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Hydrocarbonylation reactions using alkylphosphine-containing dendrimers based on a polyhedral oligosilsesquioxane core

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Radical additions of HPR_2 (R = Et, Cy) onto alkenyl groups or nucleophilic substitution reactions on chlorosilanes by $LiCH_2PR_2$ (R = Me, Hex) are used to prepare first and second-generation alkylphosphine-containing dendrimers based on a polyhedral oligomeric silsesquioxane (POSS) core. The first generation dendrimers (G1) are built on 16 or 24 arms, which are chlorides, vinyl groups or allyl moieties. Hydrosilylation (chlorosilane) followed by vinylation or allylation of octavinyl-functionalised POSS gave these G1 dendrimers. Successive hydrosilylation/allylation followed by hydrosilylation/vinylation produce the framework for the second-generation dendrimer (G2). The phosphorus-containing dendrimers are used as ligands for the hydrocarbonylation of alkenes (hex-1-ene, oct-1-ene, non-1-ene, prop-1-en-2-ol) in polar solvents (ethanol or THF) using the complexes $[Rh(acac)(CO)_2]$ or $[Rh_2(O_2CMe)_4]$ as metal source. Linear to branched ratios up to 3 : 1 for the alcohol products are obtained for the diethylphosphine dendrimers. The reactions were found to proceed mainly *via* the formation of the corresponding aldehydes.

Introduction

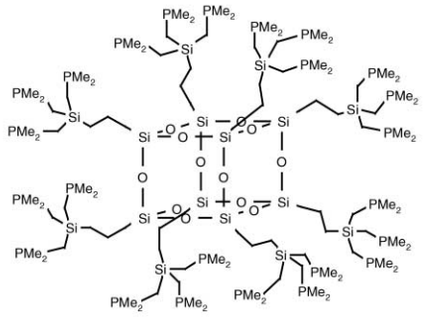
Dendrimers are well-defined macromolecules characterised by the presence of a large number of functional groups on their surface and by their ability to encapsulate guest species.[1] Recently they have triggered interest in the field of homogeneous catalysis since they are relatively large molecules and can be separated from reaction mixtures using ultra-filtration techniques.[2] Their application as ligands/catalysts ranges from C–C coupling[3–5] to hydrogenation[6–8] reactions. Successful recovery of the dendritic catalysts by ultra-filtration techniques has been achieved in several research groups giving high expectations for future industrial applications.[3,9,10] In addition, the diversity of functional groups, branching patterns, size and crowding of dendrimers can affect the activity or selectivity of the catalyst. Indeed, various 'dendrimer effects' from total inhibition of the reaction[11] to enhanced reactivity[3,4,12,13] and selectivity[14] have been identified.

Jaffrès and Morris have previously developed a dendrimer based on a polyhedral oligosilsesquioxane (POSS) core with up to 72 arms.[15] During this work, it became apparent that the groups introduced in successive generations, *i.e.* chloro- and vinyl-silane substituents, would be easily functionalisable by phosphorus-containing species. Using simple organic/inorganic reactions (nucleophilic substitution and radical addition) we have introduced different phosphorus substituents (PR_2, R = Cy, Et, Hex, Me) on the periphery of the dendrimers. In this way dendrimers of different generations with varying numbers of peripheral functionality can be prepared in a relatively facile manner. In general, the chemical properties of the dendrimers are expected to be similar to their small molecule phosphine complexes, modified only by the steric effects of the dendrimer architecture itself.

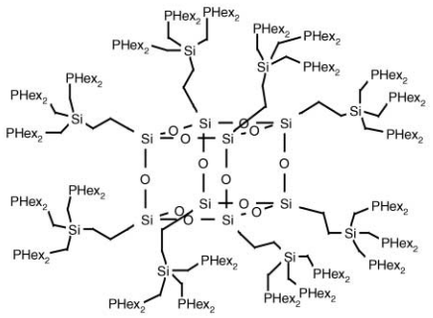
The use of a silsesquioxane as the core of the dendrimer has certain advantages. Above all, the $R_8Si_8O_{12}$ POSS molecule has an almost cubic shape, with a functional group at each corner, and so there are eight sites from which to develop the dendrimer. Most dendrimers are based on tetravinylsilane, tetraallylsilane, pentaerythritol or propyl amino compounds with only four such sites.[16–19] Using the POSS cube as a framework, the dendrimer can be built out in three dimensions leading to a very globular structure which, by the second generation, has 72 end groups suitable for functionalisation with a catalytic species.[15] In contrast 2nd generation dendrimers based on tetrahedral cores have a maximum of only 36 end groups. The large number of catalytic species that can be supported on the external surface of POSS-based dendrimers can lead to interesting effects on catalytic activity and selectivity.[14] In addition, overcrowding on the periphery may also limit the extension of the dendrimer, leading to globular, rigid dendrimers at lower generation numbers than is seen for other dendrimer cores. The relatively rigid dendrimers produced in this way should allow better recovery of POSS-based dendrimers by ultrafiltration techniques when compared to more deformable dendrimers.

Trialkylphosphines are effective ligands to rhodium catalysts, and are used to prepare alcohols from terminal alkenes under pressure of CO/H_2. Using a protic solvent and mild conditions, Cole-Hamilton and co-workers showed that this hydrocarbonylation reaction did not necessarily proceed through aldehyde intermediates.[20,21] This reaction is suitable for testing the catalytic ability of dendrimer bound alkyl phosphines, as simple product analysis will be diagnostic as to whether the dendrimers are bound to the catalytic metal or not. If the ligand binds and a trialkylphosphine rhodium complex is formed, alcohols (*e.g.* heptan-1-ol and 2-methylhexan-1-ol from hex-1-ene) will be the hydrocarbonylation products. If binding does not occur, the products will be aldehydes and acetals. In addition, since hydrocarbonylation can give two different regio isomers of the product (linear and branched), any changes in the balance of the products brought about by the environment of the dendrimer surface will be apparent.

In preliminary communications, two of which relate to this work,[22] we have described the synthesis of a dendrimer structure based on a POSS core and introduced phosphine moieties



G1-24methylPMe$_2$



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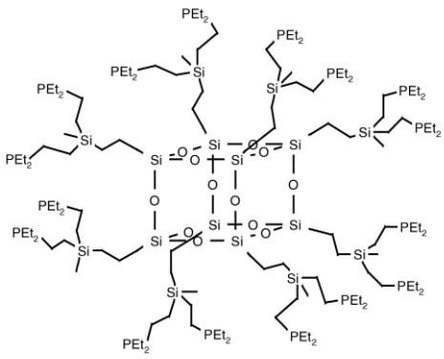
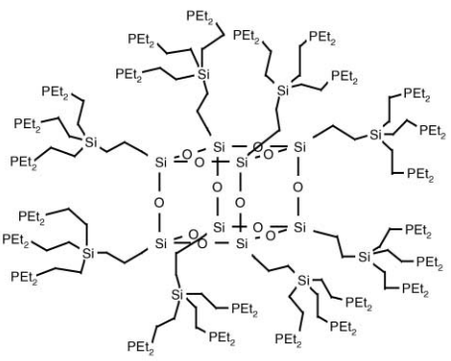


G1-16ethylPEt$_2$



G1-24ethylPEt$_2$

at its periphery.[14,22] 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.[14] We report here a comparative study of the hydrocarbonylation of various alkenes (hex-1-ene, oct-1-ene, non-1-ene, prop-1-en-2-ol) by rhodium complexes of different alkylphosphine functionalised POSS dendrimers (R = PMe_2, PEt_2, $PHex_2$, PCy_2).

Results and discussion

Synthesis of POSS dendrimer cores

Polyhedral octavinyl oligosilsesquioxane (zeroth generation dendrimer or G0) is commercially available or easily synthesised[23] from hydrolysis of readily available trichlorovinylsilane. The hydrosilylation of G0 under rigorously dry conditions by different silanes ($HSiCl_3$ or $HSiMeCl_2$ in excess) catalysed by Speier's catalyst, H_2PtCl_6, introduces substituents on the dendrimer with quantitative yield.[15] The bulkiness and electronic properties of the POSS cube hinder unwanted β-addition to the vinyl groups. Hydrosilylation using trichlorosilane or dichloromethylsilane yield 24 or 16 'reactive' chlorosilane groups respectively at the external surface of the first generation dendrimer.[15] Chloro-functionalised G1 dendrimers can then be modified by introduction of vinyl or allyl groups through nucleophilic substitution of the chloro groups by Grignard reagents as has been done for many other carbosilane dendrimers. Compounds with 16- or 24-vinyl,[15] or allyl groups (G1-16vinyl, G1-24vinyl, G1-24allyl) were prepared in high yields. NMR techniques and microanalysis were used to characterise the products, and G1-16vinyl was partially characterised by single crystal X-ray diffraction after crystals were obtained by recrystallisation from cold light petroleum. However, only partial refinement was obtained due to the extensive disorder of the carbon atoms of the vinyl and methyl groups at the periphery of the dendrimer. Similar problems of external group disorder have been seen in a crystal structure determination of the 24-vinyl POSS (G1-24vinyl).[15] The structure of G1-16vinyl is shown in Fig. 1 and confirms that the POSS core remains intact. In addition, at least in this crystal, all of the chlorides in G1-16Cl have been successfully replaced with vinyl groups to give the fully substituted vinyl dendrimer.

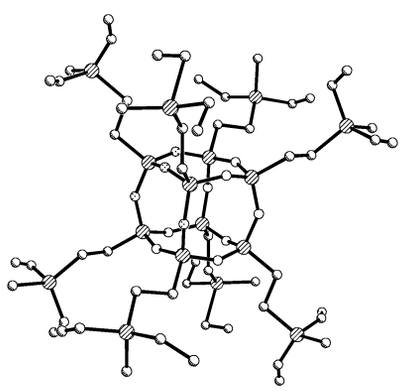
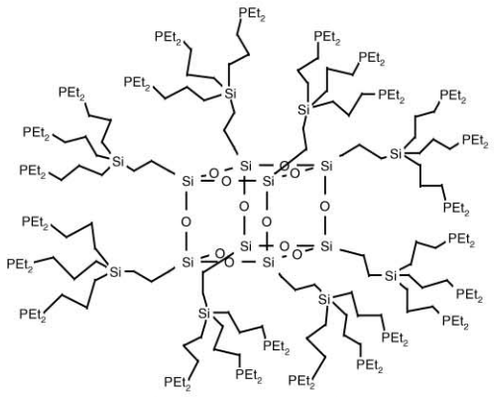
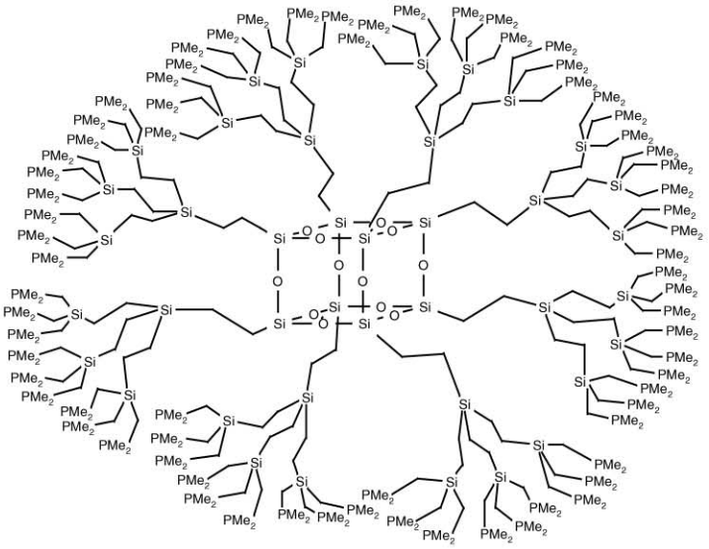


Fig. 1 X-Ray structure of G1-16vinyl. Si represented by diagonal bottom left to top right lines, O by open circles C by partially shaded circles. The hydrogen atoms are omitted for clarity.

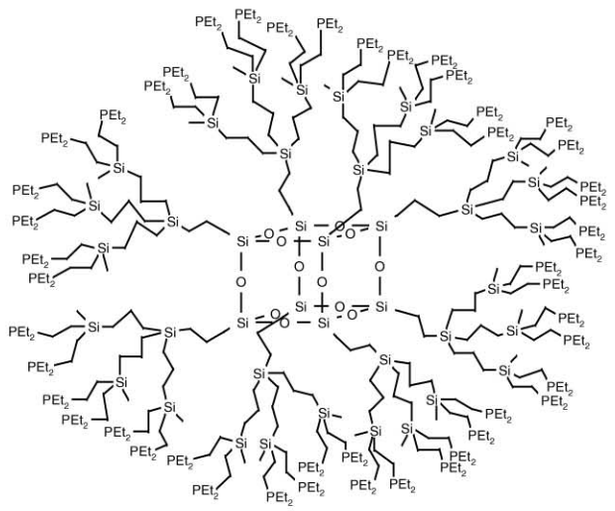
Second generation POSS-based dendrimers (48 and 72 groups) were obtained from the reaction of G1-24vinyl or G1-24allyl with $HSiMeCl_2$ or $HSiCl_3$. When starting from G1-24vinyl, reaction with $HSiCl_3$ as described previously gave the compound G2-ethyl-72Cl as a white solid in 88% yield.[15] From the G1-24allyl POSS, different reaction conditions are necessary as the solubility and reactivity of the starting materials and product are different. Toluene was used as the solvent in the hydrosilylation reaction ($HSiMeCl_2$) as the use of diethyl ether led to fast precipitation of partially functionalised product while THF (in conjugation with some chlorosilane) was trapped after reaction inside the dendritic structure. Longer reaction times (up to 96 h) are also needed as the allyl groups are less reactive toward hydrosilylation than their vinyl counterparts. The 48-chloro compound, G1-propyl-48Cl, was isolated as a white solid in quantitative yield (> 95%). The ^{1}H NMR spectra



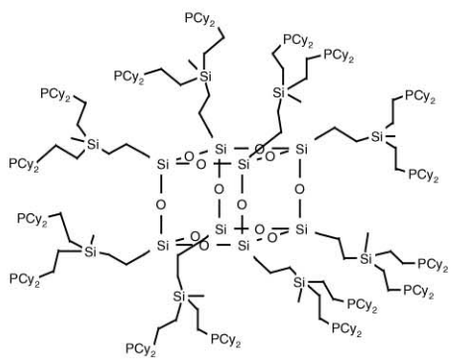
G1-24propylPEt$_2$



G2-ethyl-72methylPMe$_2$



G2-propyl-48ethylPEt$_2$



G1-16ethylPCy$_2$

showed traces of β-substitution, although it was in such small amounts that it was difficult accurately to quantify the relative amount of this 'side-reaction'. Subsequent addition of the vinyl magnesium bromide in excess gave the corresponding G2-propyl-48vinyl as a heavy oily product in 70% yield. NMR and microanalysis showed high conversion (>95%) of the chloro functionality to vinyl groups.

Functionalisation with alkylphosphine groups

Nucleophilic substitution. The first method used to introduce alkylphosphine groups onto the surface of the dendrimer was a nucleophilic substitution of the chlorine atoms of the Cl-functionalised dendrimers. Deprotonation of different dialkylphosphinomethyl compounds forms the corresponding lithium dialkylphosphinomethyl salt. The first reaction used $LiCH_2P(CH_3)_2$ as the nucleophile, which was prepared by reaction of $P(CH_3)_3$ with Bu^{t}Li.[24] Stoichiometric additions of this reagent to G1-24Cl and G2-ethyl-72Cl were carried out leading to G1-24methylPMe$_2$ and G2-ethyl-72methylPMe$_2$ respectively. Because of difficulties in determining the conversion of the substrate to G1-24methylPMe$_2$ by ^{1}H NMR due to the overlapping of the proton resonances, we used a subsequent reaction to characterise the product. Addition of methyllithium after the reaction had been going for 24 hours, revealed that ≈22 % of the chlorosilane groups of G1-24Cl were unreacted as ^{1}H NMR shows clearly the formation of methylsilane groups. The result suggests that the steric bulk of the dendrimer (steric hindrance, back-folded arms) hampers the reaction since both chlorosilane and the phosphorus compound are highly reactive species. However, higher conversion was obtained after 36 hours (>95%). The elimination of the LiCl salts was obtained by precipitation in dichloromethane. The ^{31}P NMR spectrum shows a single signal at −54.5 ppm attributed to the bound $CH_2P(Me)_2$. The white product decomposed rapidly in air or non-degassed solvent to form the oxide. The MALDI-TOF spectrum of the compounds showed the high conversion of the product (>95%) (*m*/*z* 2667 (broad), *m*/*z* expected 2667). However, due to the sensitivity to moisture and air, low resolution was obtained. Addition of $LiCH_2P(CH_3)_2$ to the G2-ethyl-72Cl compound led to slow precipitation (over 3 days) of the compound G2-ethyl-72methylPMe$_2$.

The substitution by di-n-hexylphosphine groups was achieved by addition of $LiCH_2P(C_6H_{13})_2$ to the G1-24Cl dendrimer. $LiCH_2P(C_6H_{13})_2$ was prepared by addition of the Grignard $C_6H_{13}MgBr$ to methyldichlorophosphine ($PMeCl_2$) and subsequent lithiation by ^{t}BuLi.[24] Addition of $LiCH_2P(C_6H_{13})_2$ in excess to G1-24Cl yielded a colourless low melting point solid G1-24methylPHex$_2$ after 3 days. The conversion reached 90% to the desired dihexylphosphine POSS (as measured by ^{1}H NMR spectroscopy). The purification of the product was less easy than for the dimethylphosphine dendrimer but a 40% yield of the compound was obtained after removal of the LiCl. The ^{31}P NMR spectrum of the reaction product showed a signal at −36.3 ppm, which is attributed to the bound $CH_2P(C_6H_{13})_2$.

Radical addition. The second type of reaction considered was the radical reaction of dialkylphosphines onto the double bonds of the vinyl-functionalised dendrimers. A radical reaction was

performed to affect an anti-Markownikoff type addition of the phosphine to the alkenes so that it would promote the formation of the desired terminal phosphine groups. Similar work had been previously carried out with the octavinyl oligosilsesquioxane and diethylphosphine[22] and dimethylphosphine[25] leading to POSS compounds with eight phosphine moieties.

The 24-vinyl POSS molecules were reacted in this way with $HPEt_2$ in cyclohexane at 50–60 °C. The reaction was initiated by AIBN (azoisobutyronitrile). The addition of an excess of diethylphosphine (3 fold excess) gave conversion up to 96% for the 24-branched compound G1-24ethylPEt$_2$. The solvent and the excess of phosphine were removed under vacuum to give an oily colourless product. The product was characterised by NMR (^{31}P δ −15.9 ppm) and MALDI-TOF techniques. Although no vinylic protons were detected by ^{1}H NMR, the mass spectrum seemed to indicate that on average between 23 and 24 of the arms were converted to diphosphine groups. Two main broad signals in the MS spectrum were found at *m*/*z* 3582 (M − PEt$_2$) and 3676 (*m*/*z* expected 3677). This may be due to a small amount of fragmentation occurring during the MALDI-TOF analysis as a similar phenomenon has been encountered for a similar compound with PPh_2 groups.[26] The radical addition was extended to the G1-24allyl POSS. The product obtained G1-24propylPEt$_2$ was a colourless oil in 98% yield with a conversion reaching at least 87% after 15 days. The conversion was calculated from the MALDI-TOF, which showed a broad signal centered at *m*/*z* = 3730 corresponding to ≈21 arms functionalised (*m*/*z* expected = 4014). Again this conversion differs with that suggested by the ^{1}H NMR since no alkenyl protons were detected and the integration indicating a high phosphine loading (>94%). It is therefore, as discussed above, difficult to determine the exact conversion. Interestingly various ^{31}P chemical shifts were found at δ −22.1 (minor), −23.3 (minor), −23.5 (major), −23.7 (major), −24.2 (major), −28.2 (minor) and −29.3 ppm (minor). This may be due to back folding of some of the outermost arms so that they are encapsulated inside the dendrimer, and therefore in a different environment to the ones remaining on the surface of the dendrimer. This back folding is relatively well characterised for other high generation POSS-based dendrimers.[27] G1-16ethyl-PEt$_2$ and the 2nd generation dendrimer, G2-propyl-48ethyl-PEt$_2$, were prepared by a similar reaction from G1-16vinyl and G2-propyl-48vinyl respectively. These G1 and G2 dendrimers containing diethylphosphine functionality were isolated as oily products (as expected the G2 dendrimer is the more viscous of the two) in quantitative yields and with conversions of >99% (6 days, ^{1}H NMR, MALDI-TOF) and >96% (12 days, ^{1}H NMR) respectively. The MALDI-TOF spectrum of G1-16ethylPEt$_2$ showed a peak at *m*/*z* 2923 (*m*/*z* expected 2860) possibly corresponding to partial oxidation of the phosphines {M + 3 × 'O'}. However, the 2nd generation product could not be characterised by MALDI-TOF as no peak in the expected *m*/*z* 8502 is found. We suspect that this is due to more severe fragmentation of this dendrimer than is seen for the smaller ones. A single ^{31}P chemical shift was found at δ −15.2 ppm for the 16-branched product, while for the 48 arm molecule two broad signals were detected at δ −15.8 and −16.1 ppm, again indicating possible back folding of some arms. All these diethylphosphine dendrimers showed high solubility except in highly polar solvents (alcohols, *etc*.).

Dicyclohexyl phosphine was also reacted with G1-16vinyl. After 10 days at 50 °C with an excess of diphosphine (3–4 fold) and AIBN as radical initiator, an air sensitive product was obtained. The compound, G1-16ethylPCy$_2$, is a colourless low melting point solid. A single ^{31}P chemical shift was detected at δ 4.1 ppm corresponding to the expected $CH_2P(Cy)_2$ group. MALDI-TOF and ^{1}H NMR show that only ≈12 of the 16 arms (on average) had reacted.

Reaction of dicyclohexylphosphine with G1-24vinyl was even less successful, with a very low conversion (≈55%), probably caused by increased steric problems with the larger number of vinyl groups.

A randomly dispersed diethyl- and dicyclohexyl-phosphine functionalised POSS was synthesized by addition to G1-16vinyl POSS of $HPCy_2$ (phosphine/vinyl ratio of 1.5 : 1) followed by the much smaller $HPEt_2$ (1 equivalent to the vinyl groups) 3 days later. Excess of phosphines were removed under vacuum with heating to give a quantitative yield of the derivatised dendrimer as a colourless oil. The product contained 68% of dicyclohexylphosphine groups and 32% of diethylphosphine substituents (determined by ^{1}H and ^{31}P NMR). No vinyl groups were detected in the ^{1}H NMR spectrum. When both phosphines were added at the same time only the smaller diethylphosphine groups were incorporated (conversion 99%). Details of the phosphine-functionalised dendrimers are given in Table 1.

Preparation of Rh-dendrimer complexes

Upon addition of ethanol to a mixture of [Rh$_2$(O$_2$CMe)$_4$] and G1-24ethylPEt$_2$ (P : Rh ratio = 3 : 1) a brown homogeneous solution was obtained after 3–4 hours, whilst a yellow solution was obtained with [Rh(acac)(CO)$_2$] and the dendritic ligand (<1 h). Although these solutions have not been investigated, it is normal for phosphines to add to [Rh$_2$(O$_2$CMe)$_4$] and to displace one or more carbonyl ligands in [Rh(acac)(CO)$_2$]. Under CO and H_2, however, both systems give the catalytically active [RhH(CO)$_2$(PR$_3$)$_2$].[21] Interestingly lower phosphine/rhodium ratios (below 3 : 1) led to the formation of gels when using the rhodium-based complex [Rh(acac)(CO)$_2$] or under CO/H_2 atmosphere using [Rh$_2$(O$_2$CMe)$_4$]. The gels precipitated with time to form insoluble materials, which could not be dissolved again even at higher temperature or on addition of excess ligands. It is believed that cross-linking between two dendrimers, (*i.e.* two phosphine groups of two different dendritic ligands bind to the same rhodium atom) occurs under these conditions leading to insoluble 'oligomeric' species. Steric hindrance within such complexes would then prevent the new complexation of a phosphine ligand on the metal centre on addition of excess ligand.

The G1-16ethylPEt$_2$ and G1-24propylPEt$_2$ dendrimers were readily complexed with [Rh(acac)(CO)$_2$] in the ethanol solution while the 2nd generation dendrimer necessitated stirring overnight to obtain a homogeneous phase.

In order to clarify the mode of chelation of the dendritic structure, *i.e.* whether or not bidendate or tridentate coordination of the phosphine to the rhodium centre occurred or if bimetallic species were formed, a ^{31}P NMR study of the dendrimer rhodium complexes was carried out. The ^{31}P NMR spectrum of the solution formed under CO/H_2 from the [Rh(acac)(CO)$_2$]/G1-24ethylPEt$_2$ species (P/Rh = 4/1) shows several species in solution. Two resonances were observed under 1 atmosphere of CO/H_2 at room temperature in ethanol solution. One signal (δ_P − 16.0 ppm) was found corresponding to the free P atoms (G1-24ethylPEt$_2$ resonates at δ_P −16.0 ppm) (width at half maximum = 50 Hz) and the other resonance centred at δ_P 29.6 ppm (broad signal, width at half maximum = 660 Hz) was attributed to [RhH(CO)$_2$(P)$_2$] ([RhH(CO)$_2$(PEt$_3$)$_2$] resonates at δ_P 24.5 ppm)[20] or [RhH(CO)(P)$_3$] species ([RhH(CO)(PEt$_3$)$_3$] resonates at δ_P 26.2 ppm)[20] (P = Dend-PR$_2$, Dend for dendrimer). At −50 °C, the resonance of the free P atoms stayed unchanged while the rhodium complex species showed some asymmetric broadening suggesting fluxionality within the bound complex. The fact that the resonances for the Rh bound P atoms are broad at all temperatures suggests that there are different coordination environments, whilst the fact that two resonances are observed at least up to room temperature and the peak width for the free phosphine does not vary in this temperature range suggests that the rhodium is fixed to individual P atoms and is not migrating over the surface.

Table 1 Preparation of phosphine-functionalised POSS

Dendrimer	^{31}P NMR, δ/ppm	Conversion of end groups (%)	Chemical yield (%)
G1-24methylPMe$_2$ [a]	−54.5	>95 [c,d]	97
G2-ethyl-72methylPMe$_2$ [a]	−54.4	nd [e]	80
G1-24methylPHex$_2$ [a]	−36.3 (br)	90 [c]	40
G1-16ethylPEt$_2$ [b]	−15.2 (br)	>99 [c,d]	99
G1-24ethylPEt$_2$ [b]	−15.9. −16	>96 [c,d]	97
G2-propyl-48ethylPEt$_2$ [b]	−15.8, −16.1	>90 [c,d]	96
G1-24propylPEt$_2$ [b]	−23.6, −23.9, −24.3	>87 [c,d]	98
G1-16ethylPCy$_2$ [b]	4.1 (br)	75 [c]	98
G1-24ethylPCy$_2$ [b]	4.1 (br)	55 [c]	95
G1-16ethylPCy$_{1.64}$Et$_{0.36}$ [b]	−14.9, 4.8	98 [c]	95

[a] Reaction of R_2PCH_2Li with $-SiCl_3$ derivatised dendrimer. [b] Reaction of HPR_2 with vinyl derivatised dendrimer. [c] ^{1}H NMR. [d] MALDI-TOF. [e] Not measured due to low solubility.

Table 2 Hydrocarbonylation reactions of hex-1-ene catalysed by Rh complexes of POSS derived dimethyl- and dihexyl-phosphine dendrimers

Ligand	[Rh]/10^{-3} mol dm^{-3}	Time/h	Conversion (%)	Aldehydes (%)	Alcohols (%)	l : b ratio
PMe$_3$	8	16	>99	—	99	2.4
G1-24methylPMe$_2$	8	16	>99	tr [a]	98	2.1
G1-24methylPMe$_2$	8	4	>95	80	14	2.2 [b]
G1-24methylPMe$_2$	4.4	16	>99	5 [c]	94	2.1
G2-ethyl-72methylPMe$_2$	8	16	>99	2	97	2.4
G1-24methylPHex$_2$	8	16	>99	tr [a]	99	2.4

Reaction conditions: catalyst prepared *in situ* from [Rh$_2$(O$_2$CMe)$_4$] and alkylphosphine species, batch autoclave, P/Rh = 3/1, substrate 8.3×10^{-3} mol, ethanol (4 cm^3), 120 °C, CO/H$_2$ 40 bar. [a] Traces not quantified. [b] Overall linear to branched ratio of alcohols and aldehydes. [c] Diethyl acetals of the C$_7$ aldehydes.

Catalysis

Hydrocarbonylation of hex-1-ene, oct-1-ene, non-1-ene and prop-2-en-1-ol catalysed by rhodium complexes formed from [Rh$_2$(O$_2$CMe)$_4$] or [Rh(acac)(CO)$_2$] and dimethylphosphine (G1-24methylPMe$_2$, G2-ethyl-72methylPMe$_2$), dihexylphosphine (G1-24methylPHex$_2$) or diethylphosphine (G1-16ethylPEt$_2$, G1-24ethylPEt$_2$, G1-24propylPEt$_2$, and G2-propyl-48PEt$_2$) functionalised dendrimers was carried out at 120 °C and 40 bar of CO/H$_2$ in ethanol or THF.

Hydrocarbonylation of hex-1-ene. The rhodium complexes formed with PMe$_3$, G1-24methylPMe$_2$, G2-ethyl-72methylPMe$_2$ and G1-24methylPHex$_2$ show good activity for the catalytic hydrocarbonylation of hex-1-ene to heptan-1-ol and 2-methylhexan-1-ol at the optimal conditions found previously [21] (solvent ethanol, [Rh$_2$(O$_2$CMe)$_4$] = 8.0×10^{-3} mol dm^{-3}, phosphine/rhodium ratio of 3/1, 40 bar CO/H$_2$ (1/1), 120 °C, 16 h, autoclave stirred using a stirrer bar) (Table 2). The use of [Rh$_2$(O$_2$CMe)$_4$] and [Rh(acac)(CO)$_2$] as the Rh source at higher P/Rh ratios (P/Rh = 4/1 to 6/1) gave similar results. The dendrimers must be bound to the rhodium since only reactions involving trialkylphosphine complexes give alcoholic products. The hydrocarbonylation of hex-1-ene using [Rh$_2$(O$_2$CMe)$_4$] and G1-24methylPMe$_2$ as catalyst complex in ethanol (batch reactor) gave mainly C$_7$ alcohols (over 94%) (Table 2) and the substrate was totally converted to products after 16 hours. Heptan-1-ol and 2-methylhexan-1-ol were the products of the reaction (determined by gas chromatography (GC)) in a ratio of 2.1 : 1. Traces of C$_7$ aldehydes and diethyl acetals (formed from C$_7$ aldehydes and ethanol) were also detected in some cases. The solutions recovered after reaction were clear yellow although a small amount of yellow precipitate was sometimes present. Interestingly, after 4 hours the conversion had reached 95% with 80% of the substrate converted to the aldehydes (heptan-1-al and 2-methylhexan-1-al, l : b ratio of 1.8 : 1). The other products were the alcohols (14%) with a l : b ratio of 4.6 : 1 (Table 2). This result suggests that the aldehydes are formed initially, and then reduced to the alcohols, the linear isomer being hydrogenated faster as expected since the l : b ratios of aldehydes and alcohols were not the same. The overall linear to branched selectivity was 2.2 : 1, which is similar to that obtained after the longer reaction time. This result is in contrast with earlier studies showing the one-step formation of alcohol products.[20,21] The origins of this difference are currently being investigated. Lower concentrations of Rh-dendrimer complexes increase the amount of side products (*i.e.* diethyl acetals). Indeed the hydrocarbonylation of hex-1-ene produced 5% of diethyl acetals (from C$_7$ aldehydes) when the concentration of rhodium was reduced to 4.4×10^{-3} mol dm^{-3}. Increased amounts of aldehydes were also observed at lower catalyst concentrations, when using PEt$_3$ as the ligand.[21]

Use of the 72-dimethylphosphine functionalised POSS, G2-ethyl-72methylPMe$_2$, leads to the formation of C$_7$ alcohols (heptan-1-ol and 2-methylhexan-1-ol) and a small amount of heptan-1-al diethyl acetal (2%). The catalytic solution was partially heterogeneous (before and after reaction). Traces of isomerisation products were also detected but not quantified. The l : b ratio of the alcohols obtained was 2.4 : 1 (Table 2). This regioselectivity is slightly higher than that found for the 1st generation dendrimer, but similar to that seen when using PMe$_3$ as the ligand.

Hydrocarbonylation of hex-1-ene in ethanol was also carried out using the dendrimer G1-24methylPHex$_2$ containing dihexylphosphine moieties. After 16 hours (yellow clear solution), the conversion of the substrate was higher than 99% (GC). As expected the main products of reaction were heptan-1-ol and 2-methylhexan-1-ol in a ratio of 2.4 : 1. No trace of aldehydes or side-products were detected.

Total conversion of the hex-1-ene was obtained using a catalyst derived from G1-24ethylPEt$_2$ after 16 hours in a batch autoclave, while only 6 hours were necessary using a reactor, which operates under constant pressure by feeding gas through a mass flow controller from a ballast vessel and has more efficient stirring leading to better transport across the gas–liquid interface (Table 3). Interestingly the linear to branched ratio (3.1 : 1) was slightly higher than for PEt$_3$ (2.4 : 1) under identical conditions, perhaps suggesting that the large dendrimer-based

Table 3 Hydrocarbonylation reactions catalysed by Rh complexes of POSS derived 24-diethylphosphine dendrimer G1-24ethylPEt$_2$

Substrate	Reaction time/h	Conversion (%)	Aldehydes (%)	Alcohols (%)	l : b ratio (alcohol)	Rate constant/10^{-4} s^{-1}
Hex-1-ene	16[a] or 8[b]	>99	tr	98	3.1	3.7[b]
Non-1-ene	16[a]	>99	tr	98	2.6	—

Reaction conditions: catalyst prepared *in situ* from $[Rh_2(O_2CMe)_4]$ and dendrimer (Rh = 4.0×10^{-5} mol, P/Rh = 4/1), substrate 8.0×10^{-3} mol (hex-1-ene 1 cm^3, non-1-ene 1.4 cm^3), ethanol 4 cm^3, 120 °C, CO/H_2 40 bar. [a] Batch autoclave. [b] Constant pressure apparatus.

ligand was exerting some steric control over the reaction. Small amounts of isomerisation products (hex-2-ene and hex-3-ene < 2%) were formed during the catalytic process. The graph representing the consumption of syngas (CO/H_2) during the hydrocarbonylation of hex-1-ene is shown in Fig. 2. An inflection at the beginning of the graph and a long tail at the end may indicate that different reactions dominate at different times. Based on the results obtained with G1-24methylPMe$_2$ (see also below), the hydrocarbonylation is probably a two step reaction with hydroformylation followed by subsequent hydrogenation of the aldehydes. Such a mechanism would explain the traces of aldehydes found in the reaction products. A first order rate constant for the rate of reaction was calculated for this reaction ($k = 3.7 \times 10^{-4}$ s^{-1}).

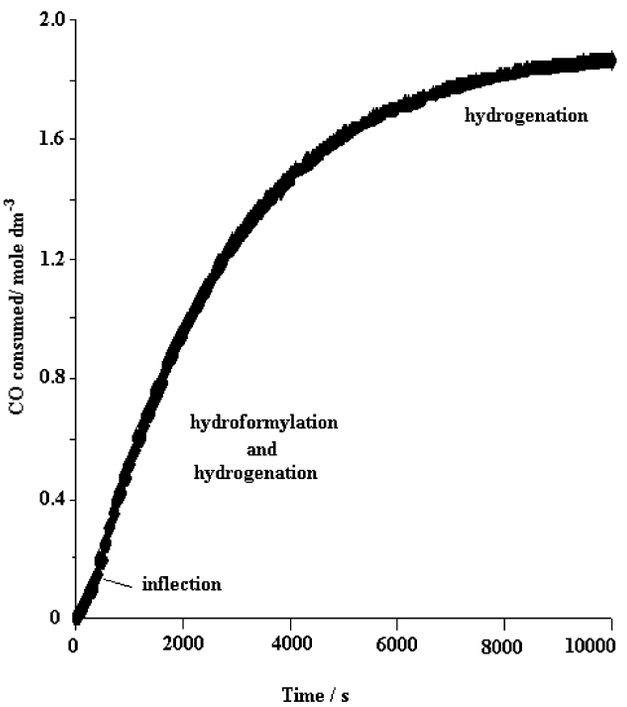


Fig. 2 Kinetics of the hydrocarbonylation of hex-1-ene in ethanol at 120 °C at 40 bar of CO/H_2 catalysed by the complexes [Rh $(CO)_2$(acac)]/ G1-24ethylPEt$_2$.

Hydrocarbonylation of oct-1-ene and non-1-ene. The hydrocarbonylation of oct-1-ene catalysed by the complexes formed from $[Rh(acac)(CO)_2]$ and the diethylphosphine-containing dendrimers (G1-24ethylPEt$_2$, G1-16ethylPEt$_2$, G1-24propylPEt$_2$, G2-propyl-48ethylPEt$_2$) led to the formation of nonan-1-ol and 2-methyloctan-1-ol as the only products (Table 4). The complexes were initially formed in a Schlenk tube and injected into the autoclave when homogeneous solutions were obtained. All complexes formed from ligands G1-24ethylPEt$_2$ (5 atoms between the phosphorus atoms, 3 P atoms/Si), G1-16ethylPEt$_2$ (5 atoms between the P atoms, 2 P atoms/Si), G2-propyl-48PEt$_2$ (2nd generation, 5 atoms between the P atoms, 2 P atoms/Si) and G1-24propylPEt$_2$ (7 atoms between the P atoms, 3 P atoms/Si) showed similar selectivity to the linear alcohol nonan-1-ol (*ca.* 73%), with a linear to branched ratio of *ca.* 3 : 1. 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 give different selectivities when using different spacers between the two phosphorus atoms.[14,21,26] For the first generation dendrimer a decreasing rate (Table 4) was observed when using ligands G1-24propylPEt$_2$ (longer spacer atoms), G1-16ethylPEt$_2$ (only 16 phosphine groups) and G1-24ethylPEt$_2$ respectively. It is possible that crowding at the dendrimer surface leads to a slower reaction. However, the 48-branched diethylphosphine POSS, G2-propyl-48ethylPEt$_2$, leads to slightly higher reactivity than its 1st generation counterparts G1-16ethylPEt$_2$ and G1-24ethylPEt$_2$ with a spacer of two carbons between the silicon and phosphorus atoms. The reaction probably does not proceed through direct formation of alcohols when using G1-24propylPEt$_2$ since aldehydes (6.1%, *i.e.* 10.5% of the total amount of products) were found after 1 hour of reaction (conversion 57.9%). In addition, since the linear to branched ratio for the alcohols and the aldehydes were respectively 3.8 : 1 and 1 : 3, a two step reaction is more likely. The overall linear to branched ratio (aldehyde and alcohols) was identical to that obtained after a longer reaction time (2.9 : 1), when alcohols were the only products.

Dendrimers G1-16ethylPCy$_2$ and G1-16ethyl$_{(PCy_2)_{0.32}(PEt_2)_{0.68}}$ with dicyclohexylphosphine moieties were also used as ligands for the hydroformylation/hydrocarbonylation of oct-1-ene (Table 5). Hydroformylation in toluene at 120 °C and 10 bar of syngas by the complex formed from $[Rh(acac)(CO)_2]$ (2.0×10^{-5} mol) and G1-24ethylPCy$_2$ (P : Rh = 6/1) led to the formation of nonan-1-al (57.2%) and 2-methyloctan-1-al (40.3%). A poor selectivity to the linear aldehyde, l : b ratio of only 1.4 : 1, was obtained. A likely explanation of this result is that the bis ligand species responsible for the selectivity cannot form due to the steric hindrance of such dicyclohexylphosphine ligands. When using the di-substituted diethyl- and dicyclohexyl-phosphine dendrimer (G1-16ethyl$_{(PCy_2)_{0.32}(PEt_2)_{0.68}}$) as ligand of the rhodium-based catalyst derived from $[Rh(acac)(CO)_2]$ (4.0×10^{-5} mol) for the hydrocarbonylation of oct-1-ene, in ethanol at 120 °C under 40 bar of syngas, the alcohols (59.9% of nonan-1-ol and 32.4% of 2-methyloctan-1-ol) were the main products of reaction. A slightly higher linear to branched ratio was obtained (l : b = 1.8 : 1). This value is however low compared to those obtained from the diethylphosphine dendrimers showing that the catalytic active species were affected by the bulky cyclohexyl substituents.

The hydrocarbonylation of non-1-ene using G1-24ethylPEt$_2$ as ligands led to the formation of decan-1-ol and 2-methyl-nonan-1-ol in 98% yield (Table 3). A linear to branched ratio of 2.6 : 1 was obtained. Traces of aldehydes and 2- and 3-nonene were also detected.

After reaction, the catalytic mixtures (all diethyl- and dicyclohexyl-phosphine dendrimers) were bright yellow solutions although the use of batch autoclaves occasionally led to formation of a yellow precipitate, which was not further analysed.

Hydrocarbonylation of prop-2-en-1-ol in protic solvents. The synthesis of butane-1,4-diol is an important industrial process since the diol is used as an intermediate in the formation of tetrahydrofuran and of polyester resins.[28] The preparation of

Table 4 Hydrocarbonylation reactions of oct-1-ene catalysed by Rh complexes of POSS derived diethylphosphine dendrimers

Ligand	Time/h	$k/10^{-4}$ s^{-1}	Conversion (%)	Isomerisation (%)	Nonan-1-ol (%)	l : b ratio
G1-16ethylPEt$_2$	8	1.5	>99.9	3.1	73.5	3.1
G1-24ethylPEt$_2$	8	1.7	>99.9	2.1	73.2	3.1
G1-24propylPEt$_2$	4	3.7	>99.9	1.4	72.8	2.9
G1-24propylPEt$_2$	1	—	57.9	0.6	40.3[a]	3.8
G2-propyl-48ethylPEt$_2$	8	2.1	>99.9	2.6	72.8	3.0

Reaction conditions: [Rh(acac)(CO)$_2$] = 4.0×10^{-5} mol, P/Rh = 6/1, ethanol (4 cm^3) heated under CO/H$_2$ (6 bar) for 1 h. Substrate oct-1-ene (8.3×10^{-3} mol) injected and the pressure increased to and maintained at 40 bar by a constant supply of CO/H$_2$, 120 °C. [a] Nonan-1-al 6.1 %, aldehyde l : b = 0.33.

Table 5 Hydroformylation or hydrocarbonylation of oct-1-ene catalysed by [Rh(acac)(CO)$_2$]/dicyclohexylphosphine-containing dendrimers

Ligand	Solvent	Time/h	$k/10^{-4}$ s^{-1}	Conversion (%)	Nonan-1-ol (%)	Nonan-1-al (%)	l : b ratio
G1-16ethylPCy$_2$	Toluene[a]	5	1.9	>99.9	—	57.2	1.4
G1-16ethyl$_{(PCy_2)_{0.32}(PEt_2)_{0.68}}$	Ethanol[b]	8	2.4	>99.9	59.9	—	1.8

Reaction conditions: [Rh(acac)(CO)$_2$], P/Rh = 6/1, substrate 8.3×10^{-3} mol, solvent (4 cm^3), 120 °C. [a] Rh = 2.0×10^{-5} mol, CO/H$_2$ 10 bar. [b] Rh = 4.0×10^{-5} mol, CO/H$_2$ 40 bar.

Table 6 Hydrocarbonylation of prop-2-en-1-ol catalysed by rhodium/G1-24ethylPEt$_2$ complexes at 120 °C and 40 bar H$_2$/CO

Solvent	Time/h	k_1[a] /10^{-3} s^{-1}	k_2[b] /10^{-3} s^{1}	Conversion (%)	BDO (%)	MPO (%)	MPD (%)	MPA (%)	HBA (%)
Ethanol	2	1.2	—	99.9	60.8	26.1	4.4	2.5	0.5
Ethanol	0.25	—	—	67.5	14.1	3.6	1.8	15.6	25.0
Ethanol[c]	—	—	—		20.9	5.4	2.7	23.2	37.1
THF	3	1.2	0.23	99.8	59.3	17.1	5.5	8.0	4.1
THF	9	—	—	99.9	64.9	21.9	6.9	1.1	0.2

Reaction conditions [Rh(acac)(CO)$_2$] (4.0×10^{-5} mol), G1-24ethylPEt$_2$ (1.0×10^{-5} mol), solvent 4 cm^3, substrate 1 cm^3 (14.7×10^{-3} mol), 120 °C, 40 bar H$_2$/CO BDO = butane-1,4-diol, MPO = 2-methylpropan-1-ol, MPD = 2-methylpropane-1,3-diol, MPA = 2-methylpropan-1-al, HBA = 4-hydroxybutan-1-al. [a] k_1 = rate constant for the hydroformylation step. [b] k_2 = rate constant for the hydrogenation step. [c] After 0.25 h (as second entry in this Table but the selectivity to the various products is shown for direct comparison with the first entry).

butane-1,4-diol by the hydrocarbonylation in a protic solvent of prop-2-en-1-ol was also used to test the catalytic properties of the dendrimer ligands. The products expected from prop-2-en-1-ol are butane-1,4-diol and 2-methylpropane-1,3-diol if the reaction follows a similar stepwise pathway to that of the hydrocarbonylation of hex-1-ene.[20,21] However the reaction carried out in ethanol led to butane-1,4-diol in 60.8% yield and to the branched alcohols 2-methylpropan-1-ol (26.1%) and only 4.4% of 2-methylpropane-1,3-diol (Fig. 3 and Table 6). The

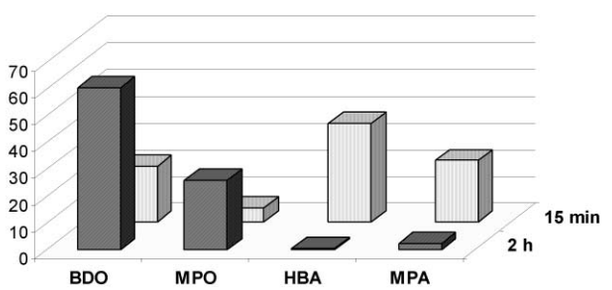


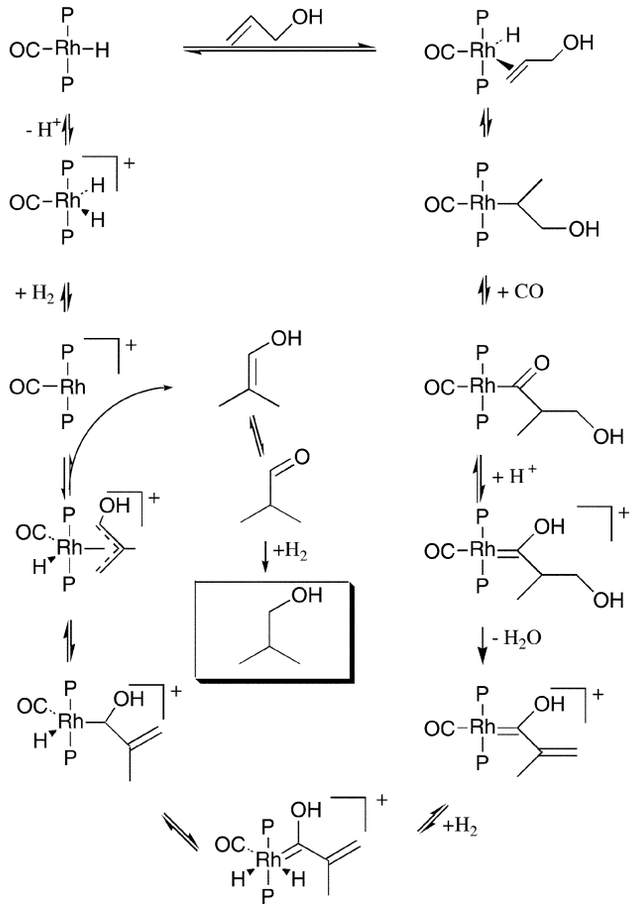
Fig. 3 Distribution of the major products of the hydrocarbonylation of prop-2-en-1-ol in ethanol catalysed by Rh dendritic complexes after 15 minutes and 2 hours (abbreviations used are given in Table 6).

other products detected were 2-methylpropan-1-al (2.5%), propanol (1.4%), 2-methylprop-2-en-1-ol (0.3%), 4-hydroxybutan-1-al (0.5%) and 2-methylprop-2-en-1-al (0.2%). Traces of propan-1-al, 2-methyl-3-hydroxypropan-1-al and the cyclic products, γ-butyrolactone (0.4%) and 2,3-dihydrofuran, were present with 3.4% of undetermined products. The linear to branched ratio (taking account of all the different products) was 1.8 : 1. This distribution of products is similar to those obtained in earlier studies using PEt$_3$.[20]

The production of 2-methylpropan-1-ol as the major branched product requires some interpretation since it cannot be a direct product of the hydrocarbonylation of the substrate, but must involve dehydration at some stage of the reaction followed by hydrogenation. It was previously proposed that the hydrocarbonylation of hex-1-ene and prop-2-en-1-ol in protic solvents using PEt$_3$ as ligand may involve a single step reaction to the alcohols *via* a hydroxycarbene intermediate.[20,21] The 2-methylpropan-1-ol was proposed to be formed from this hydroxycarbene intermediate in the Markownikoff cycle by dehydration followed by hydrogen transfer, η^3-allyl formation, a second hydrogen transfer to form the vinyl alcohol and tautomerisation to 2-methylpropan-1-al, which was then hydrogenated to 2-methylpropan-1-ol (see Scheme 1).[20] However in our reaction using the dendrimer based ligand, after 15 minutes more than 67% of the substrate had reacted, with the aldehydes being the major products. 37.1% of the product was the linear aldehyde 4-hydroxybutan-1-al, while the main branched product was 2-methylpropan-1-al. Only 20.9% and 5.4% of the products were respectively butane-1,4-diol and 2-methylpropan-1-ol.

As shown in Fig. 4, corresponding to the gas consumption during the hydroformylation of prop-2-en-1-ol in ethanol catalysed by the complex formed between [Rh(acac)(CO)$_2$] and dendrimer G1-24ethylPEt$_2$, two reaction regimes are visible. Firstly, a hydroformylation reaction occurred with possibly a concurrent hydrocarbonylation reaction (see below), followed by a slower process, presumed to be hydrogenation. The first step was first order in substrate ($k_1 = 1.2 \times 10^{-3}$ s^{-1}).

These results show that, for butane-1,4-diol, the reaction proceeds, at least in part, through a sequential pathway (*via* aldehyde), but for the branched pathway leading to 2-methylpropan-1-ol, this is less certain. The failure to observe more



Scheme 1 Mechanism proposed in ref. 20 for the production of 2-methylpropan-1-ol from the hydrocarbonylation of prop-2-en-1-ol.

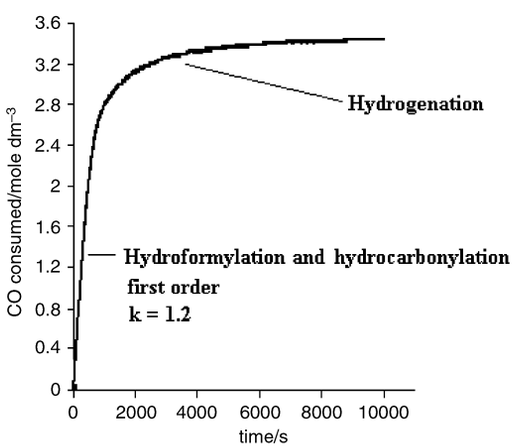
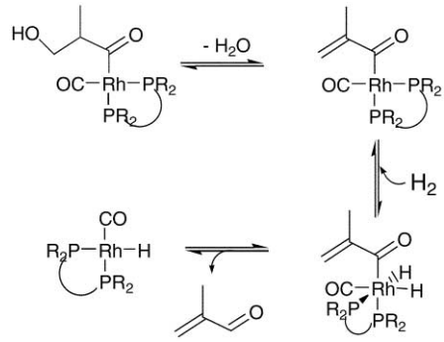


Fig. 4 Kinetics of the hydrocarbonylation of prop-2-en-1-ol catalysed by [Rh(CO_2)(acac)]/G1-24ethylPEt_2 at 120 °C and 40 bar (H_2/CO) in ethanol (k in 10^{-3} s^{-1}).

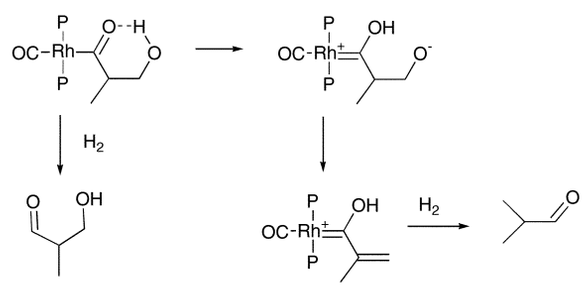
than traces of the expected branched hydroxyaldehyde, 2-methyl-3-hydroxypropan-1-al (selectivity of 1.4%),[29] and of its hydrogenated product, 2-methylpropane-1,3-diol (selectivity of 2.7%), after 15 min suggests that neither of these is an initial product nor can they be intermediates in the formation of 2-methylpropan-1-ol (see Table 6). Similar conclusions were drawn when using PEt_3 as the ligand.[20]

Since dehydration of 2-methylpropane-1,3-diol would lead to 2-methyl prop-2-en-1-ol, which cannot easily give the observed 2-methylpropanal, this means that the dehydration must occur from a rhodium bound intermediate. This cannot be the acyl complex as this would give 2-methylprop-2-en-1-al (Scheme 2), which is also probably not an intermediate (not observed after 15 min), so we propose that the branched cycle does go through



Scheme 2 Formation of 2-methylprop-2-en-1-al *via* dehydration of an acyl intermediate.

the hydroxycarbene intermediate. The relative rate of protonation of the acyl intermediate and oxidative addition of H_2 to the same intermediate determine which route will be followed (Scheme 3). The branched acyl intermediate complex has its



Scheme 3 Proposed routes to the branched products from the hydrocarbonylation of 2-propen-1-ol.

hydroxy proton in such a position that it may act to protonate the carbonyl oxygen *via* a six membered transition state. This may greatly enhance the rate of formation of the hydroxycarbene intermediate. For the linear acyl complex, the equivalent intermediate would involve a seven membered ring, which would not be expected to give such a rate enhancement. A similar mechanism was proposed for the formation of 2-methylpropan-1-ol in the hydrocarbonylation of 2-propen-1-ol using PEt_3 complexes of rhodium in toluene as solvent.[20]

If this explanation is correct, there is clearly a fine balance between the "normal" hydroformylation mechanism and the hydroxycarbene route. Further evidence for this comes from the observation of 2-methyl-3-hydroxypropan-1-al (1.7% selectivity) after short reaction times, since this must come from the "normal" hydroformylation pathway *via* the branched acyl intermediate. This suggests that both pathways are occurring for the branched aldehyde, but that the hydroxycarbene route dominates.

The hydrocarbonylation of prop-2-en-1-ol in THF (Table 6) gave similar results with the formation of butane-1,4-diol (64.9% after 9 h), 2-methylpropan-1-ol (21.9%) and 2-methylpropane-1,3-diol (6.9%). Interestingly the selectivity (including all the linear and branched products) was somewhat higher in THF (l : b = 2.2 : 1 instead of 1.8 : 1 in ethanol). The rate of formation of the desired alcohol products was much lower (*ca.* half) in the less polar solvent despite a similar rate of hydroformylation ($k_1 = 1.2 \times 10^{-3}$ s^{-1}) being found (first order reaction). The hydrogenation step was much slower in THF ($k_2 = 0.23 \times 10^{-3}$ s^{-1}) (first order reaction). Similar results were previously found with PEt_3.[20]

The observation of 2-methylpropanol as the major branched product (2-methylpropanal after shorter reaction time) for reactions carried out in THF is consistent with the explanation given in Scheme 3 for the production of these products. Since the protonation occurs *via* a cyclic transition state from the alcoholic proton of the allyl alcohol, this reaction should be

little affected by the reaction medium, as is observed. The slightly higher yield of 2-methylpropane-1,3-diol (6.9% instead of 4.4% in ethanol) at the expense of 2-methylpropan-1-ol and other dehydrated products (23.1% instead of 29.1% in ethanol) may indicate that the protonation is marginally less effective in the aprotic solvent, THF.

Conclusion

1st and 2nd generation alkylphosphine dendrimers based on POSS cores have been synthesised by two different routes. They have then been successfully applied as ligands to rhodium for the hydrocarbonylation of linear alkenes leading to alcohols as the major products. In some cases slightly higher l : b ratios in the alcohol products are obtained with the dendrimer based phosphines (3.1 : 1) than with free triethylphosphine (2.4 : 1). The reaction was shown to occur *via* formation of the aldehydes and subsequent hydrogenation to the alcohols. This result contrasts with those obtained in previous studies using PEt_3 as the ligand.[20,21]

The hydrocarbonylation of propen-1-ol using the dendritic ligand G1-24ethylPEt$_2$ led to the formation of identical products (mainly butane-1,4-diol and 2-methylpropan-1-ol) to those obtained with PEt_3. However the formation of the linear alcohol (butane-1,4-diol) clearly occurred *via* a two step reaction *i.e.* hydroformylation to form 4-hydroxybutan-1-al and subsequent hydrogenation to the diol. The formation of 2-methylpropan-1-ol (branched product) probably occurred *via* a hydroxycarbene route, with intramolecular protonation of the acyl intermediate.

The different functionalised dendrimers show different properties depending upon the nature of the phosphine and the complexity of the dendrimer itself. Hexyl and ethyl groups on the phosphine promoted better solubility than their methyl analogues (in toluene for example). Indeed, whichever diethylphosphine dendrimer was used, its ability to form homogeneous systems with rhodium complexes was higher than that for its dimethylphosphine counterpart. It seems that the longer alkyl chains on the dendrimers increase the solubility of the dendrimers in these solvents.

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. Whilst the dendrimer generation did not seem to modify the selectivity of the hydroformylation reaction, the branching pattern had a large influence on the reaction rate. Indeed, the number of functional groups and the length of the bridge between the phosphines were determining factors in the reactivity of the rhodium complexes.

Experimental

Microanalyses were carried out by the University of St. Andrews Microanalysis service on a Carlo Erba 1110 CHNS analyser. NMR spectra were recorded on a Bruker AM 300 or a Varian 300 NMR spectrometer. The ^{1}H and ^{13}C NMR spectra were recorded with reference to tetramethylsilane (external). ^{31}P NMR spectra were referenced externally to 85% H_3PO_4. ^{13}C and ^{31}P NMR spectra were recorded with broad band proton decoupling. Infrared spectra were recorded using either a Perkin-Elmer 1710 or a Nicolet 460 Protege FTIR spectrometer. GC analyses were carried out using a Phillips PU4000 instrument fitted with a capillary column with nitrogen as the carrier gas. GCMS analyses were carried out using a Hewlett-Packard 5890 GC interfaced with an Incos quadrupole mass spectrometer fitted with a SGE BP1 column or using a Hewlett-Packard HP6890 GC with a 5973 mass selective detector fitted with a 5% phenyl methyl siloxane capillary column. Matrix assisted laser desorption/ionisation (MALDI) mass spectra were obtained using a micromass TOF Spec 2E mass spectrometer system equipped with a 337 nm N_2 laser operating in positive ion reflection mode. Samples were prepared by addition of the matrix (α-cyano-4-hydroxycinnamic acid, 2.6-dihydroxyacetophenone, or 2,5-dihydroxybenzoic acid). The mixtures were then dissolved in a suitable solvent (THF, MeCN or CH_2Cl_2) before being transferred to the sample holder and dried. All mass measurements refer to peaks for the most common isotopes (^{1}H, ^{12}C, ^{16}O, ^{29}Si, ^{31}P).

All manipulations were carried out under dry, deoxygenated (Cr^{II} on silica) argon, using standard Schlenk line and catheter tubing techniques. Solvents were degassed before use having been dried by distillation from sodium diphenyl ketyl (THF, diethyl ether, light petroleum (boiling range 40–60 °C)), sodium (toluene, cyclohexane), CaH_2 (CH_2Cl_2) or magnesium alkoxide (methanol, ethanol). Water was distilled and stored under argon. Deuteriated solvents (Cambridge Isotope Laboratories) were degassed by repeated freeze–pump–thaw cycles and stored under argon over molecular sieves.

PMe_3 (Strem), Et_2PH (Strem), Cy_2PH (Strem), vinylMgBr (Aldrich), allylMgBr (Aldrich), Bu^{n}Li (Aldrich), Bu^{t}Li (Aldrich), H_2PtCl_6 (Johnson Matthey), AIBN (Aldrich), 1-bromohexane (Aldrich), $PMeCl_2$ (Strem), $[Rh_2(OAc)_4]$ (Aldrich) and [Rh(acac)(CO)$_2$] (Alfa) were all standard laboratory reagents and were used as received. $HSiMeCl_2$ and $HSiCl_3$ (both Aldrich) were distilled under argon before use.

G0-8vinyl,[15] G1-24Cl,[15] G1-24vinyl[15] and Me_2PCH_2Li[24] were prepared by standard literature methods.

Syntheses

1,3,5,7,11,13,15-Octakis[2-(dichloromethylsilyl)ethyl]pentacyclo[9.5.1.1^{3,9}.1^{5,15}.1^{7,13}]octasiloxane (G1-16Cl). The compounds $HSiMeCl_2$ (6.7 cm^3, 59.3 mmol) and $H_2[PtCl_6]$ (0.1 mol dm^{-3} in ^{i}PrOH, 10 drops) were added to a solution of G0-8vinyl (1.0 g, 1.58 mmol) in diethyl ether (50 cm^3). The resulting mixture was heated under reflux for 8 h and stirred at 20 °C for 15 h. The solvent was removed *in vacuo* to give 2.40 g (98%) of G1-16Cl as a white solid. ^{1}H NMR ($CDCl_3$): δ_H (ppm) 1.52 (m, 16 H, CH_2), 0.83 (m, 16 H, CH_2), 0.80 (s, 24 H, CH_3). ^{13}C-{^{1}H} NMR ($CDCl_3$): δ_C (ppm) 16.77 (CH_2SiCl_2), 14.53 ($SiCH_3$), 3.41 (O_3SiCH_2).

1,3,5,7,11,13,15-Octakis[2-(divinylmethylsilyl)ethyl]pentacyclo[9.5.1.1^{3,9}.1^{5,15}.1^{7,13}]octasiloxane (G1-16vinyl). Vinylmagnesium bromide (1.0 mol dm^{-3} in THF, 35 cm^3) was added to a solution of G1-16Cl (2.65 g, 1.71 mmol) in THF (40 cm^3). The resulting solution was stirred at room temperature for 17 h. The mixture was slowly added to a cooled (ice bath) aqueous solution of ammonium chloride (1.0 mol dm^{-3} in water, 50 cm^3). The aqueous solution was extracted with petroleum (2 × 80 cm^3). The combined organic layers were washed with a saturated aqueous solution of NaCl (20 cm^3), dried over Na_2SO_4 and concentrated *in vacuo*. The residue was loaded onto a column of silica gel and eluted with petroleum to afford compound G1-16vinyl (2.06 g, 85%). A crystalline compound was obtained by recrystallisation in cold petroleum. Microanalysis found C, 47.1; H, 7.3; $Si_{16}O_{12}C_{56}H_{104}$ requires C, 47.0; H, 7.3%. ^{1}H NMR ($CDCl_3$): δ_H (ppm) 6.13 (dd, $^3J_{HH}$ = 19.5 Hz, $^2J_{HH}$ = 14.2 Hz, 24 H, CH_2=), 6.02 (dd, $^3J_{HH}$ = 14.2 Hz, $^3J_{HH}$ = 4.4 Hz, 24 H, =CH_2), 5.71 (dd, $^3J_{HH}$ = 19.5 Hz, $^3J_{HH}$ = 4.4 Hz, 24 H, SiCH=), 0.62 (m, 16 H, $SiCH_2$), 0.76 (m, $SiCH_2$, 16H), ^{13}C-{^{1}H} NMR ($CDCl_3$): δ_C (ppm) 136.65 (CH=CH_2), 133.14 (CH=CH_2), 5.35 ($O_3SiCH_2CH_2$), 4.27 ($O_3SiCH_2CH_2$), −5.90 ($SiCH_3$).

1,3,5,7,11,13,15-Octakis[2-(diallylmethylsilyl)ethyl]pentacyclo[9.5.1.1^{3,9}.1^{5,15}.1^{7,13}]octasiloxane (G1-16allyl). Allylmagnesium bromide (1.0 mol dm^{-3} in THF, 35 cm^3) was added to a solution of G1-16Cl (2.65 g, 1.71 mmol) in THF (40 cm^3). The resulting solution was stirred at room temperature for 17 h.

The mixture was slowly added to a cooled (ice bath) aqueous solution of ammonium chloride (1.0 mol dm^{-3} in water, 50 cm^3). The aqueous solution was extracted with petroleum (2 × 80 cm^3). The combined organic layers were washed with a saturated aqueous solution of NaCl (20 cm^3), dried over Na_2SO_4 and concentrated *in vacuo*. The residue was loaded onto a column of silica gel and eluted with petroleum to afford 2.5 g (90% yield) of the oily G1-16allyl. Microanalysis found C, 52.3; H, 8.3; $Si_{16}O_{12}C_{72}H_{136}$ requires C, 52.6; H, 8.3%. ^{1}H NMR ($CDCl_3$): δ_H (ppm) 5.77 (m, 16 H, $CH{=}CH_2$), 4.86 (m, 32 H, $CH{=}CH_2$), 1.57 (d, $^3J_{HH}$ = 7.1 Hz, 32 H, $SiCH_2CH{=}CH_2$), 0.59 (m, 32 H, $SiCH_2CH_2Si$), 0.00 ($SiCH_3$). ^{13}C-{^{1}H} NMR ($CDCl_3$): δ_C (ppm) 134.26 ($CH{=}CH_2$), 113.86 ($CH{=}CH_2$), 19.32 ($CH_2CH{=}CH_2$), 4.27 ($O_3SiCH_2CH_2$), 2.75 ($O_3CH_2CH_2$), −5.40 ($SiCH_3$).

1,3,5,7,11,13,15-Octakis[2-(triallylsilyl)ethyl]pentacyclo-[9.5.1.1^{3,9}.1^{5,15}.1^{7,13}]octasiloxane (G1-24allyl). Allylmagnesium bromide (1.0 mol dm^{-3} in THF, 45 cm^3) was added to a solution of G1-24Cl (2.65 g, 1.54 mmol) in THF (40 cm^3). The resulting solution was stirred at room temperature for 17 h. The mixture was slowly added to a cooled (ice bath) aqueous solution of ammonium chloride (1.0 mol dm^{-3} in water, 50 cm^3). The aqueous solution was extracted with petroleum (2 × 80 cm^3). The combined organic layers were washed with a saturated aqueous solution of NaCl (20 cm^3), dried over Na_2SO_4 and concentrated *in vacuo*. The residue was loaded onto a column of silica gel and eluted with petroleum to afford the desired compound G1-24allyl (1.90 g, 81%) as an oil. Microanalysis found C, 56.6; H, 8.8; $Si_{16}O_{12}C_{88}H_{152}$ requires C, 57.1; H, 8.3%. ^{1}H NMR ($CDCl_3$): δ_H (ppm) 5.79 (m, 24 H, $CH{=}CH_2$), 4.90 (m, 48 H, $CH{=}CH_2$), 1.61 (d, $^3J_{HH}$ = 8.0 Hz, 48 H, $SiCH_2CH{=}CH_2$), 0.63 (m, 32 H, $SiCH_2CH_2Si$). ^{13}C-{^{1}H} NMR ($CDCl_3$): δ_C (ppm) 134.28 ($CH{=}CH_2$), 113.83 ($CH{=}CH_2$), 19.06 ($CH_2CH{=}CH_2$), 4.28 ($O_3SiCH_2CH_2$), 2.76 ($O_3CH_2CH_2$).

1,3,5,7,11,13,15-Octakis{2-{tris[2-(dichloromethylsilyl)-propyl]silyl}ethyl}pentacyclo[9.5.1.1^{3,9}.1^{5,15}.1^{7,13}]octasiloxane (G2-propyl-48Cl). The compounds $HSiMeCl_2$ (15 cm^3, 0.15 mol) and $H_2[PtCl_6]$ (0.1 mol dm^{-3} in ^{i}PrOH, 15 drops) were added to a solution of G1-24allyl (2.0 g, 1.08 mmol) in toluene (50 cm^3). The resulting mixture was heated at reflux for 96 h. The solvent was removed *in vacuo* to give G2-propyl-48Cl as a white solid (4.7 g, 95%). ^{1}H NMR ($CDCl_3$): δ_H (ppm) 1.84 (β hydrosilylation, $MeCl_2SiCH(CH_3)CH_2$–) (<5%) 1.55 (m, $CH_2CHMeSiCl_2$, $CH_2CH_2SiCl_2$), 1.20 (m, 48 H, CH_2CH_2-$SiCl_2$), 0.78 (s, 72 H, $SiCH_3$), 0.76–0.55 (m, 80 H, $SiCH_2$). ^{13}C-{^{1}H} NMR ($CDCl_3$): δ_C (ppm) 28.36 (27.65), 17.37 (16.64), 14.71, 4.41 (br, $O_3SiCH_2CH_2Si$).

1,3,5,7,11,13,15-Octakis{2-{tris[2-(divinylmethylsilyl)propyl]-silyl}ethyl}pentacyclo[9.5.1.1^{3,9}.1^{5,15}.1^{7,13}]octasiloxane (G2-propyl-48vinyl). Vinylmagnesium bromide (1.0 mol dm^{-3} in THF, 60 cm^3) was added to a solution of G2-propyl-48Cl (4.52 g, 0.98 mmol) in THF (50 cm^3). The resulting solution was stirred at room temperature for 48 h. The mixture was slowly added to a cooled (ice bath) aqueous solution of ammonium chloride (1.0 mol dm^{-3} in water, 50 cm^3). The aqueous solution was extracted with petroleum (2 × 80 cm^3). The combined organic layers were washed with a saturated aqueous solution of NaCl (20 cm^3), dried over Na_2SO_4 and concentrated *in vacuo*. The residue was loaded onto a column of silica gel and eluted with petroleum to afford compound G2-propyl-48vinyl as a colourless oil (3.83 g, 70%). Microanalysis found C, 59.3; H, 10.1; $Si_{40}O_{12}C_{208}H_{392}$ requires C, 59.4; H, 9.3%. ^{1}H NMR ($CDCl_3$): δ_H (ppm) 6.20–5.94 (m, 96 H, $=CH_2$), 5.73 (dd, $^3J_{HH}$ = 19.8 Hz, $^2J_{HH}$ = 4.3 Hz, 48 H, $SiCH{=}CH_2$), 1.80 (br, SiCH), 1.36 (m br, CH_2), 0.78–0.40 (m, $SiCH_2$), 0.12 (br, 72 H, CH_3Si). ^{13}C-{^{1}H} NMR ($CDCl_3$): δ_C (ppm) 137.23 ($CH{=}CH_2$), 132.78 ($CH{=}CH_2$), 18.92, 18.47, 16.76, 4.57 (br, $O_3SiCH_2CH_2$), −5.08 (CH_3Si).

1,3,5,7,11,13,15-Octakis{2-[bis(diethylphosphinoethyl)methylsilyl]ethyl}pentacyclo[9.5.1.1^{3,9}.1^{5,15}.1^{7,13}]octasiloxane (G1-16-ethylPEt$_2$). G1-16vinyl (0.25 g, 0.176 mmol) was added to a dry 20 cm^3 round bottomed Schlenk flask. AIBN (0.0078 g) was added and the flask was charged with cyclohexane (5 cm^3) and diethylphosphine (1.0 g, 11.3 mmol). The flask was sealed and heated to 60 °C for 8 days. The resulting solution was allowed to cool and taken to dryness *in vacuo*. The resulting crude product was a colourless oil (0.497 g, 99% yield for a conversion >96%). MALDI-TOF: *m*/*z* 2923 (M + 3 oxide)$^+$, (M expected 2860) not found, small peak at 2645. ^{31}P-{^{1}H} NMR ($CDCl_3$): δ_P (ppm) −15.2 (br). ^{1}H NMR ($CDCl_3$): δ_H (ppm) 1.44 (m, $^3J_{H-H}$ = 7.7 Hz, 96 H, PCH_2–), 1.15 (dt, $^3J_{H-H}$ = 7.7 Hz, J_{P-H} = 13.5 Hz, 96 H, PCH_2CH_3), 0.66 (br, 64 H, Si–CH_2), 0.10 (s, 24 H, Si–CH_3). ^{13}C-{^{1}H} NMR ($CDCl_3$): δ_C (ppm) 19.45 (d, J_{C-P} = 15.0 Hz, $SiCH_2CH_2P$), 18.66 (d, J_{C-P} = 12.7 Hz, PCH_2CH_3), 9.95 (d, J_{C-P} = 12.7 Hz, PCH_2CH_3), 7.91 (d, J_{C-P} = 6.0 Hz, PCH_2CH_2Si), 5.16 ($SiCH_2CH_2Si$), 4.82 ($SiCH_2CH_2Si$), −5.52 ($SiCH_3$). IR/cm^{-1} (KBr disc): 2956s, 2919s, 2873s, 1455vs, 1409vs (PCH_2), 1260vs ($SiCH_2$), 1120vs ($SiCH_2CH_2Si$), 1040vs (SiOSi), 952s, 800m, 750vs, 707vs.

1,3,5,7,11,13,15-Octakis{2-[tris(diethylphosphinoethyl)silyl]-ethyl}pentacyclo[9.5.1.1^{3,9}.1^{5,15}.1^{7,13}]octasiloxane (G1-24ethyl-PEt$_2$). G1-24vinyl (0.245 g, 0.162 mmol) was added to a dry 20 cm^3 round bottomed Schlenk flask. AIBN (0.0078 g) was added and the flask was charged with cyclohexane (7 cm^3) and diethylphosphine (1.40 g, 15.6 mmol). The flask was sealed and heated to 60 °C for 10 days. The resulting solution was allowed to cool and taken to dryness *in vacuo*. The resulting crude product was a colourless oil (0.573 g, 97% yield for a conversion >96%). MALDI-TOF: *m*/*z* 3676.3 (M expected 3677.4), other peaks at *m*/*z* 3803 (M + matrix), 3582.0 (M − PEt_2), 3497.9 (M − {2 × PEt_2}), 3406.2 (M − {3 × PEt_2}), 3315.7 (M − {4 × PEt_2}). If Na^+ is omitted from the matrix, two peaks are observed at *m*/*z* 3808 (M+ matrix) and 3713 (M − PEt_2 + matrix). Microanalysis found C, 51.7; H, 10.5; $C_{160}H_{368}O_{12}P_{24}Si_{16}$ requires C, 52.3; H, 10.9%. ^{31}P-{^{1}H} NMR ($CDCl_3$): δ_P (ppm) −15.9, −16.0. ^{1}H NMR ($CDCl_3$): δ_H (ppm) 1.34 (m, 122 H, PCH_2–), 1.04 (dt, $^3J_{PH}$ = 14.0 Hz, $^3J_{H-H}$ = 7.7 Hz, 122 H, PCH_2CH_3), 0.66 (br, 80 H, Si–CH_2). ^{13}C-{^{1}H} NMR ($CDCl_3$): δ_C (ppm) 19.21 (d, J_{C-P} = 14.7 Hz, $SiCH_2CH_2P$), 18.66 (d, J_{C-P} = 14.7 Hz, PCH_2CH_3), 9.95 (d, J_{C-P} = 12.1 Hz, PCH_2CH_3), 5.95 (d, J_{C-P} = 6.0 Hz, PCH_2CH_2Si), 4.44 ($SiCH_2$-CH_2Si), 3.07 ($SiCH_2CH_2Si$), −5.52 ($SiCH_3$). IR/cm^{-1} (KBr disc): 2957s, 2919s, 2874s, 1458vs, 1409vs (PCH_2), 1259vs ($SiCH_2$), 1120vs ($SiCH_2CH_2Si$), 1040vs (SiOSi), 952s, 800m, 750vs, 706vs.

1,3,5,7,11,13,15-Octakis{2-[tris(diethylphosphinopropyl)silyl]-ethyl}pentacyclo[9.5.1.1^{3,9}.1^{5,15}.1^{7,13}]octasiloxane (G1-24propyl-PEt$_2$). G1-24allyl (0.30 g, 0.162 mmol) was added to a dry 20 cm^3 round bottomed Schlenk flask. AIBN (0.0078 g) was added and the flask was charged with cyclohexane (7 cm^3) and diethylphosphine (1.40 g, 15.6 mmol). The flask was sealed and heated to 60 °C for 10 days. The resulting solution was allowed to cool and taken to dryness *in vacuo*. The resulting crude product was a colourless oil (0.592 g, 98% yield for a conversion >87%). MALDI-TOF: *m*/*z* 4012 (small) (M expected 4014.2), other major peaks at *m*/*z* 3921 (M −{PEt_2}); 3839 (M − 2 × {PEt_2}); 3789; 3750 (M − 3 × {PEt_2}) (major); 3660 (M − 4 × {PEt_2}); 3632; 3569 (M − 5 × {PEt_2}). ^{31}P-{^{1}H} NMR ($CDCl_3$): δ_P (ppm) −23.6, −23.9, −24.3. ^{1}H NMR ($CDCl_3$): δ_H (ppm) 1.37 (m, 170 H, $CH_2CH_2CH_2$, PCH_2–), 1.04 (dt, $^3J_{PH}$ = 14.6 Hz, $^3J_{H-H}$ = 7.7 Hz, 122 H, PCH_2CH_3), 0.69 (br, 48 H, $SiCH_2$), 0.53 (br, 32 H, $SiCH_2CH_2Si$). ^{13}C-{^{1}H} NMR ($CDCl_3$): δ_C (ppm) 31.10 (br, CH_2), 20.64 (d, $^1J_{C-P}$ = 13.4 Hz, CH_2CH_2P), 18.95 (d, J_{C-P} = 10.7 Hz, PCH_2CH_3), 14.39 (d, $^2J_{C-P}$ = 10.7 Hz, PCH_2CH_2), 9.68 (d, $^1J_{C-P}$ = 12.1 Hz, PCH_2CH_3), 4.58 ($SiCH_2$-CH_2Si), 4.05 ($SiCH_2CH_2Si$).

1,3,5,7,11,13,15-Octakis{2-{tris{3-[bis(diethylphosphinoethyl)-methylsilyl]propyl}silyl}ethyl}pentacyclo[9.5.1.1^{3,9}.1^{5,15}.1^{7,13}]octasiloxane (G2-propyl-48ethylPEt$_2$). G2-propyl-48vinyl (0.22 g, 5.2×10^{-5} mol) was added to a dry 20 cm^3 round bottomed Schlenk flask. AIBN (0.008 g) was added and the flask was charged with cyclohexane (5 cm^3) and diethylphosphine (0.9 g, 0.01 mol). The reaction mixture was heated to 50 °C for 12 days. The resulting solution was allowed to cool and taken to dryness *in vacuo*. The resulting crude product was a colourless oil (0.411 g, 96% yield for a conversion >90%). Microanalysis found C, 54.0; H, 12.2; $C_{400}H_{920}O_{12}P_{48}Si_{40}$ requires C, 56.3; H, 10.9%. ^{31}P-{^{1}H} NMR ($CDCl_3$): δ_P (ppm) −15.8, −16.1. ^{1}H NMR ($CDCl_3$): δ_H (ppm) 1.30 (m, $^3J_{H-H}$ = 7.7 Hz, 96 H, PCH_2–), 1.03 (dt, $^3J_{H-H}$ = 7.7 Hz, J_{P-H} = 13.7 Hz, 96 H, PCH_2CH_3), 0.66 (br, 68 H, Si–CH_2), 0.10 (s, 24 H, Si–CH_3). ^{13}C-{^{1}H} NMR ($CDCl_3$): δ_C (ppm) 19.55 (d, J_{C-P} = 15.0 Hz, CH_2CH_2P), 18.73 (d, J_{C-P} = 12.7 Hz, PCH_2CH_3), 10.08 (d, J_{C-P} = 11.5 Hz, PCH_2CH_3), 8.75 ($CH_2CH_2CH_2$), 6.38 (d, J_{C-P} = 7.0 Hz, CH_2CH_2P), 5.5 (br, $SiCH_2$), 4.90 (br, $SiCH_2$), 1.34, −5.34 9 (br, $SiCH_3$).

1,3,5,7,11,13,15-Octakis{2-[(dicyclohexylphosphinoethyl)-(diethylphosphinoethyl)methylsilyl]ethyl}pentacyclo-[9.5.1.1^{3,9}.1^{5,15}.1^{7,13}]octasiloxane (G1-16ethyl$_{(PCy_2)_{0.32}(PEt_2)_{0.68}}$). G1-16vinyl (0.133 g, 0.0939 mmol) was added to a dry 20 cm^3 round bottomed Schlenk flask. AIBN (0.007 g) was added and the flask was charged with cyclohexane (5 cm^3) and dicyclohexylphosphine (0.446 g, 2.25 mmol). The flask was sealed and heated to 60 °C for 3 days. Diethylphosphine (0.270 g, 3.0 mmol) was then added. The flask was heated to 60 °C for 5 further days. The resulting solution was allowed to cool and the excess phosphine was removed by vacuum distillation (100 °C, 0.1 mmHg). The resulting crude product was a colourless solid (0.360 g, 95% yield for a conversion >98%). ^{31}P-{^{1}H} NMR ($CDCl_3$): δ_P (ppm) 4.8, −14.9. ^{1}H NMR ($CDCl_3$): δ_H (ppm) 1.86 (br, 96 H, CH_2), 1.70–1.20 (br m, CH_3 and CH_2), 1.15 (dt, $^3J_{H-H}$ = 7.7 Hz, J_{P-H} = 13.7 Hz, 30 H, PCH_2CH_3), 0.90–0.55 (br, 64 H, Si–CH_2), 0.20–0.02 (br, 24 H, Si–CH_3). ^{13}C-{^{1}H} NMR ($CDCl_3$): δ_C (ppm) 33.48 (d, J_{C-P} = 13.4 Hz, CH_2P), 30.47 (d, J_{C-P} = 12.1 Hz, CH_2P), 29.38, 27.04, 26.66, 19.50 (d, J_{C-P} = 15.0 Hz, $SiCH_2CH_2P$), 18.66 (d, J_{C-P} = 12.6 Hz, PCH_2CH_3), 9.95 (d, J_{C-P} = 12.5 Hz, PCH_2CH_3), 7.80 (d, J_{C-P} = 6.0 Hz, PCH_2CH_2Si), 5.5–4.8 (br, $SiCH_2CH_2Si$), −5.45 ($SiCH_3$).

1,3,5,7,11,13,15-Octakis{2-[(dicyclohexylphosphinoethyl)-methylsilyl]ethyl}pentacyclo[9.5.1.1^{3,9}.1^{5,15}.1^{7,13}]octasiloxane (G1-16ethylPCy$_2$). G1-16vinyl (0.133 g, 0.0939 mmol) was added to a dry 20 cm^3 round bottomed Schlenk flask. AIBN (0.007 g) was added and the flask was charged with cyclohexane (5 cm^3) and dicyclohexylphosphine (0.446 g, 2.25 mmol). The flask was sealed and heated to 60 °C for 10 days. The resulting solution was allowed to cool and the excess phosphine was removed by vacuum distillation (100 °C, 0.1 mmHg). The resulting crude product was a colourless solid (0.356 g, 98% yield for a conversion >75%). MALDI-TOF: *m*/*z* 3746 (very broad) (*ca.* 12 arms substituted due to poor quality G1-16vinyl), M expected 4591.5. ^{31}P-{^{1}H} NMR ($CDCl_3$): δ_P (ppm) 4.1. ^{1}H NMR ($CDCl_3$): δ_H (ppm) 1.75 (br, 120 H, CH_2), 1.53 (br, 32 H, CH_2), 1.26 (br, 158 H, CH_2 and CH_3), 0.75–0.45 (br, 64 H, Si–CH_2), 0.20–0.02 (br, 24 H, Si–CH_3). ^{13}C-{^{1}H} NMR ($CDCl_3$): δ_C (ppm) 33.45 (d, J_{C-P} = 13.4 Hz, CH_2P), 30.47 (d, J_{C-P} = 12.1 Hz, CH_2P), 29.38, 27.04, 26.66, 4.44 (br, $SiCH_2CH_2Si$), −5.40 (br, $SiCH_3$).

1,3,5,7,11,13,15-Octakis{2-[tris(dicyclohexylphosphinoethyl)-silyl]ethyl}pentacyclo[9.5.1.1^{3,9}.1^{5,15}.1^{7,13}]octasiloxane (G1-24-ethylPCy$_2$). G1-24vinyl (0.245 g, 0.162 mmol) was added to a dry 20 cm^3 round bottomed Schlenk flask. AIBN (0.0078 g) was added and the flask was charged with cyclohexane (7 cm^3) and dicyclohexylphosphine (3.08 g, 15.5 mmol). The flask was sealed and heated to 60 °C for 10 days. The resulting solution was allowed to cool and the excess phosphine was removed by vacuum distillation (100 °C, 0.1 mmHg). The resulting crude product was a colourless solid (0.621 g, 95% yield for a conversion 55%). ^{31}P -{^{1}H} NMR ($CDCl_3$): δ_P (ppm) 4.1. ^{1}H NMR ($CDCl_3$): δ_H (ppm) 6.10 (m, 22 H, =CH_2), 5.45 (m, 11 H, SiCH=), 1.70 (br, H, CH_2), 1.52 (br, CH_2), 1.26 (br, CH_2 and CH_3), 0.75–0.45 (br, 58 H, Si–CH_2). ^{13}C-{^{1}H} NMR ($CDCl_3$): δ_C (ppm) 33.45 (d, J_{C-P} = 13.4 Hz, CH_2P), 30.47 (d, J_{C-P} = 12.1 Hz, CH_2P), 29.38, 27.04, 26.66, 4.44 (br, $SiCH_2CH_2Si$).

1,3,5,7,11,13,15-Octakis{2-[tris(dimethylphosphinomethyl)-silyl]ethyl}pentacyclo[9.5.1.1^{3,9}.1^{5,15}.1^{7,13}]octasiloxane (G1-24-methylPMe$_2$). $LiCH_2PMe_2$[24] (0.272 g, 3.32 mmol) was dissolved at −78 °C in a flask containing THF (20 cm^3). The solution was transferred *via* cannula to a Schlenk flask containing G1-24Cl (0.218 g, 0.127 mmol) in THF (10 cm^3). The mixture was stirred for 60 hours. The solvent was removed *in vacuo*. Dichloromethane was added (40 cm^3). After LiCl had settled, the liquid was transferred *via* cannula to another flask and taken to dryness *in vacuo*. The solid was washed twice with hexane. The resulting product was a white solid (0.329 g, 97%). MALDI-TOF *m*/*z* 2677 (very broad) (*m*/*z* expected 2667.5). Other peak at *m*/*z* 2603 (M − {CH_2PMe_2}). Microanalysis found C, 32.7; H, 7.5; $C_{88}H_{24}O_{24}P_{16}Si_{16}$ requires C, 36.9; H, 8.5%. ^{31}P-{^{1}H} NMR (CD_2Cl_2): δ_P (ppm) −54.5. ^{1}H NMR (CD_2Cl_2): δ_H (ppm) 1.0 (br, 144 H, $P(CH_3)_2$), 0.78 (br, 48 H, –$CH_2P(CH_3)_2$), 0.66 (m, 32 H,Si–CH_2CH_2–Si). ^{13}C-{^{1}H} NMR (CD_2Cl_2): δ_C (ppm) 18.5 (br, P–CH_3), 13.8 (br, P–CH_2), 5.0 (br, $SiCH_2CH_2Si$). IR/cm^{-1} (KBr disc): 2951m, 2892m, 1428m ($SiCH_2P$), 1417m (PCH_3), 1292m (PCH_3), 1274m–1262m ($SiCH_2P$), 1143vs ($SiCH_2$-CH_2Si), 1097vs (SiOSi), 938m (PCH_3), 895m (PCH_3), 761s (PCH_3), 707m, 665m.

1,3,5,7,11,13,15-Octakis{2-{tris{2-[tris(dimethylphosphino-methyl)silyl]ethyl}silyl}ethyl}pentacyclo[9.5.1.1^{3,9}.1^{5,15}.1^{7,13}]octasiloxane (G2-ethyl-72methylPMe$_2$). $LiCH_2P(Me)_2$ (0.202 g, 2.47 mmol) was dissolved at −78 °C in a flask containing THF (20 cm^3). The solution (room temperature) was transferred *via* cannula to a Schlenk flask containing POSS G2-ethyl-72Cl (0.25 g, 0.0052 mmol) in THF (10 cm^3). The mixture was stirred for 60 h (a precipitate appeared). The solid (precipitate) was collected by filtration and washed twice with THF. The resulting product was a white solid (80%) with poor solubility. IR/cm^{-1} (KBr disc): 2952m, 2893m, 1416s ($SiCH_2P$ and PCH_3), 1289w (PCH_3), 1260m ($SiCH_2P$), 1140vs ($SiCH_2CH_2Si$), 1097vs (SiOSi), 1027m, 946w (PCH_3), 894m (PCH_3), 758s −743s (PCH_3), 712s, 465m.

Di-n-hexylmethylphosphine (ref. 24). Magnesium turnings (3.5 g, 0.144 mol) were charged into a three neck Schlenk flask fitted with a reflux condenser and a gas bubbler. Diethyl ether (250 cm^3) was added, followed dropwise by 1-bromohexane (17 cm^3, 0.121 mol) causing an exothermic reaction (reflux). After completion of the addition, the grey reaction mixture was stirred at room temperature for 1 hour, and then the unreacted magnesium was allowed to settle. The solution was filtered to give a Grignard solution of $C_6H_{13}MgBr$. Dichloromethylphosphine (5 cm^3, 55.7 mmol) was added to a Schlenk flask containing diethyl ether. The flask was then cooled (ice bath) and $C_6H_{13}MgBr$ was added slowly (1 hour) to the well-stirred solution. A white precipitate of magnesium halides was formed. The solution mixture was stirred overnight. The liquid was filtered into another flask. The precipitate was twice washed with petroleum (20 cm^3) and the washings added to the second flask. The liquid was distilled under vacuum (10^{-2} mmHg, 120 °C) to give a colourless liquid (3.3 g, 26%). ^{31}P-{^{1}H} NMR ($CDCl_3$): δ_P (ppm) −41.4. ^{1}H NMR ($CDCl_3$): δ_H (ppm) 1.46–1.20 (m, 26 H, hexyl CH_2), 0.95 (d, $^2J_{PH}$ = 1.8 Hz, 3 H, PCH_3), 0.74 (m, 4 H, CH_2P). ^{13}C-{^{1}H} NMR ($CDCl_3$): δ_C (ppm) 31.67, 31.15 (d,

J_{PC} = 11.6 Hz), 29.87 (d, J_{PC} = 9.7 Hz), 25.79 (d, J_{PC} = 12.6 Hz), 22.59, 14.08, 11.65 (d, J_{PC} = 14.5 Hz, PCH_3).

Dihexylphosphinomethyllithium. $PMe(C_6H_{13})_2$ (3.23 g, 14.9 mmol) was dissolved in petroleum (40 cm^3). Bu^tLi (8.8 cm^3, 14.9 mmol) (1.7 M in pentane) was added at room temperature and the reaction mixture was stirred for 5 days. The solvent was removed *in vacuo* to give a pale yellow heavy liquid. The conversion was only 78% (determined by ^{31}P NMR). ^{31}P-{^1H} NMR (C_6D_6): δ_P (ppm) −24.9 ($LiCH_2P$), −43.2 (CH_3P). ^1H NMR (C_6D_6): δ_H (ppm) 1.8–1.10 (m, 26 H, CH_2), 0.95 (m, PCH_3), 0.82 (br, 6 H, CH_2CH_3), −0.35 (br, PCH_2Li).

1,3,5,7,11,13,15-Octakis{2-[tris(dihexylphosphinomethyl)-silyl]ethyl}pentacyclo[9.5.1.1^{3,9}.1^{5,15}.1^{7,13}]octasiloxane (G1-24-methylPHex$_2$). $LiCH_2P(C_6H_{13})_2$ (0.3236 g, 1.09 mmol) was dissolved at −78 °C in a Schlenk flask containing THF (20 cm^3). The solution (room temperature) was transferred *via* cannula to a Schlenk flask containing G1-24Cl (0.0778 g, 0.0453 mmol) in THF (10 cm^3). The mixture was stirred for 60 h. The solvent was removed *in vacuo*. Dichloromethane was added (20 cm^3). After settling overnight, the liquid was transferred *via* cannula and taken to dryness *in vacuo*. The product was washed with diethyl ether (3 × 5 cm^3) and dried *in vacuo*. The resulting product was a white solid (yield 40%). ^{31}P-{^1H} NMR ($CDCl_3$): δ_P (ppm) −36.3. ^1H NMR ($CDCl_3$): δ_H (ppm) 1.64–1.20 (m, 384 H, hexyl CH_2), 0.95 (br, 115 H, CH_3), 0.74 (br, $SiCH_2P$), 0.7–0.45 (m, 32 H, Si–CH_2CH_2–Si). ^{13}C-{^1H} NMR ($CDCl_3$): δ_C (ppm) 31.7, 31.2 (d, J_{PC} = 11.5 Hz), 29.8 (d, J_{PC} = 10 Hz), 25.79 (d, J_{PC} = 12.3 Hz), 22.6, 14.1, 10.3 (d, J_{PC} = 14.5 Hz, PCH_2Si).

Catalytic reactions

The functionalised POSS dendrimer, the rhodium source ([$Rh_2(O_2CMe)_4$] or [$Rh(CO)_2(acac)$]) (amounts are shown in the Tables) and ethanol or THF (4 cm^3) were charged into a Schlenk tube and stirred until complexation of the rhodium with the phosphine species had occurred. The catalytic solution and substrate were then injected into a degassed autoclave and pressurised/heated to the desired pressure and temperature. When using the CATS rig the catalytic solution was heated under CO/H_2 (6 bar) for 1 h. The substrate was injected and the pressure of CO/H_2 was increased to 40 bar, 120 °C. The pressure was kept constant through a mass flow controller and fed from a ballast vessel (pressure drop in ballast vessel monitored every 5 s). After reaction, the products were analysed by GC-MS.

Crystallography

X-Ray diffraction studies on crystals of G1-16vinyl were performed at 293 K using a Bruker SMART diffractometer with graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å). The structure was solved by direct methods. The carbon atoms were refined isotropically, with the geometries of the terminal Si-vinyl and methyl carbon atoms having been refined in modelled positions with fixed isotropic thermal positions. The inner ethyl carbon atoms were not modelled, but allowed to refine isotropically. All other non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were refined in idealised positions. Structural refinements were by the full-matrix least-squares method on F^2 using the program SHELXTL[30] with absorption corrected data.[30]

Crystal data and structure refinement. G1-16vinyl. $C_{56}H_{104}O_{12}Si_{16}$, colourless crystal 0.12 × 0.1 × 0.1 mm, M = 1418.8, space group $P2_1/c$, a = 13.6425(7), b = 13.8802(6), c = 23.2237(8) Å, β = 96.445(3)°, U = 4369.9(3) $Å^3$, Z = 2 (the molecule was located about a centre of symmetry), μ = 0.277 mm^{-1} (λ = 0.71073 Å), D_c = 1.078 Mg m^{-3}, $F(000)$ = 1520, 18587 measured reflections (minimum and maximum transmission factors 0.448671 and 1.0000), 6252 independent [R_{int} = 0.1085] and 1940 observed data ($I > 2\sigma(I)$) to give R = 0.1343, R_w = 0.3871 with goodness-of-fit on F^2 0.951.

CCDC reference number 177248.

See http://www.rsc.org/suppdata/dt/b2/b200303a/ for crystallographic data in CIF or other electronic format.

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