[2] For example complete addition of $HPPh_2$ on divinyldimethylsilane is obtained after only 2 h [21].

Table 1
^{31}P NMR spectra and yields data for the dendrimer-bound phosphines

Compound	End group	Number of end groups	^{31}P NMR δ	Conversion[a] (%)	Yield (%)[b]
5b	$(CH_2)_2PEt_2$	16	−15.2 (br)	>96[c,d]	99
3	$(CH_2)_2PEt_2$	24	−15.9, −16	>96[c,d]	97
9	$(CH_2)_3PEt_2$	24	−23.6, −23.9, −24.3	87[c,d]	98
11b	$(CH_2)_2PEt_2$	48	−15.8, −16.1	>90[c]	96
5a	$(CH_2)_2PPh_2$	16	−9.4, −9.5	94[c,d]	85
8	$(CH_2)_3PPh_2$	16	−14.5, −17.2, −17.3	56[c]	87
11a	$(CH_2)_2PPh_2$	48	−9.9 (br)	84[c]	75

[a] Refers to the average % arms converted to phosphine.
[b] The chemical yields based on that expected for the given conversion.
[c] ^{1}H NMR.
[d] MALDI-TOF.

determined by MALDI-TOF is 87% (average of three –PEt_2 groups missing) although no allylic protons could be found by ^{1}H NMR. When using $HPPh_2$, only 56% of the allyl moieties are however functionalised after 2 weeks (determined by ^{1}H NMR).

Interestingly for all these dendrimers the phosphines incorporated into the same dendritic framework were found to have different environments since broad and/or various ^{31}P chemical shifts are identified in the NMR spectra (see Table 1). No correlation between the degree of conversion and the multiplicity of signals is however noticed.

We have previously reported [13] that using $[Rh(acac)(CO)_2]$ compound **5a** gives high linear to branched ratio (up to 14:1) in the hydroformylation of oct-1-ene at 120 °C and 10 bar of CO/H_2 (phosphine/rhodium ratio of 6/1). In contrast, the small molecule analogue, $Me_2Si(CH_2CH_2PPh_2)_2$, gives an *l*:*b* ratio of 3.8:1 under identical conditions. Using identical conditions, hydroformylation of oct-1-ene by a rhodium complex of **11a** has been carried out. It is found that the 2nd generation dendrimer acts similarly since the rate and selectivity are similar to those of the 16-functionalised POSS (see Table 2). The regioselectivity to the linear aldehyde nonan-1-al is 84% with a *l*:*b* ratio of 11.5, while the 16 arms ligand **5a** gave a selectivity of 86% and a *l*:*b* ratio of 13.9. A drop in the rate of reaction by a factor of 2 is nevertheless noted, perhaps because the steric hindrance of such bulky ligands interferes with the approach of the alkene to the metal centre. Due to the poor conversion obtained during the synthesis of the compound **8**, we did not perform any catalytic reactions with this ligand.

Hydrocarbonylation of oct-1-ene catalysed by rhodium complexes formed from $[Rh(acac)(CO)_2]$ and diethylphosphine dendrimers was carried out at 120 °C and 40 bar of CO/H_2 (phosphine/rhodium ratio of 6/1) in ethanol. As expected on the basis of studies with PEt_3 [19,20], the only carbonylation products are nonan-1-ol and 2-methyloctanol. All complexes formed from ligands **3** (5 atoms between the phosphorus atoms, 3 P atoms/Si), **5b** (5 atoms between the P atoms, 2 P atoms/Si), **11b** (2nd generation, 5 atoms between the P atoms, 2 P atoms/Si) and **9** (7 atoms between the P atoms, 3 P atoms/Si) show similar

Table 2
Hydroformylation reactions catalysed by Rh complexes of POSS derived dendrimer diphenylphosphines[a]

Compound	End group	Number of end groups	Reaction time (h)	Rate constant[b] ($\times 10^{-3}$ s^{-1})	Conversion (%)	Isomerisation (%)	Nonan-1-al (%)	*l*:*b* ratio
5a	$(CH_2)_2PPh_2$	16	2	1.2	>99.9	6.7	86	13.9
11a	$(CH_2)_2PPh_2$	48	3	0.6	>99.9	7.5	84	11.5

[a] Reaction conditions: $[Rh(acac)(CO)_2] = 2.0 \times 10^{-5}$ mol, P:Rh = 6:1, substrate 8.3×10^{-3} mol, toluene (4 cm^3), 120 °C, CO/H_2 10 bar.
[b] From gas uptake measurements at constant pressure.

Table 3
Hydrocarbonylation reactions catalysed by Rh complexes of POSS derived diethylphosphine dendrimers[a]

Compound	End group	Number of end groups	Reaction time (h)	Rate constant[b] ($\times 10^{-4}$ s^{-1})	Conversion (%)	Isomerisation (%)	Linear alcohol (%)	*l*:*b* ratio
5b	$(CH_2)_2PEt_2$	16	8	1.5	>99.9	3.1	73.5	3.1
3	$(CH_2)_2PEt_2$	24	8	1.7	>99.9	2.1	73.2	3.1
9	$(CH_2)_3PEt_2$	24	4	3.7	>99.9	1.4	72.8	2.9
9	$(CH_2)_3PEt_2$	24	1	–	57.9	0.6	40.3 (69.6)[c]	3.8
11b	$(CH_2)_2PEt_2$	48	8	2.1	>99.9	2.6	72.8	3.0

[a] Reaction conditions: $[Rh(acac)(CO)_2] = 4.0 \times 10^{-5}$ mol, P:Rh = 6:1, substrate 8.3×10^{-3} mol, ethanol (4 cm^3), 120 °C, CO/H_2 40 bar.
[b] From gas uptake measurements at constant pressure.
[c] Selectivity, 6.1% of linear (10.5% selectivity) is also formed.

selectivity to the linear alcohol nonan-1-ol (≈73%), with a linear to branched ratio of 3:1 (see Table 3). Therefore, it is likely that the active complexes formed during hydroformylation are very similar. This result differs from those obtained with the diphenylphosphine dendrimers, which lead to different selectivity when using different spacers between the two phosphorus atoms [21]. Similar rates of reaction are found for the hydroformylation using ligands **3** and **5b**, while **9** (longer spacer group) shows a higher rate constant (Table 3). Again crowding at the dendrimer surface leads to slower reaction. However, the 48-branched diethylphosphine POSS leads to slightly higher reactivity than its 1st generation counterparts **3** and **5b** with a spacer of two carbons between the silicon and phosphorus atoms. It is not clear at the moment if the reaction proceeds to direct formation of alcohol [19,20] since aldehydes (6.1%) are found in the products of reaction after 1 h (conversion 57.9%) when using ligand **9**.

3. Conclusion

Dendrimers with up to 48 phosphine groups were synthesised by simple reactions. These 1st and 2nd generation diphenyl- and diethylphosphine dendrimers were successfully applied as ligands for the hydroformylation of oct-1-ene leading, in some cases (diphenyl compounds), to high *l*:*b* ratios. Understanding the effect of the dendrimer structure in the rates and selectivity of hydroformylation reaction is not straightforward since the different generation dendrimers may show different properties depending on the phosphine end groups.

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