

Increased selectivity in hydroformylation reactions using dendrimer based catalysts; a positive dendrimer effect

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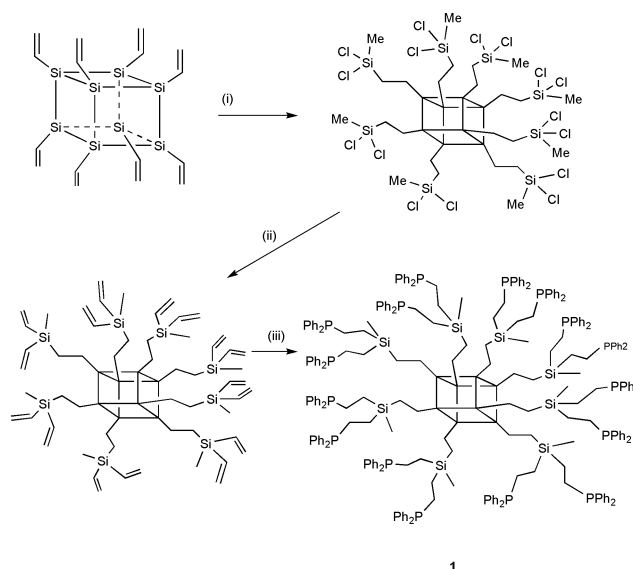
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Dendrimers based on polyhedral oligomeric silsesquioxanes (POSS) cores with 16 PPh₂ arms give much higher linear selectivities (14:1) than their small molecule analogues (3–4:1) in the hydroformylation of oct-1-ene.

Dendrimers are globular molecules in which the groups on the periphery are all the same. They have been used for a variety of applications, but interesting opportunities are offered if the dendrimer is used as a ligand in homogeneous catalysis. Most research in this area is aimed at using the dendrimer to overcome the main problem of homogeneous catalysts, that the reaction products can be hard to separate from the catalyst and the solvent. Because of their persistent shape and size (1–10 nm), there is interest in attempting to remove the catalyst by nanofiltration through a suitable membrane. Filtration of this kind has been demonstrated.^{1–3} Another possible advantage of dendrimers is that crowding in the periphery might lead to constrained geometries in the metal binding, which might affect the activity or selectivity of the catalyst. In many cases, reaction rates are slowed in the presence of a dendrimer, but there are also examples of reactions being totally or partially inhibited because the dendrimer is present. In one case it is believed that an unpaired electron is passed from metal to metal on the dendrimer, thus inhibiting its use in the Kharasch reaction.⁴

Examples of enhanced reactivity in C–C coupling reactions have been reported^{3,5} and very recently it has been shown that epoxidation reactions can be accelerated if the catalyst is bound to the dendrimer and this is thought to be because the oxidising peroxide binds to one metal, whilst the substrate is activated by another. Having the two metals held in close proximity increases the reaction rate.⁶ To our knowledge, examples of positive dendrimer effects on the selectivity of catalytic reactions have not been reported, but we now report such an effect in the hydroformylation of oct-1-ene. Hydroformylation using metals bound to dendrimers with phosphines on the periphery have been reported,^{7,8} but generally the selectivity to the desired linear product is similar to that using model small molecule ligands, although we noted a slightly enhanced linear selectivity using dendrimer-bound trialkylphosphines.⁸

Dendrimers based on polyhedral oligomeric silsesquioxane (POSS) cores were prepared as shown in Scheme 1 such that they had up to 16 PPh₂ groups on the periphery (**1**). Attempts to prepare the dendrimer with 24 PPh₂ arms leads to incomplete conversion to phosphines, presumably because of excessive steric crowding.⁸ Analysis of **1** by NMR and by MALDI-TOF mass spectrometry shows that they have 14, 15 or 16 PPh₂ groups per dendrimer, with the average number being *ca.* 15. Within one arm of the dendrimer, the P atoms are separated by five atoms. Simple diphosphines separated by five or six atoms are only expected to favour bidentate binding when constrained, as in the case of Xantphos⁹ and bis(diphenylphosphino-methyl)biphenyl (BISBI)¹⁰ ligands. For such constrained ligands, the linear:branched ratios can be very high. Indeed, using the unconstrained small molecules, **2** and **3**, 1:b ratios are only of the order of 3–4 (Table 1 and Fig. 1). In contrast, under



Scheme 1 Synthesis of 16-arm dendrimer phosphine **1**. Reagents and conditions: i, MeSiHCl₂, H₂PtCl₆ (catalyst); ii, (vinyl)MgBr; iii, Ph₂PH, azodi(isobutryl)nitride. **1** has an average of 15 PPh₂P groups, **5** has an average of 12 PPh₂ groups. In the POSS core, each edge of the cube represents Si–O–Si.

exactly the same conditions, catalysts prepared *in situ* from **1** and [Rh(acac)(CO)₂] (acacH = pentane-2,4-dione) give 1:b ratios of up to 14. A ratio this high would be very unusual for an unconstrained ligand of this size and certainly shows that a positive dendrimer effect is operating. The reaction rate and 1:b ratio increase with increasing temperature or decreasing gas pressure (Table 1) but are only slightly affected by the Rh:P ratio (3.6–10.8) at a given Rh concentration. The generally high 1:b ratios suggest that strong bidentate coordination occurs or that the high local concentration of P atoms on the surface of the dendrimer increases the concentration of complexes containing three P donors. Further confirmation that the metal is strongly bound to the dendrimer comes from ³¹P NMR studies of solutions prepared from [Rh(acac)(CO)₂] and **1** (1:3) under CO and H₂. Two resonances are observed at room temperature, one (δ 37) for P bound to Rh and the other (δ – 9.5) from the free P atoms (**1** resonates at δ – 9.5). Both resonances are very broad (width at half maximum = 470 and 88 Hz respectively), possibly because of different binding environments for the rhodium since the spectrum is the same in different solvents (CH₂Cl₂, tetrahydrofuran) and the linewidth at half maximum of the signal from the unbound P atoms only changes slightly

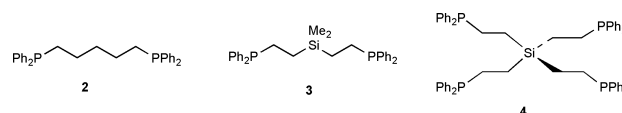
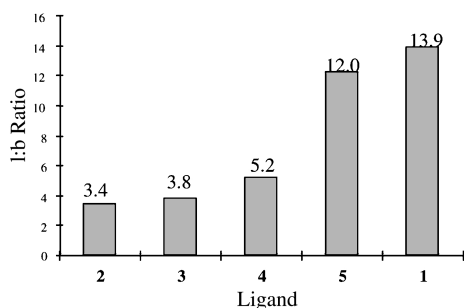


Table 1 Results of hydroformylation reactions using various ligands^a

Ligand	<i>T</i> /°C	<i>p</i> /bar	<i>k_b</i> /10 ⁻³ s ⁻¹	Conversion (%)	l:b	Nonanal (%)
1	120	10	1.2	>99.9	13.9	86
5^c	120	10	1.1	>99.9	12.0	86
5^{c,d}	100	10	0.42	>99.9	10.8	86
5^{c,e}	80	10	0.08	>99.9	8.8	84
5^{c,f}	100	20	0.33	>99.9	7.5	85
5^g	120	10	1.5	>99.9	12.2	85
5^h	120	10	0.95	>99.9	11.9	84
2	120	10	3.6	>99.9	3.4	70
3	120	10	3.0	>99.9	3.8	73
4	120	10	2.1	>99.9	5.2	77

^a [Rh(acac)(CO)₂] (2.0 × 10⁻⁵ mol); P:Rh = 6:1, toluene (4 cm³), heated under CO/H₂ (6 bar) for 1 h. Oct-1-ene (8.3 × 10⁻³ mol) injected and pressure increased. Pressure kept constant through mass flow controller and fed from a ballast vessel. Pressure drop in ballast vessel monitored every 5 s. Total reaction time, 2 h. ^b First-order rate constant measured from gas uptake plots at constant pressure. ^c P:Rh = 5.4:1. ^d *t* = 4 h. ^e *t* = 19 h. ^f *t* = 6 h. ^g P:Rh = 10.8. ^h P:Rh = 3.6.

**Fig. 1** 1:b Ratio of product C₉ aldehydes at 120 °C and 10 bar. P:Rh = 6:1, except for **5** (P:Rh = 5.4:1).

between -40 (63 Hz) and +60 °C (150 Hz). This shows that the rhodium is not migrating rapidly around the surface of the dendrimer, nor dissociating on the NMR timescale. The resonance from the Rh-bound phosphines appears as two broad overlapping doublets (δ 37 and 36) at -40 °C, but as a single broad doublet (δ 37 $J_{P-H} \approx 130$ Hz) at +60 °C, suggesting fluxionality within the bound complex. A broad hydride signal is observed at δ -10.5 (width at half maximum = 80 Hz) in the ¹H NMR spectrum at room temperature.

In order to try to understand the higher 1:b ratios observed with the dendrimer bound catalysts, we have carried out some molecular modelling of the dendrimer using the Discovery programme contained in the Insight(II) Molecular Modelling Suite of Molecular Simulations Inc.¹¹ This shows that within an arm, the P atoms are separated by 4–7 Å, whilst between arms there are always some distances in the 5–10 Å region. Rh–P distances are of the order of 2.5 Å, so very little disruption of the ground state structure of the dendrimer is required to facilitate bidentate binding. Presumably the orientation of the PPh₂ groups relative to one another is determined by steric repulsions on the surface of the dendrimer whilst models of the small molecules show that the lowest energy structures have the phosphine groups far away from one another. If this is the case, one might expect that the compound prepared from addition of Ph₂PH across the double bonds of tetravinylsilane **4**, for which the X-ray crystal structure shows that the P atoms are 6.94 and 8.33 Å apart,¹² might show intermediate behaviour between **1** and **3**. Indeed this is the case, with the 1:b ratio being 6 (Table 1 and Fig. 1). Reducing the PPh₂ loading on the dendrimer to an average value of 12 PPh₂ groups (**5**)[†] gives a slightly lower 1:b ratio (12.0, Table 1, Fig. 1) than the more completely substituted dendrimer, again suggesting that steric crowding on the dendrimer periphery is important.

It seems that the chain length between the two P atoms is also important since extensive studies on a compound derived from

tetravinylsilane containing 16 Ph₂P arms, but with only one CH₂ spacer between Si and P, *i.e.* with a potential ring size of six atoms for bidentate bonding, shows no special enhancement over the small molecule analogue.⁷

We conclude that the dendrimers synthesised here have sufficient steric crowding to make eight-membered ring bidentate coordination favourable and that these rings enhance the linear selectivity in hydroformylation reactions. Whether the binding in five-coordinate intermediates is equatorial–equatorial, which has been shown to give enhanced selectivity,^{9,10} whether the P atoms are mutually *trans* throughout the reaction, which may also give enhanced selectivity, or whether the reason for the enhanced selectivity is the locally high Ph₂P concentration is not clear at present, although the low-temperature ³¹P NMR spectrum of the rhodium complex under CO/H₂ suggests that the P atoms bound to rhodium are not all equivalent.

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Notes and references

[†] This dendrimer was prepared for **1**, but the reaction was not taken to completion. It was shown to have an average of 12 PPh₂ groups by MALDI-TOF mass spectrometry.

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