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Review

Dendritic catalysis: Major concepts and recent progress

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Received 26 October 2005; accepted 24 November 2005
Available online 7 February 2006

Contents

Abstract

Metallodendrimers are now a mature area of nanosciences with multiple potential applications [G.R. Newkome, C.N. Moorefield, F. Vögtle, Dendrons and dendrimers, in: Concepts, Synthesis and Applications, Wiley-VCH, Weinheim, 2001; D. Tomalia, J.M.J. Fréchet (Eds.), Dendrimers and other Dendritic Polymers , Wiley-VCH, New York, 2002; D. Astruc (Guest Ed.), C. R. Chimie 6 (2003) 709]. Among them, catalysis stands as a major objective given the need to design environmentally safe processes [P.T. Anastas, T.C. Williamson (Eds.), Green Chemistry ACS Symp. Ser. 626, ACS, Washington DC, 1996]. with regeneratable catalysts. Indeed, dendritic catalysts are nanosized, and as such they are, as biomolecules, easily isolable from homogeneous reaction media by precipitation, filtration, ultrafiltration or ultracentrifugation [D. Astruc (Guest Ed.), C. R. Chimie, 6 (2003) 709; D. Astruc, F. Chardac, Chem. Rev. 101 (2001) 2991; G.E. Oosterom, J.N.H. Reek, P.C.J. Kamer, P.W.N.M. van Leeuwen, Angew. Chem. Int. Ed. Engl. 40 (2001) 1828; R. van Heerbeeck, P.C.J. Kamer, P.W.N.M. van Leuwen, J.N.H. Reek, Chem. Rev. 102 (2002) 3717; R. Kreiter, A.W. Kleij, R.J.M. Klein Gebbink, G. van Koten, in: F. Vögtle, C. Schalley (Eds.), Dendrimers IV: Metal Coordination, Self-assembly, Catalysis, vol. 217, Springer Verlag, Berlin, 2001, p. 163]. The idea of using metallodendritic was first raised by van Leeuwen in 1992 [R.A. Kleij, P.W.N.M. van Leeuwen, A.W. van der Made; EP0456317, 1991 [Chem. Abstr. 116 (1992) 129870], and the first example of recycling dendritic catalysts was reported by Reetz in 1997 [M.T. Reetz, G. Lohmer, R. Schwickardi, Angew. Chem. Int. Ed. Engl. 36 1997) 1526]. Since the first reviews on the subject that appeared in 2001, several other more or less related reviews were reported [J.N.H. Reek, D. de Groot, G.E. Oosterom, P.C.J. Kamer, P.W.N.M. van Leeuwen, Rev. Mol. Biotechnol. 90 (2002) 159; M. Dasgupta, M.B. Peori, A.K. Kakkar, Coord. Chem. Rev. 233–234 (2002) 223; S. Hecht, J.M.J. Fréchet, Angew. Chem. Int. Ed. 40 (2001) 74; J.M.J. Fréchet, J. Polym. Sci.: Part A: Polym. Chem. 41 (2003) 3713; P.A. Chase, R.J.M. Klein Gebbink, G. van Koten, J. Organometal. Chem. 689 (2004) 4016; C. Liang, J.M.J. Fréchet, Prog. Polym. Sci. 30 (2005) 385. R. van de Coevering, R.J.M. Klein Gebbink, G. van Koten, Prog. Polym. Sci. 30 (2005) 474; A. Dahan, M. Portnoy, J. Polym. Sci.: Part A: Polym. Chem. 43 (2005) 235; D. Astruc, K. Heuzé, S. Gatard, D. Méry, S. Nlate, L. Plault; Adv. Synth. Catal. 347 (2005) 2005; D. Astruc, C. R. Chimie 8 (2005) 1101] and dendritic catalysis was the subject of a multi-chapter section of the special triple issue of C.R. Chimie in 2003 [Y. Niu, R.M. Crooks, J.N.H. Reek, D. de Groot, G. E. Oosterom, P. J. Kamer, P. W. N. M. van Leeuwen, G. P. M. van Klink, H. P. Dijktra, G. van Koten, Y. Ribourdouille, G.D. Engel, L.H. Gade, K. Soai, I. Sato, C.-M. Che, J.-S. Huang, J.-L. Zhang, D. Astruc, J.-C. Blais, M.-C. Daniel, S. Gatard, S. Nlate, J. Ruiz,in: D. Astruc (Guest Ed.), C. R. Chimie 6–8 (2003) 1049]. The purpose of the present review is to summarize the major

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doi:10.1016/j.ccr.2005.11.012

concepts and recent advances in the field. For extensive references older than 2001, the reader is referred to our comprehensive Chem. Rev. article [D. Astruc, F. Chardac, Chem. Rev. 101 (2001) 2991].

Keywords: Dendrimer; Homogeneous catalysis; Heterogeneous catalysis; Complexes

1. Major concepts

Several approaches to dendritic catalysis and dendrimers in catalysis have been reported [1–21], and a general picture of this diversity is shown on Fig. 1 [5].

Indeed, the catalytically active metal centers can be located at the termini of the dendritic branches. In this case (a) in Fig. 1, bulk at the periphery increases as the dendrimer generation increases, and these branch termini have all the less tendency to back fold toward the dendrimer center as the terminal group is larger. This means that, for a given generation that depends on the length of the tethers, the dendrimer topology and the size of the termini, bulk will inhibit further dendritic construction. This may be related to the de Gennes dense packing limit whereby the limit generation is provided by the dendrimer surface area [22]. Recall that with small termini, the Astruc group has demonstrated dendrimer construction far beyond the dense packing limit and the aforementioned theory is not generally applicable [23], as suggested by other theoretical papers on dendrimers [24–27]. It applies, however, with large terminal groups [23]; therefore, the Astruc group has suggested that stars (case b) in Fig. 1) represent a better topology than dendrimers for the purpose of catalysis, especially because substrate approach to the metal center is often a rate-limiting step is catalytic reactions [28]. The first experimental observation of kinetics that do not decrease with star-shaped catalysts compared to monometallic catalysts, was reported by the Astruc group for the redox catalyzed cathodic reduction of nitrate in aqueous solution (Scheme 1, [29,30]). Note that sterically bulky metal centers undergo a dramatic kinetic limitation.

On the other hand, it has been demonstrated on several occasions with various types of catalytic reactions using DAB-derived phosphine–metal catalysts (Ru in C=C metathesis [31,32], Pd in cross C–C coupling [33–35]) that a negative dendritic effect of the catalytic reaction kinetics encourages the use of low-generation dendrimers. This dichotomy further encourages the use of star-shaped recyclable catalysts in the future as their size is sufficient for recovery and re-use. Another example of such classic dendrimer catalyst in which the nickel groups are located at the dendrimer periphery is that published in 1984 by van Koten and represented in Fig. 2. Its efficiency in Kharash reaction (addition of polyhanogenoalkanes onto double C=C bonds) slightly decreases from the monometallic catalyst to the corresponding metallodendritic one of Fig. 2 [8,36].

Another distinct approach is that using ionic bonds in connection with hydrogen bonds to attach the catalyst to the dendrimer, pioneered by the van Leeuwen and Meijer groups. In this method, the phosphine–metal catalyst bearing a carboxylate chain is bonded to a tertiary ammonium ending of the polypropyleneimine dendrimer branches [21,37]. The reactivity does not decrease in the metallodendrimers compared to the monomers, although recycling attempts show a decrease of activity due to leaching. The topology (c) of Fig. 1 whereby the phosphine ligands of the catalyst are located at the branching points all along the dendritic construction is rarely found but has been reported by Kakkar [12]. The challenging approach to locate the catalyst at the center of the dendrimer was reported *inter alia* with porphyrin-centered dendrimers for selective olefin epoxidation [38] and ferrocenylphosphine-centered dendrimers [39] shown in Fig. 3. In the latter case, the kinetics decrease as expected as

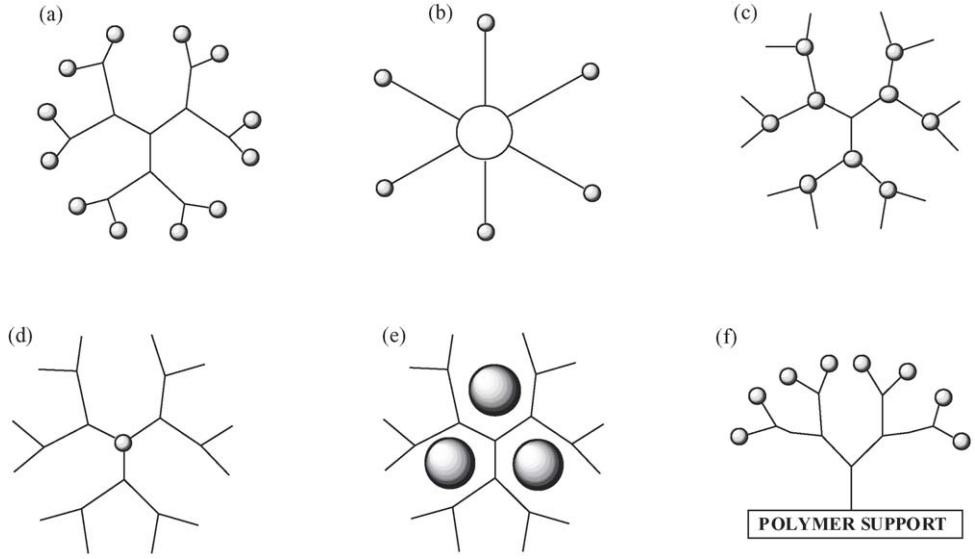
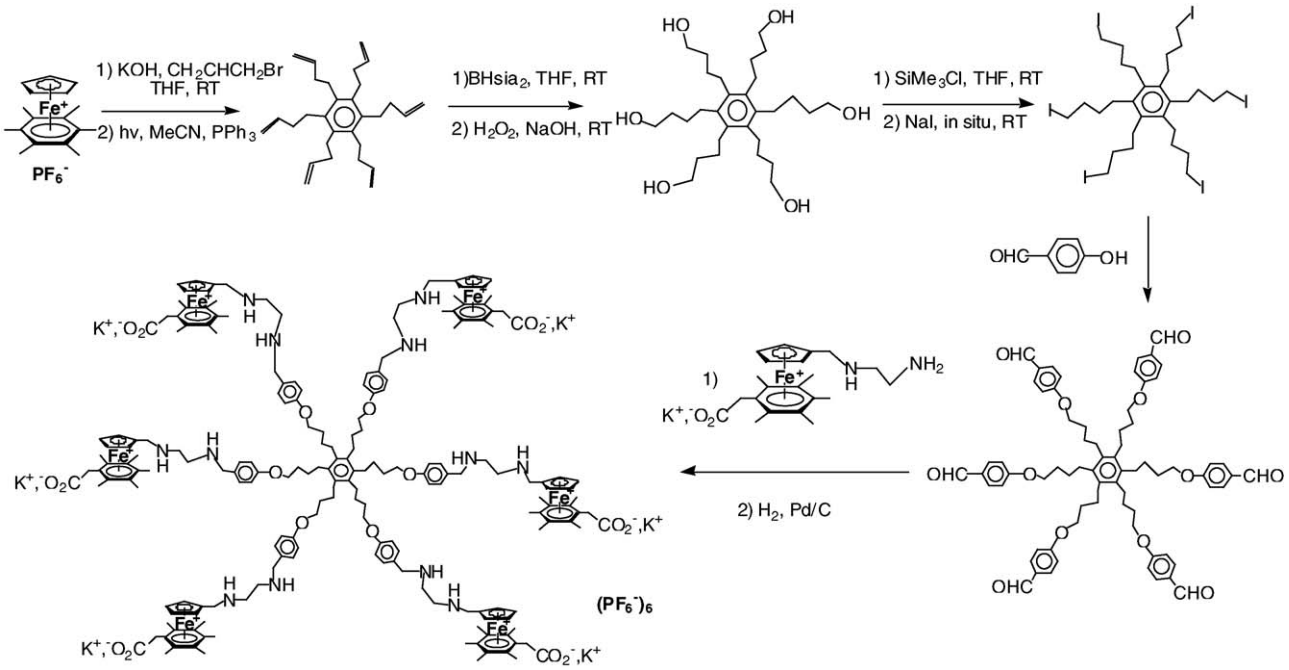


Fig. 1. The various dendrimer topologies and metal locations in catalytically active metallodendrimers [5].



Scheme 1. Design and synthesis of a water-soluble star-shaped catalyst for cathodic reduction of nitrates and nitrites to ammonia showing no kinetic drop from the monometallic to the star-shaped catalyst.

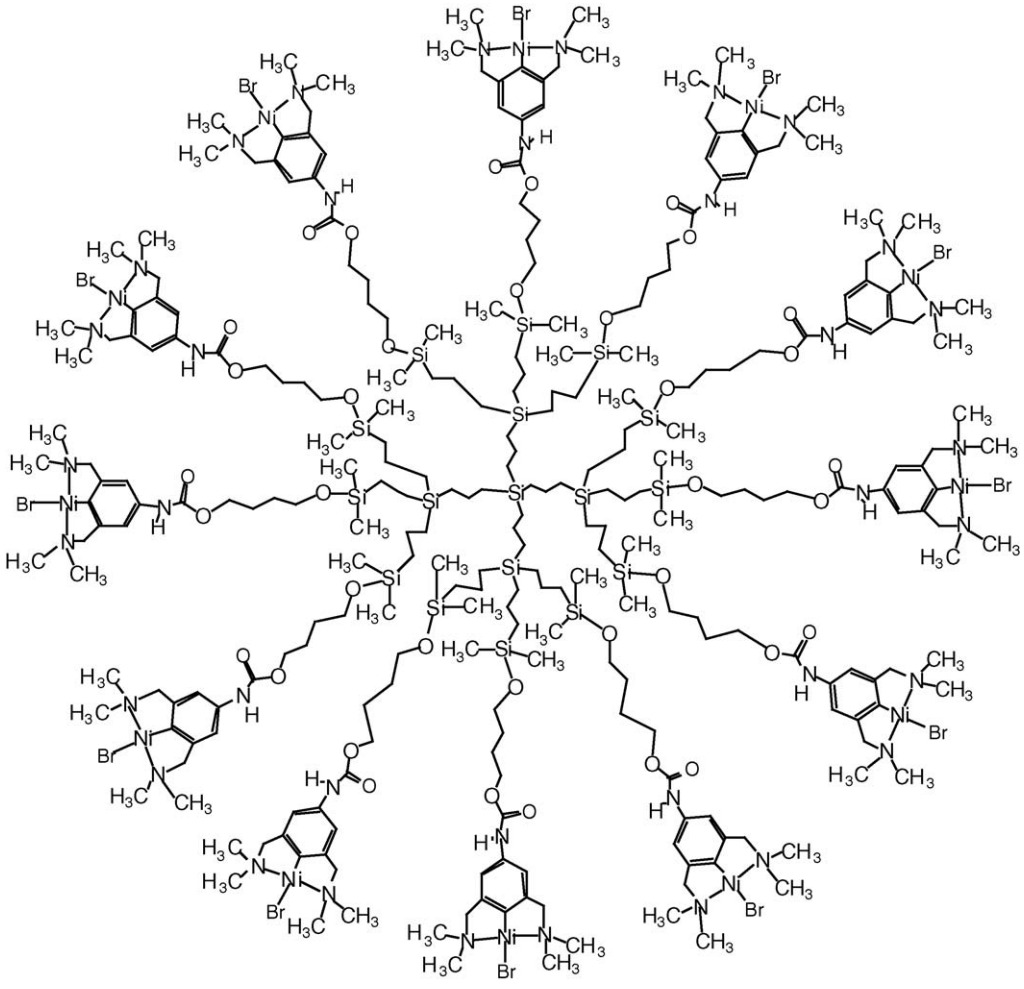


Fig. 2. van Koten's pioneering dendritic nickel complex that catalyses the Kharash reaction with a slightly negative dendritic effect on the reaction kinetics [8,36].

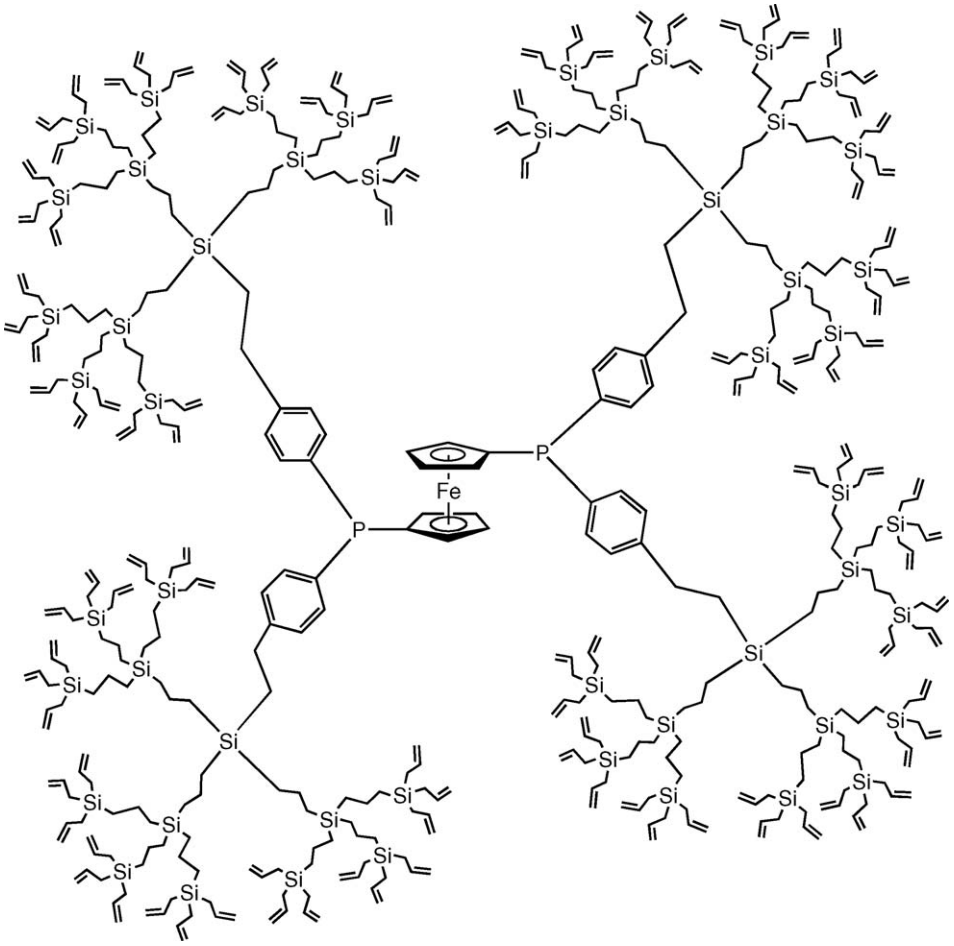
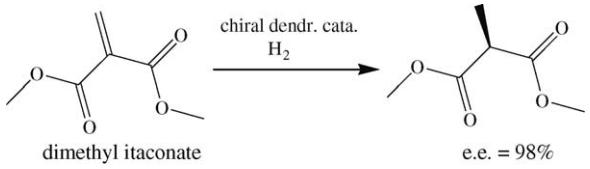


Fig. 3. van Leeuwen's dendritic ferrocenyldiphosphine for Pd catalysis of allylic alkylation.

the dendrimer generation increases due to the increased steric bulk inhibiting approach to the catalytic metal center.

An elegant approach largely developed by Crooks involved the formation of catalytically active metal nanoparticles formed by reduction of metal cations coordinated to dendrimers containing amines such as the commercial polyamidoamines (PAMAM) synthesized by Tomalia. This strategy is shown in (e) of Fig. 1 and has been applied to various catalytic reactions in green media such as supercritical CO_2 or water and has involved nanoparticles prepared in this way from dendrimers and further fixed on heterogeneous supports [21,40–63].

Asymmetric catalysis has been pioneered by Brunner with dendrizymes [64], developed by Seebach [65,66] and an example by Togni [67] is shown in Fig. 4 in which a dendritic optically active ferrocenyl phosphine is used for the following enantioselective hydrogenation reaction:



Another approach pioneered by Alper [68,69] is that using polymer-supported metallodendrons shown in Figs. 1, (f) and Fig. 5, that have been used *inter alia* for hydroformylation and Heck reactions. This strategy has been reviewed [70] and applied by Portnoy with dendritic effects [70–72].

In our research group, we have also pioneered the dendritic protection of a catalyst by a dendronic periphery using ionic bonding between polyoxometallate core and dendrons that are cationic at the focal point using an ammonium or pyridinium group. Indeed, polyoxometallates are excellent catalysts for various oxidation reactions (epoxidation of alkenes, oxidation of alcohols and sulfides). With linear ammonium counter cations, however, the catalyst is not recyclable and is decomposed as witnessed by the change of ^{31}P NMR of the phosphotungstate moiety. With dendritic encapsulation by tridentate ammonium cations of controlled size, it is possible to recycle and re-use the catalyst several times without decomposition as confirmed by ^{31}P NMR (Fig. 6) [73–75].

2. Recent advances

2.1. The classic approach using homogeneous catalysts

2.1.1. Hydrogenation

The Reek-van Leeuwen group has examined the activity of Rh complexes of the dppf-type dendritic ligands in the hydro-

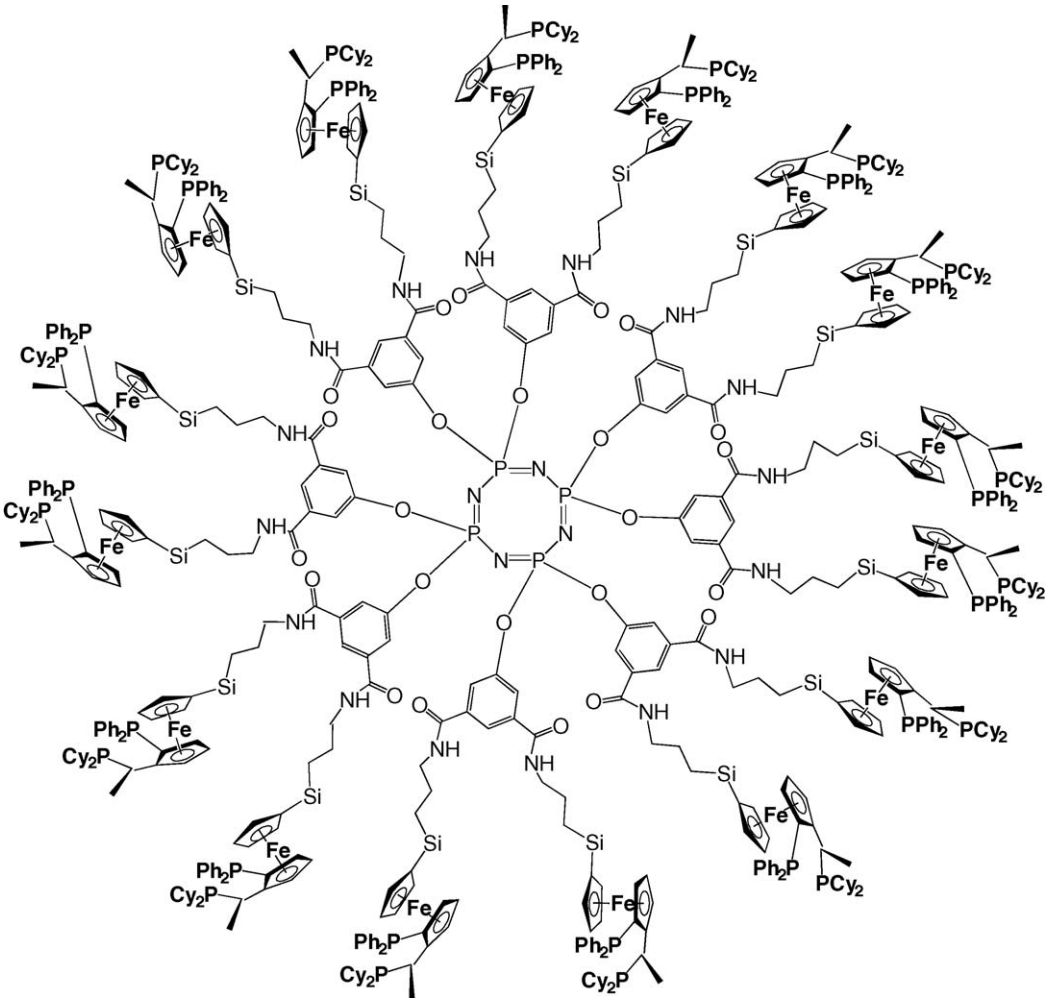


Fig. 4. Togni's chiral ferrocenyl dendrimer for enantioselective hydrogenation [67].

genation of dimethyl itaconate in a continuous-flow membrane reactor. This shows a reasonable constant of formation of the product compared to the non-dendritic catalyst [76]. Gade has used tripodal-terminated Rh-phosphine dendrimers to catalyze the hydrogenation of styrene and 1-hexene, and shown that the catalytic hydrogenation properties were not altered compared to the monomer with low-generation dendrimers [77]. Kakkar designed dendrimer containing phosphorus ligands at the branching points and looked at the catalysis of olefin hydrogenation upon variation of the dendritic structure (Fig. 7) [78].

2.1.2. Hydroformylation

Cole-Hamilton showed that Rh-phosphine-terminated dendrimers based on polyhedral silsesquioxane cores with 16 PPh_2 arms give much higher linear selectivities (14: 1) than their small analogues (3.4: 1) in the hydroformylation of cyclooct-1-ene (Fig. 8) [79,80].

The Reek-van Leeuwen Rh-dendritic phosphine catalysts used as indicated above in hydrogenation are also efficient for hydroformylation, and the activities obtained are as good as for monomers except in the case of the bulky substrate 4,4,4-triphenylbut-1-ene which gave a significant decrease of activity [76].

2.1.3. Hetero-C–C coupling: Heck, Sonogashira, Suzuki, Stille

Scretas reported that Pd complexes of DAB-dendr-(NH_2) modified with P,N ligands catalyze the Heck reaction of aryl bromides and noted a marked dependence of the conversion on the dendritic ligand/Pd ratio taken into account in terms of inhibiting steric bulk. Jayaraman compared three generations of Pd-alkylphosphine dendrimers in the Heck reactions with various olefins and reported that the second and third-generations were found to exhibit better catalytic activity than the monomer and first-generation metallodendrimer [81], a trend also noted by Mapolie with poly(propyleneime)-iminopropyl-palladium [82]. On the other hand, three generations of bidentate DAB phosphinated Pd dendrimers that were found to be active in Sonogashira coupling of iodo- and bromobenzene with phenylacetylene showed a negative dendritic effect attributed to increasing steric effect as the generation increases (example for iodobenzene at 25 °C, time for quantitative conversion: model: 30 min; first-generation: 15 h; second-generation: 40 h;

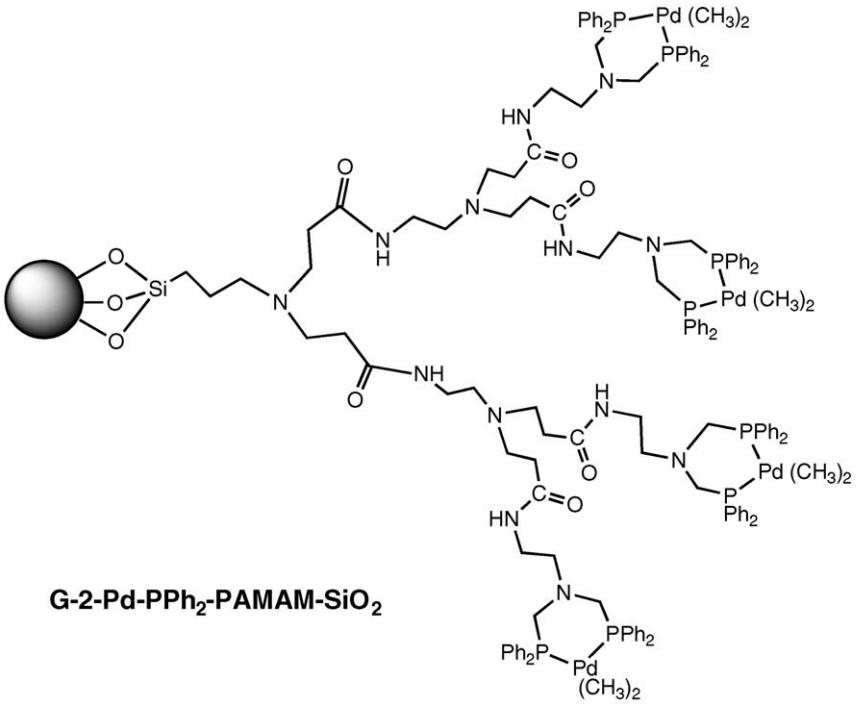


Fig. 5. Alper's polymer-attached metallodendron for Heck catalysis.

third-generation: 48 h) (Fig. 9). These metallodendrimers can be recovered and recycled with little decrease of efficiency up to seven cycles with bis-cyclohexylaminoalkylephosphine ligands (conversion is 39% after 7 cycles for the third-generation catalyst). The nature of the alkyl substituents (cyclohexyl versus *tert*-butyl) on the P ligand of the Pd catalyst also plays a role in efficiency, solubility and thus recycling ability [33–35].

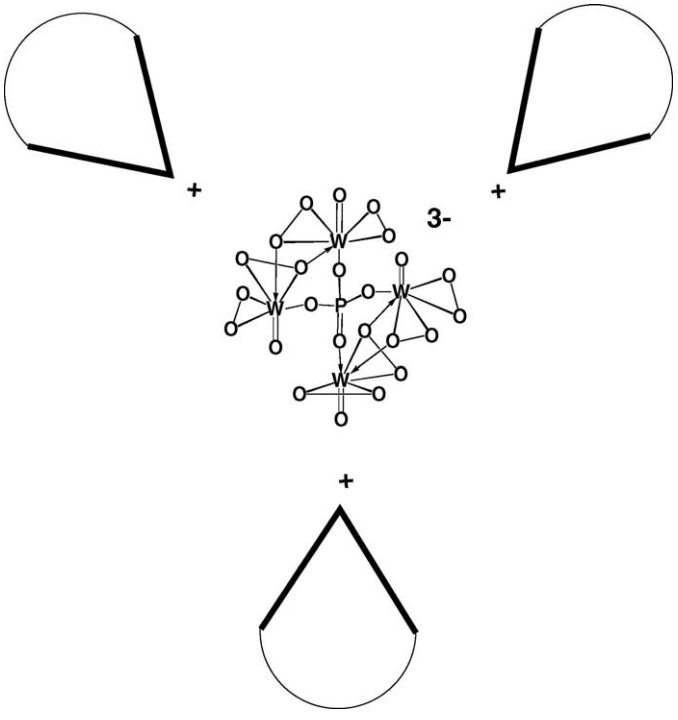


Fig. 6. Phosphotungtate trianionic catalyst for olefin epoxidation and alcohol or sulfide oxidation [74].

2.1.4. Oligomerization and polymerization

Several authors have studied the use of metallodendrimers in which the metal centers are initiators of olefin polymerization to catalyze the polymerization of ethylene (Fig. 10). This strategy allows site isolation due to well-defined hyperbranched structure. As a consequence, the metallodendritic initiators can avoid side reactions encountered with monomeric initiators and thus provide a better result with a positive dendritic effect [83–88].

2.1.5. Other homogeneous catalytic reactions

Cobalt porphyrins are used as coenzyme B12 mimics [89] and in AIBN-mediated reactions with alkynes [90]. Rhodium terminated dendrimers significantly enhance the catalytic activity of $[\{Rh(CO)_2Cl\}_2]$ for the carbonylation of methanol [91]. New reports by the van Koten group detail the good catalytic activity of nickel–pincer-terminated dendrimers [92] and platinum–pincer-terminated dendrimers [93]. PAMAM dendrimers terminated by Co(II) Schiff base groups disclose a ligand effect on the phosphoesterase activity [94]. Al-Binol complexes show slightly improved activity and enantioselectivity than monometallic analogues for Diels–Alder reactions between cyclopentadiene and oxazolidinone derivatives [95]. Pd-terminated carbosilane dendrimers were tested as catalysts in the hydrovinylation of styrene and compared to monometallic models [96]. The Thayumanavan group showed that conformationally constrained dendrimers provide better access to dendritic cores compared to the more flexible counterparts, which should have implications in using dendrimers as scaffolds in catalysis [97]. Finally, metallodendritic complexes in

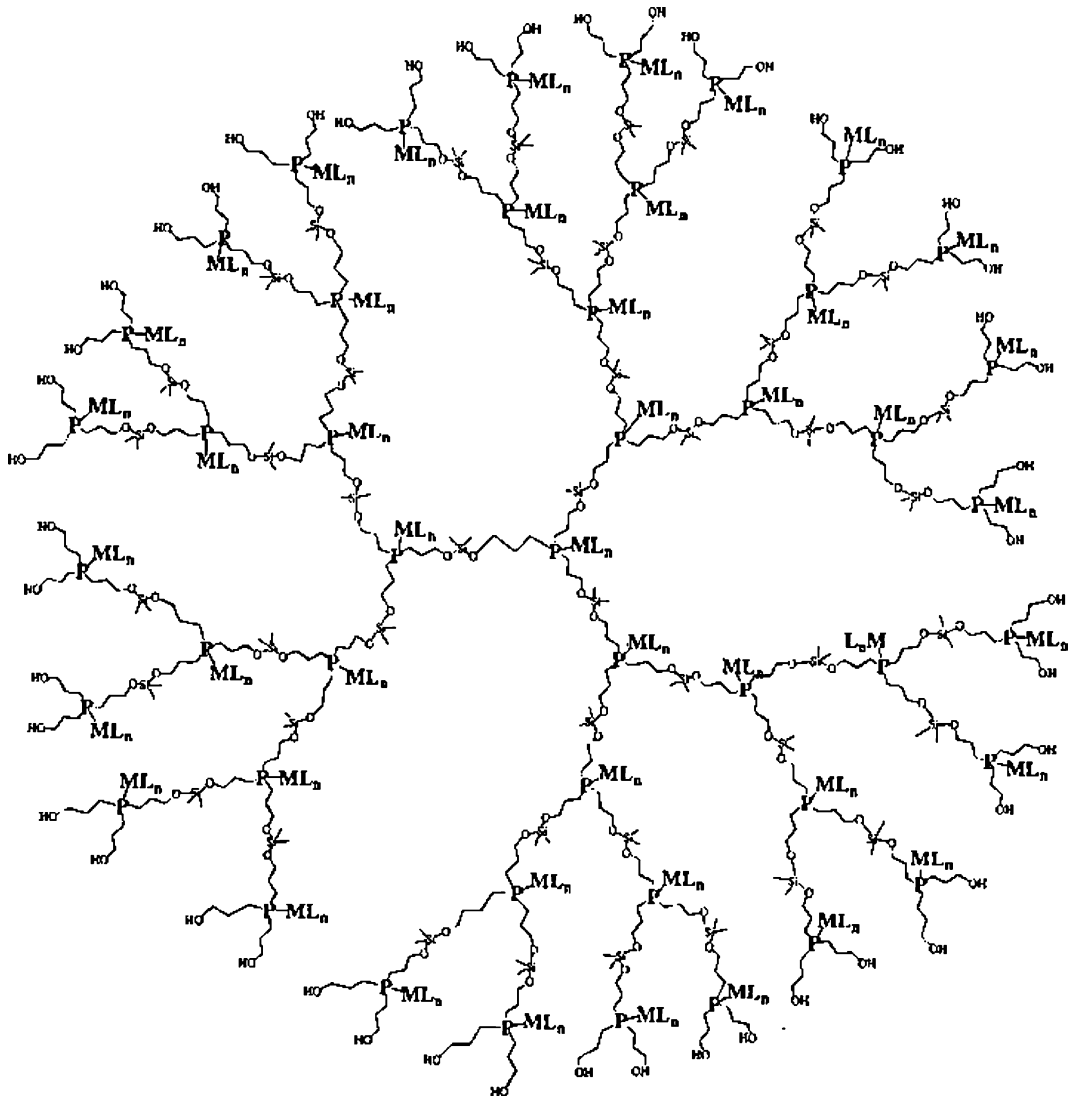


Fig. 7. Kakkar's dendritic catalyst for olefin hydrogenation [M = RhCl(COD)] [78].

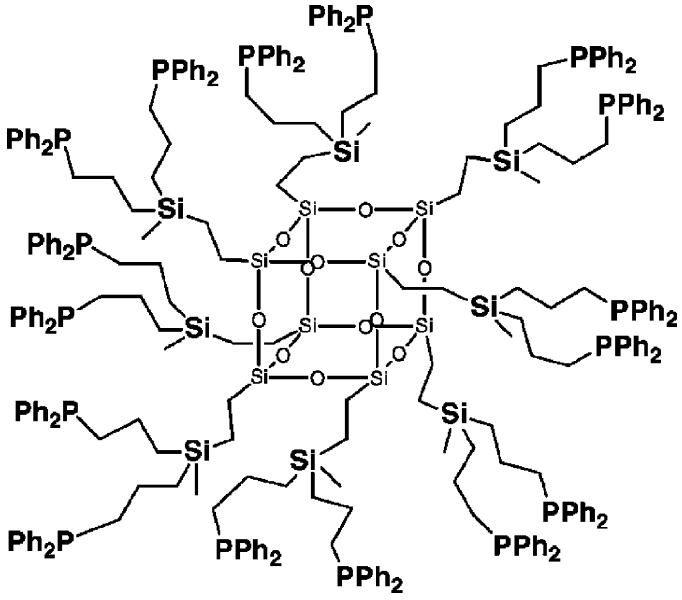


Fig. 8. Cole-Hamiltons polyhedral silsesquioxane cores [80].

electron-transfer processes and catalysis has been reviewed [98]. Palladium- and rhodium-phosphine catalysts containing benzoate substituents were linked to ammonium groups of PPI-type dendrimers by ionic bonds to achieve the Heck reaction of acrylate with iodobenzene at 100 °C in toluene (Fig. 11) [99] and one-pot hydroformylation, Knovenagel reaction and hydrogenation of styrene [100].

Using dendrimers terminated with ruthenium benzylidene complexes containing the *cis*-chelating diphosphine chains of the dendrimers, the Astruc group has achieved ring-opening-metathesis polymerization of norbornene at room temperature [31,32,101–103]. The metathesis reaction proceeds more slowly than with the Grubbs catalysts that have phosphines in *trans* position, but the *cis*-diphosphine is then firmly held in the dendrimer providing excellent stability. The metallodendrimers catalyzed the ROMP of norbornene more rapidly than the monometallic model, which was taken into account by the easier decoordination of a phosphorus ligand in the dendrimers than in the monometallic catalyst in the rate-limiting step [101]. Indeed, theoretical calculations by Kahlal and Saillard showed

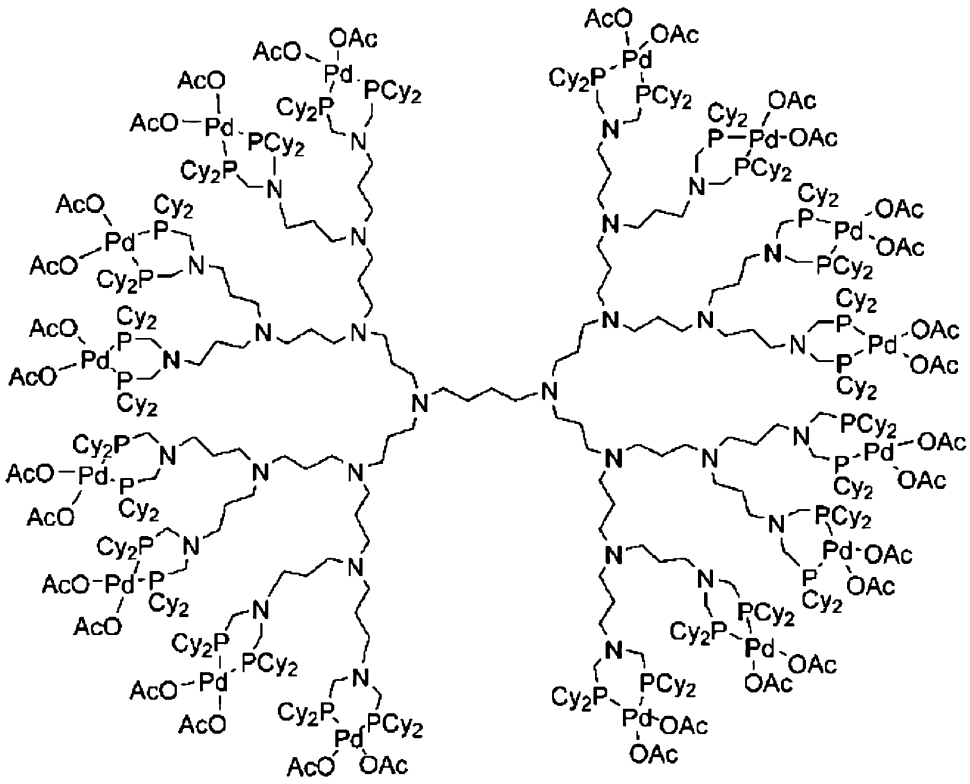


Fig. 9. Bidentate third-generation DAB phosphinated Pd dendrimer for Sonogashira and Suzuki reactions [34,35].

that the interaction of the olefin onto the ruthenium center is non-bonding before phosphine de-coordination showing that phosphine de-coordination is necessary before catalysis [102]. As expected, a negative dendritic effect is observed upon increasing the dendrimer generation from one to three because of concomitant increasing steric inhibition. This reaction leads to metallodendritic polymers, a rather new class of polymers [101–103].

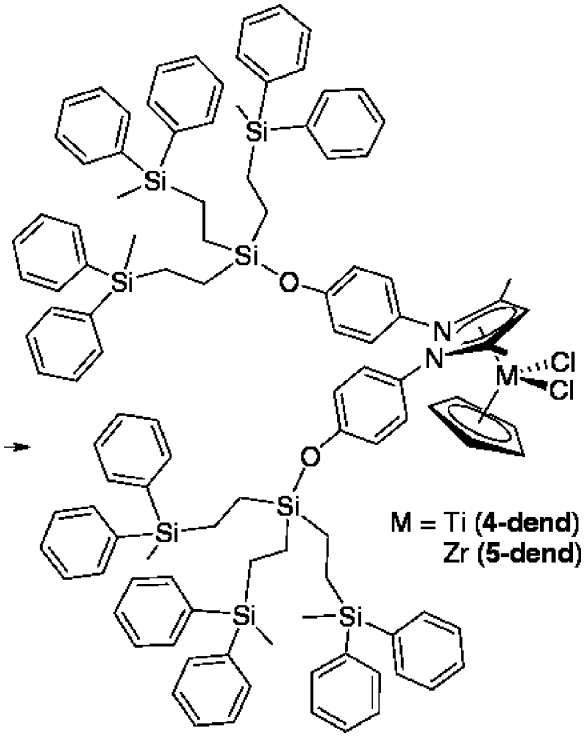


Fig. 10. Andrés's dendritic complexes for ethylene polymerization [87].

Xi's group has synthesized star-shaped polymers with relatively low polydispersity using the ATRP method in the presence of CuBr/pentamethyldiethylene triamine [104] and star-block copolymers from dendrimers initiators by combining ROMP with ATRP [105]. Hedrick's group has synthesized dendritic-linear A_xB_x block copolymers by living ring-opening polymerization (ROP) of lactones. The A blocks are composed of the first-to third-generation dendrons from 2,2-bis(hydroxymethyl)-propionic acid, and it is the B blocks that is poly(ε-caprolactone) prepared by ROP [106].

The interest in asymmetric catalytic, reviewed previously [5], is ongoing [107–114] with reports on asymmetric alkylation of aldehydes with diethyl zinc [108], allylic amination [111] and alkylation [113], aldol reactions [114], epoxidation, and hetero Diels–Alder reactions [109,110]. Most reports, however, deal with asymmetric hydrogenation [115–122].

2.2. Supported metallodendritic catalysts

Alper'strategy has been pursued with rhodium-supported resins for carbonylative ring expansion of aziridines to β-lactams [123]. Other reactions reported by the Alper group involve other carbonylation reactions including hydroformylation (Fig. 12) [124–129]. Chiral auxiliaries on silica have also been used for enantioselective addition of diethylzinc to benzaldehyde [130].

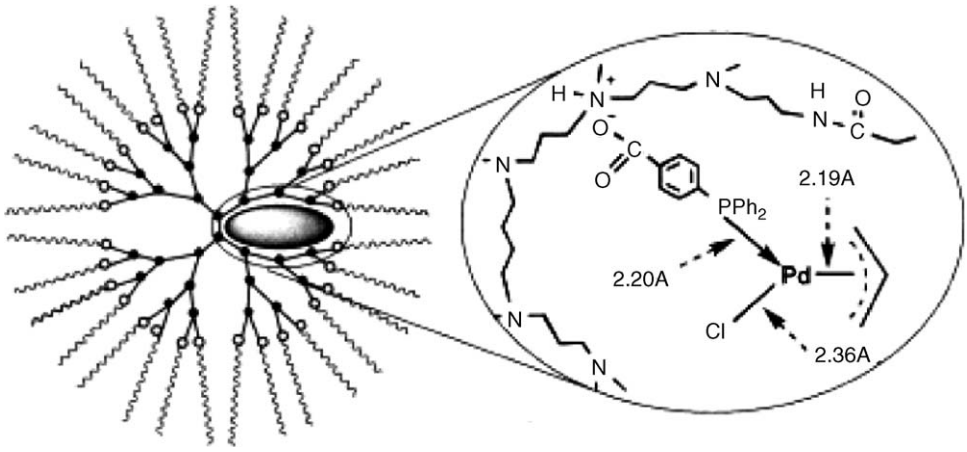


Fig. 11. Kaneda's dendrimer-encapsulated Pd complex for Heck reaction [99].

Van Koten's group has equipped dendronized polymers with NCN–palladium–pincer moieties compounds at their peripheries that catalyze the aldol condensation of benzaldehyde with methylisocyanate [131]. Portnoy has noted an increase in catalytic activity and selectivity in intramolecular Pauson–Khand reaction for Co complexes, immobilized on second and third-generation dendron-functionalized polystyrene compared to analogues on non-dendronized support [71].

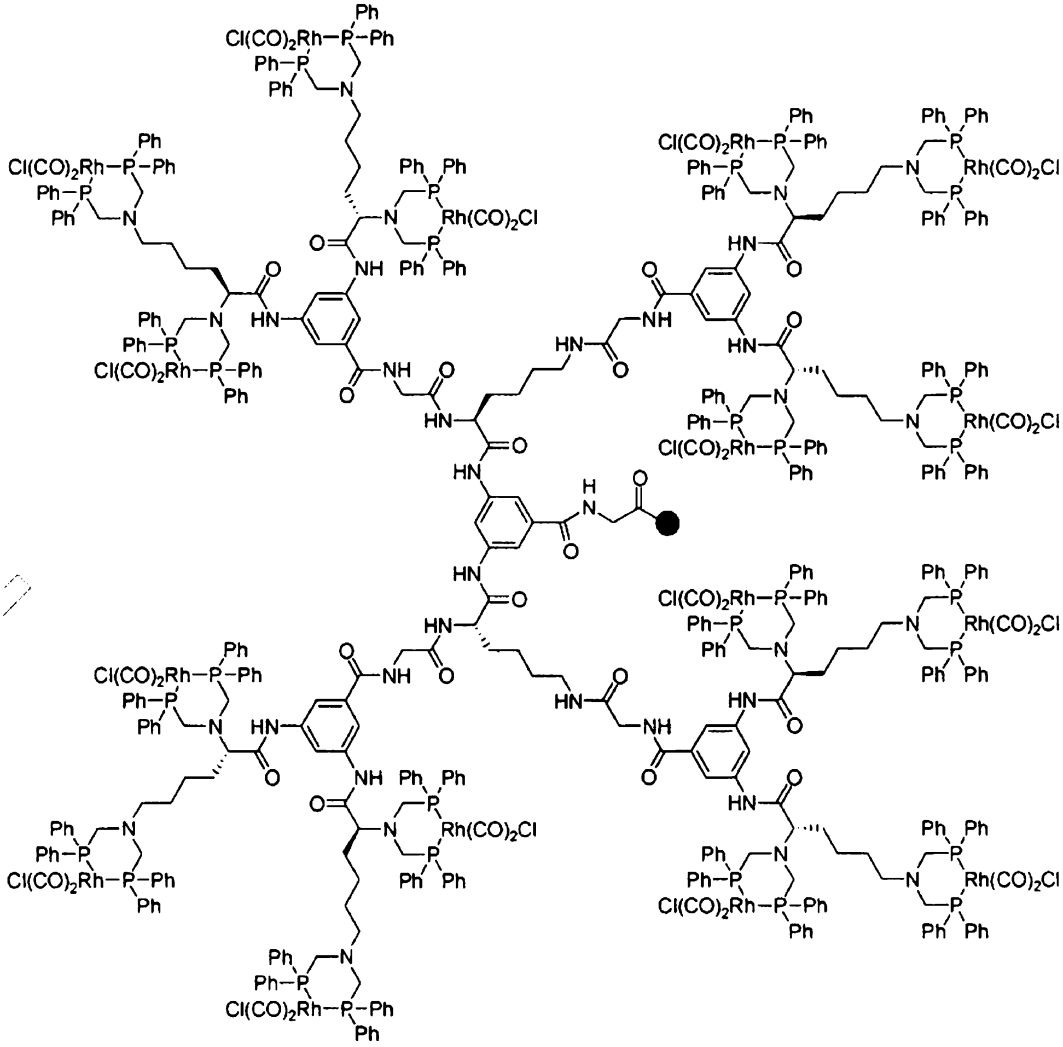


Fig. 12. Alper's rhodium complexed dendrimer on a resin for hydroformylation [125].

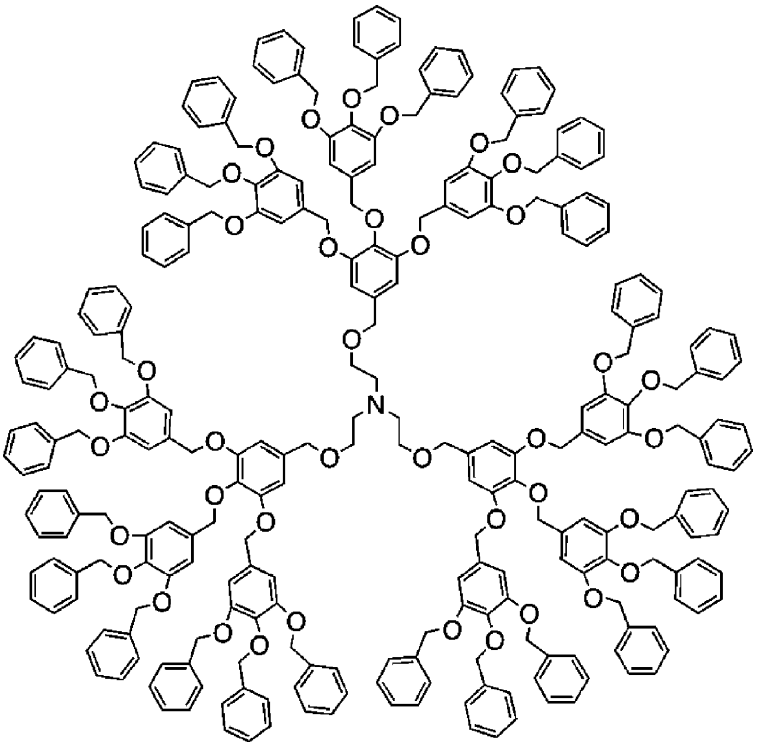


Fig. 13. Lopez's dendritic amine for nitroaldol (Henry) reaction [142].

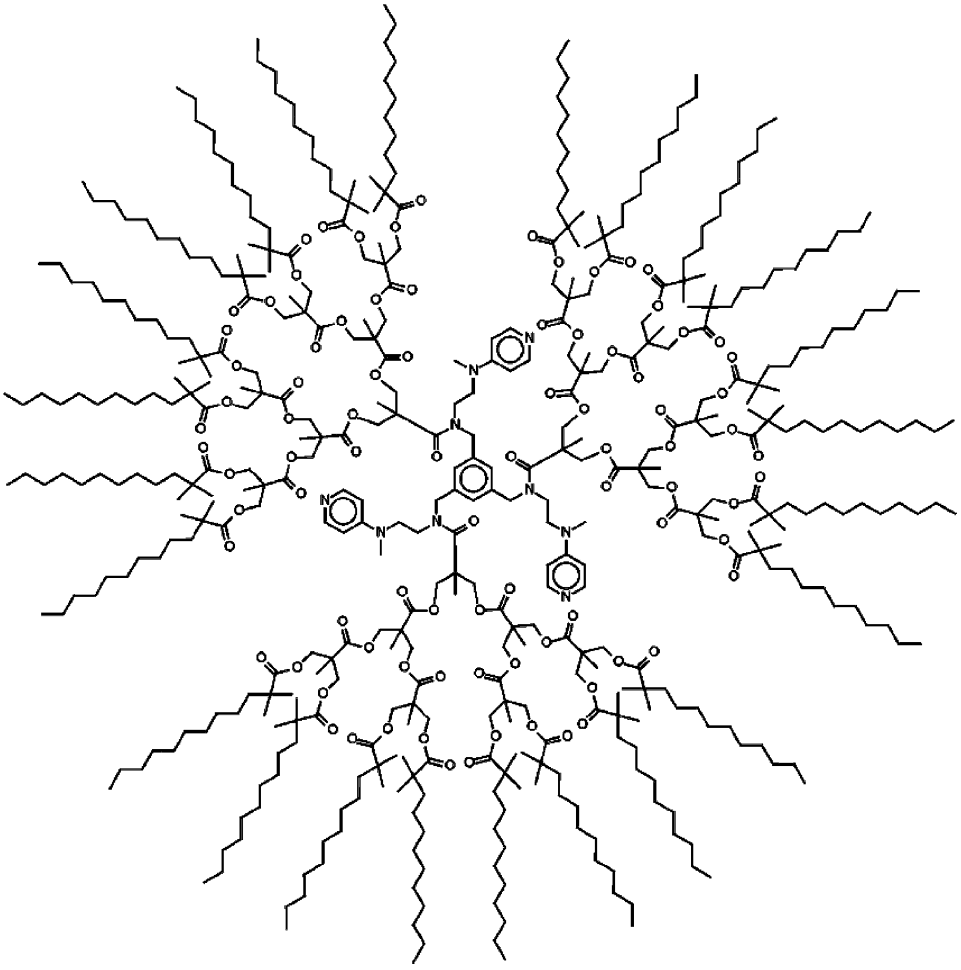


Fig. 14. Fréchet's dendritic 4-(dialkylamino)pyridine catalyst for acylation reactions [146].

2.3. Dendritic organic catalysts

Hawker and Fréchet had pioneered the area of organic dendritic catalysts behaving as reverse micelles with a high density of inner aromatic rings and hydroxy groups stabilizing positively charged transition states as in enzymes [17]. Since cationic polymers and aggregates of quaternary ammonium ions are known to catalyze reactions of anionic compounds particularly in aqueous solution, polycationic dendrimers derived from PPI have been used for this purpose and behave as micellar catalysts in water [132–134]. Reymond has used peptide dendrimers for selective catalysis, including with a combinatorial approach; for instance, esterolysis activity is enhanced [135–138]. Other uses have been found as Lewis-acid dendritic catalysts [139,140]. Organic catalysis is a growing area, and multiple uses of dendrimers are awaited shortly. Reports have appeared on the nitroaldol (Henry) reaction (Fig. 13) [141–143], mimic of glutathione peroxidase [144], esterification [145], acylation (Fig. 14) [146], aminolysis [147,148], enantioselective alkylation [149,150], and activation of hydrogen peroxide [151,152].

3. Conclusion

The field of dendritic catalysis is expanding with a variety of branches. To the classic concepts of catalysts attached to the termini of dendritic tethers that have been steadily applied to asymmetric catalysis, one now deals with new areas such as nanoparticle-encapsulated dendrimers and organic catalysis that were only in their infancy at the turn of the century. Catalysis inside dendrimers is a great idea that is difficult to apply as shown by attempts to use the metal-cored protected dendritic catalyst. The concept of dendron-protected catalytically active core works when ionic bonding between the cored catalyst and dendron is involved, but covalent dendrimers give poorer results. Emphasis is now placed on the recovery of the catalysts, and it is true that leaching is often a problem as in supported catalysis when a large number of catalytic recycling operations are desired. Progress has been made in the applied field of membrane filtration, and the recovery of catalytic material is possible with dendrimers or stars of moderate size. The concept of the reduction of the steric effect at the dendrimer periphery by using star-shaped catalysts instead of dendritic catalysts works rather well. Indeed, careful investigation of dendritic effects on the kinetics upon increase of the dendrimer generation most of the time leads to the observation of a negative dendritic effect due to increasing bulk that inhibits the approach of the catalytic metal center. Sophisticated nanomaterials combining molecular and materials aspects will undoubtedly lead to further improvement and bring this exciting area at the forefront of applicable catalysis.

Acknowledgements

We are grateful to Jocelyne Moncada for assistance in the preparation of the manuscript, and to the Institut Universitaire de France (IUF, DA), the Centre National de la Recherche Scientifique (CNRS), the Ministry of Research and Technology (MRT, thesis grant to DM) and the University Bordeaux I for financial support.

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