Catalysts based on palladium dendrimers†

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This report reviews the role of palladium dendrimers in catalysis as (a) soluble macromolecules for the support of catalysts, that are separable by nanofiltration techniques; (b) ligand-modifiers that can create specific metal nanoenvironments and tune the solubility of the catalyst; (c) spacers for the support of molecular catalysts that can proportionate a more homogeneous-like environment to the supported catalytic sites; and (d) precursors for the synthesis of mono- and bimetallic nanoparticles of controlled size and narrow size distribution. Some examples of catalysis with related metal systems, such as star-shaped molecules or hyperbranched polymers, are also given.

1 Introduction

Dendrimers[1] functionalised with transition metals[2,3] have found many applications.[4] The use of these dendrimers in catalysis has been the object of many reviews either of general scope,[5] or focused on particular issues such as catalyst recovery,[6] immobilisation,[7] dendrimer effects,[8] catalysis inside dendrimers,[9] phosphorus-containing dendrimers,[10] chiral catalysts,[11] or dendrimer-encapsulated nanoparticles,[12–14] amongst others.[15,16] Moreover, a recent issue of *Topics in Organometallic Chemistry* has been dedicated to this field.[17] Palladium compounds have played an important role in the field of organic synthesis over the past few decades due to the variety of transformations they are able to catalyse, the possibilities offered for carbon–carbon bond formation, and their tolerance of many functional groups, all of which mean that they can provide mild and selective methods for the production of valuable chemicals from simple precursors.[18] The present review summarises the advances in palladium-catalysed reactions using dendrimer-based catalysts. Sections 2 and 3 of this review are dedicated, respectively, to peripheral and core palladium dendrimers used as nanosized macromolecular catalysts with well-defined active sites, generally in homogeneous conditions. Section 4 deals with the modification of supports (silica or polymers) with dendritic wedges (*dendrons*), which, in turn, serve as supports for metal catalysts, and Section 5 describes the use of dendrimers as templates for the preparation and stabilisation of metal nanoparticles. Several of the properties that make dendrimers so interesting for catalysis are also present in related systems such as star-shaped metal molecules or hyperbranched polymers, and therefore several relevant studies using such systems will also be discussed in this review.

Dendrimers are attractive in catalysis because they combine a unique set of characteristics that are not present together in

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Ernesto de Jesús was born in 1959 in La Seu d'Urgell (Catalonia), Spain. He received his BSc degree in Chemistry from the University of Zaragoza in 1981 and his PhD in Organometallic Chemistry from the University of Alcalá in 1987 under guidance of Pascual Royo. Then, he joined as a postdoctoral fellow the group of Pierre Braunstein in the CNRS-Université Louis Pasteur in Strasbourg and in 1990 he took up a position as Profesor Titular of Inorganic Chemistry in the University of Alcalá. Since 1998, his research is focused in the synthesis, structure and applications in catalysis of transition-metal dendrimers and more recently in aqueous-phase metal-catalysed reactions for C–C bond formation.

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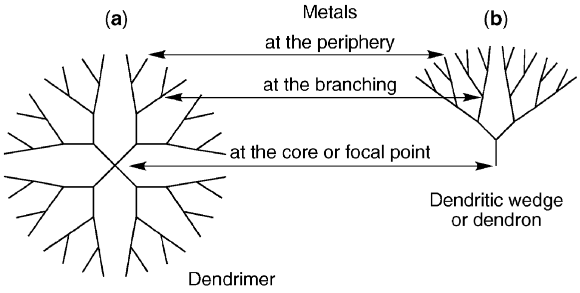

Fig. 1 Possible locations for metal centres in the dendrimer structure.

any other homogeneous or heterogeneous catalysts, such as (a) a size that enables catalyst separation and recovery, particularly by nanofiltration with membrane techniques; (b) a well-defined structure and monodisperse nature which retains the advantage of homogeneous catalysts in terms of easy tunability and rationalisation of properties, controlled metal environment and good suitability for study; (c) metal sites incorporated in nanoenvironments that can be tailored to obtain unique activities, selectivity or solubility properties; (d) a very high local catalyst concentration in peripheral systems, which makes cooperative effects possible. Those special features imparted by the dendrimer to the catalytic centres and not achievable otherwise are referred to in the literature as "dendritic effects". The exact properties of a metal dendrimer depend, in the first instance, on the location of the metallic centres in the dendritic structure (Fig. 1). Dendrimers used in homogeneous catalysis usually have the metal centres located at the periphery or at the core or focal point of the dendritic skeleton. Supported composites, such as those described in Section 4, consist of peripherally modified dendrons, whereas the encapsulation of metals within the branching framework is employed for the synthesis of precursors of dendrimer-encapsulated nanoparticles.

When the groups of van Leeuwen and van Koten jointly published their pioneering work on dendrimer-bound metal catalysts in 1994, they noted that such systems have the appropriate shape and size to be separated by nanofiltration techniques whilst also retaining the characteristics of the homogeneous systems.[19] As long as the metal centres are directly available for the substrate in peripherally modified dendrimers, as they are in mononuclear homogeneous catalysts, then comparable activities and selectivities are expected for both systems, in contrast to the behaviour generally associated with catalyst immobilization onto solid supports. However, the dendrimer can be give rise to specific catalyst performances. Thus, dendritic effects (positive or negative) on activities, stabilities, or selectivities can arise from phenomena such as cooperativity between metal groups at the macromolecule periphery or steric isolation of catalyst encapsulated into the dendritic core. In the absence of other effects, the steric crowding in dendrimers causes a general decrease in the activities of higher generation dendrimers.

Juan C. Flores was born in Talavera de la Reina (Toledo), Spain, in 1964. He graduated in Chemistry in 1988, and completed his PhD in Organometallic Chemistry at the University of Alcalá (1989–1992) under the supervision of Profs. Pascual Royo and Tomás Cuenca. After a two years postdoctoral period with Prof. Marvin D. Rausch at the University of Massachusetts (USA), working in a joint research program with Prof. James C. W. Chien, he returned to the University of Alcalá as a Senior Research Fellow (1995–1997). In 1998 he was appointed Profesor Titular of Inorganic Chemistry, and since then he has studied, together Prof. Ernesto de Jesús, the synthesis, structure, and catalytic applications of transition metal dendrimers.

The scarce application of palladium catalysts in industrial processes is primarily due to their expense and the high metal loadings required for many reactions. Pharmaceuticals are products with a high added value and therefore the use of Pd catalysts for their production is more viable. However, even though the toxicity of palladium has posed no problems so far, removal of catalyst residues is of vital importance in these products. Palladium catalysts are generally not very stable and the formation of metal is often observed. Therefore, during this review, special focus is placed on the activity, stability, separation and recyclability of dendritic and non-dendritic catalysts.

Standard acronyms (Fig. 2) and simplified formulae are used throughout the text and tables for the description of dendrimers.‡,§ Polyaminoamide (PAMAM),[20,21] poly(propylene imine) (PPI),[22] carbosilane (CS),[23] phosphorus

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‡ *Abbreviated nomenclature of dendrimers.* The schematic names and formulas describing dendritic catalysts, used mainly in tables, are based on the nomenclature and, in particular, the simplified names proposed by Friedhofen and Vögtle.[169] In this nomenclature, the name of a dendritic molecule is built as follows:

$$\text{core} : \{\text{ branching units}\}^{\text{generation}}_{\text{repetions}} : \text{endgroups}_{\text{repetitions}}$$

Encapsulated molecules, ions or metal clusters are added to the dendrimer description separated by the symbol $\subset$. For clarity, we have chosen to omit the number of repetitions of the branching units at each generation, and represent the branching units by the acronyms shown in Fig. 2 for common dendritic structures. The core unit is also omitted in the case of some "standardised" nuclei, such as those shown in the same scheme for PAMAM, PPI or carbosilane dendrimers. End-groups will be explicitly written but the formula will be abbreviated for the PAMAM and PPI end-groups shown in Fig. 2. For instance, all the following simplified names will describe the NH_2-ended dendrimer **a** with a decreasing level of detail: 1,4-diaminobutane:PAMAM^{G3}:$(CH_2CH_2C(O)NHCH_2CH_2NH_2)_{64}$, PAMAM^{G3}:$(CH_2CH_2C(O)NHCH_2CH_2NH_2)_{64}$ or PAMAM^{G3}:$(NH_2)_{64}$. As diverse chain lengths and ramifications are usual in carbosilane dendrimers, the acronym CS will be followed by the number of carbon atoms per branch (C2 or C3) or the ramification at each branching unit (*e.g.* CS–C2 × 3) in the case of deviations from the structure represented in Fig. 2.

§ *Other abbreviations used throughout this work*: BARF = $[B(C_6H_3\text{-}3,5\text{-}(CF_3)_2)_4]^-$; BSA = *N*,*O*-bis(trimethylsilyl)acetamide; dba = dibenzylideneacetone; dppf = [bis(diphenylphosphanyl)ferrocene]; dppb = 1,4-bis(diphenylphosphanyl)butane; NMP = *N*-methylpyrrolidone; py = pyridine; TFA = trifluoroacetate; *p*-TsOH = *para*-toluenesulfonic acid.

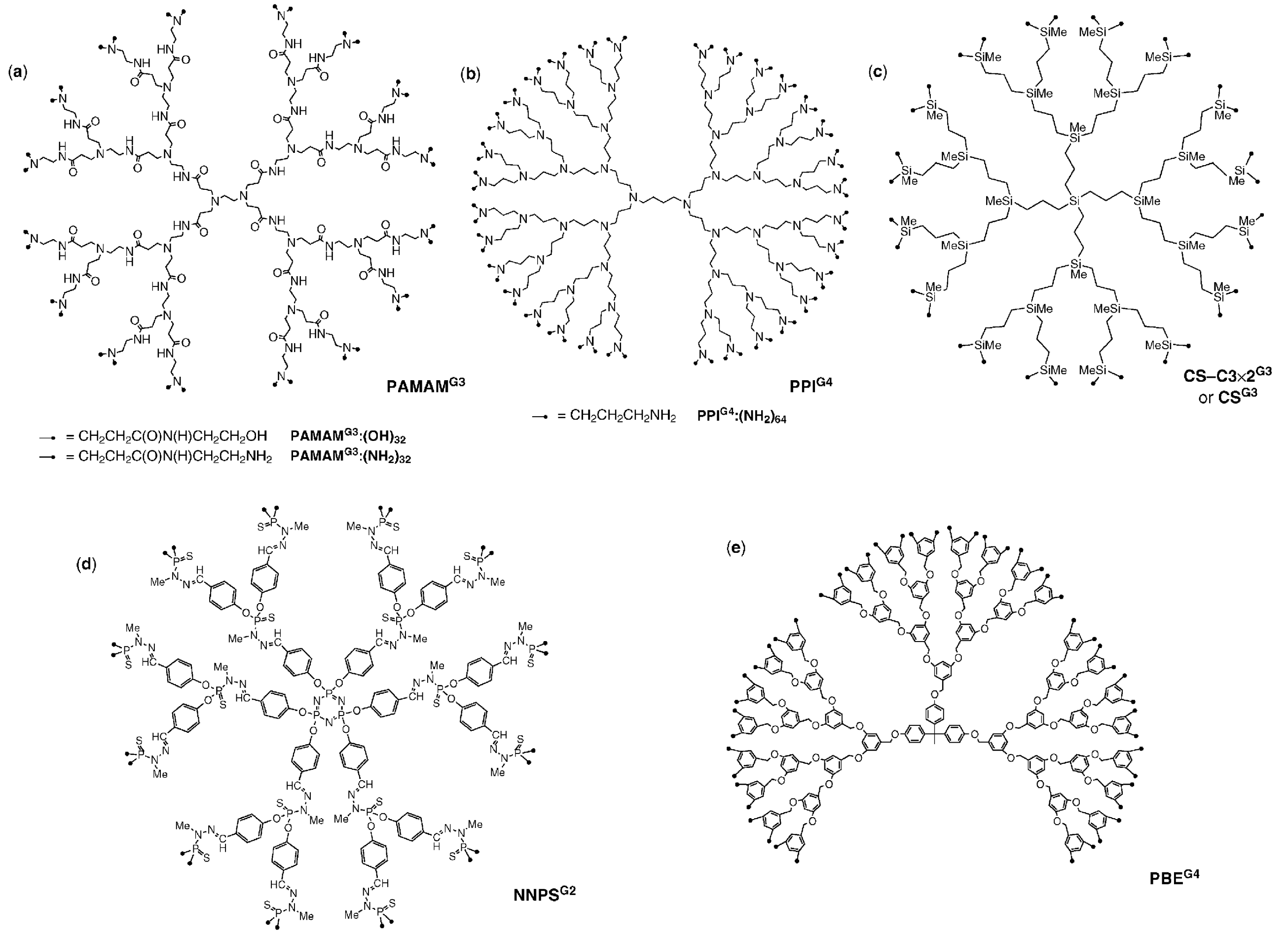


Fig. 2 Types of dendritic structures most commonly used in Pd catalysis, accompanied by the acronyms utilised in this paper: (a) polyaminoamide (PAMAM); (b) poly(propylene imine) (PPI); (c) a carbosilane dendrimer (CS); (d) a Majoral-type phosphorus dendrimer (NNPS); (e) a Fréchet-type poly(benzyl ether) dendrimer (PBE).

(NNPS),[3,24] or poly(benzyl ether) (PBE)[25] are the structures most commonly found in palladium-containing dendrimers.

2 Peripherally modified metal dendrimers

Periphery-modified dendrimers have multiple catalytic sites located at their surface that are directly available to the substrates. This enables reaction rates similar to those of their monomeric counterparts. It is expected that dendritic effects arise mainly from the elevated density of catalytic groups at the surface. Catalysed reactions proceeding by a bimetallic mechanism can benefit from the proximity of the metal centres. However, the effect may be detrimental in the case of availability of bimetallic deactivation pathways.

The first dendritic metal catalyst was reported in 1994 by DuBois and co-workers, who used palladium complexes co-ordinated tridentately to phosphorus dendrimers to catalyse the electrochemical reduction of CO_2 to CO (Fig. 3).[26] The rates and selectivities (CO *vs.* H_2) were qualitatively similar to those obtained with monometallic [Pd(triphosphane)(CH_3CN)]$(BF_4)_2$ analogues to which they were compared. However, two important concepts were recognised: (a) the metal sites in dendrimer **a** are more closely approximate to typical homogeneous catalysts because of the variety of co-ordination modes available for the five Pd atoms in dendrimer **b**; (b) the activity might increase if the palladium sites were sufficiently well separated in the dendritic catalyst to prevent the suggested formation of Pd^I species with Pd–Pd bonds. Since then an increasing number of palladium catalysts have been immobilised at the surface of dendrimers through covalent links between the terminal functionalities of the dendrimer and the metal complex. This covalent approach has been complemented in the last few years with a number of examples involving non-covalent interactions between the dendrimer and an anchoring ligand. Non-covalent metal-dendrimer

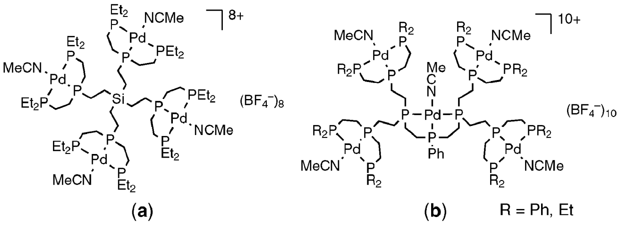


Fig. 3 Palladium catalysts described by DuBois for the electrochemical reduction of CO_2 to CO.[26]

Table 1 Reactions catalysed by peripherally modified palladium dendrimers (Part I)

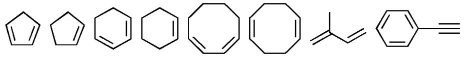
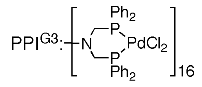
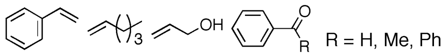
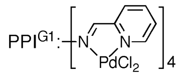
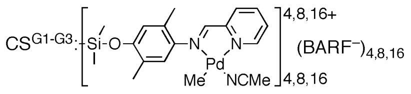
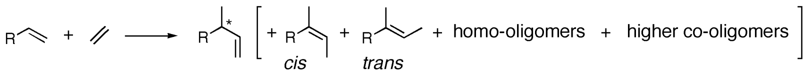
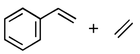
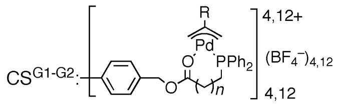
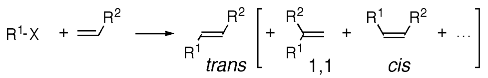
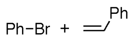
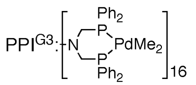
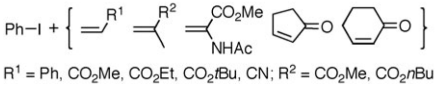
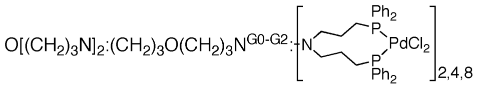
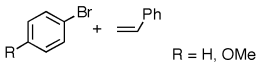
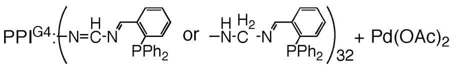
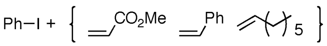
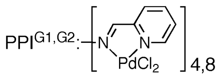
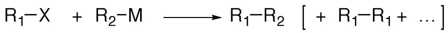
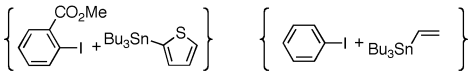
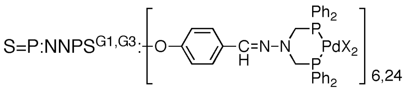
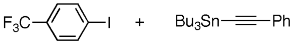
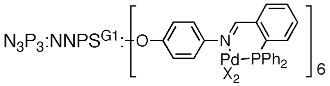
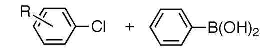
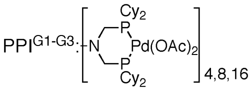
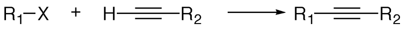
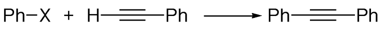
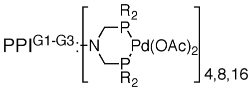
Entry	Substrates or reaction	Typical conditions	Dendritic catalysts
Hydrogenation of alkenes			
1[28]		0.8 mol% Pd, 1 atm H_2, 25 °C, EtOH	
2[29]		0.3 mol% Pd, 1 atm H_2, 30 °C, EtOH	MeSi:CS^{G2}:$(OSiMe_2(CH_2)_3NH_2)_6$ + 6 $PdCl_2{\cdot}2H_2O$
Polymerisation and copolymerisation of α-olefins			
3[31]	Polymerisation of ethylene	3 atm ethylene, MAO/Pd = 500–1500, 25 °C, toluene	
4[33]	Copolymerisation of *tert*-butylstyrene and carbon monoxide	1 atm CO, r.t., CH_2Cl_2 or neat	
Hydrovinylation			
5[35]		Styrene/Pd = 500–1000, 30 bar ethylene, r. t., CH_2Cl_2	
6[36] 7[37]		Styrene/Pd = 500–1500, 15 bar ethylene, 15–25 °C, CH_2Cl_2	CS-C2^{G1,G3}:$\{[SiMe_2(CH_2PPh_2)Pd(\eta^3\text{-}2\text{-}MeC_3H_4)][BF_4]\}_{4,8}$ CS-C2^{G1,G3}:$\{[SiMe_2(CH_2PPhR)Pd(\eta^3\text{-}2\text{-}MeC_3H_4)][A]\}_{4,8}$ A^- = $BARF^-$, BF_4^- (See Fig. 5)
Heck reaction			
8[39]		2 mol% Pd, DMF, NaOAc, 120 °C	

Table 1 (*continued*)

Entry	Substrates or reaction	Typical conditions	Dendritic catalysts
9[40]	 R^1 = Ph, CO_2Me, CO_2Et, CO_2tBu, CN; R^2 = CO_2Me, CO_2nBu	K_2CO_3, 140 °C, toluene	
10[41]		2% Pd, AcOH/NBu_3 (1 : 1), LiOAc, 130 °C, [L]/[Pd] = 2 : 1	
11[42]		4 mol% Pd, MeCN, NEt_3, 82 °C	
Stille and Suzuki cross-couplings			
12[48]		1 mol% Pd, DMF; 68 °C (thienyl) or 50 °C (vinyl)	 X = Cl, OAc
13[49]	Previous substrates plus 	2–5 mol% Pd, DMF, 50 °C or 1 mol% Pd, DMF, 20 °C (phenylethynyl)	 X = Cl, OAc
14[50]	 R = *p*-COMe, *p*-NO_2, *p*-CN, *p*-F, *p*-OMe, *o*-, *m*-, *p*-Me	1 mol% Pd, 65 °C, NaOH, THF/H_2O (2 : 1)	
Sonogashira reaction			
15[53]	 X = Cl, Br, I	1 mol% Pd, NEt_3, 25–120 °C	 R = Cy, ^{t}Bu

systems will be discussed at the end of the present section. Periphery-functionalised covalent palladium dendrimers are subsequently categorised according to the catalytic reaction they take part in.

2.1 Hydrogenation of olefins[27]

Kaneda and co-workers have observed that a PPI dendrimer decorated with sixteen diphosphane palladium complexes is much more active in the hydrogenation of cyclopentadiene under mild conditions than the scarcely active monometallic model (Table 1, entry 1).[28] This distinct behaviour was attributed to the presence of amine groups in the dendrimer matrix, which favour the formation of the active hydride species by neutralisation of the HCl liberated in the initial activation of the dichloro complexes. This dendritic catalyst is less active than Pd/C or Pd/Al_2O_3 but shows high selectivity in the hydrogenation of conjugated dienes to monoenes (*e.g.*, cyclopentadiene to cyclopentene). In a screening of several dienes, the initial rates were slowed by the substrate size when a polystyrene-bound Pd catalyst was used, but not in the case of the Pd dendrimer. This result was ascribed to the easy access of the substrates to the active sites in the dendrimer. The dendritic catalyst, which is heterogeneous in the solvent typically used (ethanol), can be readily recovered by centrifugation and reused without loss of activity or selectivity.

Feng and co-workers have reported another recyclable system, based on a CS dendrimer with peripheral aminopropyl groups, which is able to reduce C=C bonds and carbonyl groups, although the structure of the palladium dendrimer has not been completely elucidated (Table 1, entry 2).[29]

2.2 Polymerisation and copolymerisation of α-olefins[30]

Two examples of palladium dendrimers with applications in polymerisation have appeared in the literature. Mapolie and co-workers have described a PPI dendrimer with four terminal alkylpyridyliminepalladium complexes that catalyses the polymerisation of ethylene after activation with methylaluminoxane (MAO; Table 1, entry 3).[31] These dendrimers are more active than their bi- or mononuclear palladium analogues and produce linear polyethylene of high molecular weight.

Our group has prepared a series of carbosilane dendrimers bearing arylpyridylimine ligands at their surface. Initially, we employed these ligands for the synthesis of nickel complexes that were used for the oligomerisation/polymerisation of ethylene.[32] We found a strong dependence of the molecular weight, oligomer/polymer distribution and microstructure of the final product on the dendritic generation, which we ascribed to steric interactions of the growing polymer chain and the nanosized catalyst. In view of these results, we used the arylpyridylimine ligands to prepare cationic palladium dendrimers for the alternating copolymerisation of CO and 4-*tert*-butylstyrene (Fig. 4; Table 1, entry 4).[33] The activity increased somewhat with the generation of catalyst, but the half-lives of the active species were similar for the dendrimers and the mononuclear analogue. More significant changes were observed in the molecular weight, polydispersity and stereoregularity of the copolymer. Thus, an increase in generation resulted in lower molecular weights and broader molecular weight distributions, probably because the steric pressure of bulkier dendrimers on the growing chains enhances chain-transfer processes and favours the formation of an assortment of shorter polymers. Syndiotactic polyketones were mainly obtained in all cases, although a constant decrease in stereoregularity was observed with the catalyst size, which was explained as the result of increasing steric interference on the chain-end control mechanism.

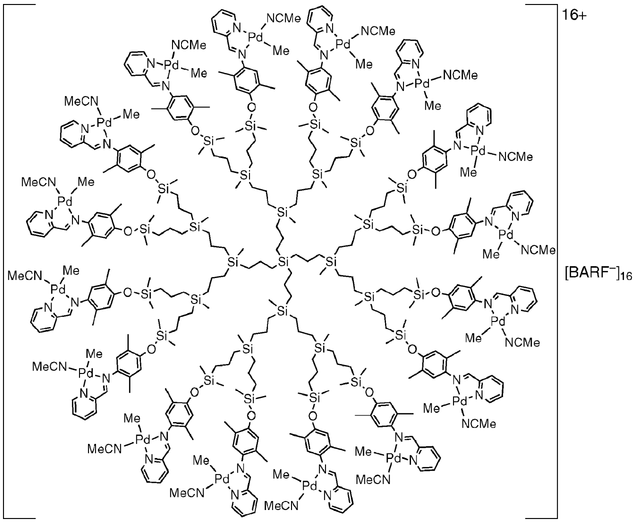


Fig. 4 Third-generation dendrimer used for the copolymerisation of *tert*-butylstyrene and carbon monoxide by Benito *et al.*[33]

2.3 Hydrovinylation[34]

The metal-catalysed co-dimerisation of styrene and ethylene to produce 3-phenyl-2-butene is the archetypal example of hydrovinylation (Table 1). However, after consumption of the styrene, the same catalyst is able to isomerise the chiral product to achiral 2-phenyl-2-butene. This isomerisation can be minimised by running the reaction at lower conversions. Therefore, Vogt, van Koten and co-workers reasoned that it might be useful to run the reaction continuously at these lower conversions by using dendritic catalysts and nanofiltration membranes.[35] The catalysts were prepared *in situ* from the palladium precursors and hemilabile P,O ligands supported on carbosilane dendrimers (Table 1, entry 5). Both mononuclear and dendritic complexes showed, in general, high chemoselectivity for the co-dimers (*versus* homo-oligomers or higher co-oligomers), but they started to deactivate within 10 h, thus limiting their efficiency. Under batch conditions, the dendrimers were less stable, and therefore less active, than the monometallic models. The deactivation and precipitation of palladium black was attributed to the formation of diphosphane complexes, which is facilitated by the high local concentration and flexibility of the arms in the dendrimers studied. Under continuous operation, the deactivation was still favoured and the retention of the smaller dendrimer in the membrane was low for practical purposes (85%). Although the dendrimers showed a limited efficiency, hardly any isomerisation or other side products could be detected in the solution.

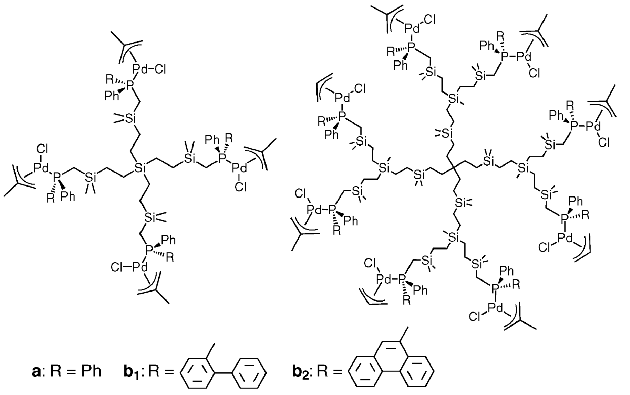


Fig. 5 Hydrovinylation catalysts containing monodentate phosphane ligands synthesised by Rossell and co-workers.[36,37]

The hydrovinylation of styrene has also been studied by Rossell, Muller and co-workers, who employed palladium monodentate complexes of diphenyl-[36] or phenyl(aryl) phosphanes[37] anchored to the surface of carbosilane dendrimers (Fig. 5). The cationic active species were generated *in situ*, by adding a chloro ligand abstractor in dichloromethane, or isolated as acetonitrile complexes. Initial studies were carried out with the diphenylphosphane ligand **a** in Fig. 5 and showed that these ligands were more active than the bidentate P,O systems described above (Table 1, entry 6). The order of activity, mononuclear > G3 ≥ G1, can be correlated with the steric crowding by taking into account that the limited branching of the G3 dendrimer results in a low surface congestion. In all cases the activity decreased with increasing reaction times as a consequence of the deactivation of the catalyst, an effect that apparently was more important for the dendrimers.

The main interest in the hydrovinylation reaction lies in the generation of a new asymmetric centre, and therefore considerable effort has been invested in obtaining high enantioselectivity by modifying the metal atom with optically active ligands. The carbosilane dendrimers **b** in Fig. 5 are the first example of dendrimers containing P-stereogenic monophosphanes.[37] The (*S*)-3-phenyl-1-butene enantiomer was preferably obtained from the (*S*)-phosphane-containing precursors $\mathbf{b_1}$ in all the experiments (Table 1, entry 7). When activated with $AgBF_4$, enantiomeric excesses in the range from 63 to 68% were obtained at moderate conversions (≈35%). At higher conversions (≈50–60%), a decrease in the activity, selectivity and enantioselectivity was observed for the dendrimers, but not for the monometallic complex. However, at least for the smaller dendrimer, excellent selectivity (92 *vs.* 77%) and enantioselectivity (77 *vs.* 56% ee-(*S*)) can be obtained at the same conversion level upon activation with Na[BARF]. Complexes $\mathbf{b_2}$ are more active, but less selective and unable to induce significant enantiomeric excesses.

2.4 Heck reaction[38]

In a seminal article published in 1997, Reetz *et al.* reported the first examples of catalyst recovery and a positive dendritic effect in catalysis with metal dendrimers.[39] They also reported the functionalisation of commercial PPI dendrimers with diphosphane $N(CH_2PR_2)_2$ end-groups by a double phosphanylmethylation, a methodology that has been used extensively since (Fig. 6). A third-generation dendrimer incorporating 16 dimethyldiphosphanepalladium complexes at the surface was tested in the Heck reaction of bromobenzene and styrene; it gave a 9 : 1 mixture of *trans* and 1,1 compounds with an overall conversion of 85–90% (Table 1, entry 8). The dendritic catalyst was significantly more active than the mononuclear complex (approx. three times in terms of TON), probably due to its reduced tendency to decompose thermally to metallic Pd. The dendritic material was recovered (>98%) by precipitation with diethyl ether and, even though the precise nature of this material was not identified, the recovered catalyst displayed comparable activity and selectivity when reused in the Heck reaction.

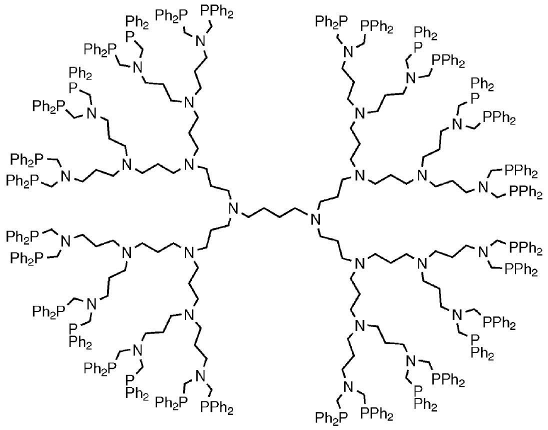


Fig. 6 A third-generation poly(propylene imine) dendrimer modified with diphenylphosphanylmethyl end-groups.

Krishna and Jayaraman have studied the Heck reaction of iodobenzene and a variety of alkenes using large-ring diphosphanes supported on poly(ether imine) dendrimers (Table 1, entry 9).[40] This reaction affords only the *trans* product and the catalytic activities decrease after recycling. Iminophosphane, aminophosphane[41] and pyridylimine[42] ligands constitute other classes of systems anchored to the surface of PPI dendrimers that have been tested in the Heck reaction. Extensive formation of Pd black was observed during the catalytic process using the Pd iminophosphane G4 dendrimers, thus precluding any categorical conclusion, and the aminophosphane ligand gave lower conversions (Table 1, entry 10).[41] In the case of the pyridylimine ligands, however, the dendritic complexes generally gave higher rates and conversions, and were more stable towards Pd precipitation, than the monomeric complex, although no attempts were made to recover the catalyst (Table 1, entry 11).[42] The formation of a significant quantity of polystyrene (14%) was observed when styrene was used as reagent.

N-Heterocyclic carbenes have yielded unexpected successes in key areas of homogeneous catalysis,[43] including the Pd-catalysed formation of carbon–carbon bonds. Although homogeneous catalysts based on palladium dendrimers and carbene ligands are unknown, the group of Díez-Barra has published a related hexacarbene Pd star-shaped complex (Fig. 7) which is more active than the corresponding

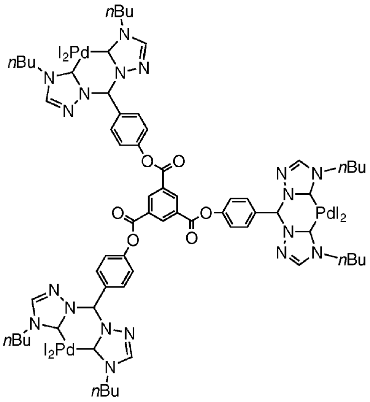


Fig. 7 The palladium hexacarbene complex synthesised by Díez-Barra *et al.* and used as a catalyst in the Heck reaction.[44]

monomeric catalyst in the Heck reaction between *p*-bromobenzaldehyde and *n*-butyl acrylate.[44] In contrast, the star-shaped trinuclear cationic PCP pincer complex reported by Belestkaya *et al.* is less active than the corresponding mononuclear complex $[(2,5\text{-}C_6H_3(CH_2PPh_2)_2)Pd(NCMe)]BF_4$ in the coupling of iodobenzene and ethyl acrylate.[45]

2.5 Suzuki[46] and Stille[47] cross-coupling reactions

Majoral and Caminade have used palladium complexes supported on phosphorus-based dendrimers[3] as catalysts in the Stille reaction. Bis(diphenylphosphanylmethyl)amine (PNP)[48] or iminophosphane[49] complexes anchored at the surface of NNPS dendrimers have been used in the cross-coupling of aryl iodides with 2-thienyl or vinyl organostannanes. In the case of the PNP ligand (Table 1, entry 12), the G3 catalysts were recovered by precipitation from the reaction mixture with diethyl ether and reused, with a small loss of activity. For instance, the conversion after three runs dropped from 86 to 79% with the thienyl stannane. This behaviour reflects the enhanced stability of the dendrimers which, contrary to the monomers, resist degradation and palladium precipitation. Similar results were obtained with the iminophosphane ligand (Table 1, entry 13). The efficiency of the dendrimer containing six metal units with respect to the corresponding monomer depends on the substrates involved, and the dendrimer could be recycled several times with only slightly decreased activities.

Recently,[50] Astruc and Heuzé have screened the Suzuki reaction between phenylboronic acid and a variety of chloroarenes using bis(dicyclohexylphosphanylmethyl)amine ligands anchored to the surface of G1 to G3 PPI dendrimers (Table 1, entry 14). They found that the mononuclear analogue is able to catalyse the coupling of both electron-poor and electron-rich (and hindered) chloroarenes, with yields ranging from 42 to 99% and reaction times from 1 to 24 h. The G1 dendrimer gave yields comparable to those obtained with the mononuclear complex, but a clear negative effect was observed with an increase of the generation. The dendritic compounds were recovered by precipitation with pentane and reused for three cycles. However, an important loss of activity, in terms of both conversion and TOF, was observed in all cases. The mononuclear complex could not be recovered since degradation occurred immediately during the first pentane precipitation, with formation of Pd black.

2.6 Sonogashira reaction[51]

Astruc and Heuzé have also found that the above-mentioned PPI dendrimers are efficient and recoverable catalysts for the Sonogashira reaction in the absence of a copper co-catalyst (Table 1, entry 15).[52,53] A negative dendritic effect on activity was observed with an increase in generation, especially on going from the second to the third generation. Moreover, the dendrimers produced only traces of cross-coupling products with aryl chlorides, whereas the monometallic complexes, especially the *tert*-butyl derivatives, gave high reactivities. Nevertheless, the G2 and G3 cyclohexyl dendrimers could be recycled by precipitation with pentane and reused at least six times without loss of activity. The integrity of the catalyst after each recovery cycle was confirmed by NMR spectroscopy.

2.7 Allylic substitution[54]

The allylic substitution reaction is an important tool for the formation of C–C and C–heteroatom bonds. In this reaction, the allylic position of an alkene, preferentially one possessing an anionic leaving group, is activated towards nucleophilic attack after conversion of the alkene into a π-allylpalladium complex (Table 2). Brinkmann, Kragl and co-workers selected this reaction to demonstrate, for the first time, the viability of performing a metal-catalysed homogeneous reaction continuously with a dendritic catalyst in a membrane reactor.[55] Palladium diphosphane complexes derived from third- (Fig. 6) and fourth-generation PPI dendrimers were studied (Table 2, entry 1), and retention rates higher than 99.9% were found for the smaller G3 dendrimer in the selected membrane. Both catalysts were used in the allylic amination of cinnamyl methyl carbonate with morpholine in a continuous process. The best results were obtained with the G4 dendrimer, with initial quantitative conversions that decreased to about 80% after 100 residence times. Leaching of palladium species was observed (0.07 to 0.14% per residence time for G4), although these values can only partially explain the decrease of conversion and therefore formation of inactive $PdCl_2$ complexes was also proposed.

Reek, van Leeuwen and co-workers have explored[56,57] the use of palladium complexes of phosphane-functionalised carbosilane dendrimers in allylic alkylations carried out in batch or continuous-flow membrane reactors. Relatively encumbered carbosilane dendrimers with one (**a**, Fig. 8) or two diphenylphosphanylmethyl substituents (**b**) at each outer silicon atom were treated with $[Pd(\mu\text{-}Cl)(\eta^3\text{-}C_3H_5)]_2$ to generate the catalyst precursors. Dendrimers **b** gave well-defined palladium complexes with a *cis* configuration whereas dendrimers **a** produced a mixture of *trans* complexes. Substituted allyl acetates and the sodium salt of diethyl 2-methylmalonate were reacted in batch processes that gave linear *trans* products very selectively (Table 2, entry 2). Dendrimers **b** were found to be more active than **a** but, otherwise, no relevant differences were observed in activities or selectivities in function of the size and nature of the dendrimer, or in comparison with monometallic analogues, thereby suggesting that the active centres act as

Table 2 Reactions catalysed by peripherally modified palladium dendrimers (Part II)

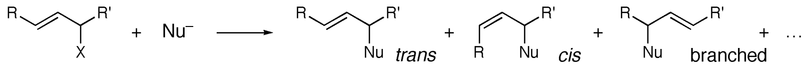
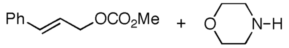
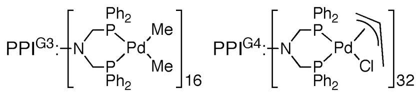
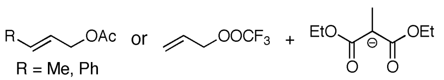
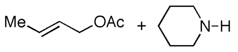
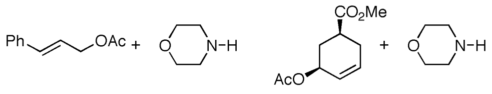
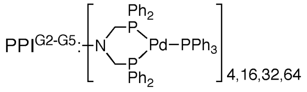
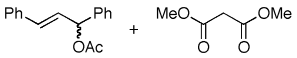
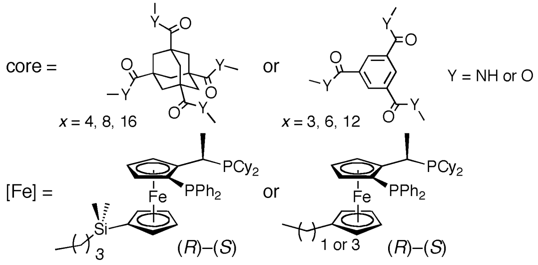
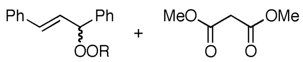
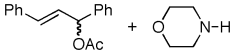
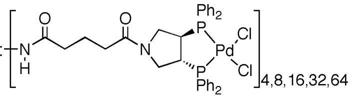
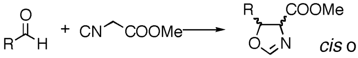
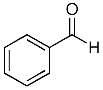
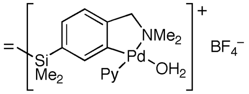
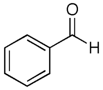
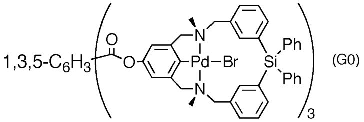
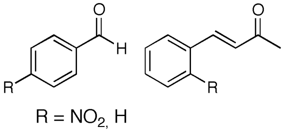
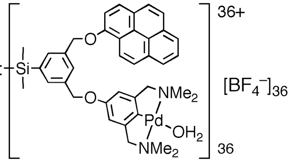
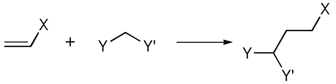
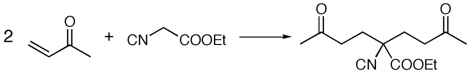
Entry	Substrates or reaction	Typical conditions	Dendritic catalysts
Allylic substitution			
1[55]		[Pd] = 30 mM, 25 °C, CH_2Cl_2	
2[56,57]		[Pd] = 0.05 mM, r.t., THF	CS-C2×3^{G1,G2}:{$SiMe_2CH_2PPh_2$}$_{4,12}$(PdClMe)$_{2,6}$ (Fig. 8a) CS-C2×3^{G1,G2}:{SiMe(CH_2PPh_2)$_2$PdClMe}$_{4,12}$ (Fig. 8b)
3[57]		[Pd] = 2 mM, r.t., CH_2Cl_2	
4[58]		[Pd] = 1 mM, 40 °C, NBu_2H, NEt_3, DMSO	
5[60]		1 mol% Pd, r.t., L/Pd = 1.1. BSA, KOAc, CH_2Cl_2	core:{C_6H_3-3,5-(CONH-)$_2$}$^{G0-G2}$:[Fe]$_x$ + [Pd(dba)$_2$] 
6[61]	 ROO^- = acetate or pivalate	2.5 mol% Pd, L/Pd = 1 or 2, r.t., BSA, LiOAc or KOAc, CH_2Cl_2	S=P:NNPS^{G3}:[OC_6H_4CH=N-(*S*)-C*H($CHMe_2$)(CH_2PPh_2)]$_{24}$ + [Pd(dba)$_2$] (Fig. 10)

Table 2 (*continued*)

Entry	Substrates or reaction	Typical conditions	Dendritic catalysts
7[62]		0.3 mol% Pd, 45 °C, DMSO	PPI or PAMAM$^{G1\text{-}G5}$: 
Aldol-type condensation of aldehydes with isocyanoacetate	 *cis* or *trans*		
8[63]		≈1 mol% Pd, NEt*i*Pr$_2$, r.t., CH$_2$Cl$_2$	CS-C2^{G1}:[Pd]$_4$ CS-C3^{G1}:[Pd]$_4$ CS-C2×2^{G2}:[Pd]$_8$ CS-C3×2^{G2}:[Pd]$_8$ CS-C3×3^{G2,G3}:[Pd]$_{12,36}$ [Pd] = 
9[68]		1 mol% Pd, NEt*i*Pr$_2$, r.t., CH$_2$Cl$_2$	
10[65]		1 mol% Pd, NEt*i*Pr$_2$, r.t., CH$_2$Cl$_2$	CS-C3×3^{G3}: 
Michael addition	 Y = electron-withdrawing groups		
11[45,70,71]	 0.5 mol% Pd, r.t., CH$_2$Cl$_2$	0.5 mol% Pd, r.t., CH$_2$Cl$_2$	See Fig. 11

independent sites. The dendrimer **b** coordinated to twelve palladium atoms was tested in a membrane reactor with allyl trifluoroacetate as the substrate. The maximum conversion (*ca.* 50%) was obtained after two reactor volumes but dropped quickly after this point. Since the size of the dendritic catalyst enables a high retention in the membrane, this decrease was attributed to leaching of small inactive palladium species under the operating conditions. The deactivation is not caused by interactions with the membrane, as demonstrated by the authors, and contrasts with the stability of the same catalysts in batch reactions.

Interesting results have also been observed for the same catalytic systems in the allylic amination reaction of crotyl acetate and piperidine,[57] which produced mainly mixtures of branched and linear *trans* products (Table 2, entry 3). Under continuous-flow conditions, a similar rapid deactivation of the catalyst was observed. Surprisingly, the replacement of the diphenylphosphanylmethyl $SiCH_2PPh_2$ end-groups in **a** (Fig. 8) by ethylene-spaced $SiCH_2CH_2PPh_2$ groups resulted in a stable catalyst that produced a high (*ca.* 80%) and almost constant conversion at a P : Pd ratio of 4 : 1. The extent of the reaction conversion decrease can be quantitatively explained simply by taking into consideration a retention factor in line with the expected values (98.5–99%).

Kaneda and co-workers have synthesised dendritic Pd^0 complexes of PPI dendrimers similar to those represented in Fig. 6 with up to 64 diphosphane groups (fifth generation).[58] In the amination of *trans*-cinnamyl acetate with morpholine (Table 2, entry 4), the regioselectivity of the reaction towards linear *trans* and branched products (90 : 10) was found to be unaffected by the generation of the dendrimer. In the reaction with *cis*-3-acetoxy-5-carbomethoxycyclohex-1-ene, on the other hand, the stereoselectivity for the *cis* product increased with the generation of the dendrimer from 8% for $[Pd(PPh_3)_4]$ to 94% for the fifth-generation catalyst. This dendritic effect was attributed to increasing surface congestion of the dendrimers that shields the (π-allyl)Pd intermediate from *endo* attack by the nucleophile. In addition, the catalysts can be easily recycled without loss of activity (99% of yield in the fourth run) using a thermomorphic system[59] consisting of a mixture of DMF and heptane.

Several authors have studied the asymmetric version of this catalytic reaction. Köllner and Togni, for example, have used $[Pd(dba)_2]$ combined *in situ* with dendrimers containing up to sixteen chiral ferrocenyl diphosphanes of the Josiphos-type (Fig. 9) as a catalyst for the reaction of racemic *trans*-1,3-diphenyl-2-propenyl acetate with dimethyl malonate (Table 2, entry 5).[60] The enantioselectivities obtained with the dendrimers were, in general, in the narrow range 89–91% ee in favour of the (*S*) isomer, which is slightly less than with the parent Josiphos ligand (93% ee). The most notable exception was found with the larger G2 dendrimers, probably because of their low solubility. More recently, Laurent *et al.* have reported a dendritic catalyst that produces a slightly higher enantiomeric excess (90% ee for the (*R*) isomer) than the mononuclear analogue (80% ee; Table 2, entry 6) under the same conditions.[61] This dendritic catalyst, which is based on a Majoral-type phosphorus dendrimer with 24 chiral iminophosphane end-groups (Fig. 10), shows good stability. It was recovered by precipitation with diethyl ether and reused with practically the same efficiency. The reaction showed a good reproducibility and, under optimised conditions, proceeded with total conversion and 95% ee in 25 h.

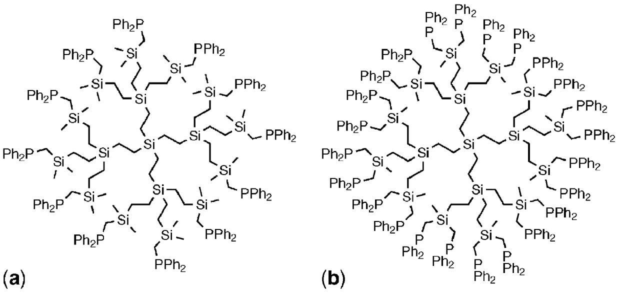


Fig. 8 Carbosilane dendrimers CS–C2 × 3^{G2} with one (a) or two (b) diphenylphosphanylmethyl groups per branch.

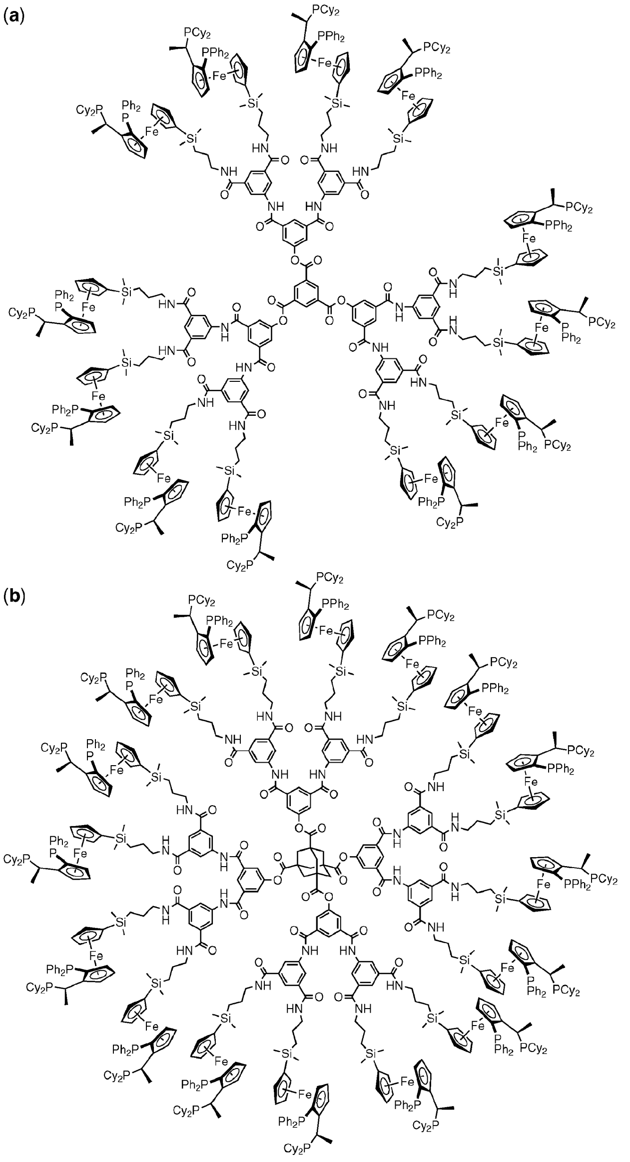


Fig. 9 Second-generation dendrimers of chiral ferrocenyl diphosphanes employed by Köllner and Togni in asymmetric catalysis.[60]

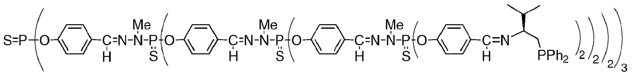


Fig. 10 Chiral iminophosphanes supported on a Majoral-type phosphorus dendrimer used for asymmetric catalysis.[61]

A strongly positive dendrimer effect on enantioselectivity has been found by Gade and co-workers, who reported the use of palladium dichloride complexes of chiral pyrphos ligands fixed on PAMAM or PPI dendrimers of zero to fifth generation in the allylic amination of *trans*-1,3-diphenyl-2-propenyl acetate with morpholine (Table 2, entry 7).[62] A steady increase in ee values was found on going from the mononuclear reference (9% ee) to the fifth-generation dendrimers, although the effect was less pronounced for the PPI catalysts (40% ee for the larger G5 dendrimer) than for the PAMAM catalysts (69% ee for G5). The remarkable changes in selectivity were preliminarily attributed to gradual conformational alteration of the aryl substituents on the diphosphane caused by an increasingly crowded periphery on going to higher generations.

2.8 Aldol-type condensation with isocyanoacetates

The group of van Koten has studied the aldol-type condensation of aldehydes—most often benzaldehyde—with methyl isocyanoacetate to give oxazolines extensively (Table 2). A variety of cyclometallated CN and NCN-pincer palladium catalysts have been used, including peripherally modified dendrimers,[63–65] and hyperbranched[66] or dendronised[67] polymers based generally on carbosilane skeletons. Cyclopalladated cationic complexes $[(CN)Pd(pyridine)(aqua)]^+$ were situated at the periphery of dendrimers having diverse levels of crowding by combining different generations, ramifications (two or three branches at each silicon) and branch lengths (C2 or C3 branches; Table 2, entry 8).[63] The rates for the dendrimers and the monometallic model were comparable, except for the lower activities found in dendrimers where a high congestion in the dendrimer periphery is to be expected. The *trans*/*cis* ratios of the oxazoline product ($\approx$1.7) were basically unaffected by the dendritic framework.

Due to the difficulty in imposing appropriate spatial constraints at the dendrimer level to encourage the (stereo)selectivity, specific combinations of dendrimers and other strategies have been investigated. The encapsulation of the catalytic centres in a macrocyclic ligand[68] or the introduction of a pyrenoxy π-system in the vicinity of the metal sites,[65] however, has no effect on the diastereoselectivity of the reaction with either mononuclear or dendritic catalysts (Table 2, entries 9 and 10). The close proximity of the pyrenoxy unit to the metal atom augments the reaction rate of the mononuclear complexes in the aldol condensation of several aromatic aldehydes, whereas the steric crowding is probably responsible for the drop in activity observed for its dendritic version containing 36 palladium metal atoms.[65] In contrast, the trimetallic compound shows an enhanced reactivity in the case of the encapsulated systems.[68]

As an alternative to carbosilane dendrimers, soluble hyperbranched carbosilane polymers can be synthesised by cheaper, one-pot polymerisation of triallylsilane by Pt-catalysed hydrosilylation. Frey, van Koten and co-workers have reported the synthesis of a hyperbranched carbosilane polymer and its functionalisation with NCN-pincer palladium complexes.[66] This system, which was the first example of a homogeneous catalyst supported on a hyperbranched polymer, was tested in the condensation of benzaldehyde and methyl isocyanoacetate. In line with the results outlined above for dendrimers, the stereoselectivity remained basically unmodified (*trans*/*cis* = 2) and the activity was only slightly lower than that of the mononuclear system.

2.9 Michael addition

The group of van Koten has synthesised a variety of star-shaped compounds with pincer ligands and palladium complexes at the ends of the arms. Although these systems are not true dendrimers, they are mentioned here because peripherally modified dendrimers and stars share several common characteristics, such as the multiple metal centres at the periphery or the viability of nanofiltration. In fact, the high rigidity in the backbone of some star-shaped complexes is of interest for optimal catalyst retention in continuous nanomembrane reactor processes. Thus, platinum complexes similar to the star-shaped palladium molecules **a** and **d** (Fig. 11) are retained more efficiently by nanofiltration membranes than carbosilane dendrimers of comparable volume, probably due to the flexibility of the latter.[69] Pincer complexes, such as those represented in Fig. 11, have been studied as Lewis acid catalysts in the double Michael reaction between ethyl cyanoacetate and methyl vinyl ketone (Table 2, entry 11). The NCN-pincer compounds showed comparable activity to the monometallic models with the exception of the hexanuclear complex **b**, whose poor solubility under catalytic conditions resulted in lower yields.[70] In contrast, the activity always decreased in related PCP systems as the number of metal atoms in the catalyst molecule increased.[45] Surprisingly, the dodecanuclear complex **d** showed a threefold increase in activity, which was ascribed to a positive cooperation between metal centres in the high peripheral concentration.[71] As this complex is retained very efficiently by nanomembranes, it was used in a continuous reactor with excellent results.[72] Only a small decrease of yield with time was observed after reaching the steady-state condition. This decrease was ascribed to the very slow leaching of the catalyst, *i.e.* the decomposition or deactivation of the catalyst was negligible during the prolonged reaction times (25 h, 65 cycles).

2.10 Complexes supported non-covalently on dendrimers

The connection of the catalyst to the dendritic support by a stable covalent attachment is preferable in order to reduce the chance of metal leaching. Nevertheless, the use of non-covalent interactions (ionic, hydrophobic or hydrogen bonds) allows a high degree of flexibility in terms of synthesis and reuse.[16] Several reports have been published in this area since the initial paper of Kimura *et al.*[73] The palladium-catalysed amination of crotyl acetate with piperidine, reported by Reek, Meijer and co-workers, was the first example using the non-covalent approach.[74] This non-covalent binding was based on

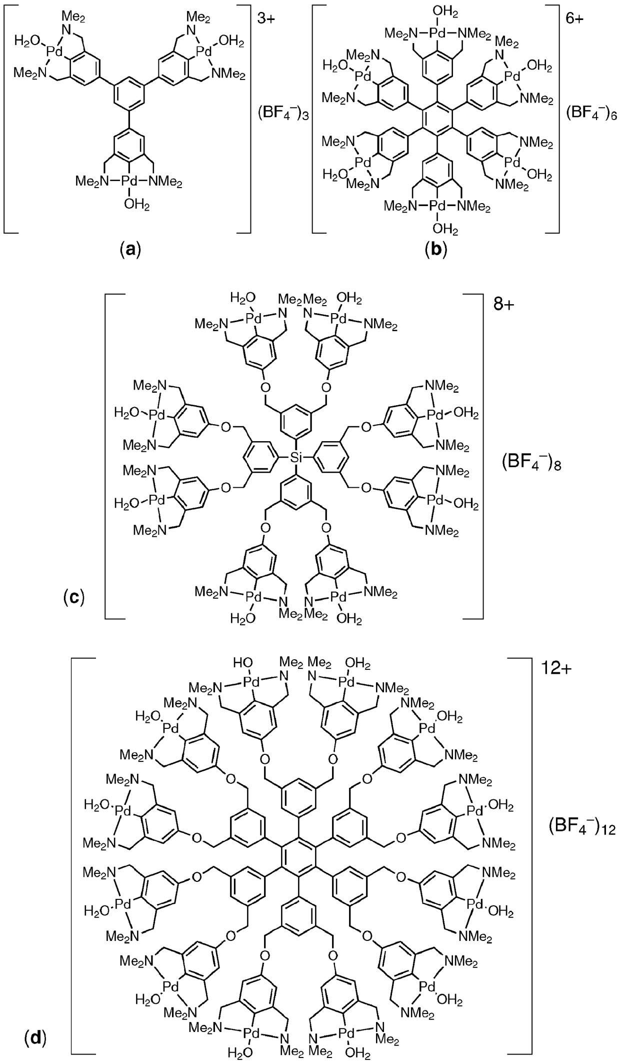


Fig. 11 Palladium star-shaped complexes prepared by van Koten and co-workers and applied in the Michael addition.[70,71]

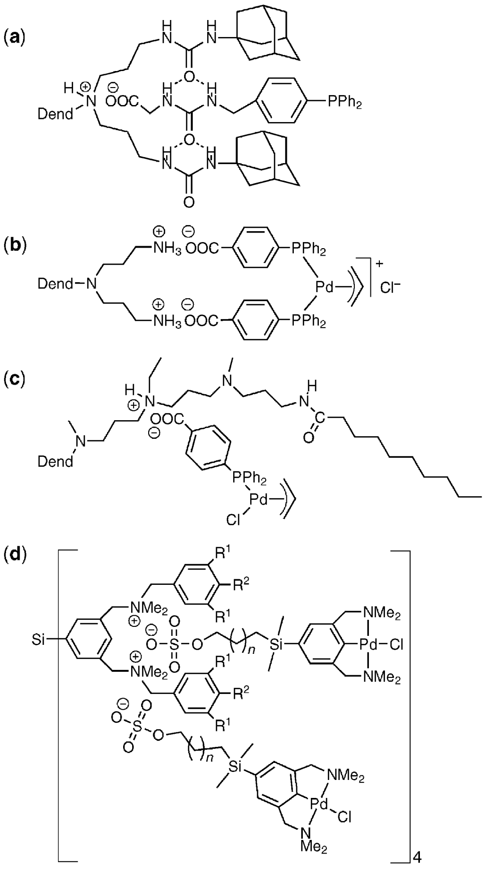
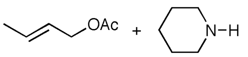
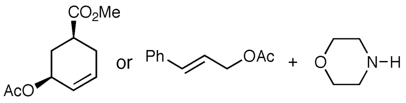
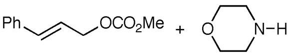
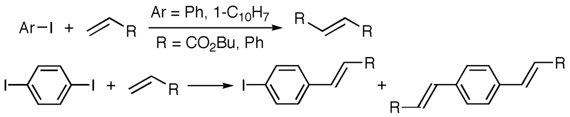
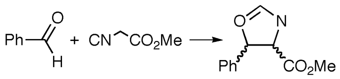


Fig. 12 Several examples of noncovalent binding between ligands and dendrimers.

a strong, but reversible, ionic interaction reinforced by hydrogen bonds between the urea acetate group of a phosphane ligand complementary to the binding motif of the dendrimer host (Fig. 12(a)). The activity and selectivity of the supramolecular assemblies was found to be comparable to that of related mononuclear complexes, although the selectivity (*trans*/*cis*/branched products) changed with the P/Pd ratio (Table 3, entry 1). The advantage of the dendritic system was emphasised when used in a continuous-flow membrane reactor. The dendrimer–ligand binding was found to be so strong as to allow retention rates of 99.4–99.9%, depending on the P/Pd loading. During the catalytic process, the conversion reached its maximum (*ca.* 80%) after approximately one hour and remained fairly constant during the first 10 hours of experiment. The slight decrease observed was attributed to the slow deactivation of the catalysts.

Kaneda and co-workers have used exclusively ionic interactions to attach phosphane ligands to the external (Fig. 12(b))[75] or internal amine groups (Fig. 12(c))[76] of PPI dendrimers by simple protonation of the amines with diphenylphosphanylbenzoic acid. The externally functionalised systems gave yields and distributions of linear *trans* and branched products almost identical to those obtained with dendrimer-free catalysts in the amination of cinnamyl acetate with morpholine (Table 3, entry 2).[75] The stereoselectivity of the amination of *cis*-3-acetoxy-5-carbomethoxycylohex-1-ene was also found to be almost insensitive to the catalyst generation (*cis*/*trans* = 1.0–1.5), in contrast to the remarkable dendritic effect found when the active centres were immobilised by covalent binding (see Table 2, entry 4).[58] These results were explained on the basis of the higher mobility of the metal centres on the dendritic surface in the ionic binding mode. The protonation of the PPI internal amines (Fig. 12(c)) was forced by modifying the more basic external amines with decanoyl dichloride.[76] The metal sites of these systems are encapsulated inside the dendrimer instead of decorating its surface and, presumably, the catalytic reactions occur in the dendritic cavities. These supramolecular systems catalyse the Heck reaction of iodobenzene with *n*-butyl acrylate very efficiently (Table 3, entry 4), with reaction rates that increase with the dendrimer generation, while the reaction hardly occurred in the absence of the dendrimer under the same conditions. Moreover, lower L/Pd ratios were sufficient to avoid the precipitation of Pd metal for bigger dendrimers than for the smaller dendrimers or the mononuclear complex. These results support the hypothesis that the bigger dendrimer acts as an effective nanoreactor that furnishes an adequate polar nanoenvironment to active species and the reaction. However, the

Table 3 Reactions catalysed by palladium complexes supported non-covalently on dendrimers

Entry	Substrates or reaction	Typical conditions	Dendritic catalysts
Allylic substitutions			
1[74]		[Pd] = 2 mM, P/Pd = 1 or 2, r.t., CH_2Cl_2	PPI^{G5}:$[N(H)C(O)N(H)(adamantyl)]_{64}$ ⊂ $[HOOCCH_2N(H)C(O)N(H)CH_2C_6H_4PPh_2]_{32}$ + $[PdCl(\eta^3\text{-2-MeC}_3H_4)]_2$ (See Fig. 12(a))
2[75]		0.3 mol% Pd, 5 °C, MeOH	$PPI^{G3,G5}$:$[(NH_3)^+(OOCC_6H_4PPh_2)^-]_{16,64}$ + $[PdCl(\eta^3\text{-2-MeC}_3H_4)]_2$ (See Fig. 12(b))
3[76]		0.25 mol% Pd, 30 °C, toluene	$PPI^{G3–G5}$:$(NHC(O)(CH_2)_8CH_3)_{16,32,64}$ ⊂ $[(HOOCC_6H_4PPh_2)PdCl(\eta^3\text{-C}_3H_5)]_{16,32,64}$ (See Fig. 12(c))
Heck reactions			
4[76]		0.5 mol% Pd, 100 °C, KOAc, toluene or DMF	$PPI^{G3–G5}$:$(NHC(O)(CH_2)_8CH_3)_{16,32,64}$ ⊂ $[(HOOCC_6H_4PPh_2)PdCl(\eta^3\text{-C}_3H_5)]_{16,32,64}$ (See Fig. 12(c))
Aldol condensations			
5[64,77]		1 mol% Pd, r.t., NEt_2iPr, CH_2Cl_2	See Fig. 12(d); n = 0, 3, R^1 = $PBE^{G0–G2}$, R^2 = H; R^1 = R^2 = $O(CH_2)_{11}CH_3$

encapsulation can also have a negative effect on the activity by restricting the accessibility of the metal centre. This could account for the decreasing productivity observed with increasing generation in the allylic amination of cinnamyl methyl carbonate with morpholine (Table 3, entry 3). Clearer evidence for the encapsulation of the catalyst was maybe found in the Heck reactions using 1,4-diiodobenzene (Table 3, entry 4), which were highly selective to the monosubstituted product in the presence of the G5 dendrimer, whereas a nearly equimolecular mixture of mono- and disubstituted products was obtained without dendrimer. With the appropriate modification of the dendrimer periphery, the catalyst was recovered using a DMF/heptane thermomorphic system and reused several times whilst retaining the high activity in the catalytic amination of cinnamyl methyl carbonate with piperidine.

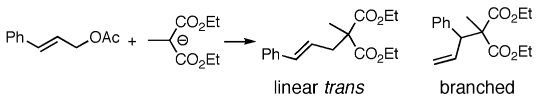
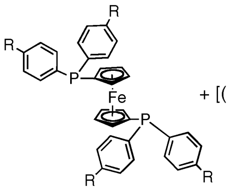
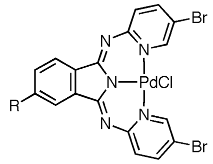
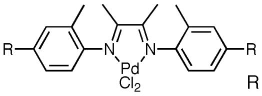
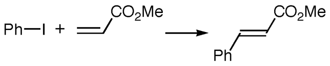
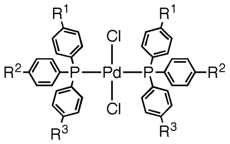
Van de Coevering *et al.* have used an octacationic dendrimer to immobilise eight anionic NCN-pincer palladium complexes (Fig. 12(d)).[64,77] Initially, the catalytic sites were located outside the dendrimer due to the use of a small R substituent at the dendrimer side (R^1 = OCH_2Ph) and a long chain (n = 3) at the side of the Pd^{II} complex. In this case, the presence of the dendrimer did not influence the catalytic activity or selectivity of the palladium complex in the aldol condensation shown in Table 3 (entry 5). In a second approach, the active sites were encapsulated within the dendritic structure by shortening the complex chain (n = 0) or, alternatively, by using bigger poly(benzyl ether) dendrons or dodecanoyl chains at the R position. The activities and selectivities of the complex with or without dendrimer remained fairly constant, except for minor decreases in catalytic activity. This means that the structure of the molecular assembly is relatively open and keeps the catalytic Pd^{II} sites easily accessible.

García-Bernabé *et al.* have immobilised a $[PdCl_2(P(C_6H_4CH_2CH_2R^F)_2)]$ catalyst (R^F = $(CF_2)_7CF_3$) in a hyperbranched poly(ethylene glycol) functionalised with perfluorinated end-chains.[78] The immobilisation was produced by the strong interaction obtained when the perfluorinated chain of the complex was intercalated in the perfluorinated shell of the polymer. This catalyst was tested in the Suzuki coupling of 4-bromoacetophenone in DMF at 80 °C. Conversions of 100% were obtained under these conditions after three recovery cycles. The reason given for the good catalytic behaviour of these supported catalysts is that the fluorine–fluorine interaction is temperature dependent and is reduced significantly at higher temperatures, thereby facilitating desorption of the catalyst at the temperature at which the catalytic process is run and readsorption at room temperature for the separation process.

3 Core-functionalised dendrimers

Dendrimer effects can arise primarily in core-functionalised dendrimers from the site isolation created by the dendritic environment. Although the encapsulation is associated with negative kinetic effects, reactions deactivated by an excess of ligand or where bimetallic deactivation mechanisms operate can benefit from site isolation. On the other hand, the catalytic centre located at the core of the molecule can also profit from a

Table 4 Reactions catalysed by core-modified palladium dendrimers

Entry	Reaction/ substrates	Typical conditions	Dendritic catalysts
1[79,80]	**Allylic substitution**  	THF, r.t., Pd:L = 1/1, 0.1 mol% Pd	 + $[(\eta^3\text{-}1\text{-}MeC_3H_4)PdCl]_2$ R = $(CH_2)_2Si{:}CS\text{-}C3\times3^{G0\text{-}G2}{:}allyl_{3,9,27}$ $(CH_2)_2Si{:}CS^{G2}{:}Me_{27}$
2[83]	**Hydrogenation of alkenes** Styrene, 1-octene	1 bar H_2, 2 mol% Pd, THF, 22 °C.	 R = $O{:}PBE^{G1\text{-}G2}{:}(CH_2Ph)_{2,4}$; $O{:}PBE^{G1}{:}(CH_2C_6H_4\text{-}tBu)_2$
3[84]	**Oligomerisation of olefins** Ethylene	1 bar ethylene, 40 °C, toluene	 R = $O{:}PBE^{G0,G1}{:}(CH_2Ph)_{1,2}$
4[85]	**Heck reaction**  	2.5 mol% Pd, 100 °C, in $scCO_2$ (170 bar), toluene, or DMF	 R_1, R_2, R_3 = H or $(CH_2)_2Si{:}CS\text{-}C3\times3^{G1}{:}(SiMe_2Et)_3$ (See Fig. 14)

nanoenvironment that is different from that of the groups situated at the periphery.

In 1999 the group of van Leeuwen reported the synthesis of carbosilane dendrimers with a [bis(diphenylphosphanyl)ferrocene] core (Fig. 13).[79] The palladium complexes of these ligands were used in the allylic alkylation of cinnamyl acetate with diethyl 2-sodio-2-methylmalonate, which only produced *trans* or branched products (Table 4, entry 1).[79,80] An increase in the size of the ligand produced a decrease in the reaction rate, as expected for a restricted accessibility of the metal centre. In contrast with the results obtained with related peripherally modified dendrimers (see above),[56,57] the regioselectivity of the reaction was modified by the ligand size: larger dendritic ligands favoured the formation of the minor, branched product. A change in the local microenvironment caused by the apolar dendritic shell was proposed as one of the possible origins of the modified selectivity. Interestingly, the larger core-functionalised dendrimer with the Pd catalyst encapsulated in the interior was found to be very stable, in a continuous-flow membrane reactor, compared with a related surface-functionalised catalyst in which the metal centres are fully accessible.[80]

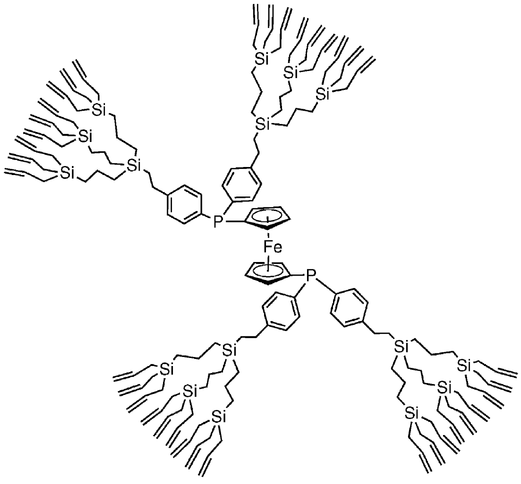


Fig. 13 A bidentate dendritic dppf ligand reported by van Leeuwen and co-workers for the preparation of core-functionalised metal dendrimers.[79]

Another interesting observation in the preceding work is that changes in activity or selectivity with the generation are not smooth as an abrupt change occurs at one point of the dendritic growth. This type of phenomenon has been observed in other cases and has been attributed to back-folding of the dendritic structure at this point.[81] In relation with this, Canovese *et al.* have studied the influence of the wedge size on the mechanism of the allyl amination reaction with palladium complexes bearing pyridyldithio ether (SNS) dendritic ligands.[82] Two concurrent processes were studied, namely the equilibrium of displacement of the SNS ligand by the amine (piperidine) and the kinetics of the attack of the piperidine at the allyl fragment. As expected, the displacement of the SNS ligand was more favourable in the case of the bulkiest ligands and the kinetics of the allyl attack was slower. However, the size of the dendritic wedge becomes relevant only on going from the second to the third generation.

A stabilisation effect of a dendritic ligand was also observed by Siggelkow and Gade in the hydrogenation of olefins with dendronised bis(2-pyridylimino)isoindole (BPI) palladium complexes (Table 4, entry 2).[83] In contrast, no correlation was found between activity and ligand size in the oligomerisation of ethane using palladium dendritic α-diimine catalysts (Table 4, entry 3).[84]

Core-functionalised dendrimers are particularly suited for the solubilisation of catalysts by an appropriate choice of peripheral groups. A number of solubilisers, especially fluorinated ligands, have been developed in recent years to improve the solubility of metal catalysts in supercritical carbon dioxide (scCO$_2$). The group of Galindo and our group have demonstrated that fluorine-free carbosilane dendrons can solubilise metal catalysts in scCO$_2$.[85] We have prepared [PdCl$_2$(PPh$_3$)$_2$] complexes in which one, two or three carbosilane dendrons are tethered to the phenyl groups of the phosphane ligand (Fig. 14). The solubility of the Pd complexes in scCO$_2$ increases with the number of carbosilane dendrons per triphenylphosphane ligand, going from the negligible solubility of the non-dendritic complex to the moderate solubility (0.87 g L^{-1}) of the completely dendronised complex. The effect of this solubilisation in the catalytic behaviour was studied using the Heck reaction of iodobenzene and methyl acrylate (Table 4, entry 4). Although the conversions obtained with the dendronised complexes were modest (close to 40%), the inclusion of the carbosilane dendrons was found to be essential as the non-dendronised PPh$_3$ complex is completely inactive under the same conditions. The activity of dendronised and non-dendronised complexes was also compared in toluene and DMF. The dendrimers are less active catalysts in DMF, a fact that could be in agreement with both the lower accessibility of the catalytic site or the local apolar environment caused by the dendritic shell. Interestingly, this behaviour is reversed in toluene, where the dendrimers are slightly more active. Conversely, the conformational flexibility of the dendritic wedges could be responsible for this by adopting more closed or open conformations depending on the solvent polarity.

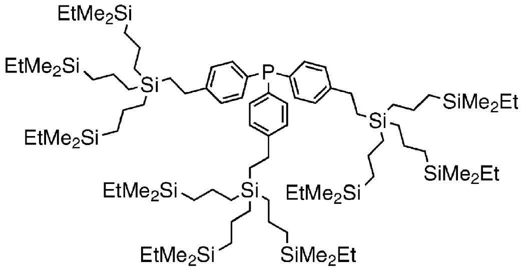


Fig. 14 A triphenylphosphane-derived ligand bearing three carbosilane dendrons that has been used for the solubilisation of palladium catalysts in supercritical carbon dioxide.[85]

The differentiation that dendrimers introduce between the internal and external microenvironment has led to them being considered for potential applications as concentrators of substrates around the catalytic centre, a concept taken from cellular processes.[86] For instance, an apolar substrate placed in an aqueous environment will tend to concentrate into a dendrimer containing inner apolar branches. However, this differentiation of internal and external microenvironments is only possible in large dendrimers with fully encapsulated cores. An alternative is the use of star polymer architectures whose size can be tuned over a wide range by adjusting the polymerisation reactions. In this sense, Fréchet and co-workers[87] have synthesised a photooxidation catalyst based on a Pd-porphyrin complex surrounded by a relatively hydrophobic block and terminated by a hydrophilic block. They found enhanced reactivity in the case of 2-furaldehyde, which is a poor substrate for the oxidation with singlet oxygen. They postulated that this is due to the capability of the macromolecule to concentrate the substrate close to the site of singlet oxygen generation in the interior of the macromolecule.

4 Supported catalysts

The immobilisation of homogeneous catalysts on organic or inorganic solid supports facilitates their separation and reuse but usually results in the partial loss of the advantages of the molecular catalyst in terms of activity and selectivity. The introduction of a dendrimer template between the support and catalyst might help to overcome this drawback by preserving the well-defined environment of the homogeneous catalyst. Most of the supported dendritic catalysts reported to date have been prepared by stepwise divergent growth of the dendrimer on the support, using solid-phase techniques,[88] and subsequent functionalisation of the supported dendrimer with the appropriate ligands and metal complexes.[7] Solid-phase techniques facilitate the use of a large excess of soluble reagents and the separation and purification of the functionalised support.

An alternative approach for the heterogenisation of dendritic catalysts that does not rely on the use of a solid support consists in the cross-linking of soluble homogeneous dendrimers.[89] Related with this, an example of heterogenisation of palladium catalysts has been reported recently in which star-shaped oxime palladacycle complexes were networked by formation of Pd–Cl–Pd bridges.[90] These materials exhibit good catalytic activity and recyclability in the Suzuki coupling of aryl bromides at room temperature and aryl chlorides at 110 °C.

4.1 Dendritic catalysts supported on silica

The most highly developed class of supported dendritic catalysts has mainly been published by the group of Alper and consists of PAMAM dendrons constructed from aminopropyl-functionalised silica gel by the usual Tomalia approach,[20] and generally phosphonated in the last step. The first report appeared in 1999, when Alper, Arya, Manzer *et al.* suggested that the dendritic support of a dendronised silica could give the catalysis a degree of homogeneous character as it would be highly solvated in a suitable solvent system. The first catalysts contained rhodium complexes and were used in hydroformylation reactions and recycled and reused without significant loss of selectivity or activity.[91,92] In many cases, these silica-supported systems should be better described as hyperbranched polymeric as opposed to perfect dendritic materials because of the elevated number of imperfections in the growth of the dendrimer, which results in an actual metal content lower than the theoretical value, especially for higher generations.[93,94] These defects are due, in part, to steric constraints in the growth and phosphonation of amine groups residing at the periphery of higher-generation dendrimers or in the pores of the support, but are also favoured by inappropriate reaction conditions.[95] The steric constraints can be partially overcome by extending the length of the PAMAM arms (Fig. 15).[92,96] Recently, Alper, Sayari and co-workers have attained average growth yields of better than 99% in the support of G4 PAMAM dendrimers using large pore PE-MCM-41 instead of amorphous silica.[97]

Alper *et al.* have also proved the usefulness of silica systems, such as those represented in Fig. 15, for the Heck coupling of bromo- or iodoarenes (but not chloroarenes) with styrene or butyl acrylate (Table 5, entry 1).[98] The stability and efficiency of supported Pd complexes in the Heck reaction was improved by using PCP pincer ligands (Table 5, entry 2).[99] In the presence of the same type of diphosphane catalysts, iodobenzene reacted with carbon monoxide in methanol at 100 °C and a CO pressure of 100 psi to give essentially quantitative yields of methyl benzoate, whereas bromobenzene did not react even at 150 °C.[94] The G1 dendrimer was recycled four times with a decrease of activity from 100 to 76%, which was to some extent due to the loss of the recovered silica-based catalyst because of its partial solubility in methanol. The carbonylation reaction was found to be applicable to a variety of iodoarenes regardless of the nature of the substituent (Table 5, entry 3). The carbonylation of alkenes in the presence of an alcohol (or hydroesterification reaction) usually gives a mixture of linear and branched products in the case of 1-alkenes. Silica-supported G0 to G4 PAMAM dendrimers have been studied in the reaction of a wide selection of terminal alkenes with carbon monoxide and methanol (Table 5, entry 4).[93] These systems are the first example of Pd-supported catalysts for hydroesterification that can be effectively recycled for several runs, although with decreasing activities due to Pd leaching. It is noteworthy that the ratio of linear to branched products, which always favours linear products, even for styrene, improved upon recycling, possibly because the branched products are more likely to be produced by the complexes grafted on the surface, which are more prone to leach away.

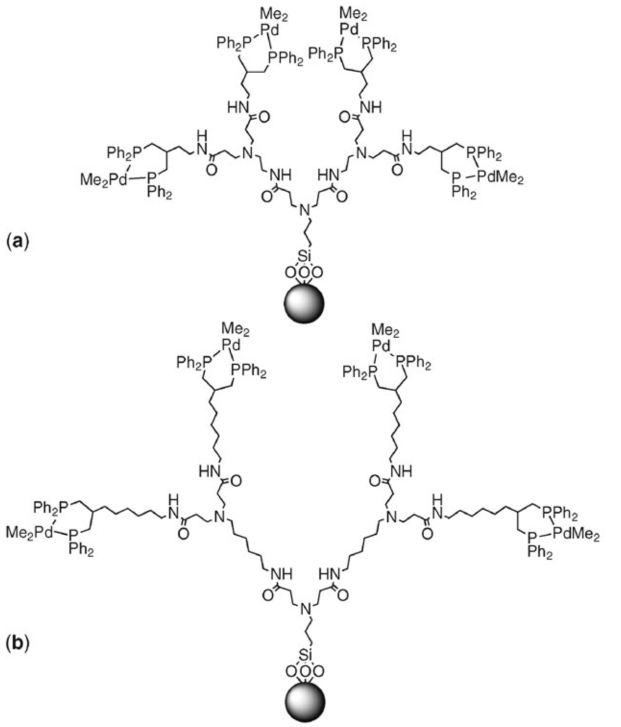


Fig. 15 (a) A second-generation PAMAM Pd dendrimer supported on silica, SiO_2-$Si(CH_2)_3N$:$PAMAM^{G2}$:$(N(CH_2PPh_2)_2PdMe_2)_4$. (b) The PAMAM-C6 analogue, which differs in the number of carbon atoms separating the intermediate amido and the branching amine functionalities.

Chanthateyanonth and Alper have reported the synthesis of five- and seven-membered ring lactones in high yields by the intramolecular cyclocarbonylation of 2-allylphenols with pincer-PCP complexes at high temperatures (120–40 °C).[100] The selectivity of the reaction could be directed, at least in the case of the G0 catalyst, towards the five- or the seven-membered ring lactone by an appropriate choice of reaction conditions. However, the catalyst could be effectively recycled only under the conditions for highly selective formation of the seven-membered ring lactone (Table 5, entry 5). Under the same conditions, the related mononuclear homogeneous catalyst gave high yields but only moderate selectivity. This difference in selectivity between the homogeneous and heterogeneous systems was ascribed to the substantial difference in size between both types of catalyst. The intramolecular cyclocarbonylation reaction has since been extended, by using diphosphane chelate palladium catalysts, to other 2-allyl- or 2-vinylphenols and -anilines to afford five-, six- and seven-membered ring lactones and lactams (Table 5, entry 6),[101] and also to the synthesis, with yields greater than 90%, of fused heterocycles containing oxygen, nitrogen or sulfur seven- and eight-membered rings (Table 5, entry 7).[102] In the latter case, the G1 dendrimer showed the best recyclability using 2-(2-iodophenoxy)aniline as substrate, maintaining conversions always greater than 95% for the desired dibenzoxazepinone for eight recycling runs. These reactions were found to be compatible with a wide variety of substituents, and double intramolecular insertions of carbon monoxide were also accomplished in high yields.

The oxidation of terminal alkenes to methyl ketones was studied by Zweni and Alper using *tert*-butyl hydroperoxide as oxidant and, as catalysts, Pd(dba) anchored to the silica support by G0 to G4 dendrimers of different arm lengths (PAMAM-C2, -C4, and -C6; see Fig. 15 and Table 5, entry 8).[96] With the G0 catalyst, the yields ranged from 27 to 42% for the linear terminal alkenes but the lowest yield (11%) was obtained, as expected, with cyclohexene. However, the activity

Table 5 Reactions catalysed by palladium dendrimers supported on silica

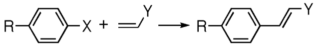
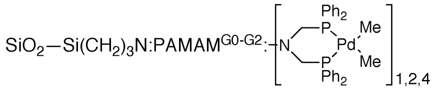
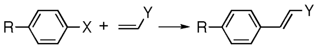
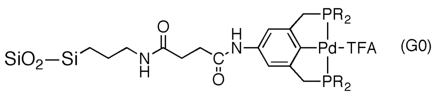
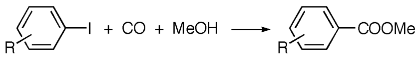
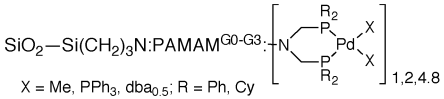
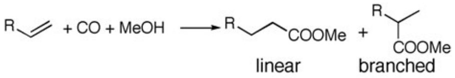
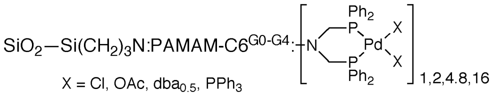
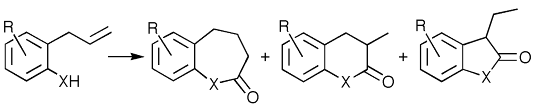
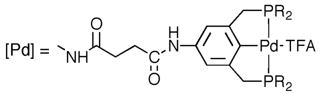
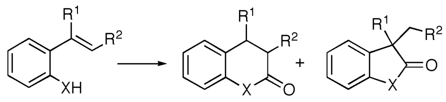
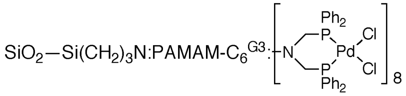
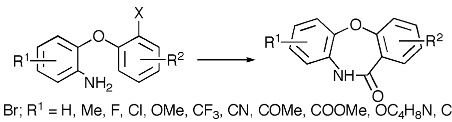
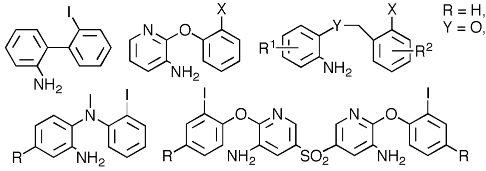
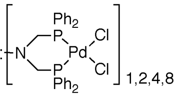
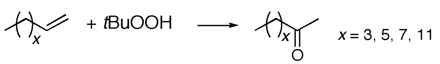
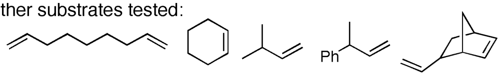
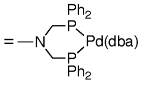
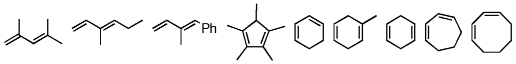
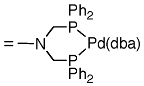
Entry	Substrates or reaction	Typical conditions	Dendritic catalysts
Heck reactions			
1[98]	 X = I, R = H, Y = Ph X = Br; R = Me, OMe, CO_2Me, NO_2, C_4H_3S; Y = Ph, CO_2Bu	120 °C, 48 h, NaOAc, DMF	
2[99]	 X = I; R = H; Y = Ph, CO_2Bu X = Br; R = Me, OMe, CO_2Me; Y = Ph, CO_2Bu, CO_2Me	Na_2CO_3, 140 °C; 0.03 mol% Pd (X = I) or 0.8 mol% Pd (X = Br)	
Carbonylation reactions			
3[94]	 R = Me, p-NO_2, p-Me, o, m, p-OMe, p-CF_3, p-I, p-Br, p-OH, p-MeCO, p-I-C_6H_4	100 °C, 100 psi CO, NEt_3, MeOH	 X = Me, PPh_3, $dba_{0.5}$; R = Ph, Cy
4[93]	 R = $CH_3(CH_2)_8$, $CH_3(CH_2)_6$, $CH_3(CH_2)_4$, Ph, o-Me-C_6H_4, p-Cl-C_6H_4, p-tBu-C_6H_4, p-(HOOC)-C_6H_4, p-MeO-C_6H_4	0.1–0.6 mol% Pd, 115 °C, 150 psi (CO), p-TsOH, THF or toluene/MeOH 1 : 1	 X = Cl, OAc, $dba_{0.5}$, PPh_3
5[100]	 X = O, R = H, 6-Me, 4–Cl	120 °C, 600 psi (CO/H_2 5 : 1), dppb, toluene	SiO_2—$Si(CH_2)_3N$:PAMAM$^{G0\text{-}G2}$:$[Pd]_{1,2,4}$ SiO_2—$Si(CH_2)_3N$:PAMAM-C6^{G1}:$[Pd]_2$ 
6[101]	Previous intramolecular carbonylation with X = O, NH; R = H, 6-Me, 4–Cl  X = O, R^1 = H, R^2 = Me; X = NH, R^1 = Me, R^2 = H	120 °C, 600 psi CO/H_2 (5 : 1), dppb, toluene	

Table 5 (*continued*)

Entry	Substrates or reaction	Typical conditions	Dendritic catalysts
7[102]	 X = I, Br; R^1 = H, Me, F, Cl, OMe, CF$_3$, CN, COMe, COOMe, OC$_4$H$_8$N, C$_5$H$_{10}$N R$_2$ = H, Me, F, Cl, COOMe Other substrates tested:  R = H, Cl, CF$_3$ Y = O, S	80 °C (X = I) or 120 °C (X = Br), 100 psi CO, NEt*i*Pr$_2$, toluene	SiO$_2$—Si(CH$_2$)$_3$N:PAMAM^{G0-G3}: 
Oxidation of alkenes			
8[96]	 Other substrates tested: 	0.5 mol% Pd, 55 °C, nonane	SiO$_2$—Si(CH$_2$)$_3$N(CH$_2$PPh$_2$)$_2$Pd(dba) SiO$_2$—Si(CH$_2$)$_3$N:PAMAM^{G1,G3,G4}:[Pd]$_{2,8,16}$ SiO$_2$—Si(CH$_2$)$_3$N:PAMAM-C6^{G1,G2}:[Pd]$_{2,4}$ SiO$_2^-$—Si(CH$_2$)$_3$N:PAMAM-C12^{G1,G2}:[Pd]$_{2,4}$ [Pd] = 
Hydrogenation of alkenes			
9[103]		14 psig H$_2$, 0.18 mol% Pd, 25 °C, MeOH	SiO$_2$—Si(CH$_2$)$_3$N(CH$_2$PPh$_2$)$_2$Pd(dba) SiO$_2$—Si(CH$_2$)$_3$N:PAMAM^{G1}:[Pd]$_2$ SiO$_2$—Si(CH$_2$)$_3$N:PAMAM-C6^{G1,G2}:[Pd]$_{2,4}$ SiO$_2$—Si(CH$_2$)$_3$N:PAMAM-C12^{G1,G2}:[Pd]$_{2,4}$ [Pd] = 

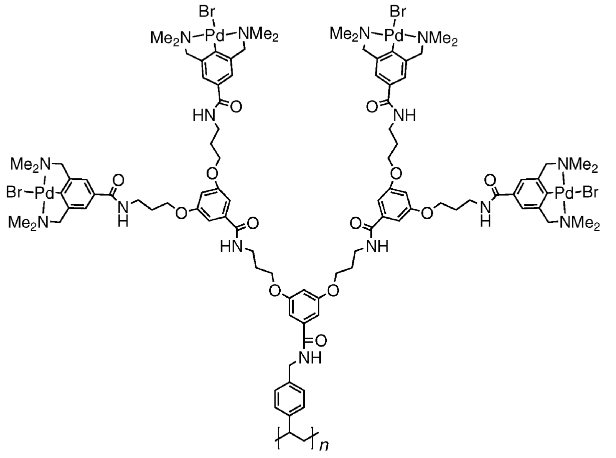


Fig. 16 A second-generation, polystyrene-based DenPol decorated with palladium NCN pincer complexes at the periphery.[67]

dropped drastically when the dendritic generation increased in the case of the short-chain PAMAM catalysts. Considering that this poor activity is due to the steric congestion of the dendrimer, long-chain PAMAM-C6 and -C12 first- and second-generation dendrimers were tested. Intriguingly, the G2-PAMAM-C6 and -C12 dendrimers gave the highest and lowest conversions, respectively, for the linear terminal olefins. These catalysts were found to be recyclable and the reaction scope was extended to other branched or cyclic olefins.

Recently, the selective hydrogenation of dienes to monoolefins has been studied using 1,3-cyclohexadiene and other cyclic and acyclic dienes (Table 5, entry 9).[103] In the case of 1,3-cyclohexadiene, the best selectivity was obtained with methanol as the solvent (73 to 88% for cyclohexene, depending on the catalyst, when complete conversion of the starting diene was achieved). The presence of small amounts of benzene in the product mixture may be an indication of traces of Pd particles within the catalyst matrix. The higher-generation catalysts displayed good recycling properties.

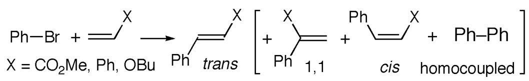
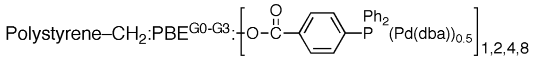
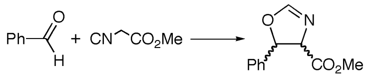
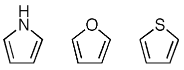
4.2 Dendritic catalysts supported on polymers (DenPols)

Dendronised polymers (DenPols) combine dendritic and polymeric segments and consist of a linear polymeric core to which dendrons are linked through their focal point (Fig. 16).[104] The ensemble has a high degree of structural rigidity due to steric congestion around the linear polymeric core, which makes it ideal for the immobilisation of catalytic sites. The first reaction tested with supported DenPols, reported by Arya, Alper and co-workers in 2000, was the hydroformylation of olefins with rhodium complexes on a PAMAM-polystyrene DenPol.[105]

Dahan and Portnoy have used dendronised polystyrene resins of generations zero to three as a convenient support for [(diphosphane)Pd(dba)] catalysts, which were found to be moderately active in the Heck reaction of bromobenzene with methyl acrylate (Table 6, entry 1).[106] A remarkable dendritic effect was observed in both activity and selectivity. Thus, the nondendritic G0 system gave conversions as low as 20% after 72 h at 80 °C, and significant amounts of biphenyl by-product resulting from the homocoupling of bromobenzene. In contrast, the G3 system produced the *trans* Heck coupling product quantitatively and selectively—a better result even than that observed under the same conditions with the related homogeneous catalysts. As precipitation of metallic palladium occurs during the reaction, the dendritic effect might be reflecting a reduced decomposition rate of the higher generation catalysts or an encapsulation effect of the DenPol on Pd nanoparticles that could be acting as the true catalyst.

Schlüter, van Koten and co-workers have used DenPols of up to the third generation and equipped with NCN-pincer palladium complexes at the periphery as catalysts for the aldol condensation of benzaldehyde with methyl isocyanoacetate (Table 6, entry 2).[67] The activity per palladium, although lower than in their homogeneous counterparts, was found to be almost independent of the generation of the dendrimer. This is in agreement with a model of active sites not interfering with each other and equally accessible to the substrates in the different generations, probably because the bulky nature of the

Table 6 Reactions catalysed by palladium dendrimers supported on polymers

Entry	Reaction/ substrates	Typical conditions	Dendritic catalysts
1[106]	**Heck reaction**  	2.5 mol% Pd, 80–120 °C, NEt_3, NMP	 $\text{Polystyrene–CH}_2\text{:PBE}^{\text{G0-G3}}\text{:}[\text{O–C(=O)–C}_6\text{H}_4\text{–PPh}_2(\text{Pd(dba)})_{0.5}]_{1,2,4,8}$
2[67]	**Aldol condensation**  	2.5 mol% Pd, NEt*i*Pr_2, CH_2Cl_2	Polystyrene–CH_2:{N(H)C(O)–C_6H_3-3,5-$(OCH_2CH_2–)_2$}$^{G1–G3}$: (N(H)C(O)–C_6H_2-3,5-$(CH_2NMe_2)PdBr_2)_{2,4,8}$ (see Fig. 16)
3[107]	**Hydrogenation**  	2.1 mol% Pd	Polystyrene–N:PAMAM$^{G1–G9}$:(N = CH–C_6H_4OH)$_x$ + $PdCl_2$

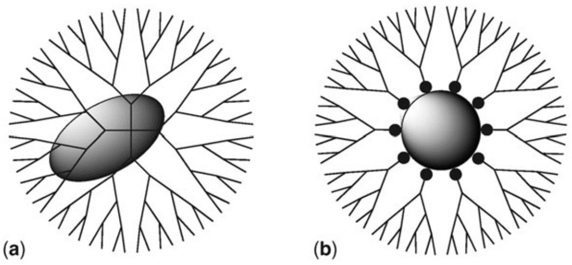


Fig. 17 Schematic representation of (a) a dendrimer-encapsulated nanoparticle (DEN) and (b) a nanoparticle-cored dendrimer (NCD).

NCN–Pd complex forces them to reside on the polymer surface. Finally, Feng and co-workers[107] have reported the hydrogenation of furan, pyrrole and thiophene with palladium dichloride and a second-generation PAMAM-polystyrene DenPol terminated with phenol groups (Table 6, entry 3). For the furan substrate, the catalyst could be recycled 10 times with conversions dropping from 0.96 in the first run to 0.58 in the last one.

5 Palladium nanoparticles

The synthesis of monodisperse and small (1–10 nm) metal nanoparticles[108] is important for many applications, including catalysis.[109–111] Because metal nanoparticles tend to aggregate, the use of stabilising agents such as polymers, surfactants, ionic compounds or ligands is necessary to control the particle size and prevent the aggregation of the nanoparticles and the associated loss of catalytic activity.[109,110,112] However, stabilisers diminish the accessibility of the nanoparticle surface to substrates and therefore produce a partial passivation of the catalyst. An ideal stabiliser should surround the nanoparticle to control the size and prevent agglomeration at the same time as being sufficiently porous to permit the passage of substrates and products between the reaction media and the metal surface. Dendrimers possess internal voids and channels and have been used in this context in two different strategies. In the first one (Fig. 17(a)), the metal nanoparticle is synthesised in the interior of the macromolecule and is stabilised by the outer part of the dendrimer. In the second case (Fig. 17(b)), the surface of the metal nanoparticle is protected by coordination of a ligand situated at the focal point of a dendron.

5.1 Dendrimer-encapsulated nanoparticles (DENs)

The encapsulation of metal nanoparticles inside a dendrimer was first demonstrated by the groups of Crooks[113] and Tomalia[114] in 1998, and has been the subject of several reviews.[12–14] DENs are generally prepared from PAMAM[113,114] or PPI[115,116] dendrimers containing interior amine groups that are able to complex metal ions.[117] The metal ions are sorbed into the dendrimer interior and subsequently reduced chemically to yield nanoparticles that remain encapsulated within the macromolecule. The number of metal ions preloaded in the dendritic structure predetermines the nanoparticle size, and the type and generation of the dendrimer limits the maximum metal loading possible to obtain true encapsulated nanoparticles stabilised by the outer branches of the host molecule. Thus, the dendritic macromolecule acts simultaneously as a template that controls the size of the nanoparticles and a stabiliser that prevents aggregation. DENs have an ensemble of characteristics derived from the unique architecture of dendrimers that are particularly advantageous for catalytic applications. First, the nanoparticles thus generated are, in many cases, nearly monodisperse, with sizes that are easily adjustable by controlling the metal preloading and usually in the range of 1 to 3 nm, and therefore contain an elevated ratio of metal atoms at the surface. Second, the dendrimer branches protect the nanoparticle from agglomeration whilst leaving a substantial part of the metal surface unpassivated and available to substrates. At the same time, they control the accessibility of the metal catalyst and, therefore, the selectivity of the catalytic process.[118,119] Third, the periphery of the dendrimer can be modified, either covalently[115,116,120] or non-covalently,[121,122] to dissolve the nanocomposite in the desired organic,[120,121,123] aqueous,[119,124] supercritical CO_2,[116] or fluorous medium.[115,122]

The encapsulation of bimetallic nanoparticles[125] in dendrimers can be carried out by metal reduction of dendrimers preloaded with a mixture of salts of the desired metals,[124,126–128] or, alternatively, the second metal can be introduced into a preformed DEN containing the other metal.[129] The first method is used to prepare bimetallic particles of the alloy type, whereas the second one is aimed at the preparation of particles formed by a core of the first metal surrounded by a shell of the second metal. Dendrimer-encapsulated metal nanoparticles can be also prepared from preformed DENs containing a less noble metal, which is completely displaced when introduced into a solution containing ions of the more noble metal.[130] It is possible to take advantage of DENs to facilitate the preparation of ligand-stabilised nanoparticles of controlled size by extraction of the preformed Pd nanoparticle with *n*-alkanethiols.[131]

Both PAMAM and PPI dendrimers are commercially available but, in order to select a dendrimer template, the differences in stability[132] and relative size should be considered (4.5 *vs*. 2.8 nm for G4 PAMAM and PPI, respectively).[13] An usual type of water-soluble palladium DENs are obtained from the hydroxy-terminated dendrimer $\text{PAMAM}^{G4}\text{:(OH)}_{64}$ preloaded with about 40 metal ions. The resulting water-soluble composites, which are stable for months in water,[118] contain a metal nanoparticle in the range of 1.3 to 1.7 (±0.3) nm encapsulated in a dendrimer of 4.5 nm, and usually give a good compromise between activity and stability.[133] The average distance between the dendrimer surface and the metal surface has been estimated[14] to be 0.7 ± 0.2 nm.[134] For the preparation of DENs within dendrimers terminated in NH_2 groups, the pH of the solution should be adjusted carefully to protonate the more basic exterior amines.[121]

Hydrogenation of alkenes. Palladium DEN catalysts were reported for the first time in 1999 by the group of Crooks, who used water-soluble $\text{PAMAM:OH} \subset (\text{Pd})_{40}$ composites for the hydrogenation of allyl alcohol and *N*-isopropyl acrylamide in water (Table 7, entry 1).[118]. The G4 DENs showed high catalytic activity but the TOF decreased very significantly for the higher-generation dendrimers with a more crowded periphery. The reduction of the hydrogenation rate upon

Table 7 Reactions catalysed by palladium dendrimer-encapsulated nanoparticles

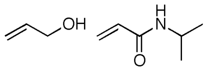
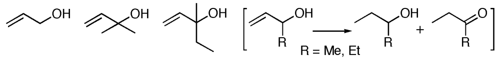
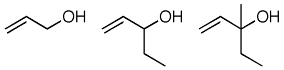
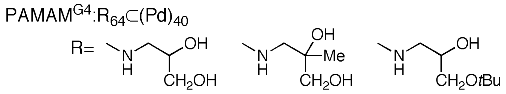
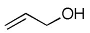
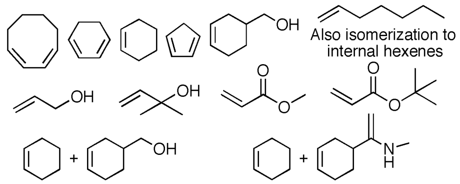
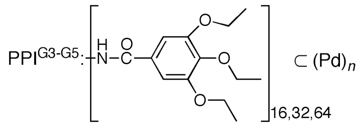
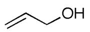
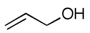
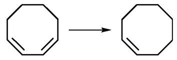
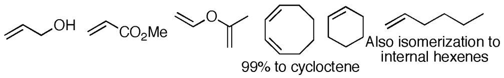
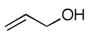
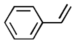
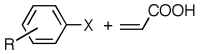
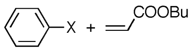
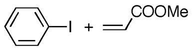
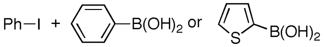
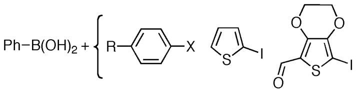
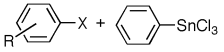
Entry	Substrates or reaction	Typical conditions	Dendritic catalysts
Hydrogenation of alkenes			
1[118]		[Pd] = 2 × 10^{-4} M, 1 atm H_2, 20 °C, H_2O	$PAMAM^{G4,G6,G8}$:$(OH)_{64,256,1024} \subset (Pd)_{40}$
2[119]		[Pd] = 2 × 10^{-4} M, 1 atm H_2, 25 °C, MeOH–H_2O (4 : 1)	$PAMAM^{G4,G6,G8}$:$(OH)_{64,256,1024} \subset (Pd)_{40}$
3[135]		[Pd] = 2 × 10^{-4} M, 1 atm H_2, r.t., MeOH–H_2O (1 : 1)	
4[137]			$PAMAM^{G6}$:$(OH)_{256} \subset (Pd)_{55,100,147,200,250}$
5[138]		[Pd] = 4 × 10^{-4} M, 1 atm H_2, 30 °C, toluene	
6[121]		[Pd] = 2 × 10^{-4} M, 1 atm H_2, 20 °C, toluene	$PAMAM^{G4}$:$[(NH_3)^+(OOC(CH_2)_{10}CH_3)^-]_{64} \subset (Pd)_n$
7[128,129]		[Pd + M] = 1–1.5 × 10^{-4} M, 1 atm H_2, ≈20 °C, H_2O	$PAMAM^{G4}$:$(OH)_{64} \subset$ (alloy-Pd_nPt_{40-n}), n = 0–40, $PAMAM^{G6}$:$(NH_2)_{140}(NH_2R^+)_{116} \subset [MM']$, $[MM']$ = alloy-Pd_nAu_{150-n}, n = 0–150, core/shell-$[Au_{55}](Pd_x)$ or Pd_{55+n}, n = 0–455
8[124,126]		[Pd + M] = 2.75–5.5 × 10^{-4} M, 1 atm H_2, 20 °C, EtOH–H_2O (4 : 1)	$PAMAM^{G4}$:$(OH)_{64} \subset [MM']_n$, $[MM']$ = Pd, Pt, Rh, alloy-Pd_xPt_y, Pd_xRh_y
9[122]		[Pd] = 10 × 10^{-6} M, 1 atm H_2, r.t., THF/FC-75 (2 : 1)	$PAMAM^{G4}$:$[(NH_3)^+(OOCR^F)^-]_{64} \subset (Pd)_n$, R^F = Perfluoropolyether chain
10[147]		[Pd] = 2 × 10^{-4} M, 1 atm H_2, 20 °C, H_2O	SBA-15–N:$PAMAM^{G0-G3}$:$(NH_2)_{2,4,8,16} \subset (Pd)_n$

Table 7 (*continued*)

Entry	Substrates or reaction	Typical conditions	Dendritic catalysts
11[116]		1–2.6 mol% Pd, 1 atm H_2, r.t., $scCO_2$	PPI^{G4}:$[C(O)CF(CF_3)\{OCF_2CF(CF_3)\}_3OCF_2CF_2CF_3]_{64} \subset (Pd)_n$
Heck reactions			
12[149]	 X = I, Br R = *o*-, *m*-, *p*-Br, *o*-, *m*-Me, *o*-COMe	0.025 mol% Pd, NaOAc, DMA or NEt_3, 140 °C	$PAMAM^{G4}$:$(OH)_{64} \subset (Pd)_{60}$
13[115]	 X = I, Br	3–5 mol% Pd, NEt_3, 90 °C, heptane/ benzene/FC-75	$PPI^{G3,G4}$:$[C(O)CF(CF_3)\{OCF_2CF(CF_3)\}_3O(CF_2)_2CF_3]_{32,64} \subset (Pd)_n$
14[116]		1–2.6 mol% Pd, NEt_3, 75 °C, $scCO_2$	
Stille and Suzuki cross-couplings			
15[133,150]		1.5 mol% Pd, reflux, Na_3PO_4, EtOH/H_2O	$PAMAM^{G2}$:$(OH)_{16} \subset (Pd)_5$, $PAMAM^{G3,G4}$:$(OH)_{32,64} \subset (Pd)_{10}$
16[151]	 X = I, R = H, COOEt X = Br, R = H	0.055 mol% Pd, K_2CO_3; 78 °C, EtOH (X = I) or 153 °C, DMF (X = Br)	$PAMAM^{G4}$:$(OH)_{64} \subset (Pd)_{60}$
17[152]	Ph–I + Ph–$B(OH)_2$	0.42–0.75 mol% Pd, NaOAc, 100 °C, CH_3CN/H_2O	PPI^{G1-G5}:$[(NH_3)^+]_{4,8,16,32,64} \subset (Pd)_n$
18[154]	 X = I, Br R = *o*-, *m*-, *p*-OH, *o*-, *m*-, *p*-COOH	0.1 mol% Pd (X = I) or 1 mol% Pd (X = Br); KOH, 23 °C, H_2O	$PAMAM^{G4}$:$(OH)_{64} \subset (Pd)_{40}$

dendrimer encapsulation is more important for larger substrates, as clearly shown in a subsequent report where allyl alcohol and four α-substituted derivatives were compared (Table 7, entry 2).[119] The steric control of the dendrimer periphery on the hydrogenation rate was corroborated by a series of experiments using fourth-generation PAMAM dendrimers with terminal groups producing various extents of steric crowding at the periphery (Table 7, entry 3).[135] These results demonstrated the possibility of performing size-selective catalysis by adjusting the "mesh" of the dendrimer nanofilter. Solvent-induced changes in the internal structure of dendrimers should also be considered, especially for lower generations with a less crowded periphery. The latter is suggested by the fact that hydrogenation rates of allyl alcohol for the G4 and G6 dendrimers were found to be significantly reduced in a MeOH/H_2O solvent mixture instead of only water, whereas the effect of changing the solvent was only very small for the G8 dendrimer.[119]

Particle size and morphology are recognised as important factors in nanocatalysis,[136] because of the potential changes in the electronic and geometric properties of the particle on the nanometre scale. It has been observed that the hydrogenation rates for allyl alcohol, at constant Pd concentrations, tend to increase as the particle size increases, even though the percentage of surface atoms it is expected to be smaller for bigger particles.[119,129] This effect has recently been studied in more detail with nanoparticles ranging from 1.3 to 1.9 nm (Table 7, entry 4).[137] In the 1.5–1.9-nm range, the hydrogenation rates correlate with the number of face atoms, whose proportion is large for bigger particles in this size range. However, the TOF values were almost invariant in the 1.3–1.5-nm size range. This was explained as a result of negative electronic effects compensating the geometrical effects.

The influence of the polar environment inside dendrimers in the specificity of the substrate using DENs was first noted by Kaneda and co-workers in a study measuring the initial hydrogenation rates of different substrates with palladium PPI catalysts,[138] where size effects of both the dendrimer and substrate similar to those described above were observed; for instance, a clear decrease of the hydrogenation rate was found with an increase of the ring size in cyclic conjugated dienes (Table 7, entry 5), especially with the bigger G5 dendrimer. This ring effect was absent when a Pd/C catalyst was used instead. However, a more complex mechanism of substrate recognition, not one based merely on molecular size, should be in operation in the specific hydrogenation of only the polar substrate, which was observed when equimolar mixtures of cyclohexene and 3-cyclohexene-1-methanol (or *N*-methyl-3-cyclohexene-1-carboxamide) were catalysed by the G5 DEN. The formation of hydrogen bonding between the polar substrate and the internal amino groups (as evidenced by NMR and FT-IR spectroscopy) might play an important role in its preferential penetration into the dendrimer and therefore in the remarkable specificity. However, the complete encapsulation of the metal nanoparticle within the dendrimer is also important, as shown by the lower specificity of the G3 dendrimer. The solubilisation of DENs in the organic solvent was achieved in this case by covalent attachment of terminal triethoxybenzamide groups. An alternative approach, developed by Chechik *et al.*, uses non-covalent binding of dodecanoic chains to the terminal amine groups of a PAMAM dendrimer (Table 7, entry 6).[121]

Indirect evidence for the true bimetallic nature of nanoparticles as PdPt[128] or PdAu[129] DEN alloys results from their ability to hydrogenate allyl alcohol at higher rates than physical mixtures of monometallic DENs with equal composition (Table 7, entry 7). In their optimal composition, these bimetallic composites are more active than Pd- or Pt-only DENs. The same effect is found in core/shell $[Au]_{55}(Pd)_x$ DENs composed of an inactive gold core of 55 atoms surrounded by a shell with a variable number of palladium atoms. For nanoparticles with a sufficiently sized Pd shell (≈250 atoms), TOF values were 30–38% higher than those obtained with similar Pd-only DENs. Bimetallic PdPt[126] and PdRh[124] PAMAM DENs have been used by Chung and Rhee for the partial hydrogenation of 1,3-cyclooctadiene to cyclooctene, with selectivities higher than 99% for complete conversion of the diene (Table 7, entry 8). A similarly high selectivity has been reported with Pd-only nanoparticles encapsulated in PPI dendrimers (Table 7, entry 5).[138] The Pd–Rh DENs were reused without loss of catalytic performance, and, again, the bimetallic catalysts were more active than physical mixtures of monometallic nanoparticles. It should be noted that similar enhancements have been observed with bimetallic PdPt,[139] PdRh and PdAu[140] nanoparticles stabilised by other methodologies.

The recovery and recycling of soluble catalysts can be facilitated by the use of biphasic fluorous/organic systems, where the efficiency of the separation relies on the preferential solubility of the catalyst in the fluorous phase.[141] Chechik and Crooks reported palladium DENs which were solubilised in the fluorous phase by non-covalent modification of the terminal amine groups with perfluoropolyethers and used for the hydrogenation of several substrates (Table 7, entry 9).[122] In one case, the catalyst was recycled 12 times without appreciable loss of catalytic activity. Another way to enable easy recovery of nanoparticles is by immobilising them on solid supports. DENs have been used as precursors of mono-[142,143] and bimetallic[144] supported nanoparticles in order to try to take advantage of the size regularity and compositional fidelity of the original nanoparticles, although removal of the dendrimer template by calcination is always associated with some degree of aggregation.[143,145] In a different approach connected with the work of Alper on dendritic catalysts supported on silica (see Section 4), Zhu, Qiu and co-workers[146] and Jiang and Gao[147] have independently reported the encapsulation of Pd nanoparticles into PAMAM dendrimers constructed on the surface of the channels in amine-functionalised SBA-15 (Fig. 18). The latter group showed that these supported nanoparticles retain their activity after several recycling runs (Table 7, entry 10).[147]

Heck reactions. Palladium nanoparticles catalyse effectively carbon–carbon coupling reactions, such as the Heck reaction.[111,148] Christensen and co-workers, for example, have studied the reaction between several haloarenes and acrylic acid in the presence of palladium nanoparticles encapsulated in a PAMAM dendrimer (Table 7, entry 12).[149] Under the

Fig. 18 DENs supported on the surface of the channels in SBA-15.[146,147]

conditions tested, the catalyst was unable to couple aryl chlorides, a modest yield of 35% was obtained with bromobenzene, but iodoarenes reacted effectively at low Pd loadings (0.025 mol%) with yields ranging from 67 to 92%. The catalyst could be recycled, although the efficiency dropped drastically and formation of Pd black was observed upon reuse. Yeung and Crooks have studied the reaction of phenyl halides and *n*-butyl acrylate in an organic/fluorous biphasic system using DENs decorated externally with perfluoropolyether chains (Table 7, entry 13).[115] Again, only the aryl iodide produced high yields and the catalytic activity decreased significantly upon successive recovery/catalytic cycles, even though Pd precipitation or leaching were not observed. As no deactivation was observed upon storage or after 24 h refluxing in the reaction solvent, it was suggested that deactivation occurs by changes in the morphology of the Pd nanocluster surface brought about by redox cycling of the Pd atom during the Heck reaction. Perfluoropolyether chains also provide solubility in supercritical carbon dioxide ($scCO_2$). Using the same type of palladium DENs, Crooks, Johnston *et al.* reported the first example of catalysis in $scCO_2$ with soluble metal nanoparticles (Table 7, entry 14).[116] The utility of this system to catalyse reactions in $scCO_2$ was demonstrated in the hydrogenation of styrene to ethylbenzene (Table 7, entry 11) and in the Heck coupling reaction of iodobenzene and methyl acrylate (Table 7, entry 14). It is worth mentioning that only the 1,1-coupled product (methyl 2-phenylacrylate) was obtained in this reaction, whereas the same reaction carried out with the same catalyst but in an organic/fluorocarbon solvent system gave only the *trans*-coupled product (butyl *trans*-formylcinnamate).

Stille and Suzuki cross-coupling reactions. Li and El-Sayed have compared the stability of Pd nanoparticles stabilised by PAMAM:OH dendrimers or polymers, as measured by their tendency to give Pd black during the reaction of iodobenzene and phenylboronic or 2-thienylboronic acid in aqueous media (Table 7, entry 15).[133] The G4 DEN was found to be a better stabiliser but a worse catalyst than the G3 and G2 nanocomposites, thus showing how the strong encapsulation of Pd particles within dendrimers results in a loss of catalytic activity. During the study of this reaction, an increase in the size of the metal nanoparticles encapsulated in the G4 dendrimer was observed after the first and second catalytic cycles.[150] It was proposed that the rate of formation of the complete nanoparticle is slow due to the fact that G4 PAMAM:OH is a strong encapsulator, which results in a high concentration of metal in solution. As the presence of phenylboronic acid inhibits the particle growth, it was suggested that it acts as a capping agent. Thus, the reaction mechanism must involve the adsorption of phenylboronic acid onto the surface of the nanoparticle, which subsequently reacts with the iodobenzene in solution. Christensen and co-workers have found that the G4 PAMAM:OH dendrimer becomes an efficient Suzuki catalyst if larger Pd loadings per macromolecule are used (60 atoms of Pd *vs.* 10 used by El-Sayed; Table 7, entry 16).[151] Iodo and bromo (but not chloro) arenes, including 2-iodothiophenes, were found to be efficiently coupled with low palladium loadings (0.055 mol%), whereas El-Sayed's composites were inactive and gave important amounts of palladium deposition when trying to couple iodobenzene with 2-thienylboronic acid.[133] It was proposed that Christensen's composites consist of palladium nanoparticles stabilised by the dendrimer (see below) rather than particles encapsulated in the dendrimer. In any case, the catalyst solutions were stable for months.[151] Recently, Lemo *et al.* have observed that Pd nanoparticles encapsulated in low-generation PPI dendrimers are more active in the coupling of iodobenzene and phenylboronic acid but are also more prone to the precipitation of Pd black (Table 7, entry 18).[152]

Several examples are known of the Stille cross-coupling reaction in water,[153] although typical conditions include the use of high temperatures. Garcia-Martinez *et al.* have obtained high yields (70–100%) in the aqueous-phase reaction of phenol or benzoic acid derivatives (bromo and iodo) with trichlorophenylstannane at room temperature using modest Pd loadings (0.1 to 1 mol% Pd), except for *ortho*-iodobenzoic acid, which poisoned the catalyst (Table 7, entry 17).[154] The aggregation of Pd nanoparticles during the catalytic reaction was almost inappreciable and the catalyst remained active after completion of the reaction, whereas precipitation of Pd black and a decrease in product yield was observed when the reaction was carried out at more elevated temperatures (>50 °C).

Non-encapsulated metal-dendrimer composites. The group of Esumi has used a different strategy for dendrimer protection in which the metal is not encapsulated in the dendritic interior but coordinated at the surface of the PAMAM[155] or PPI[156] dendrimers. Palladium monometallic[156] and Pd/Pt or Pd/Au bimetallic[157] nanoparticles thus stabilised were studied in the reduction of 4-nitrophenol with sodium borohydride. The bimetallic nanocomposites were recently used as catalysts for scavenging 1,1-diphenyl-2-picrylhydrazyl (DPPH) radicals.[158]

Hyperbranched polymers. Several reports have appeared using hyperbranched polyglycerols, which are synthetically accessible with narrow molecular weight distributions,[159] to stabilise palladium nanoparticles. Traditional encapsulating dendrimers generally contain nitrogen donor atoms that enable initial coordination of metal salt precursors but at the same time block active sites in catalysis. In contrast, polyglycerols contain weakly coordinating OH functions. The applicability of these polymer-encapsulated Pd nanoparticles has been examined in the hydrogenation of cyclohexene in both batch[160] and continuously operated membrane reactors.[161] More recently, palladium nanoparticles encapsulated into optically active hyperbranched polyglycerols have been tested in the Heck reaction of 2,3-dihydrofuran and phenyl triflate, resulting in the formation of 2-phenyl-2,3-dihydrofuran in moderate yields but with no enantiomeric excess.[162] Russo *et al.* have used hyperbranched polyamides (aramids) to stabilise Pd nanoclusters[163] which were applied, in collaboration with Bianchini, to the hydrogenation of unsaturated substrates either in non-polar or polar solvents. In most cases, the catalyst proved to be efficient, selective and recyclable, yet the nature of the solvent affected remarkably the catalysis outcome in terms of both activity and selectivity.[164] The catalyst was recyclable by filtration up to three times, maintaining the activity and selectivity and without apparent leaching.

5.2 Nanoparticle-cored dendrimers (NCDs)

Ligands bearing dendryl substituents, such as those discussed in Section 3 of this review, can be used advantageously to replace simple capping ligands (more usually, thiols, amines or phosphanes)[109] in the preparation and stabilisation of metal nanoparticles.[117,165–168] In sharp contrast to small molecules, only a very limited number of dendritic ligands have room around the nanoparticle core due to their sterically demanding dendritic structure. Thus, a substantial fraction of the metal surface area is available for participation in catalytic reactions without the need for previous ligand dissociation. Godipas *et al.* have reported the synthesis of palladium nanoparticles stabilised by thiol ligands bound to the focal-point of Fréchet-type poly(benzyl ether) dendrons (Fig. 19).[166] The resulting palladium NCD nanoparticles have a relatively wide size distribution (1–5 nm) compared to DENs and are made up of a metal core with an average diameter of 2.0 nm and containing about 300 palladium atoms that is surrounded by 14 third-generation ligands, which means that 91% of the Pd surface should be unpassivated. Despite that, the nanoparticles were found to be very stable and did not exhibit discernible aggregation after prolonged periods. No side products were observed in model Heck and Suzuki reactions (Table 8, entry 1), and the turnover numbers and frequencies were high, although yields were moderate because of the low Pd loadings (0.002 mol%). The catalyst was found to be soluble in toluene, the solvent used in the Heck reaction, but insoluble in ethanol, where the Suzuki reaction was carried out. Hydrogenations were unsuccessful, probably because the ligand carbon–sulfur bonds undergo hydrogenolysis, which leads to metal precipitation. Recently, Wu *et al.* have used dendronised phosphanes instead of thiols as capping agents and have obtained high efficiency in both Suzuki and hydrogenation reactions (Table 8, entries 2 and 3, respectively).[167] Suzuki reactions of aryl iodides and bromides occurred with low Pd loadings (0.06 mol%) and yields ranging from 86 to 100%. Even aryl chlorides gave good yields, although higher Pd loadings were required (2 mol%). The catalysts were recovered by precipitation with methanol and reused eight times without any loss of activity in the first four runs. The leaching of palladium in the firsts runs was of the order of a few parts per million.

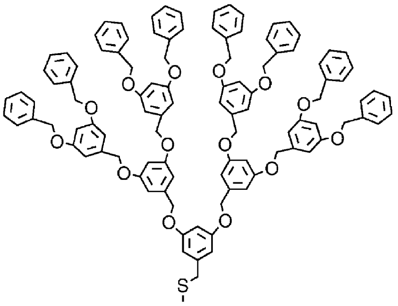
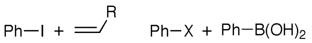
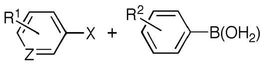
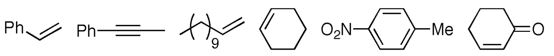
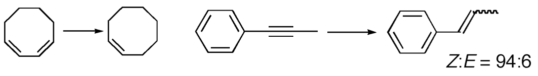


Fig. 19 Thiol ligand employed for the preparation of palladium NCDs.[166]

Table 8 Reactions catalysed by NCDs

Entry	Substrates or reaction	Typical conditions	Dendritic catalysts
Heck and Suzuki C–C couplings			
1[166]	 X = Br, I; R = COOEt, Ph	0.02 mol% Pd, NEt_3, reflux, toluene (Heck) or 40% ethanol (Suzuki)	[Pd]–[S:PBE^{G3}:$(CH_2Ph)_8$]$_n$, (See Fig. 19)
2[167]	 Z = C; X = Cl, Br, I; R^1 = H, *p*-OH, *p*-COMe, *m*-, *p*-COOMe, *o*-, *m*-NO$_2$, *o*-, *p*-CHO, *o*-, *p*-CH$_3$; R^2 = H, *p*-CH$_3$, *p*-COMe, *p*-F Z = N, X = 2,3–Br, 2,3–Cl , R^1 = R^2 = H	0.06 mol% Pd (X = Br, I) or 2 mol% Pd (X = Cl); K_3PO_4, reflux, dioxane	[Pd]–[PPh$_2$:PBE$^{G1–G3}$:$(CH_2Ph)_{2,4,8}$]$_n$
Hydrogenation of alkenes			
3[167]		0.5 mol% Pd, 5–30 atm H_2, 40 °C, $CHCl_3$	[Pd]–[PPh$_2$:PBE^{G3}:$(CH_2Ph)_8$]$_n$
4[168]		1.6 × 10^{-3} M, r.t., CH_2Cl_2	[PdM]–[py-4-CH$_2$N: PAMAM$^{G1,\ G2}$:R$_{4,8}$], [MM″] = Pd, Pd$_x$Pt$_y$, Pt R = –CH$_2$CH$_2$CONH(CH$_2$)$_5$CH$_3$

Bimetallic PdPt nanoparticles stabilised with pyridine-PAMAM ligands have been studied as catalysts for the selective hydrogenation of dienes (Table 8, entry 4).[168] Hydrogenation of 1,3-cyclooctadiene yielded cyclooctene exclusively without formation of any insoluble metal aggregate. The activity of the bimetallic nanoparticles was found to be higher than that found for physical mixtures of monometallic nanoparticles of equal composition. In agreement with parallel observations made in the preceding examples, a notable increase in the activity (1.9 times) was observed on going from G1-Pd_4Pt to G2-Pd_4Pt: an increase in dendron generation provides a less congested Pd surface, which facilitates substrate access to the active sites. The catalyst, which could be separated using a DMF/*n*-heptane thermomorphic system,[59] was found to retain its activity after four recycling cycles. An extremely high selectivity for the monoene was also achieved in the hydrogenation of 1-phenyl-1-propyne, which afforded 1-phenyl-1-propene in 94% yield ($Z : E = 94 : 6$).

6 Conclusions and outlook

During the last decade, palladium dendrimers have been used as (a) soluble systems in homogeneous catalysis, (b) spacers for catalyst immobilization on silica or polymers, and (c) precursors for the synthesis and stabilisation of mono- and bimetallic palladium nanoparticles. Carbon–carbon bond-formation and hydrogenation reactions are the main focus of research in this area, with a particular emphasis on the catalyst recyclability and the influence of the dendritic architecture on the catalytic outcome.

Palladium complexes have been grafted at both the periphery and core of dendrimers, although the former approach has been largely predominant in homogeneous catalysis driven by the idea of a better accessibility of the active sites. In fact, peripherally modified dendrimers and monometallic complexes often show a similar behaviour in terms of activity, stability or selectivity, thus showing that the dendritic metal catalysts are probably acting in these cases as independent sites, with a similar accessibility to the substrates in both types of catalysts. In other cases, the specific catalytic profiles observed for peripherally modified dendrimers are generally ascribed to the consequences of the physical constraint of the metal complexes at the limited surface of the macromolecule in terms of steric congestion, local concentration of metals and ligands, or interaction between metal centres. Surface congestion tends to decrease the activity of high-generation dendrimers but presumably has an important role in the selectivity by restricting the conformations available. The effect of the dendrimer on the stability of the palladium species is contradictory, and both stabilising and destabilising effects have been observed. This illustrates the importance of the design of the dendritic catalyst. In this review, several examples have been discussed in which a small modification of the dendritic molecule stabilizes the Pd catalyst significantly. When the catalyst deactivation is favoured by the interaction between metal centres, the generation number, the core or branch multiplicity, or the segment length can be modified to diminish the metal density at the dendritic surface. However, it is also important to note that the interaction between metal complexes located at the dendritic surface can be avoided through the use, for instance, of more rigid dendrimers, which shows the importance of the appropriate choice of dendrimer backbone. In the same sense, ligands can cause specific effects on the dendrimer catalysts by modifying, for example, the surface congestion or the arm back-folding.

Enhanced stabilities are more generally associated with dendrimers in which the palladium centres are encapsulated within the dendrimer interior. In fact, it is somewhat surprising that only a few studies have been devoted to the catalytic behaviour of core palladium dendrimers. Core dendrimers are *a priori* more suited to the observation of site-isolation effects originating from the steric hindrance or dipolar characteristics of the dendrimer branches. Small dendritic substituents might be sufficient for the stabilisation of Pd catalysts and, even if the activity is lowered by the encapsulation effect of the substituent, this can be compensated by the longer durability of the catalyst. Moreover, the peripheral groups of encapsulated catalysts can be varied to obtain a better solubility in the desired solvent and this enhanced solubility should favour fast kinetics. The use of dendritic ligands to solubilise Pd complexes in non-conventional solvents such as water is essentially unexplored. In contrast to core systems, the solubility of periphery-modified dendrimers is controlled by the metal groups and the scarce solubility of the higher-generation molecules is often a drawback.

If the catalytic behaviour of a monometallic catalyst is modulated by the electronic and steric properties of the first coordination sphere constituted by the ligands, the specific behaviour of a dendritic catalyst depends additionally on the secondary dendritic structure. However, this secondary structure is often far from being perfectly defined, at least in low-generation dendrimers containing flexible arms. Moreover, the conformational dynamism can be significantly altered by the solvent, the ionic charge of the metal complex, the pH, or the ionic strength of the solution, which is changed for instance by salts formed in some C–C reactions. The presence of catalytic sites with slightly different abilities to interact with substrates should be considered in the interpretation of the catalytic results, and more theoretical and experimental studies are needed in this direction.

Even though they have a similar catalytic behaviour, dendrimers differ from mononuclear complexes in their nanoscopic dimensions, which enable separation by membranes and use in continuous-flow reactors. However, recuperation and reuse of the palladium catalysts has been achieved in most cases by precipitation, or by using thermomorphic systems. Although the latter methods are not always *directly* related to the intrinsic characteristics of the dendrimer, and in some cases the same results might be obtained with monometallic complexes, the interest in these studies also lies in the information extracted about the nature and stability of the recuperated catalysts. Metal leaching and catalyst deactivation are the most common problems for catalyst recovery.

A priori, non-covalent connections between the dendritic support and the anchoring ligand are more suited to metal or dendrimer leaching, although it has been demonstrated that these interactions can be sufficiently strong for the effective retention of the non-covalently functionalized dendrimers in continuous-flow membrane reactors. Of course, the possibility of the catalysis occurring in the dissociated metal complexes should not be ruled out, although the changes in catalyst activity, selectivity or stability observed in several examples provide evidence that supports the proposal that the catalysis occurs under the dendrimer influence.

In contrast to dendrimers, hyperbranched molecules are randomly branched but easily accessible by controlled one-pot reactions that can produce materials with a narrow dispersion of molecular weights. Hyperbranched polymers compete favourably with dendrimers when size effects are considered, as for continuous-flow uses, and no special advantages are obtained from the well-defined dendritic structure in terms of enhanced activity or selectivity. Alternatively, star-shaped polymetallic complexes with rigid cores share the well-defined structure of dendrimers and can also be efficiently retained by membranes.

The main advantage of the support of palladium dendrimers on silica or polymers lies in the easy separation of the catalyst. The large disparity found in the structural perfection of these materials complicates the evaluation of the dendrimer effect in the catalysis outcomes. However, interesting findings can result from enhancements in the synthetic procedures and the use of crystalline silicas of adequate pore size to minimize crowding problems associated with the irregular nature of amorphous silica.

Their controlled size and narrow dispersion make dendrimer-encapsulated nanoparticles excellent models for fundamental studies. Encapsulation can serve to control the selectivity of the reactions, whereas the modification of the end-groups can tune the solubility. Bimetallic palladium-platinum, -gold and -rhodium alloy or core–shell nanoparticles have been prepared. The introduction of dendritic ligands as stabilisers in nanoparticle-core dendrimers is of special interest because it focuses on the precise molecular definition of catalytic materials at the same time as minimizing the passivation of the metal surface.

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References

1 (*a*) *Dendrimers and Other Dendritic Polymers*, ed. J. M. J. Fréchet and D. A. Tomalia, Wiley-VCH, New York, 2002; (*b*) *Dendrimers and Dendrons: Concepts, Syntheses, Applications*, ed. G. R. Newkome, C. N. Moorefield and F. Vögtle, Wiley-VCH, Weinheim, 2001.

2 Several reviews on metallodendrimers: (*a*) C. Gorman, *Adv. Mater.*, 1998, **10**, 295–309; (*b*) M. A. Hearshaw and J. R. Moss, *Chem. Commun.*, 1999, 1–8; (*c*) G. R. Newkome, E. F. He and C. N. Moorefield, *Chem. Rev.*, 1999, **99**, 1689–1746; (*d*) F. J. Stoddart and T. Welton, *Polyhedron*, 1999, **18**, 3575–3591; (*e*) I. Cuadrado, M. Morán, C. M. Casado, B. Alonso and J. Losada, *Coord. Chem. Rev.*, 1999, **193–195**, 395–445; (*f*) M. A. Hearshaw, A. T. Hutton, J. R. Moss and K. J. Naidoo, *Adv. Dendritic Macromol.*, 1999, **4**, 1–60; (*g*) H. J. van Manen, F. C. J. M. van Veggel and D. N. Reinhoudt, *Top. Curr. Chem.*, 2001, **217**, 121–162; (*h*) K. Onitsuka and S. Takahashi, *Top. Curr. Chem.*, 2003, **228**, 39–63; (*i*) O. Rossell, M. Seco and I. Angurell, *C. R. Chim.*, 2003, **6**, 803–817; (*j*) P. A. Chase, R. Gebbink and G. van Koten, *J. Organomet. Chem.*, 2004, **689**, 4016–4054.

3 J. P. Majoral, A. M. Caminade and R. Laurent, in *Metal-Containing and Metallosupramolecular Polymers and Materials*, ed. U. S. Schubert, G. R. Newkome and I. Manners, Oxford University Press, 2006, pp. 230–243.

4 J. M. J. Fréchet, *J. Polym. Sci., Part A: Polym. Chem.*, 2003, **41**, 3713–3725.

5 (*a*) G. E. Oosterom, J. N. H. Reek, P. C. J. Kamer and P. W. N. M. van Leeuwen, *Angew. Chem., Int. Ed.*, 2001, **40**, 1828–1849; (*b*) D. Astruc and F. Chardac, *Chem. Rev.*, 2001, **101**, 2991–3023; (*c*) R. Kreiter, A. W. Kleij, R. J. M. Klein Gebbink and G. van Koten, *Top. Curr. Chem.*, 2001, **217**, 163–199; (*d*) J. N. H. Reek, S. Arévalo, R. van Heerbeek, P. C. J. Kamer and P. W. N. M. van Leeuwen, *Adv. Catal.*, 2006, **49**, 71–151; (*e*) D. Méry and D. Astruc, *Coord. Chem. Rev.*, 2006, **250**, 1965–1979.

6 (*a*) R. van Heerbeek, P. C. J. Kamer, P. W. N. M. van Leeuwen and J. N. H. Reek, *Chem. Rev.*, 2002, **102**, 3717–3756; (*b*) G. P. M. van Klink, H. P. Dijkstra and G. van Koten, *C. R. Chim.*, 2003, **6**, 1079–1085.

7 A. Dahan and M. Portnoy, *J. Polym. Sci., Part A: Polym. Chem.*, 2005, **43**, 235–262.

8 B. Helms and J. M. J. Fréchet, *Adv. Synth. Catal.*, 2006, **348**, 1125–1148.

9 L. J. Twyman, A. S. H. King and I. K. Martin, *Chem. Soc. Rev.*, 2002, **31**, 69–82.

10 A. M. Caminade, V. Maraval, R. Laurent and J. P. Majoral, *Curr. Org. Chem.*, 2002, **6**, 739–774.

11 (*a*) B. Romagnoli and W. Hayes, *J. Mater. Chem.*, 2002, **12**, 767–799; (*b*) Y. Ribourdouille, G. D. Engel and L. H. Gade, *C. R. Chim.*, 2003, **6**, 1087–1096.

12 (*a*) R. M. Crooks, M. Q. Zhao, L. Sun, V. Chechik and L. K. Yeung, *Acc. Chem. Res.*, 2001, **34**, 181–190; (*b*) R. W. J. Scott, O. M. Wilson and R. M. Crooks, *J. Phys. Chem. B*, 2005, **109**, 692–704.

13 R. M. Crooks, B. I. Lemon, L. Sun, L. K. Yeung and M. Q. Zhao, *Top. Curr. Chem.*, 2001, **212**, 81–135.

14 Y. Niu and R. M. Crooks, *C. R. Chim.*, 2003, **6**, 1049–1059.

15 (*a*) J. N. H. Reek, D. de Groot, G. E. Oosterom, P. C. J. Kamer and P. W. N. M. van Leeuwen, *Rev. Mol. Biotechnol.*, 2002, **90**, 159–181; (*b*) M. Dasgupta, M. B. Peori and A. K. Kakkar, *Coord. Chem. Rev.*, 2002, **233–234**, 223–235; (*c*) D. Astruc, *C. R. Chim.*, 2005, **8**, 1101–1107; (*d*) D. Astruc, K. Heuzé, S. Gatard, D. Méry, S. Nlate and L. Plault, *Adv. Synth. Catal.*, 2005, **347**, 329–338.

16 Non-covalent immobilization of homogeneous catalysts in soluble organic supports has been revised in: R. van de Coevering, R. J. M. Klein Gebbink and G. van Koten, *Prog. Polym. Sci.*, 2005, **30**, 474–490.

17 *Dendrimer Catalysis*, ed. L. H. Gade, Springer, Berlin, 2006.

18 (*a*) *Handbook of Palladium-Catalysed Organic Reactions*, ed. J. L. Malleron, J. C. Fiaud and J. Y. Legros, Academic Press, London, 1997; (*b*) *Handbook of Organopalladium Chemistry for Organic Synthesis*, ed. E. Negishi and A. de Meijere, Wiley-Interscience, New York, 2002; (*c*) *Palladium Reagents and Catalysts New Perspectives for the 21st Century*, ed. J. Tsuji, Wiley, New York, 2004; (*d*) *Palladium in Organic Synthesis*, ed. J. Tsuji, Springer, Berlin/Heidelberg, 2005.

19 J. W. J. Knapen, A. W. van der Made, J. C. de Wilde, P. W. N. M. van Leeuwen, P. Wijkens, D. M. Grove and G. van Koten, *Nature*, 1994, **372**, 659–663.

20 (*a*) D. A. Tomalia, H. Baker, J. Dewald, M. Hall, G. Kallos, S. Martin, J. Roeck, J. Ryder and P. Smith, *Polym. J.*, 1985, **17**, 117–132; (*b*) D. A. Tomalia, H. Baker, J. Dewald, M. Hall, G. Kallos, S. Martin, J. Roeck, J. Ryder and P. Smith, *Macromolecules*, 1986, **19**, 2466–2468.

21 E. Esfand and D. A. Tomalia, in *Dendrimers and Other Dendritic Polymers*, ed. J. M. J. Fréchet and D. A. Tomalia, Weinheim, VCH, 2002, p. 587.

22 (*a*) E. M. M. de Brabander-van den Berg and E. W. Meijer, *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 1308–1311; (*b*) M. H. P.

van Genderen, E. M. M. de Brabander-van den Berg and E. W. Meijer, *Adv. Dendritic Macromol.*, 1999, **4**, 61–105.

23 (*a*) A. W. van der Made and P. W. N. M. van Leeuwen, *J. Chem. Soc., Chem. Commun.*, 1992, 1400–1401; (*b*) A. W. van der Made, P. W. N. M. van Leeuwen, J. C. de Wilde and R. A. C. Brandes, *Adv. Mater.*, 1993, **5**, 466–468; (*c*) L. L. Zhou and J. Roovers, *Macromolecules*, 1993, **26**, 963–968; (*d*) C. Schlenk and H. Frey, *Monatsh.Chem.*, 1999, **130**, 3–14; (*e*) H. Frey and C. Schlenk, *Top. Curr. Chem.*, 2000, **210**, 69–129.

24 (*a*) J. P. Majoral and A. M. Caminade, *Top. Curr. Chem.*, 1998, **197**, 79–124; (*b*) A. M. Caminade and J. P. Majoral, *Acc. Chem. Res.*, 2004, **37**, 341–348; (*c*) A. M. Caminade and J. P. Majoral, *Coord. Chem. Rev.*, 2005, **249**, 1917–1926; (*d*) U. O. Turrin, B. Donnadieu, A. M. Caminade and J. P. Majoral, *Z. Anorg. Allg. Chem.*, 2005, **631**, 2881–2887; (*e*) A. M. Caminade, A. Maraval and J. P. Majoral, *Eur. J. Inorg. Chem.*, 2006, 887–901.

25 (*a*) C. Hawker and J. M. J. Fréchet, *J. Chem. Soc., Chem. Commun.*, 1990, 1010–1013; (*b*) C. J. Hawker and J. M. J. Frechet, *J. Am. Chem. Soc.*, 1990, **112**, 7638–7647.

26 A. Miedaner, C. J. Curtis, R. M. Barkley and D. L. DuBois, *Inorg. Chem.*, 1994, **33**, 5482–5490.

27 H. Brunner, in *Applied Homogeneous Catalysis with Organometallic Compounds*, ed. B. Cornils and W. A. Herrmann, Wiley-VCH, Weinheim, Second, revised edn, 2002, vol. 1, pp. 195–122.

28 T. Mizugaki, M. Ooe, K. Ebitani and K. Kaneda, *J. Mol. Catal. A: Chem.*, 1999, **145**, 329–333.

29 C. F. Li, D. X. Li, Z. J. Zhang and S. Y. Feng, *Chin. Chem. Lett.*, 2005, **16**, 1389–1392.

30 (*a*) S. D. Ittel, L. K. Johnson and M. Brookhart, *Chem. Rev.*, 2000, **100**, 1169–1204; (*b*) S. Mecking, *Coord. Chem. Rev.*, 2000, **203**, 325–351; (*c*) W. Kaminsky and M. Arndt-Rosenau, in *Applied Homogeneous Catalysis with Organometallic Compounds*, ed. B. Cornils and W. A. Herrmann, Wiley-VCH, Weinheim, Second revised edn, 2002, vol. 1, pp. 213–230; (*d*) V. C. Gibson and S. K. Spitzmesser, *Chem. Rev.*, 2003, **103**, 283–316.

31 G. Smith, R. Chen and S. Mapolie, *J. Organomet. Chem.*, 2003, **673**, 111–115.

32 (*a*) J. M. Benito, E. de Jesús, F. J. de la Mata, J. C. Flores and R. Gómez, *Chem. Commun.*, 2005, 5217–5219; (*b*) J. M. Benito, E. de Jesús, F. J. de la Mata, J. C. Flores, R. Gómez and P. Gómez-Sal, *Organometallics*, 2006, **25**, 3876–3887.

33 J. M. Benito, E. de Jesús, F. J. de la Mata, J. C. Flores and R. Gómez, *Organometallics*, 2006, **25**, 3045–3055.

34 (*a*) T. V. RajanBabu, N. Nomura, J. Jin, B. Radetich, H. Park and M. Nandi, *Chem. Eur. J.*, 1999, **5**, 1963–1968; (*b*) P. W. Jolly and G. Wilke, in *Applied Homogeneous Catalysis with Organometallic Compounds*, ed. B. Cornils and W. A. Herrmann, Wiley-VCH, Weinheim, Second, revised edn, 2002, vol. 3, pp. 1164–1189.

35 (*a*) N. J. Hovestad, E. B. Eggeling, H. J. Heidbüchel, J. T. B. H. Jastrzebski, U. Kragl, W. Keim, D. Vogt and G. van Koten, *Angew. Chem., Int. Ed.*, 1999, **38**, 1655–1658; (*b*) E. B. Eggeling, N. J. Hovestad, J. T. B. H. Jastrzebski, D. Vogt and G. van Koten, *J. Org. Chem.*, 2000, **65**, 8857–8865.

36 M. Benito, O. Rossell, M. Seco, G. Muller, J. I. Ordinas, M. Font-Bardia and X. Solans, *Eur. J. Inorg. Chem.*, 2002, 2477–2487.

37 L. I. Rodríguez, O. Rossell, M. Seco, A. Grabulosa, G. Muller and M. Rocamora, *Organometallics*, 2006, **25**, 1368–1376.

38 S. Bräse and A. de Meijere, in *Metal-Catalyzed Cross-Coupling Reactions*, ed. A. de Meijere and F. Diederich, Wiley-VCH, Weinheim, Second, revised edn, 2004, vol. 1, pp. 217–315.

39 M. T. Reetz, G. Lohmer and R. Schwickardi, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 1526–1529.

40 T. R. Krishna and N. Jayaraman, *Tetrahedron*, 2004, **60**, 10325–10334.

41 D. P. Catsoulacos, B. R. Steele, G. A. Heropoulos, M. Micha-Screttas and C. G. Screttas, *Tetrahedron Lett.*, 2003, **44**, 4575–4578.

42 G. S. Smith and S. F. Mapolie, *J. Mol. Catal. A: Chem.*, 2004, **213**, 187–192.

43 (*a*) W. A. Herrmann, *Angew. Chem., Int. Ed.*, 2002, **41**, 1290–1309; (*b*) *N-Heterocyclic Carbenes in Transition Metal Catalysis*, ed. F. Glorius, Springer, Berlin, 2007.

44 E. Díez-Barra, J. Guerra, R. I. Rodríguez-Curiel, S. Merino and J. Tejeda, *J. Organomet. Chem.*, 2002, **660**, 50–54.

45 I. P. Beletskaya, A. V. Chuchuryukin, G. van Koten, H. P. Dijkstra, G. P. M. van Klink, A. N. Kashin, S. E. Nefedov and I. L. Eremenko, *Russ. J. Org. Chem.*, 2003, **39**, 1268–1281.

46 (*a*) A. Suzuki, *Chem. Rev.*, 1995, **95**, 2457–2483; (*b*) A. Suzuki, *J. Organomet. Chem.*, 1999, **576**, 147–168; (*c*) T. N. Mitchell, in *Metal-Catalyzed Cross-Coupling Reactions*, ed. A. D. Meijere and F. Diederich, Wiley-VCH, Weinheim, Second, revised edn, 2004, vol. 1, pp. 125–161.

47 (*a*) J. K. Stille, *Angew. Chem., Int. Ed. Engl.*, 1986, **25**, 508–524; (*b*) N. Miyaura, in *Metal-Catalyzed Cross-Coupling Reactions*, ed. A. d. Meijere and F. Diederich, Wiley-VCH, Weinheim, Second, revised edn, 2004, vol. 1, pp. 41–123.

48 V. Maraval, R. Laurent, A. M. Caminade and J. P. Majoral, *Organometallics*, 2000, **19**, 4025–4029.

49 M. Koprowski, R. M. Sebastián, V. Maraval, M. Zablocka, V. Cadierno, B. Donnadieu, A. Igau, A. M. Caminade and J. P. Majoral, *Organometallics*, 2002, **21**, 4680–4687.

50 J. Lemo, K. Heuzé and D. Astruc, *Org. Lett.*, 2005, **7**, 2253–2256.

51 K. Sonogashira, Y. Tohda and N. Hagihara, *Tetrahedron Lett.*, 1975, **16**, 4467–4470.

52 D. Méry, K. Heuzé and D. Astruc, *Chem. Commun.*, 2003, 1934–1935.

53 (*a*) K. Heuzé, D. Méry, D. Gauss and D. Astruc, *Chem. Commun.*, 2003, 2274–2275; (*b*) K. Heuzé, D. Méry, D. Gauss, J.-C. Blais and D. Astruc, *Chem. Eur. J.*, 2004, **10**, 3936–3944.

54 (*a*) B. M. Trost and D. L. Van Vranken, *Chem. Rev.*, 1996, **96**, 395–422; (*b*) M. Johannsen and K. A. Jørgensen, *Chem. Rev.*, 1998, **98**, 1689–1708; (*c*) U. Kazmaier and M. Pohlman, in *Metal-Catalyzed Cross-Coupling Reactions*, ed. A. de Meijere and F. Diederich, Wiley-VCH, Weinheim, Second, revised edn, 2004, vol. 2, pp. 531–583.

55 N. Brinkmann, D. Giebel, G. Lohmer, M. T. Reetz and U. Kragl, *J. Catal.*, 1999, **183**, 163–168.

56 D. de Groot, E. B. Eggeling, J. C. de Wilde, H. Kooijman, R. J. van Haaren, A. W. van der Made, A. L. Spek, D. Vogt, J. N. H. Reek, P. C. J. Kamer and P. W. N. M. van Leeuwen, *Chem. Commun.*, 1999, 1623–1624.

57 D. de Groot, J. N. H. Reek, P. C. J. Kamer and P. W. N. M. van Leeuwen, *Eur. J. Org. Chem.*, 2002, 1085–1095.

58 T. Mizugaki, M. Murata, M. Ooe, K. Ebitani and K. Kaneda, *Chem. Commun.*, 2002, 52–53.

59 D. E. Bergbreiter, *Chem. Rev.*, 2002, **102**, 3345–3384.

60 C. Köllner and A. Togni, *Can. J. Chem.*, 2001, **79**, 1762–1774.

61 R. Laurent, A. M. Caminade and J. P. Majoral, *Tetrahedron Lett.*, 2005, **46**, 6503–6506.

62 Y. Ribourdouille, G. D. Engel, M. Richard-Plouet and L. H. Gade, *Chem. Commun.*, 2003, 1228–1229.

63 A. W. Kleij, R. J. M. Klein Gebbink, P. A. J. van den Nieuwenhuijzen, H. Kooijman, M. Lutz, A. L. Spek and G. van Koten, *Organometallics*, 2001, **20**, 634–647.

64 R. van de Coevering, M. Kuil, R. J. M. Klein Gebbink and G. van Koten, *Chem. Commun.*, 2002, 1636–1637.

65 M. Q. Slagt, J. T. B. H. Jastrzebski, R. J. M. Klein Gebbink, H. J. van Ramesdonk, J. W. Verhoeven, D. D. Ellis, A. L. Spek and G. van Koten, *Eur. J. Org. Chem.*, 2003, 1692–1703.

66 (*a*) C. Schlenk, A. W. Kleij, H. Frey and G. van Koten, *Angew. Chem., Int. Ed.*, 2000, **39**, 3445–3447; (*b*) C. Schlenk, A. W. Kleij, H. Frey and G. Van Koten, *Angew. Chem., Int. Ed.*, 2000, **39**, 3736.

67 B. M. J. M. Suijkerbuijk, L. J. Shu, R. J. M. Klein Gebbink, A. D. Schlüter and G. van Koten, *Organometallics*, 2003, **22**, 4175–4177.

68 G. Rodríguez, M. Lutz, A. L. Spek and G. van Koten, *Chem. Eur. J.*, 2002, **8**, 46–57.

69 H. P. Dijkstra, C. A. Kruithof, N. Ronde, R. van de Coevering, D. J. Ramón, D. Vogt, G. P. M. van Klink and G. van Koten, *J. Org. Chem.*, 2003, **68**, 675–685.

70 H. P. Dijkstra, M. D. Meijer, J. Patel, R. Kreiter, G. P. M. van Klink, M. Lutz, A. L. Spek, A. J. Canty and G. van Koten, *Organometallics*, 2001, **20**, 3159–3168.

71 H. P. Dijkstra, M.Q. Slagt, A. McDonald, C. A. Kruithof, R. Kreiter, A. M. Mills, M. Lutz, A. L. Spek, W. Klopper, G. P. M. van Klink and G. van Koten, *Eur. J. Inorg. Chem.*, 2003, 830–838.

72 H. P. Dijkstra, N. Ronde, G. P. M. van Klink, D. Vogt and G. van Koten, *Adv. Synth. Catal.*, 2003, **345**, 364–369.

73 M. Kimura, M. Kato, T. Muto, K. Hanabusa and H. Shirai, *Macromolecules*, 2000, **33**, 1117–1119.
74 D. de Groot, B. F. M. de Waal, J. N. H. Reek, A. P. H. J. Schenning, P. C. J. Kamer, E. W. Meijer and P. W. N. M. van Leeuwen, *J. Am. Chem. Soc.*, 2001, **123**, 8453–8458.
75 M. Ooe, M. Murata, A. Takahama, T. Mizugaki, K. Ebitani and K. Kaneda, *Chem. Lett.*, 2003, **32**, 692–693.
76 M. Ooe, M. Murata, T. Mizugaki, K. Ebitani and K. Kaneda, *J. Am. Chem. Soc.*, 2004, **126**, 1604–1605.
77 R. van de Coevering, A. P. Alfers, J. D. Meeldijk, E. Martínez-Viviente, P. S. Pregosin, R. J. M. Klein Gebbink and G. van Koten, *J. Am. Chem. Soc.*, 2006, **128**, 12700–12713.
78 A. Garcia-Bernabé, C. C. Tzschucke, W. Bannwarth and R. Haag, *Adv. Synth. Catal.*, 2005, **347**, 1389–1394.
79 G. E. Oosterom, R. J. van Haaren, J. N. H. Reek, P. C. J. Kamer and P. W. N. M. van Leeuwen, *Chem. Commun.*, 1999, 1119–1120.
80 J. N. H. Reek, D. de Groot, G. E. Oosterom, P. C. J. Kamer and P. W. N. M. van Leeuwen, *C. R. Chim.*, 2003, **6**, 1061–1077.
81 H.-F. Chow and C. C. Mak, *J. Org. Chem.*, 1997, **62**, 5116–5127.
82 (*a*) L. Canovese, G. Chessa, C. Santo, F. Visentin and P. Uguagliati, *Organometallics*, 2002, **21**, 4342–4349; (*b*) L. Canovese, G. Chessa, F. Visentin and P. Uguagliati, *Coord. Chem. Rev.*, 2004, **248**, 945–954.
83 B. A. Siggelkow and L. H. Gade, *Z. Anorg. Allg. Chem.*, 2005, **631**, 2575–2584.
84 B. Blom, M. J. Overett, R. Meijboom and J. R. Moss, *Inorg. Chim. Acta*, 2005, **358**, 3491–3496.
85 F. Montilla, A. Galindo, R. Andrés, M. Córdoba, E. de Jesús and C. Bo, *Organometallics*, 2006, **25**, 4138–4143.
86 C. Liang and J. M. J. Fréchet, *Prog. Polym. Sci.*, 2005, **30**, 385–402.
87 W. R. Dichtel, K. Y. Baek, J. M. J. Fréchet, I. B. Rietveld and S. A. Vinogradov, *J. Polym. Sci., Part A: Polym. Chem.*, 2006, **44**, 4939–4951.
88 (*a*) K. E. Uhrich, S. Boegeman, J. M. J. Fréchet and S. R. Turner, *Polym. Bull.*, 1991, **25**, 551–558; (*b*) S. Lebreton, S. Monaghan and M. Bradley, *Aldrichimica Acta*, 2001, **34**, 75–83.
89 M. T. Reetz and D. Giebel, *Angew. Chem., Int. Ed.*, 2000, **39**, 2498–2501.
90 Q. P. Liu, Y. C. Chen, Y. Wu, J. Zhu and J. G. Deng, *Synlett*, 2006, 1503–1506.
91 S. C. Bourque, F. Maltais, W.-J. Xiao, O. Tardif, H. Alper, P. Arya and L. E. Manzer, *J. Am. Chem. Soc.*, 1999, **121**, 3035–3038.
92 S. C. Bourque, H. Alper, L. E. Manzer and P. Arya, *J. Am. Chem. Soc.*, 2000, **122**, 956–957.
93 J. P. K. Reynhardt and H. Alper, *J. Org. Chem.*, 2003, **68**, 8353–8360.
94 S. Antebi, P. Arya, L. E. Manzer and H. Alper, *J. Org. Chem.*, 2002, **67**, 6623–6631.
95 K. Sakai, T. C. Teng, A. Katada, T. Harada, K. Yoshida, K. Yamanaka, Y. Asami, M. Sakata, C. Hirayama and M. Kunitake, *Chem. Mater.*, 2003, **15**, 4091–4097.
96 P. P. Zweni and H. Alper, *Adv. Synth. Catal.*, 2004, **346**, 849–854.
97 J. P. K. Reynhardt, Y. Yang, A. Sayari and H. Alper, *Adv. Funct. Mater.*, 2005, **15**, 1641–1646.
98 H. Alper, P. Arya, S. C. Bourque, G. R. Jefferson and L. E. Manzer, *Can. J. Chem.*, 2000, **78**, 920–924.
99 R. Chanthateyanonth and H. Alper, *J. Mol. Catal. A: Chem.*, 2003, **201**, 23–31.
100 R. Chanthateyanonth and H. Alper, *Adv. Synth. Catal.*, 2004, **346**, 1375–1384.
101 R. Touzani and H. Alper, *J. Mol. Catal. A: Chem.*, 2005, **227**, 197–207.
102 S.-M. Lu and H. Alper, *J. Am. Chem. Soc.*, 2005, **127**, 14776–14784.
103 P. P. Zweni and H. Alper, *Adv. Synth. Catal.*, 2006, **348**, 725–731.
104 (*a*) A. D. Schluter, *Top. Curr. Chem.*, 1998, **197**, 165–191; (*b*) A. D. Schluter and J. P. Rabe, *Angew. Chem., Int. Ed.*, 2000, **39**, 864–883; (*c*) A. F. Zhang, L. J. Shu, Z. S. Bo and A. D. Schluter, *Macromol. Chem. Phys.*, 2003, **204**, 328–339; (*d*) A. Zhang, *Prog. Chem.*, 2005, **17**, 157–171; (*e*) H. Frauenrath, *Prog. Polym. Sci.*, 2005, **30**, 325–384.
105 P. Arya, N. V. Rao, J. Singkhonrat, H. Alper, S. C. Bourque and L. E. Manzer, *J. Org. Chem.*, 2000, **65**, 1881–1885.
106 A. Dahan and M. Portnoy, *Org. Lett.*, 2003, **5**, 1197–1200.
107 Z. Guo, H. Feng, H.-C. Ma, Q.-X. Kang and Z.-W. Yang, *Polym. Adv. Technol.*, 2004, **15**, 100–104.
108 *Metal Nanoparticles: Synthesis, Characterization, and Applications*, ed. D. L. Feldheim and C. A. Foss, Jr, Marcel Dekker, New York, 2002.
109 (*a*) A. Roucoux, J. Schulz and H. Patin, *Chem. Rev.*, 2002, **102**, 3757–3778; (*b*) D. Astruc, F. Lu and J. Ruiz Aranzaes, *Angew. Chem., Int. Ed.*, 2005, **44**, 7852–7872.
110 H. Bönnemann and R. M. Richards, *Eur. J. Inorg. Chem.*, 2001, 2455–2480.
111 M. Moreno-Mañas and R. Pleixats, *Acc. Chem. Res.*, 2003, **36**, 638–643.
112 Q. Yang, L. Wang, W. D. Xiang, C. L. Wang and J. F. Zhou, *Prog. Chem.*, 2006, **18**, 290–297.
113 M. Q. Zhao, L. Sun and R. M. Crooks, *J. Am. Chem. Soc.*, 1998, **120**, 4877–4878.
114 L. Balogh and D. A. Tomalia, *J. Am. Chem. Soc.*, 1998, **120**, 7355–7356.
115 L. K. Yeung and R. M. Crooks, *Nano Lett.*, 2001, **1**, 14–17.
116 L. K. Yeung, C. T. Lee, K. P. Johnston and R. M. Crooks, *Chem. Commun.*, 2001, 2290–2291.
117 Other interesting examples are poly(phenylene-pyridyl) dendrimers: Z. B. Shifrina, M. S. Rajadurai, N. V. Firsova, L. M. Bronstein, X. L. Huang, A. L. Rusanov and K. Muellen, *Macromolecules*, 2005, **38**, 9920–9932.
118 M. Zhao and R. M. Crooks, *Angew. Chem., Int. Ed.*, 1999, **38**, 364–366.
119 Y. H. Niu, L. K. Yeung and R. M. Crooks, *J. Am. Chem. Soc.*, 2001, **123**, 6840–6846.
120 K. Esumi, R. Nakamura, A. Suzuki and K. Torigoe, *Langmuir*, 2000, **16**, 7842–7846.
121 V. Chechik, M. Zhao and R. M. Crooks, *J. Am. Chem. Soc.*, 1999, **121**, 4910–4911.
122 V. Chechik and R. M. Crooks, *J. Am. Chem. Soc.*, 2000, **122**, 1243–1244.
123 K. Esumi, T. Hosoya, A. Suzuki and K. Torigoe, *J. Colloid Interface Sci.*, 2000, **229**, 303–306.
124 Y.-M. Chung and H.-K. Rhee, *J. Mol. Catal. A: Chem.*, 2003, **206**, 291–298.
125 Reviews on bimetallic nanoparticles: (*a*) J. H. Sinfelt, *Acc. Chem. Res.*, 1987, **20**, 134–139; (*b*) N. Toshima and T. Yonezawa, *New J. Chem.*, 1998, 1179–1201.
126 Y.-M. Chung and H.-K. Rhee, *Catal. Lett.*, 2003, **85**, 159–164.
127 Y.-M. Chung and H.-K. Rhee, *Catal. Surv. Asia*, 2004, **8**, 211–223.
128 R. W. J. Scott, A. K. Datye and R. M. Crooks, *J. Am. Chem. Soc.*, 2003, **125**, 3708–3709.
129 R. W. J. Scott, O. M. Wilson, S.-K. Oh, E. A. Kenik and R. M. Crooks, *J. Am. Chem. Soc.*, 2004, **126**, 15583–15591.
130 M. Zhao and R. M. Crooks, *Chem. Mater.*, 1999, **11**, 3379–3385.
131 (*a*) J. C. Garcia-Martinez, R. W. J. Scott and R. M. Crooks, *J. Am. Chem. Soc.*, 2003, **125**, 11190–11191; (*b*) J. C. Garcia-Martinez, O. M. Wilson, R. W. J. Scott and R. M. Crooks, in *Metal-Containing and Metallosupramolecular Polymers and Materials*, 2006, vol. 928, pp. 215–229.
132 PAMAM dendrimers undergo retro-Michael addition at temperatures higher than about 100 °C, whereas the onset of weight loss for G4 PPI is 470 °C. M. Q. Zhao, Y. L. Liu, R. M. Crooks and D. E. Bergbreiter, *J. Am. Chem. Soc.*, 1999, **121**, 923–930.
133 Y. Li and M. A. El-Sayed, *J. Phys. Chem. B*, 2001, **105**, 8938–8943.
134 Nanoparticles are not necessarily spherical and might be significantly displaced from the centre of the dendrimer. F. Gröhn, B. J. Bauer, Y. A. Akpalu, C. L. Jackson and E. J. Amis, *Macromolecules*, 2000, **33**, 6042–6050.
135 S.-K. Oh, Y. H. Niu and R. M. Crooks, *Langmuir*, 2005, **21**, 10209–10213.
136 R. Schlögl and S. B. Abd Hamid, *Angew. Chem., Int. Ed.*, 2004, **43**, 1628–1637.

137 O. M. Wilson, M. R. Knecht, J. C. Garcia-Martinez and R. M. Crooks, *J. Am. Chem. Soc.*, 2006, **128**, 4510–4511.

138 M. Ooe, M. Murata, T. Mizugaki, K. Ebitani and K. Kaneda, *Nano Lett.*, 2002, **2**, 999–1002.

139 (*a*) N. Toshima, M. Harada, T. Yonezawa, K. Kushihashi and K. Asakura, *J. Phys. Chem.*, 1991, **95**, 7448–7453; (*b*) N. Toshima, T. Yonezawa and K. Kushihashi, *J. Chem. Soc., Faraday Trans.*, 1993, **89**, 2537–2543.

140 Y. Mizukoshi, T. Fujimoto, Y. Nagata, R. Oshima and Y. Maeda, *J. Phys. Chem. B*, 2000, **104**, 6028–6032.

141 (*a*) I. T. Horváth and J. Rábai, *Science*, 1994, **266**, 72–75; (*b*) I. T. Horváth, *Acc. Chem. Res.*, 1998, **31**, 641–650; (*c*) E. de Wolf, G. van Koten and B.-J. Deelman, *Chem. Soc. Rev.*, 1999, **28**, 37–41; (*d*) L. P. Barthel-Rosa and J. A. Gladys, *Coord. Chem. Rev.*, 1999, **190–192**, 587–605.

142 (*a*) R. Velarde Ortiz and G. Larsen, *Chem. Mater.*, 2002, **14**, 858–866; (*b*) H. C. Choi, W. Kim, D. W. Wang and H. J. Dai, *J. Phys. Chem. B*, 2002, **106**, 12361–12365; (*c*) R. W. J. Scott, O. M. Wilson and R. M. Crooks, *Chem. Mater.*, 2004, **16**, 5682–5688; (*d*) H. F. Lang, S. Maldonado, K. J. Stevenson and B. D. Chandler, *J. Am. Chem. Soc.*, 2004, **126**, 12949–12956.

143 H. F. Lang, R. A. May, B. L. Iversen and B. D. Chandler, *J. Am. Chem. Soc.*, 2003, **125**, 14832–14836.

144 R. W. J. Scott, C. Sivadinarayana, O. M. Wilson, Z. Yan, D. W. Goodman and R. M. Crooks, *J. Am. Chem. Soc.*, 2005, **127**, 1380–1381.

145 L. Sun and R. M. Crooks, *Langmuir*, 2002, **18**, 8231–8236.

146 C. L. Wang, G. S. Zhu, J. Li, X. H. Cai, Y. H. Wei, D. L. Zhang and S. L. Qiu, *Chem. Eur. J.*, 2005, **11**, 4975–4982.

147 Y. J. Jiang and Q. M. Gao, *J. Am. Chem. Soc.*, 2006, **128**, 716–717.

148 (*a*) M. Beller, H. Fischer, K. Kühlein, C. P. Reisinger and W. A. Herrmann, *J. Organomet. Chem.*, 1996, **520**, 257–259; (*b*) M. T. Reetz and G. Lohmer, *Chem. Commun.*, 1996, 1921–1922.

149 E. H. Rahim, F. S. Kamounah, J. Frederiksen and J. B. Christensen, *Nano Lett.*, 2001, **1**, 499–501.

150 R. Narayanan and M. A. El-Sayed, *J. Phys. Chem.B*, 2004, **108**, 8572–8580.

151 M. Pittelkow, K. Moth-Poulsen, U. Boas and J. B. Christensen, *Langmuir*, 2003, **19**, 7682–7684.

152 J. Lemo, K. Heuzé and D. Astruc, *Inorg. Chim. Acta*, 2006, **359**, 4909–4911.

153 (*a*) H.-C. Zhang and G. D. Daves, Jr, *Organometallics*, 1993, **12**, 1499–1500; (*b*) A. I. Roshchin, N. A. Bumagin and I. P. Beletskaya, *Tetrahedron Lett.*, 1995, **36**, 125–128; (*c*) R. Rai, K. B. Aubrecht and D. B. Collum, *Tetrahedron Lett.*, 1995, **36**, 3111–3114; (*d*) C. Wolf and R. Lerebours, *J. Org. Chem.*, 2003, **68**, 7551–7554; (*e*) J. Fresneda, E. de Jesús, P. Gómez-Sal and C. López Mardomingo, *Eur. J. Inorg. Chem.*, 2005, 1468–1476.

154 J. C. Garcia-Martinez, R. Lezutekong and R. M. Crooks, *J. Am. Chem. Soc.*, 2005, **127**, 5097–5103.

155 (*a*) K. Esumi, A. Suzuki, N. Aihara, K. Usui and K. Torigoe, *Langmuir*, 1998, **14**, 3157–3159; (*b*) K. Esumi, K. Satoh, A. Suzuki and K. Torigoe, *Shikizai Kyokaishi*, 2000, **73**, 434.

156 K. Esumi, R. Isono and T. Yoshimura, *Langmuir*, 2004, **20**, 237–243.

157 T. Endo, T. Kuno, T. Yoshimura and K. Esumi, *J. Nanosci. Nanotechnol.*, 2005, **5**, 1875–1882.

158 T. Endo, T. Fukunaga, T. Yoshimura and K. Esumi, *J. Colloid Interface Sci.*, 2006, **302**, 516–521.

159 (*a*) A. Sunder, R. Hanselmann, H. Frey and R. Mülhaupt, *Macromolecules*, 1999, **32**, 4240–4246; (*b*) A. Sunder, J. Heinemann and H. Frey, *Chem. Eur. J.*, 2000, **6**, 2499–2506; (*c*) A. Sunder, H. Frey and R. Mülhaupt, *Macromol. Symp.*, 2000, **153**, 187–196.

160 (*a*) S. Mecking, R. Thomann, H. Frey and A. Sunder, *Macromolecules*, 2000, **33**, 3958–3960; (*b*) S. Mecking, U. Schlotterbeck, R. Thomann, M. Soddemann, M. Stieger, W. Richtering and H. Kautz, *Polym. Mater. Sci. Eng.*, 2001, **84**, 511.

161 R. Sablong, U. Schlotterbeck, D. Vogt and S. Mecking, *Adv. Synth. Catal.*, 2003, **345**, 333–336.

162 Y. Chen, H. Frey, R. Thomann and S. E. Stiriba, *Inorg. Chim. Acta*, 2006, **359**, 1837–1844.

163 D. Tabuani, O. Monticelli, H. Komber and S. Russo, *Macromol. Chem. Phys.*, 2003, **204**, 1576–1583.

164 (*a*) D. Tabuani, O. Monticelli, A. Chincarini, C. Bianchini, F. Vizza, S. Moneti and S. Russo, *Macromolecules*, 2003, **36**, 4294–4301; (*b*) D. Tabuani, O. Monticelli, A. Chincarini, C. Bianchini, F. Vizza, S. Moneti and S. Russo, *Macromolecules*, 2004, **37**, 680.

165 (*a*) R. Y. Wang, J. Yang, Z. P. Zheng, M. D. Carducci, J. Jiao and S. Seraphin, *Angew. Chem., Int. Ed.*, 2001, **40**, 549–552; (*b*) M. K. Kim, Y. M. Jeon, W. S. Jeon, H. J. Kim, S. G. Hong, C. G. Park and K. Kim, *Chem. Commun.*, 2001, 667–668; (*c*) K. R. Gopidas, J. K. Whitesell and M. A. Fox, *J. Am. Chem. Soc.*, 2003, **125**, 6491–6502; (*d*) W. H. Guo, J. J. Li, Y. A. Wang and X. G. Peng, *J. Am. Chem. Soc.*, 2003, **125**, 3901–3909; (*e*) C. S. Love, V. Chechik, D. K. Smith and C. Brennan, *J. Mater. Chem.*, 2004, **14**, 919–923; (*f*) G. H. Jiang, L. Wang, T. Chen, H. J. Yu and C. Chen, *Mater. Chem. Phys.*, 2006, **98**, 76–82; (*g*) W. Zhang, Y.-K. Du, N.-P. Hua, X.-M. Wang and P. Yang, *Wuji Huaxue Xuebao*, 2006, **22**, 263–267.

166 K. R. Gopidas, J. K. Whitesell and M. A. Fox, *Nano Lett.*, 2003, **3**, 1757–1760.

167 L. Wu, B.-L. Li, Y.-Y. Huang, H.-F. Zhou, Y.-M. He and Q.-H. Fan, *Org. Lett.*, 2006, **8**, 3605–3608.

168 M. Murata, Y. Tanaka, T. Mizugaki, K. Ebitani and K. Kaneda, *Chem. Lett.*, 2005, **34**, 272–273.

169 J. H. Friedhofen and F. Vögtle, *New J. Chem.*, 2006, **30**, 32–43.