Dendritic Catalysts

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Abstract. After the publication of the first papers on dendritic catalysts in 1994, many different examples in this class of (macro)molecular catalysts have been reported in recent years. This chapter provides an overview of (recent) highlights and developments in the field of dendrimer catalysis, with an emphasis on homogeneous catalysis. The distinctive features of periphery-functionalized, chiral and non-chiral metallo-dendrimers are discussed and are compared to those of core-functionalized metallo-dendrimers and metallo-dendrimers containing metal complexes throughout their structure. Furthermore, the class of non-metal-containing dendritic catalysts is described. Special attention is focused on the different types of selectivity encountered in dendrimer catalysis and the concept of dendritic catalyst recycling. A summary of the various reactions catalyzed by dendritic catalysts is provided at the end of this chapter.

Keywords: Dendrimers, (Homogeneous) catalysis, Metals

Topics in Current Chemistry, Vol. 217

1 Introduction

Dendrimers have a particular position within the broad spectrum of macromolecules. One of the most striking features of dendrimers is surely their well-defined structure, in contrast to many other types of macromolecules. The elegance often expressed in the fractal-like dendrimer structure has inspired many research groups over the years [1]. Many of the dendrimer properties are introduced by the applied iterative synthesis, and the use of either convergent or divergent strategies allows for the fine-tuning thereof. Among these are monodispersity, often pseudo spherical structure, and amplification of functional groups. The wide range of possibilities offered by dendritic molecular systems has led to the description of many applications in several fields of science [2]. Potential (bio)chemical applications include host-guest chemistry, drug delivery, self-assembly, and usage as sensor materials. One of the most promising applications of dendrimers is found in homogeneous catalysis, in which the usage of a wide variety of dendritic catalysts and catalyst supports is currently being pursued. Some of these systems are based mainly on the amplification of functional groups at the periphery of the structure. This amplification could lead to dendritic catalysts that are large enough to be recovered from a reaction mixture by ultrafiltration or size-exclusion techniques, thereby solving one of the classical separation problems in homogeneous catalysis. It is also possible that the amplification of functional groups enables cooperative effects between peripheral catalytic sites. Other systems make use of a (single) catalytic group at the interior of a dendrimer. In this way, interactions of the catalyst with the reaction medium or with other catalytic sites can be diminished, possibly resulting in substrate selective catalysis. Dendritic catalysts can then become selective and/or tailor-made catalysts, with properties reminiscent of those often encountered for enzymes. Whereas the high degree of perfection of enzymes might be an unreachable goal, the idea of designing catalytic systems with tunable properties, is a true challenge. A last class of dendritic systems combines the properties of a larger structure with the amplification of functional groups within the structure. In these systems the dendrimer backbone functions not only as a "support", but also holds ligating groups in a highly repetitive and uniform manner. This can result in a high catalyst-to-dendrimer ratio, thereby preventing extensive dilution of active material.

Here, we present an overview of the more recent and important earlier achievements in the field of dendritic catalysis, with an emphasis on homogeneous (organo)metallic catalysis. Dendrimers that are functionalized with metal complexes at their periphery (Sect. 2) as well as a their core (Sect. 3) are discussed. Subsequently, dendrimers that contain metal complexes throughout their structure (Sect. 4) and dendritic catalysts that operate without metals (Sect. 5) will be discussed. At the end, a graphical summary of the catalyzed reactions involved is provided (Sect. 6).

2
Metal Functionalities at the Periphery of a Dendrimer

Starting from the concept of attaching metal complexes to the periphery of a dendrimer, many new dendritic catalysts have been developed. Numerous examples involve the attachment of earlier-developed complexes to a dendrimer "support". These dendritic species exhibit new properties including catalyst deactivation due to proximity effects, catalyst stabilization, and even site co-operativity. Dendrimers with non-chiral and chiral peripheral catalytic sites are described below.

2.1
Non-Chiral Metal Complexes at the Periphery of a Dendrimer

The first example of a catalytically active metallo-dendrimer, having catalytic groups at the periphery, was prepared in the group of Van Koten [3], in a collaboration with the group of Van Leeuwen. The synthesis of this metallo-dendrimer started from carbosilane molecules [4] containing silicon-chlorine bonds at their periphery to which (NCN)-type terdendate ligands {NCN=[$C_6H_3(CH_2NMe_2)_2$-2,6]} were connected. To prevent possible interactions between the different metal sites 1,4-butanediol linkers were placed between the carbosilane backbone and the ligating site. Nickel was introduced in the activated position of the ligands by oxidative addition to a zero-valent nickel source [e.g., $Ni(PPh_3)_4$]. The resulting dendritic aryl-nickel(II)-species **1** (Fig. 1) was applied as a homogeneous catalyst in the *a*tom *t*ransfer *r*adical *a*ddition reaction (ATRA or Kharasch addition reaction) of CCl_4 to methyl methacrylate (MMA). Compared to the mononuclear catalyst, having a similar *para*-functional group, this polynuclear system shows similar behavior, indicating that each NCN-NiX-site (X=Cl, Br) acts independently. The activity per Ni-site is only slightly lower than that of the mononuclear system, which has been ascribed to the non-perfect composition of the metallo-dendrimer. Furthermore, the reaction catalyzed by the polynuclear system involves a clean, regioselective 1 : 1 addition without telomerization/polymerization or the formation of side products. Due to the dimensions of this metallo-dendrimer (2.5 nm) it was the first example of a metallo-dendritic catalyst that was, in principle, suitable for recovery by membrane filtration techniques.

Stimulated by these results, other periphery-functionalized metallo-dendrimer catalysts based on similar carbosilane backbones were prepared, having NCN-metal units connected directly to the carbosilane backbone [5]. Metal introduction in these systems was possible via lithiation followed by a transmetallation of the polylithiated species using an appropriate d^8 metal salt. This new procedure yielded different generations of polynuclear nickelated carbosilane dendrimers (**2**, Fig. 2) [6], which were again tested as homogeneous catalysts in the Kharasch addition reaction [7]. For this series of dendrimers an interesting dependency of the activity on the generation number was found. The G_0-$(NCN\text{-}NiX)_4$ dendrimer showed an activity comparable to that of the mononuclear catalyst. However, for the G_1-$(NCN\text{-}NiX)_{12}$ and G_2-$(NCN\text{-}NiX)_{36}$ dendrimers a dramatic decrease in activity was observed. A nearly complete loss of activity was found for these

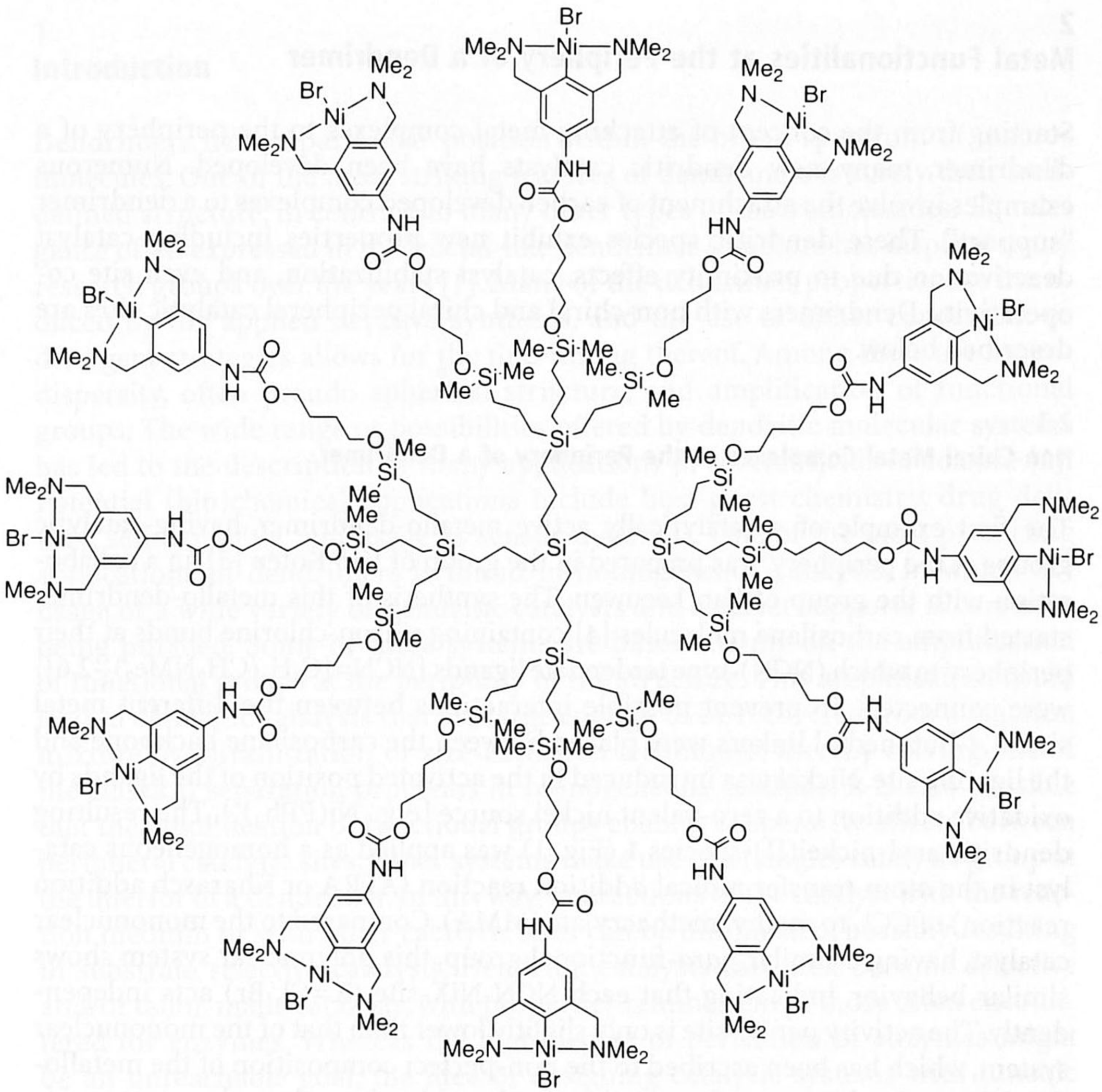
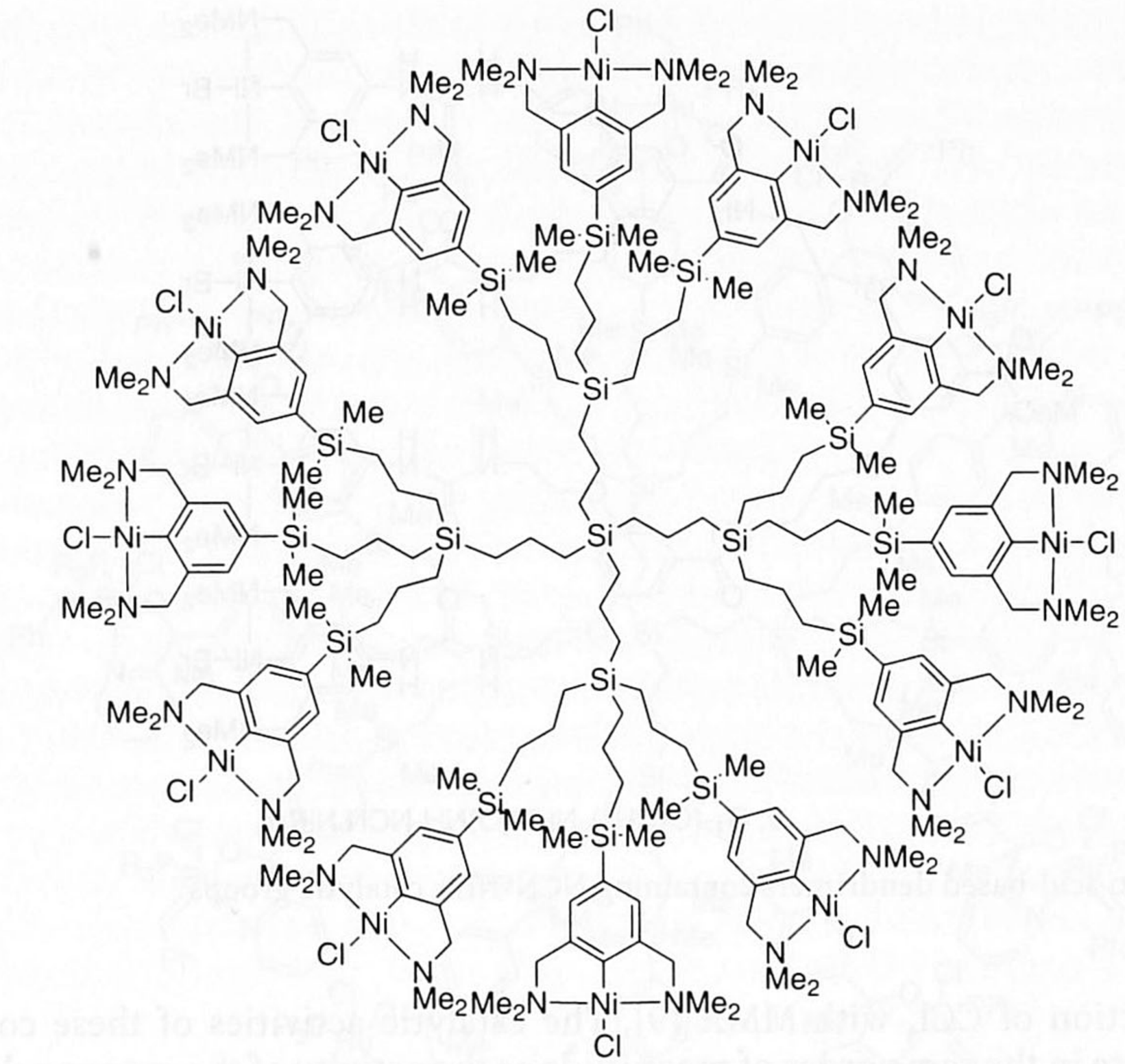
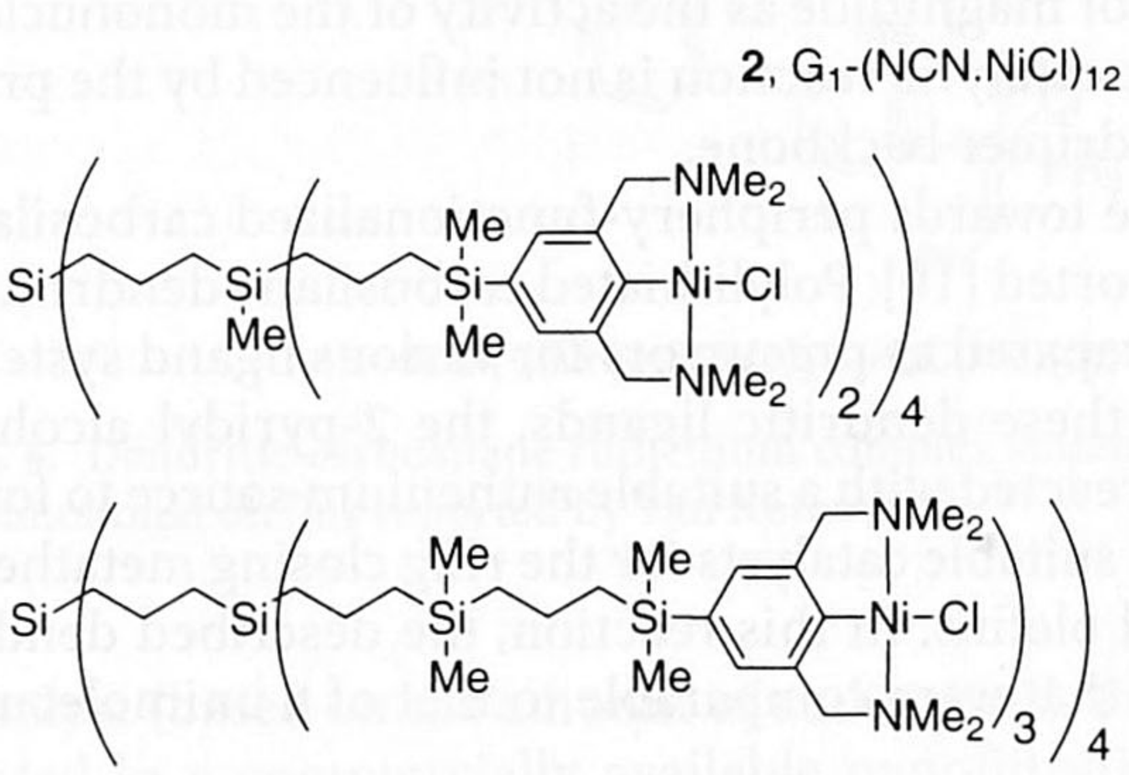


Fig. 1. Van Koten's dendritic polynickel complex

higher generation dendrimers with the conversions of MMA being only 18 and 1.5%, respectively. The loss of activity was ascribed to a proximity effect between different Ni(II)-sites, i.e., a (negative) dendritic effect. During the catalytic process a Ni(III) center can interact with a neighboring site (forming a mixed valence complex) rather than with the transient radicals in solution. This effect is very pronounced in the ATRA catalytic process, which involves a Ni(II)/Ni(III) redox couple. In order to test this hypothesis, modifications of the carbosilane backbone were carried out to yield modified dendrimers **3** and **4** (Fig. 2), which have less congested dendrimer peripheries. These species were successfully applied as homogeneous catalysts in the ATRA reaction and indeed showed activities that were again comparable to the mononuclear catalyst. The dendritic G_0-(NCN-NiX)$_4$ and G_1-(NCN-NiX)$_{12}$ (**2**) complexes were also tested in



2, G_1-(NCN.NiCl)$_{12}$



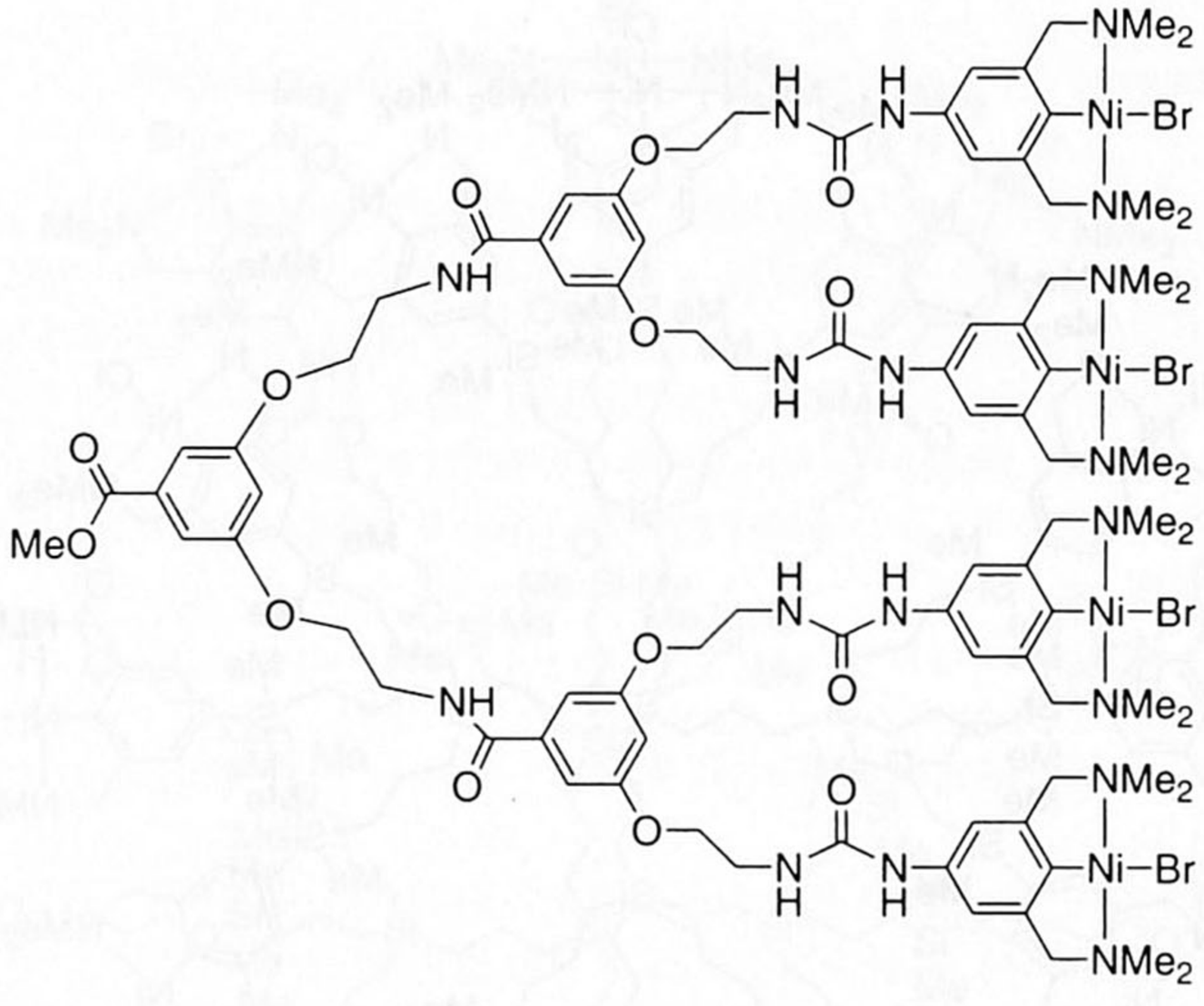
3, G_1'-(NCN.NiCl)$_8$

4, G_1-((CH$_2$)$_3$Si(Me)$_2$NCN.NiCl)$_{12}$

Fig. 2. Modified dendritic polynickel complexes prepared by Van Koten et al.

a continuous membrane reactor equipped with a SelRO MPF-50 nanofiltration membrane [8]. These species showed retentions of 97.4% and 99.8%, respectively, which should be sufficient for many applications. In conclusion, it was shown that the dendritic NCN-NiX complex can very well be applied as a recyclable homogeneous catalyst in the ATRA reaction if proximity effects are taken into account.

Organometallic NCN-NiX catalysts were also connected to the periphery of a dendritic framework built up from amino acids (**5**, Fig. 3), in order to investigate systems that are suitable supports for other functionalized materials. A series of these highly polar compounds was prepared and tested as catalysts in the

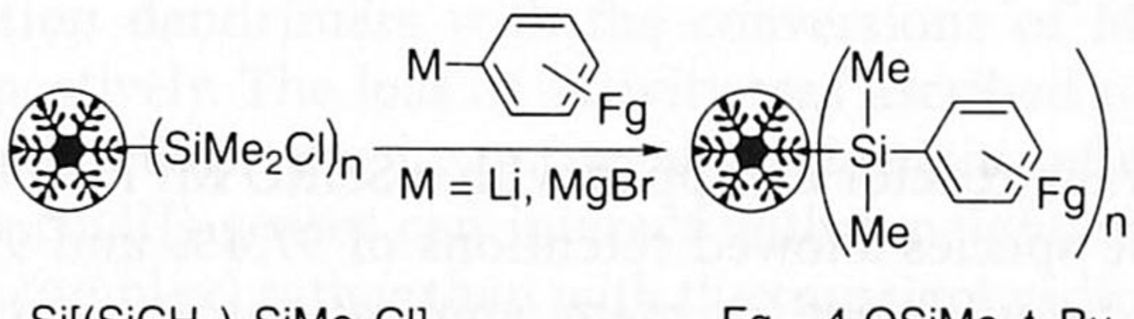


5, G_1-$(O(CH_2)_2NHC(O)NH\text{-}NCN.NiBr)_4$

Fig. 3. Amino acid-based dendrimers containing NCN-NiBr catalytic groups

ATRA reaction of CCl_4 with MMA [9]. The catalytic activities of these compounds were in the same order of magnitude as the activity of the mononuclear complex. This indicates that the catalytic reaction is not influenced by the presence of polar groups in the dendrimer backbone.

Recently, a general procedure towards periphery-functionalized carbosilane dendrimers (Scheme 1) was reported [10]. Polylithiated carbosilane dendrimers of different generations were prepared as precursors for various ligand systems including phosphines. One of these dendritic ligands, the 2-pyridyl alcohol-functionalized dendrimer, was reacted with a suitable ruthenium source to form complexes (**6**, Fig. 4) that were a suitable catalysts for the ring closing metathesis (RCM) reaction of bifunctional olefins. In this reaction, the described dendrimer catalysts showed activities that were comparable to that of a unimolecular

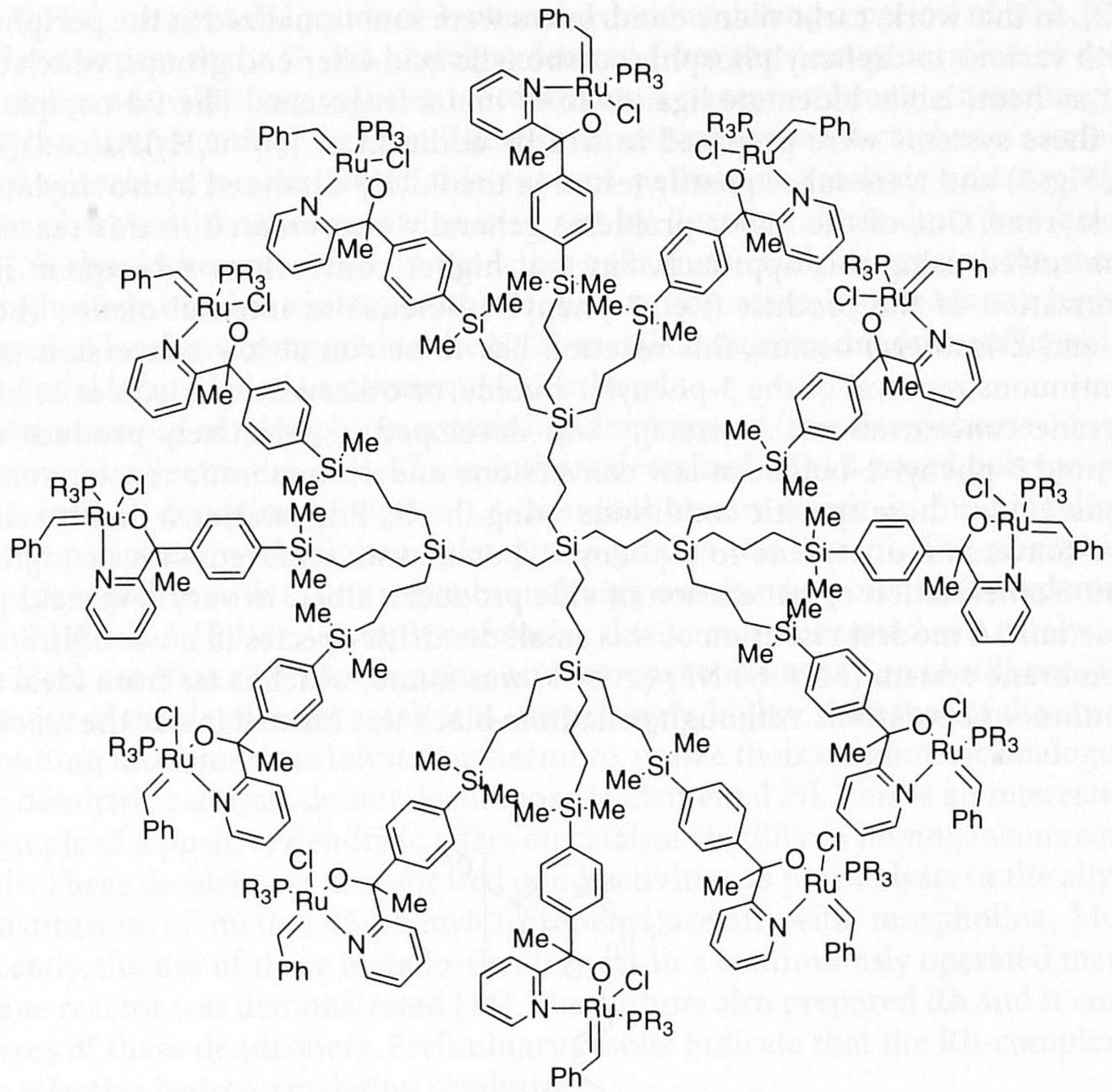


$Si[(SiCH_2)_3SiMe_2Cl]_4$
$Si\{(CH_2)_3Si[(CH_2)_3SiMe_2Cl]_3\}_4$

Fg = 4-$OSiMe_2t$-Bu, n = 4, 12
Fg = $N(Me)SiMe_2t$-Bu, n = 4
Fg = 4-Br, n = 4, 12
Fg = H, n = 4
Fg = PR_2

= dendrimer backbone

Scheme 1. General route towards periphery functionalized carbosilane dendrimers



6, G_1-$((CH_2)_3Si(Me)_2C_6H_4C(Me)(py)ORuCl(CHPh)(PPh_3))_{12}$

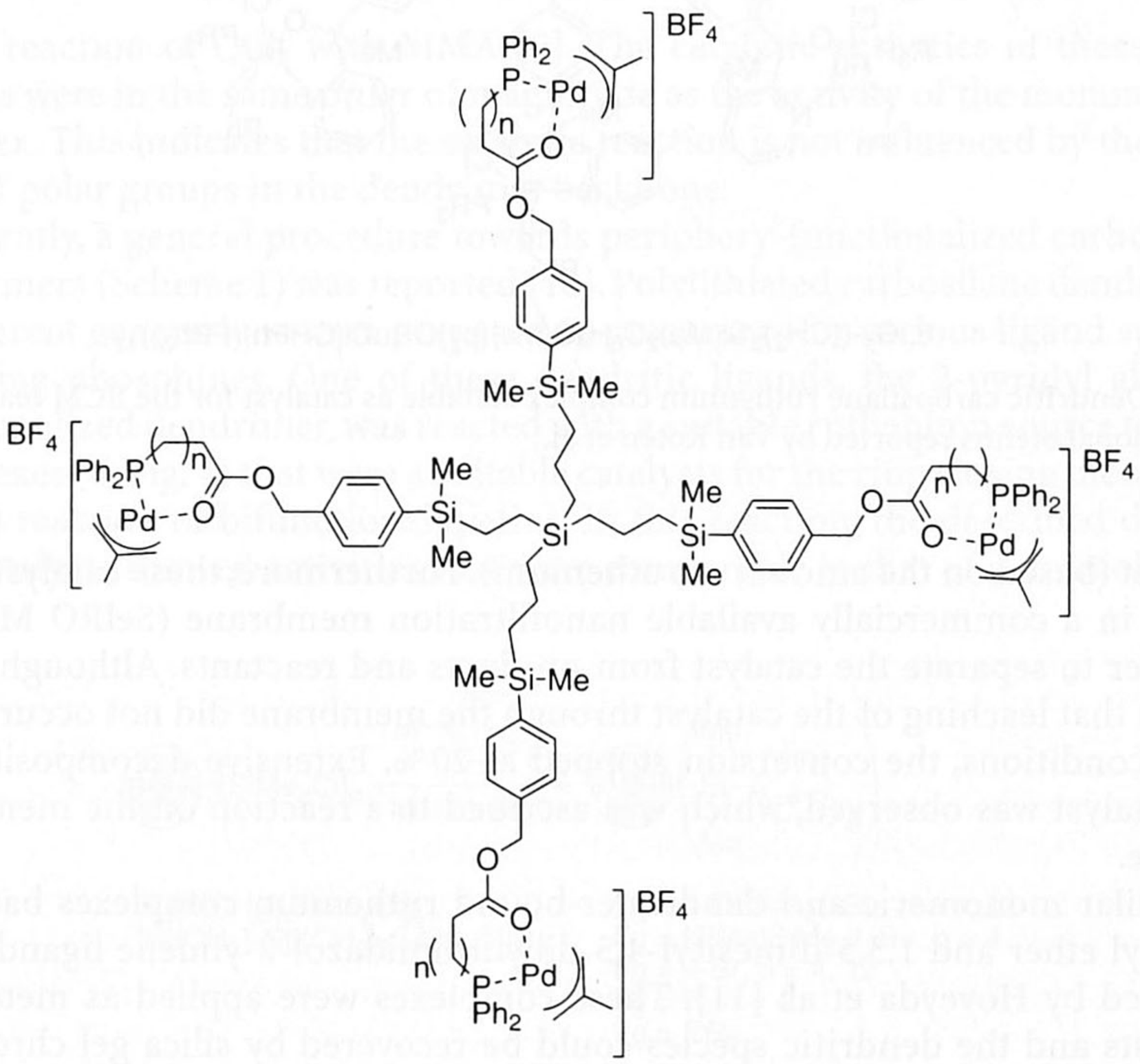
Fig. 4. Dendritic carbosilane ruthenium complex suitable as catalyst for the RCM reaction of bifunctional olefins reported by Van Koten et al.

catalyst (based on the amount of ruthenium). Furthermore, these catalysts were tested in a commercially available nanofiltration membrane (SelRO MPS-60) in order to separate the catalyst from products and reactants. Although it was shown that leaching of the catalyst through the membrane did not occur under these conditions, the conversion stopped at 20%. Extensive decomposition of the catalyst was observed, which was ascribed to a reaction on the membrane surface.

Similar monomeric and dendrimer-bound ruthenium complexes based on styrenyl ether and 1,3,5-dimesityl-4,5-dihydroimidazol-2-ylidene ligands were reported by Hoveyda et al. [11]. These complexes were applied as metathesis catalysts and the dendritic species could be recovered by silica gel chromatography.

An elegant demonstration of the use of membrane technology for the effective recovery of metallo-dendritic catalysts and for selective product formation was presented by the Van Koten group in collaboration with the group of Vogt

[12]. In this work, carbosilane dendrimers were functionalized at the periphery with various ω-diphenylphosphinocarboxylic acid ester end groups, which can act as hemi-labile bidentate ligands to d^8 metal fragments. The Pd-complexes of these systems were prepared in situ by addition of $[(\eta^3\text{-}C_4H_7)Pd(cod)]BF_4$ (7, Fig. 5) and were subsequently tested in the Pd(II)-catalyzed hydrovinylation of styrene. One of the major problems generally encountered in this reaction was solved using this approach. Since at higher conversions subsequent isomerization of the product (i.e., 3-phenyl-1-butene) to internal olefins (both *E*- and *Z*-isomers) occurs, this reaction has to be run at low conversion with continuous removal of the 3-phenyl-1-butene, or otherwise carried out at high styrene concentrations. A strategy was developed to selectively produce the desired 3-phenyl-1-butene at low conversions under membrane reactor conditions. Under these specific conditions using the $G_0\text{-}Pd_4$ catalyst, a highly selective conversion of styrene to 3-phenyl-1-butene was achieved with no significant isomerization or generation of side products, albeit in very low yield per time unit. A modest retention of this small dendritic species in a nanofiltration membrane system (MPF-60 NF) ($\geq 85\%$) was found, which is far from ideal for continuous operations. Although palladium black was formed inside the reactor,



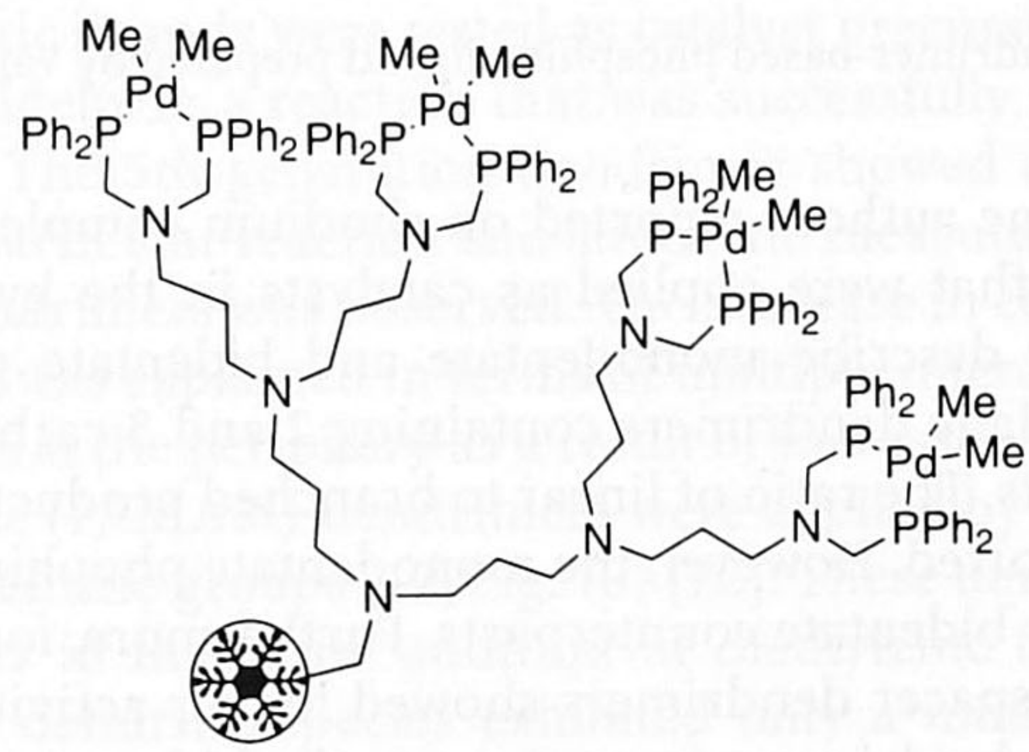
7, $[G_0\text{-}(C_6H_4CH_2OC(O)(CH_2)_nPPh_2.Pd(allyl))_4](BF_4)_4$

Fig. 5. Hemilabile dendrimer palladium catalyst applied in a membrane reactor, prepared by Van Koten, Vogt et al.

the G_0-Pd_4 catalyst did produce 3-phenyl-1-butene during a period of 80 h. The authors expect that a G_1-Pd_{12} catalyst derived from the next generation of dendritic ligands will show sufficient retention in a nanomembrane reactor to give effective catalyst immobilization. The decomposition of the Pd-catalyst is ascribed to the intrinsic properties of this type of palladium catalysis and has also been observed in experiments carried out by Reetz et al., as described below [13]. It should be noted that, in the latter palladium catalytic species, the metal is exclusively bonded via heteroatom donor coordination. This leads to a higher degree of leaching compared to the NCN-metal containing dendrimers in which the metal is bonded via a covalent M–C σ-bond.

An example of phosphine-containing dendrimers (see also Scheme 1) was reported by Reetz et al. [13]. These authors described a DAB-based poly(propylene imine) dendrimer (DAB = 1,4-diaminobutane) which is functionalized at the periphery with diphenylphosphine groups (**8a**, Fig. 6). The phosphine groups together with the nitrogen branching point form a potentially terdentate P,N,P-ligand. A [$PdMe_2$] complex of such a dendrimer was tested as a catalyst in the Heck reaction of bromobenzene and styrene with formation of stilbene. The activity of the dendrimer catalyst is, surprisingly, higher than that of the corresponding monomeric catalyst. Furthermore, unlike their monomeric analogues the dendritic catalysts do not decompose to elemental Pd. This is an interesting example of a positive dendritic effect on catalyst stability in homogeneous catalysis. These dendrimers also showed good activities as precatalysts in the allylic substitution of methyl (3-phenyl-2-propenyl)acetate with morpholine. More recently, the use of these metallo-dendrimers in a continuously operated membrane reactor was demonstrated [14]. The authors also prepared Rh and Ir complexes of these dendrimers. Preliminary results indicate that the Rh-complexes are effective hydroformylation catalysts.

Recently, Reetz and co-workers have shown that sulfonylated DAB-based poly(propylene imine) dendrimers can be cross-linked using scandium triflate [15]. This yields a material that can serve as a heterogeneous catalyst in several reactions, such as the reaction of benzaldehyde, aniline, and an enolsilane to



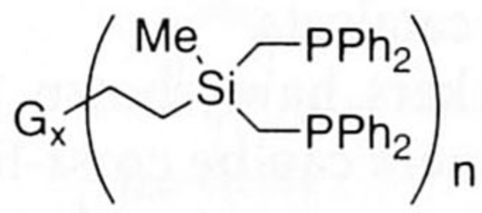
8a, G_2-$(PNP.PdMe_2)_8$
8b, G_3-$(PNP.PdCl_2)_{16}$

Fig. 6. Phosphine dendrimer catalyst prepared by Reetz et al.

yield β-amino ketones, Mukaiyama aldol additions, and the Diels-Alder reaction of methyl vinyl ketone with cyclopentadiene. The authors showed that the cross-linked dendrimer material could be recycled without loss of activity.

Kaneda and co-workers applied a ligand system comparable to that of Reetz et al. [16]. These ligands were used to introduce [$PdCl_2$] units to form dendritic Pd(II) complexes (**8b**, Fig. 6) that were applied in the hydrogenation of conjugated and non-conjugated olefins. In the case of the conjugated olefins the dendrimer complex proved to be a highly effective hydrogenation catalyst. Remarkably as observed for **8a**, the activity of this polynuclear complex was higher compared to that of the corresponding mononuclear complex. The authors also performed the same hydrogenation reaction under heterogeneous conditions and recovered the dendritic catalyst. They showed that the activity as well as the XPS and IR spectra of the spent catalyst were comparable to those of the fresh catalyst.

The research group of Van Leeuwen reported on carbosilane dendrimers appended with peripheral diphenylphosphino end groups [17]. After in situ complexation with allylpalladium chloride, the resultant metallo-dendrimer (**9**, Fig. 7) was used as catalyst in the allylic alkylation of sodium diethyl malonate with allyl trifluoroacetate in a continuous flow reactor. Unlike in the batch reaction, in which a very high activity of the dendrimer catalyst and quantitative conversion of the substrate was observed, a rapid decrease in space-time yield of the product was noted inside the membrane reactor. The authors concluded that this can most probably be ascribed to catalyst decomposition. The product flow (i.e., outside the membrane reactor) was also investigated and it was shown that no active catalyst had leached through the membrane.



9

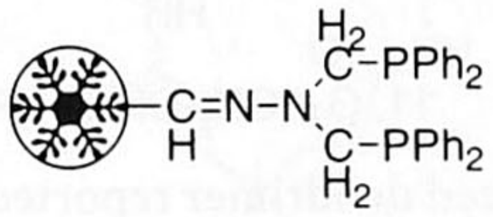
For **9**: x =1 and n = 12

Fig. 7. Carbosilane dendrimer-based phosphine ligand prepared by Van Leeuwen et al.

Recently, the same authors reported on rhodium complexes of these phosphine dendrimers that were applied as catalysts in the hydroformylation of 1-octene[18]. They describe monodentate and bidentate phosphine ligands attached to carbosilane dendrimers containing 2 and 3 carbon atoms between the branching points. The ratio of linear to branched product is about the same for all catalysts reported. However, the monodentate phophines showed higher activities than their bidentate counterparts. Furthermore, for the monodentate phosphines the C_3-spacer dendrimers showed higher activities than the more compact C_2-spacer dendrimers, in contrast to the bidentate phosphines where no effect of the spacer was observed. Higher generation dendrimers generally gave slower rates. The authors suggested that the change in activity for the monodentate phophines is due to the distance between the individual phosphines

and thus the (dendrimer)-P-Rh-P ring size. Preliminary results on membrane ultrafiltration using a commercially available membrane (SelRO MPF-60) showed that this membrane was not compatible with the applied hydroformylation conditions, due to solvent and temperature restrictions.

Other phosphorus-based dendrimers have been described by Majoral, Chaudret and co-workers (**10**, Fig. 8). The authors describe the incorporation of Pd, Pt, and Rh in the diphosphine moieties of these dendrimers [19]. Furthermore, they describe organometallic experiments on the surfaces of these complexes, which indicate that such complexes can serve as homogeneous catalysts. More recently, the authors showed that palladium(II) and ruthenium(II) complexes of these phosphorus-based dendrimers can indeed be applied as homogeneous catalysts in organic transformations such as Stille couplings, Knoevenagel condensations, and Michael additions [20].



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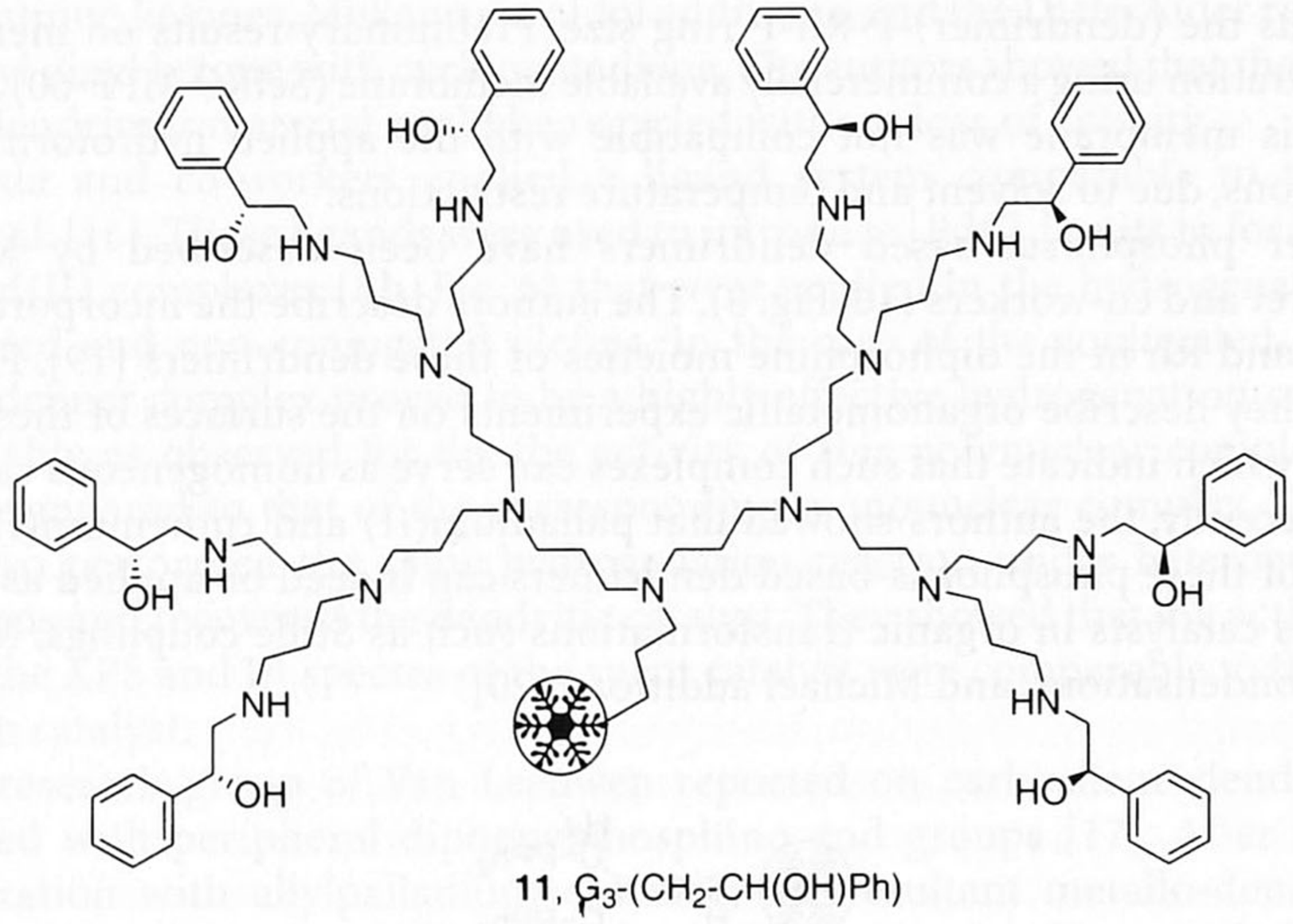
= dendrimer surface of generations 1 to 4

Fig. 8. Phosphine dendrimers prepared by Majoral, Chaudret and co-workers

2.2 Chiral Metal Complexes at the Periphery of a Dendrimer

Meijer et al. prepared different generations of DAB-based poly(propylene imine) dendrimers, which were substituted at the periphery with chiral amino alcohols (see, e.g., **11**, Fig. 9) [21]. The latter functionalities act as chiral ligand sites from which chiral alkylzinc aminoalcoholate catalyst sites can be generated in situ. The dendritic ligands were tested as catalyst precursors in the reductive allylation of benzaldehyde, a reaction that was successfully studied by Seebach et al. (vide infra). The 5th generation dendrimer showed almost no enantioselectivity in this particular reaction and almost no measurable optical rotation for these chiral dendrimers was observed. The decrease in conversion as well as product selectivity was explained in terms of multiple interactions between the terminal groupings at the periphery as a result of increased steric congestion.

Polyamidoamine (PAMAM) dendrimers were applied by Soai et al. as a support for chiral ephedrine groups (**12**, Fig. 10) [22]. These dendritic ligands were applied as catalysts in the chiral addition of diethylzinc to *N*-diphenylphosphinylimines. The dendritic species exhibited only a moderate effect on the product ees, whereas a high chiral induction was found for the non-dendritic model species. Furthermore, quite large amounts of dendrimer catalyst (up to 50 mol %) were needed to obtain these moderate ees. Recently, the same authors applied dendrimers based on rigid hydrocarbon backbones using the same

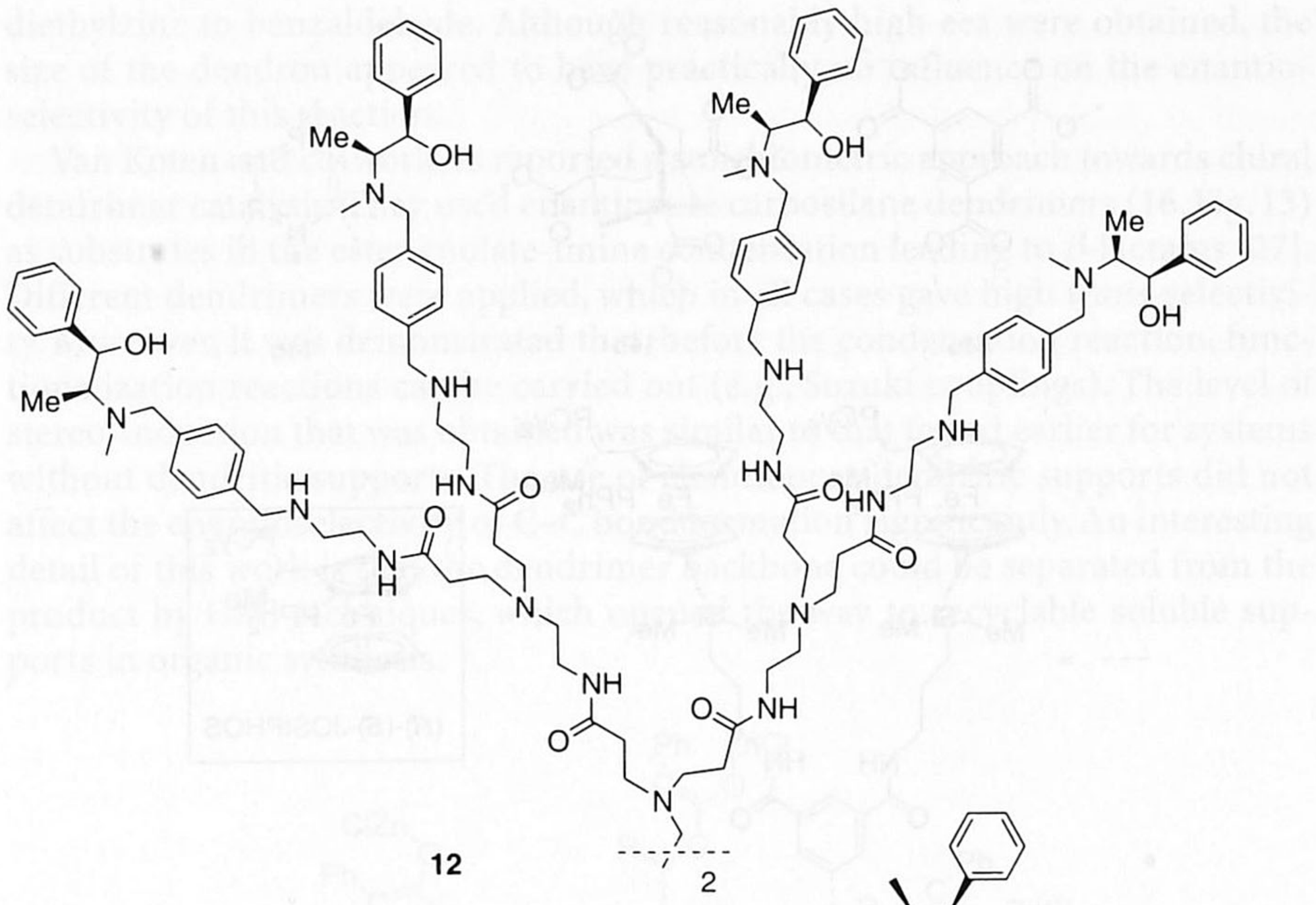


11, G_3-(CH_2-CH(OH)Ph)

Fig. 9. Chiral periphery-functionalized dendrimer reported by Meijer et al.

ephedrine groups (**13**, Fig. 10) [23]. With these systems ees up to 86% were obtained with a catalyst concentration of only 3.3 mol %. The authors explain the different results of the flexible and rigid systems by suggesting that due to the flexibility of the PAMAM dendrimer arms, different ephedrine groups can interact with each other. This may prevent the effective transfer of chiral information during the C–C coupling reaction. In contrast, the hydrocarbon backbone in **13** is much more rigid, thereby diminishing interaction between the chiral groups and resulting in a stereoselective process.

A further example of the application of chiral dendrimers is provided by the group of Togni that has developed dendrimers with asymmetric diphosphine ferrocenyl groups [so-called (*R*)-(*S*)-Josiphos] attached to the surface [24]. The dendrimer backbone is constructed from benzene-1,3,5-tricarboxylic acid (**14a**) or adamantane-1,3,5,7-tetracarboxylic acid (**14b**) as core. In a more recent paper Togni et al. describe the same type of dendrons, attached to a cyclophosphazene core (**14c**, Fig. 11) [25]. These dendrimer ligands were converted in situ into the Rh(I) complexes, by a complexation reaction of the dendritic ligand with [Rh(COD)]BF_4. The adamantane core-based dendrimer complexes were tested as hydrogenation catalysts in the asymmetric hydrogenation of dimethyl itaconate in methanol. In all cases, the measured enantioselectivity was high (98.0–98.7%), and only slightly lower than the ees found for the monomeric rhodium complex of Josiphos. Likewise, for the cyclophosphazene-core based dendrimers preliminary catalysis experiments indicated that comparable ees were obtained. The authors concluded that in both cases the catalytic units act as independent units (compare polynickel complexes **1**–**4**) and that the dendritic structure was not influencing the stereoselection process. Furthermore, preliminary experiments for the adamantane core-based dendrimer indicate that it is completely retained by a commercially available nanofiltration membrane.



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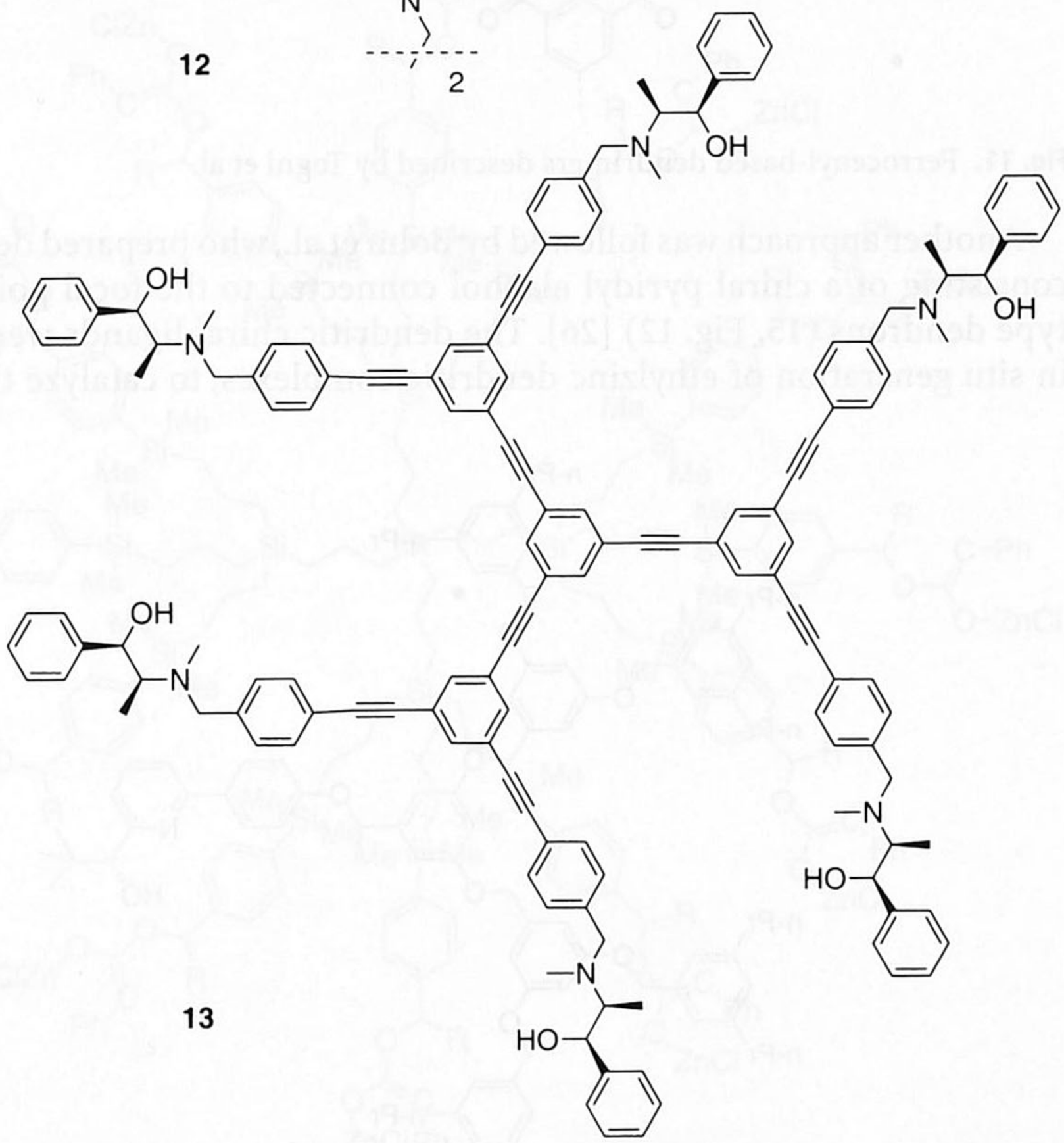

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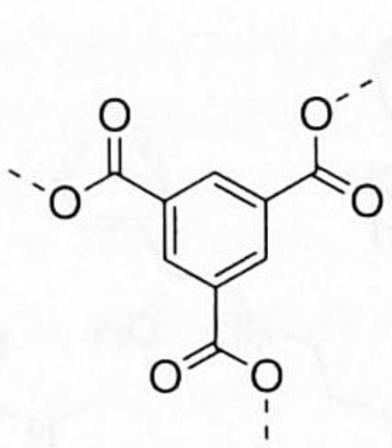
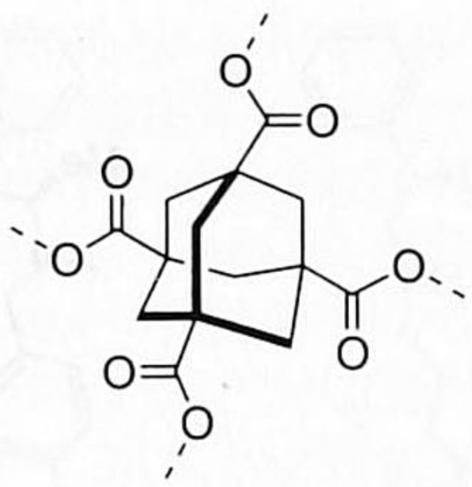
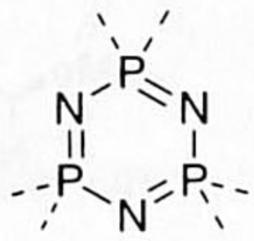
Fig. 10. Flexible and rigid chiral dendrimers prepared by Soai et al.



14a



14b



14c

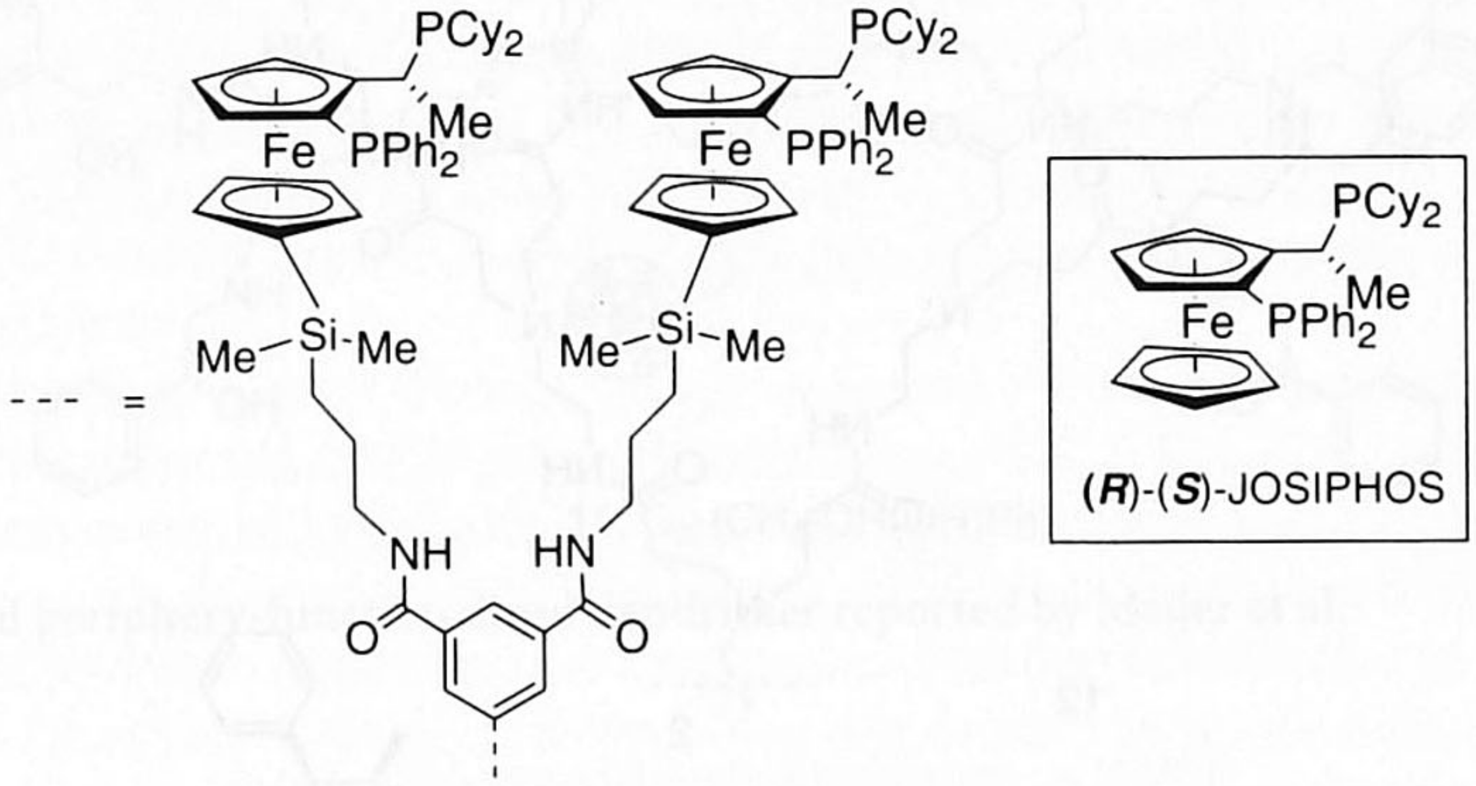
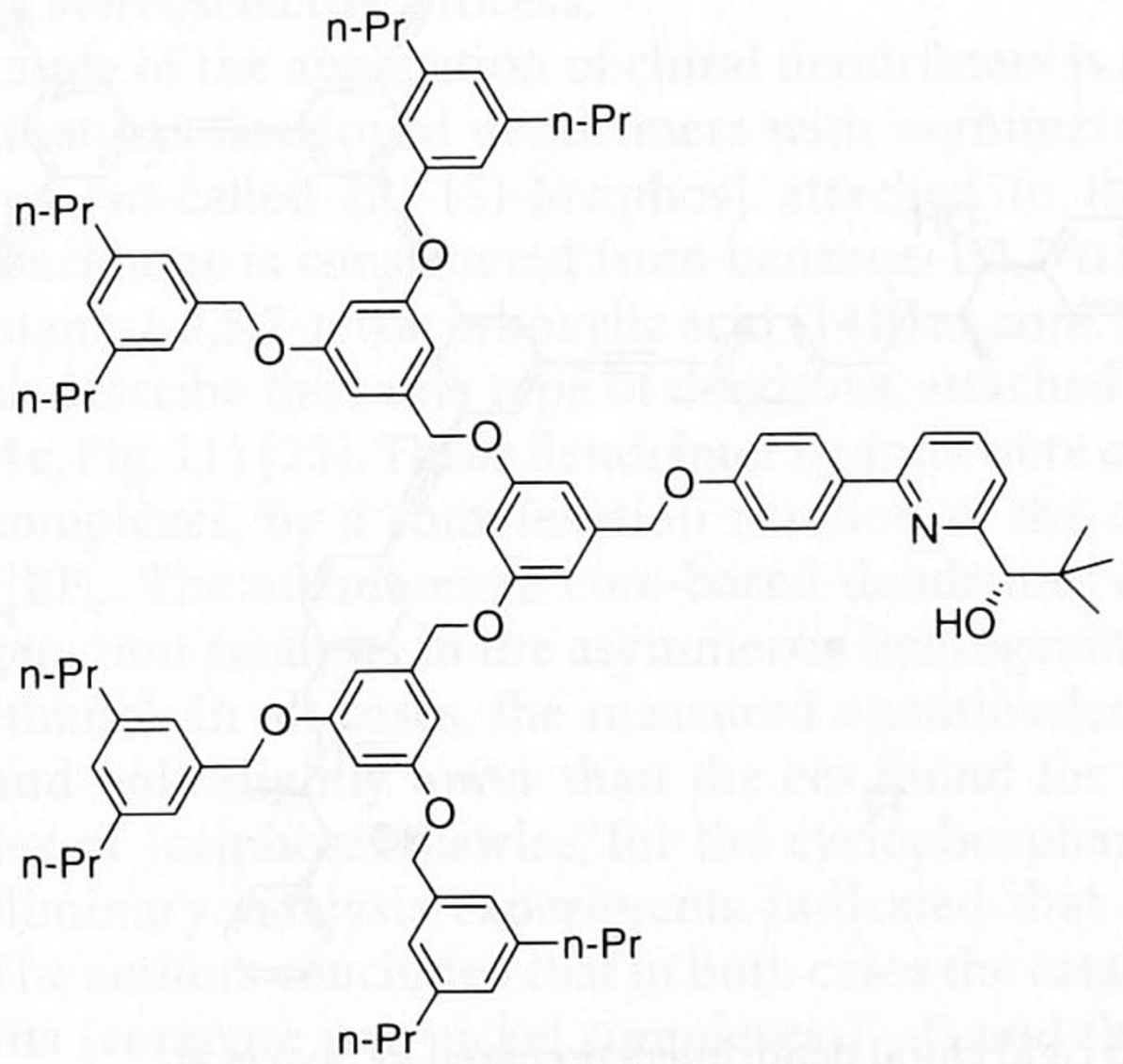


Fig. 11. Ferrocenyl-based dendrimers described by Togni et al.

Another approach was followed by Bolm et al., who prepared dendron ligands consisting of a chiral pyridyl alcohol connected to the focal point of Fréchet-type dendrons (**15**, Fig. 12) [26]. The dendritic chiral ligands were used for the in situ generation of ethylzinc dendritic complexes, to catalyze the addition of

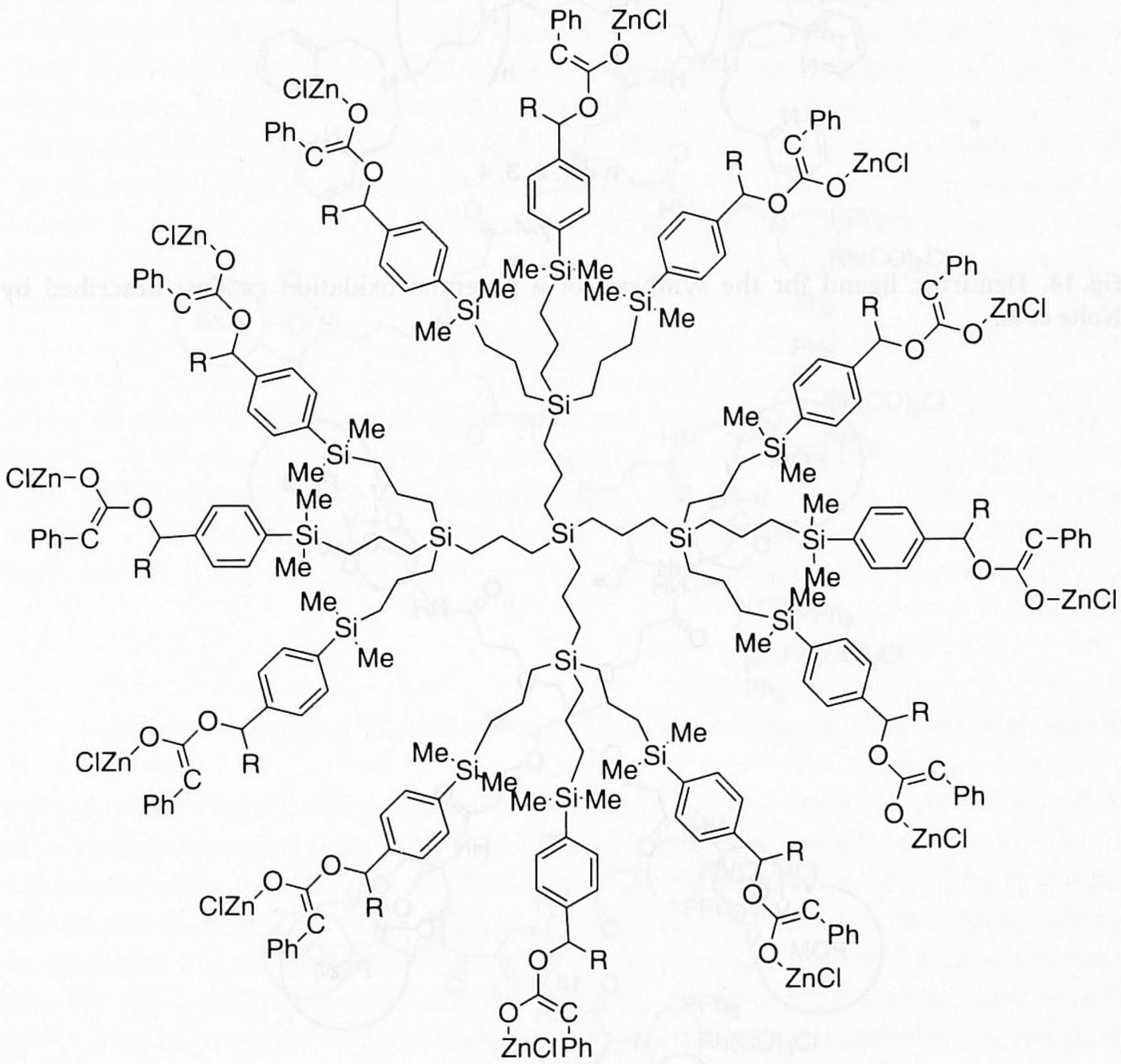


15, G_2-(C_6H_4-py-CH_2(OH)*t*-Bu)

Fig. 12. Monofunctional dendritic catalyst described by Bolm et al.

diethylzinc to benzaldehyde. Although reasonably high ees were obtained, the size of the dendron appeared to have practically no influence on the enantioselectivity of this reaction.

Van Koten and co-workers reported a stoichiometric approach towards chiral dendrimer catalysis. They used enantiopure carbosilane dendrimers (**16**, Fig. 13) as substrates in the ester enolate-imine condensation leading to β-lactams [27]. Different dendrimers were applied, which in all cases gave high *trans*-selectivity. Moreover, it was demonstrated that, before the condensation reaction, functionalization reactions can be carried out (e.g., Suzuki couplings). The level of stereo-induction that was obtained was similar to that found earlier for systems without dendritic supports. The use of enantiopure dendritic supports did not affect the enantioselectivity of C–C bond formation significantly. An interesting detail of this work is that the dendrimer backbone could be separated from the product by GPC techniques, which opened the way to recyclable soluble supports in organic synthesis.



16, G_2-CH_2(R)OC(CPh)OZnCl

Fig. 13. Chiral dendrimers applied as stoichiometric reagents by Van Koten et al.

2.3 Miscellaneous Periphery-Functionalized Dendritic Metal Complexes

As a model for the O_2-transport copper protein hemocyanin, multicopper dendrimers were prepared by Nolte and co-workers [28]. The dendrimers employed consist of a DAB-based poly(propylene imine) backbone, which is functionalized with pyridylethyl moieties (**17**, Fig. 14). These terdentate ligands are able to form copper(II) and zinc(II) complexes upon addition of the metal ion perchlorates. The authors also succeeded in the preparation of the corresponding

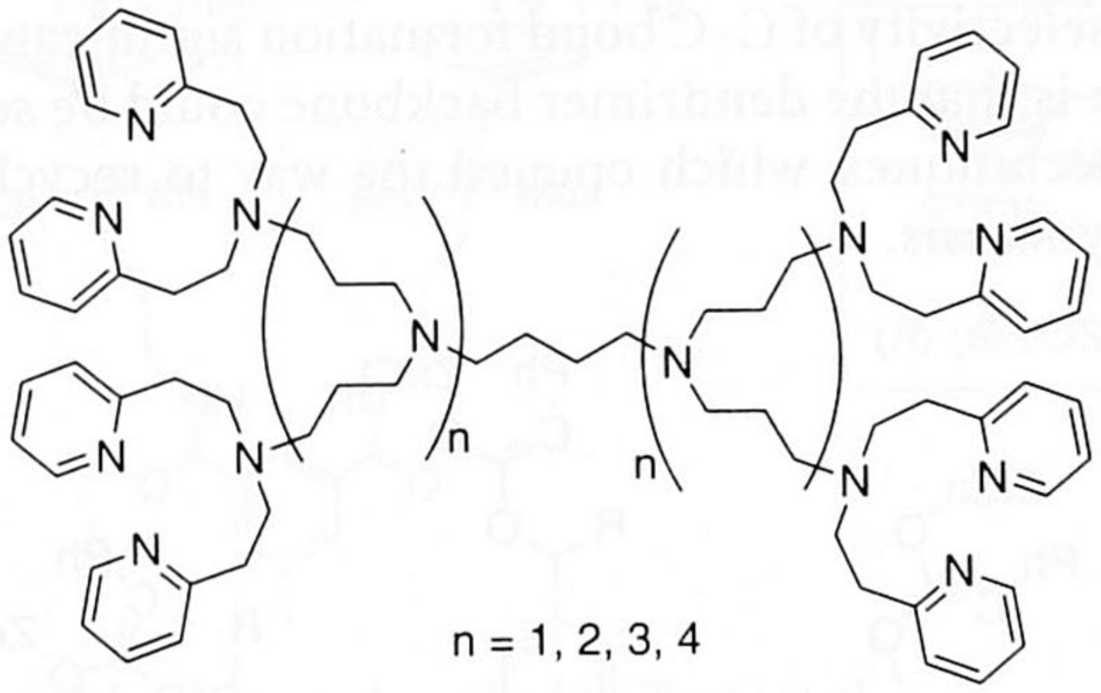


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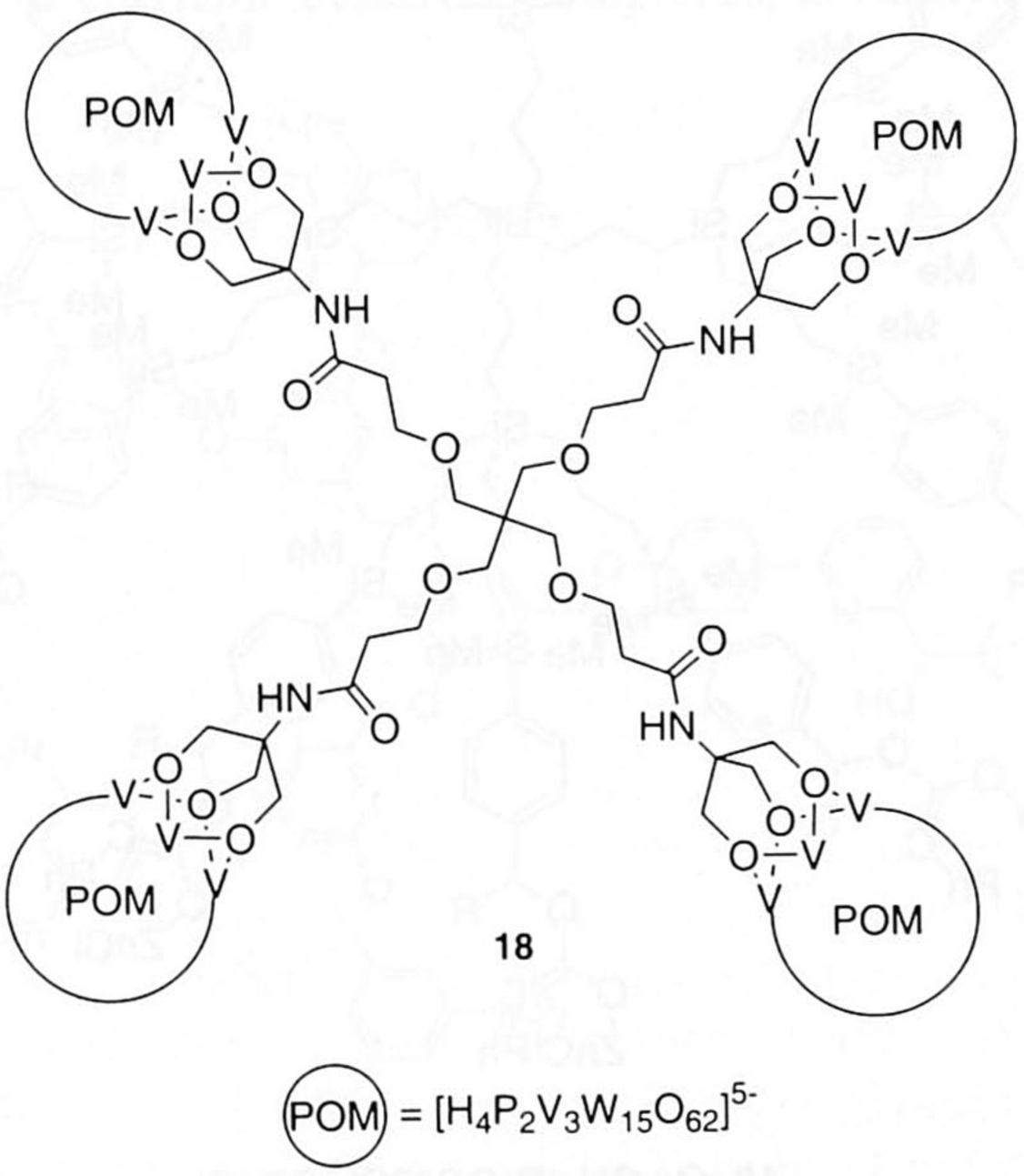
Fig. 14. Dendritic ligand for the synthesis of a potential oxidation catalyst described by Nolte et al.



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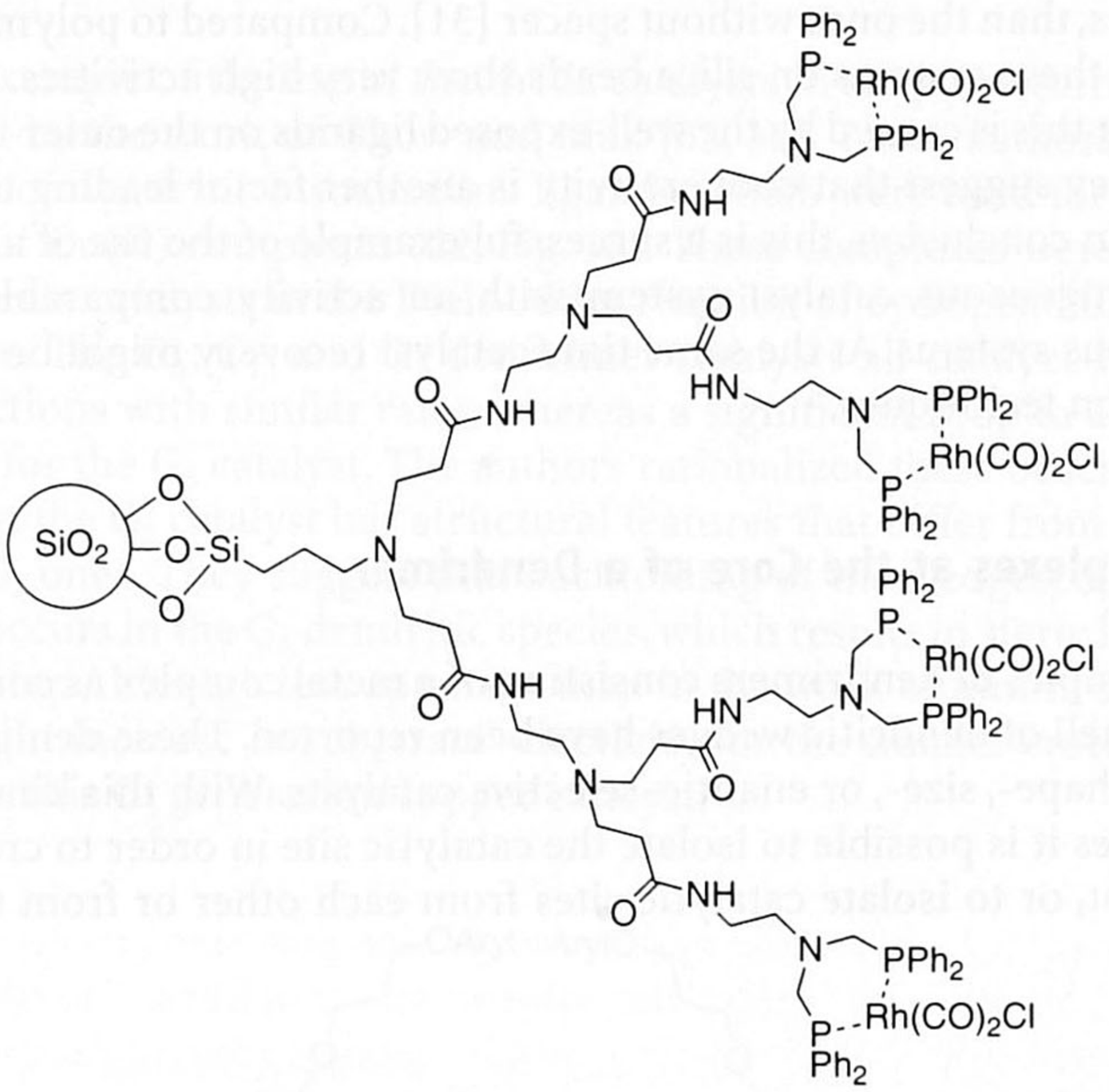
POM = $[H_4P_2V_3W_{15}O_{62}]^{5-}$

Fig. 15. Simple dendritic structures with polyoxometalate functionalities described by Newkome et al.

copper(I) complexes and showed for the $Cu(I)_{32}$ complex that, upon treatment of this complex with O_2, 65–70% of the copper centers are involved in dioxygen binding. These complexed dioxygen molecules may be regarded as highly activated, which would make this dendritic complex a good candidate for an oxidation catalyst.

The attachment of inorganic polyoxometalates (POM) to simple dendrimer surfaces was reported by Newkome and Hill [29]. The authors describe the attachment of four $[H_4P_2V_3W_{15}O_{62}]^{5-}$ units to simple dendrimer backbones by ester bonds (**18**, Fig. 15). These POM derivatives were applied as homogeneous catalysts in the oxidation of tetrahydrothiophene (THT) by both *t*-BuOOH and H_2O_2. Although this reaction is catalyzed by strong acids, catalysis by the (less acidic) POM derivatives is more efficient than catalysis by *p*-toluenesulfonic



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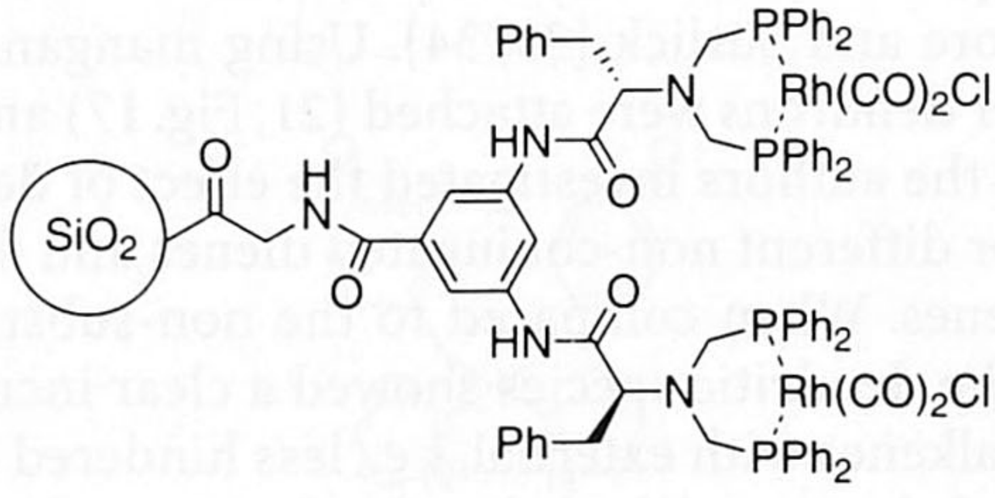

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Fig. 16. Heterogeneous dendrimer catalysts prepared by Alper et al.

acid. Furthermore, these systems can be recovered by precipitation followed by filtration, and used again without loss of activity.

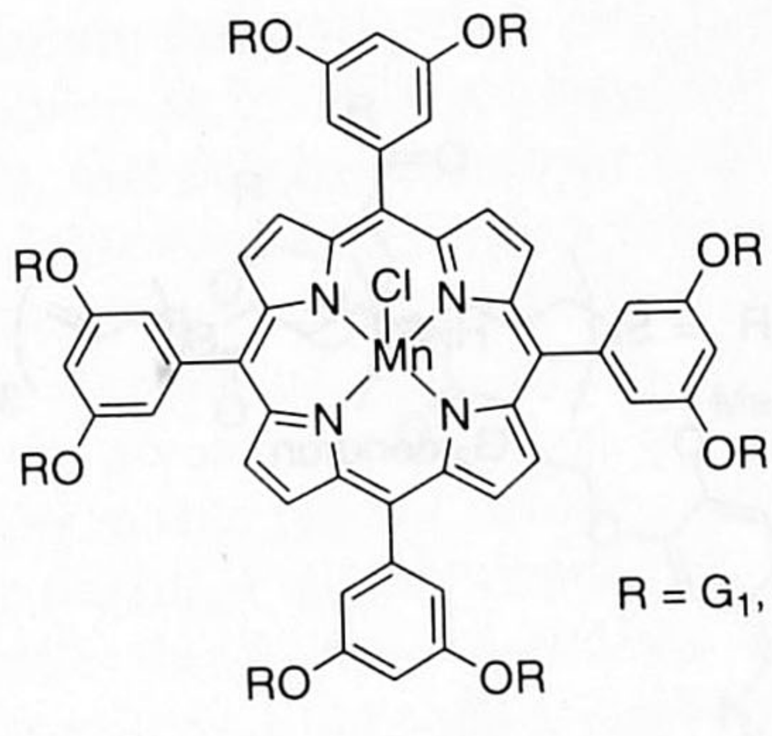
Heterogeneous periphery-functionalized dendrimer catalysts were described by the group of Alper, who made use of dendritic wedges grafted on silica beads [30]. For this purpose PAMAM and branched phenyl propionaldehyde dendritic wedges were used to which diphosphine ligands were connected. Rhodium(I) complexes of these dendrimers were applied as hydroformylation catalysts (**19**, **20**, Fig. 16). The rhodium content of these compounds was estimated using ICP analysis. In catalysis, both kinds of complexes are highly active and show excellent selectivities towards branched aldehydes using a variety of olefins. However, higher generation dendrimers of these systems showed lower activities. The authors ascribe this to steric congestion of the dendrimer surface and tested this hypothesis by introducing a spacer arm. Although slow leaching of rhodium was observed, the dendrimers containing a spacer showed higher activities, even after 4 cycles, than the ones without spacer [31]. Compared to polymer-supported catalysts these systems on silica beads show very high activities. The authors propose that this is caused by the well-exposed ligands on the outer-core of these systems. They suggest that cooperativity is another factor leading to high reactivity [32]. In conclusion, this is a successful example of the use of a dendrimer-based heterogeneous catalyst system with an activity comparable to that of homogeneous systems. At the same time catalyst recovery might be possible via size exclusion techniques.

3
Metal Complexes at the Core of a Dendrimer

Several examples of dendrimers consisting of a metal complex as core and a surrounding shell of dendritic wedges have been reported. These dendrimers were applied as shape-, size-, or enantio-selective catalysts. With this kind of dendritic complexes it is possible to isolate the catalytic site in order to create a chiral environment, or to isolate catalytic sites from each other or from the reaction medium.

3.1
Shape-Selective or Regioselective Catalysis in the Core of a Metallo-Dendrimer

A first example of shape-selective catalysis by metallo-dendrimers was reported by the groups of Moore and Suslick [33, 34]. Using manganese porphyrins to which phenylpolyester dendrons were attached (**21**, Fig. 17) and iodosylbenzene as the oxygen source, the authors investigated the effect of dendron size on the rate of epoxidation for different non-conjugated dienes and for 1:1 mixtures of linear and cyclic alkenes. When compared to the non-substituted manganese porphyrin complex, the dendritic species showed a clear increase in selectivity for conversion of the alkenes with external, i.e., less hindered double bonds and a higher affinity toward electron-rich olefins. Furthermore, an increased stability of the metalloporphyrin core towards oxidation was observed for the dendritic species.



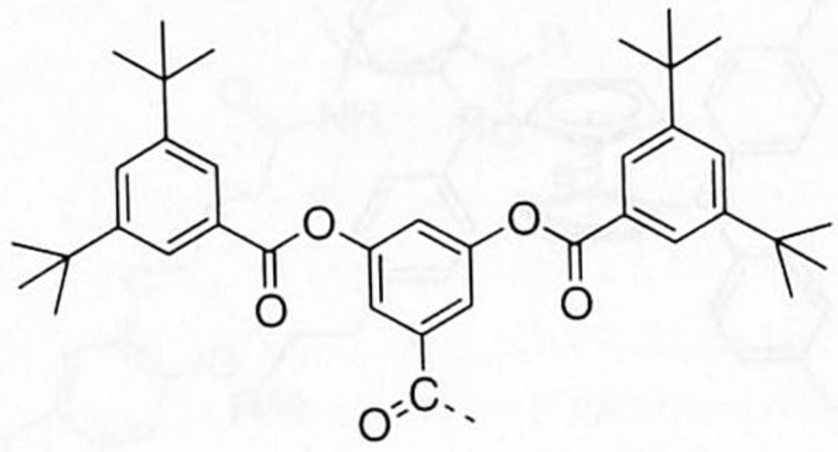


Fig. 17. Shape-selective manganese porphyrins prepared by Moore and Suslick et al.

Another example of the use of dendritic catalysts in shape-selective catalysis was provided by the work of Chow and Mak [35, 36]. These authors described the synthesis of dendritic bisoxazoline ligands, which were used for the in situ preparation of Cu(II) complexes (**22**, Fig. 18). These complexes were employed as homogeneous catalysts in the Diels-Alder reaction of cyclopentadiene with a crotonylimide. The G_0, G_1, and G_2 dendrimer catalysts all catalyzed the cycloaddition reactions with similar rates, whereas a significant drop in activity was encountered for the G_3 catalyst. The authors rationalized these observations by assuming that the G_3 catalyst has structural features that differ from that of the G_0, G_1, and G_2 ones. They suggest that backfolding of the wedges, due to steric constraints, occurs in the G_3 dendritic species, which results in steric blocking of the metal center. Although less apparent than in the work of Moore and Suslick [33, 34], a slight increase in substrate selectivity for the smaller crotonylimides was found for this G_3 generation copper catalyst.

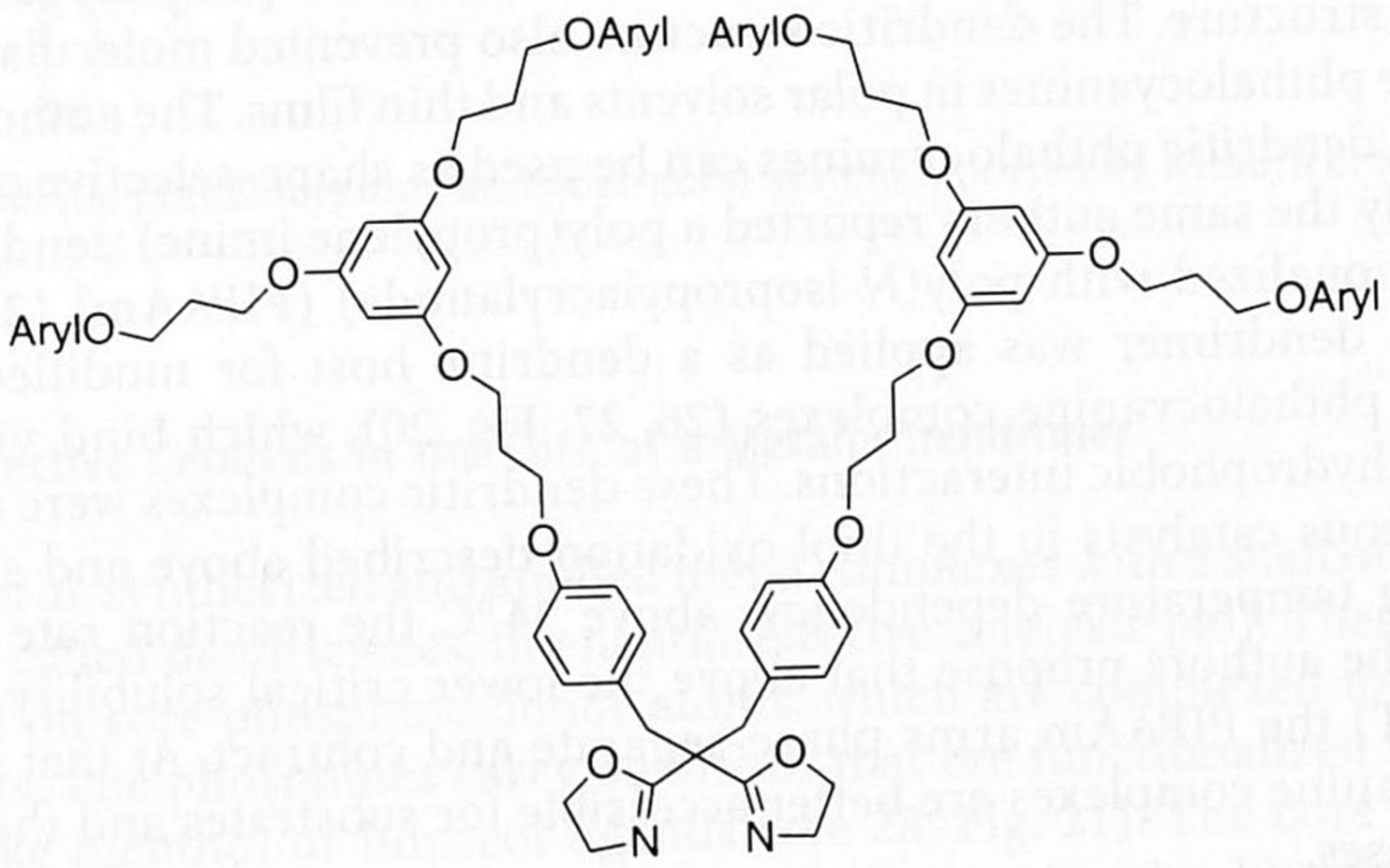


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Fig. 18. Dendritic bisoxazoline ligand prepared by Chow and Mak

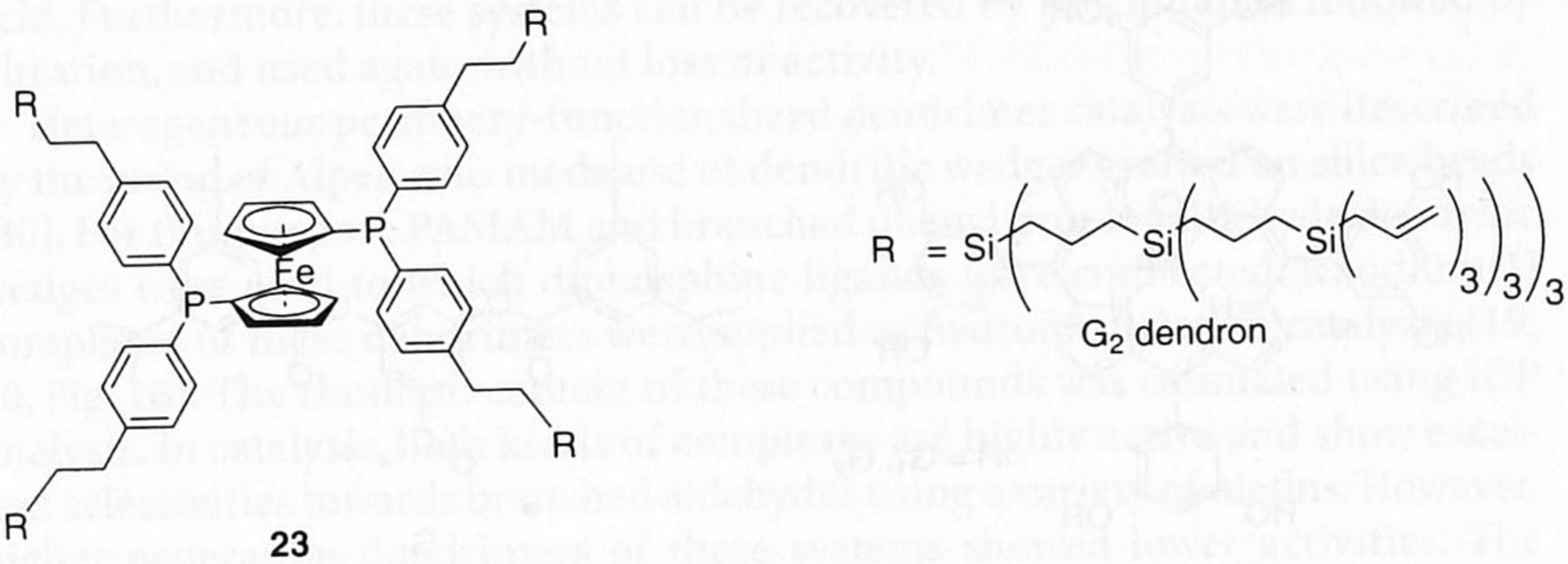

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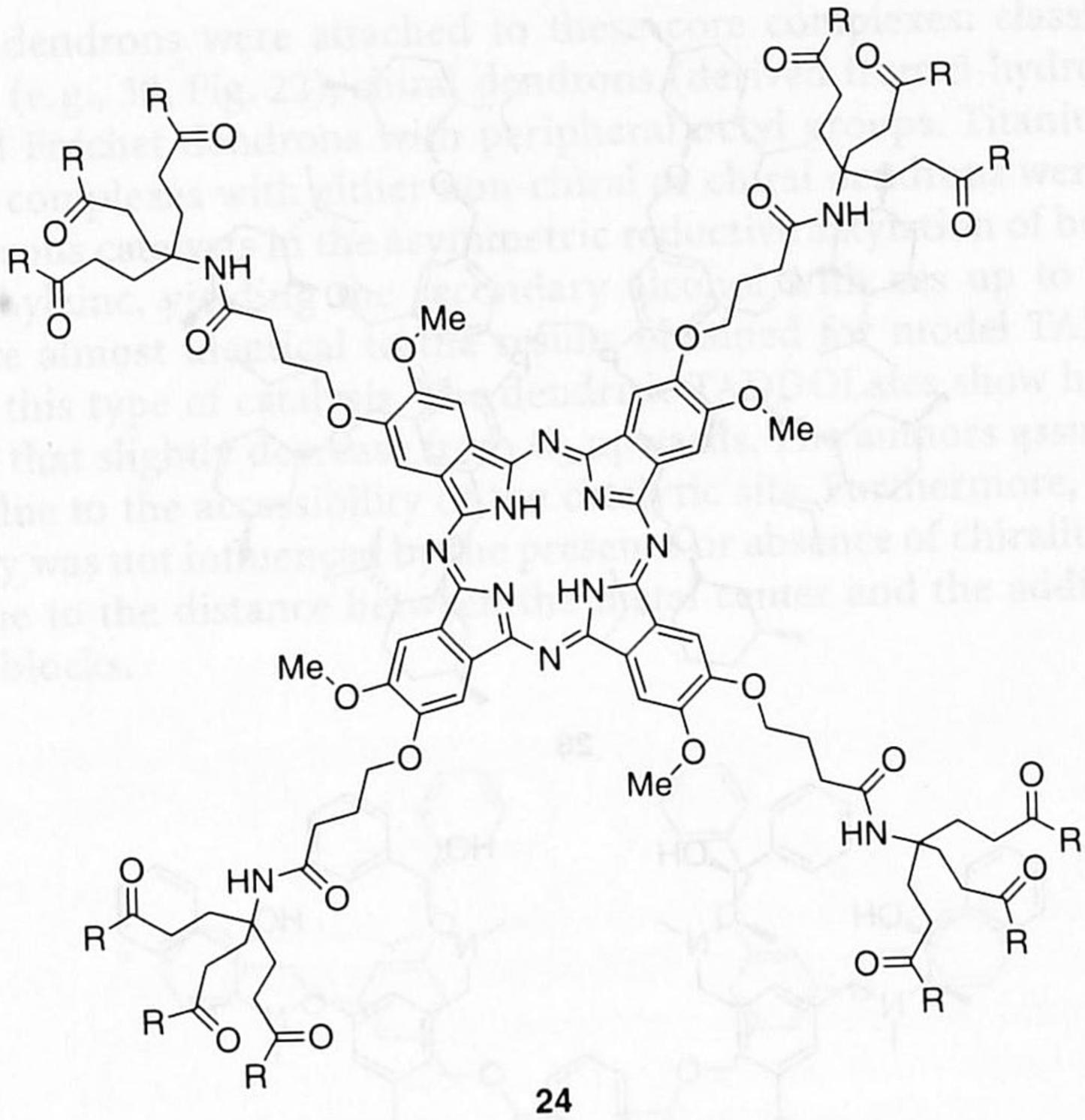
Fig. 19. Ferrocenyldiphosphine core dendrimer prepared by Van Leeuwen et al.

Stereo-selective catalysis at the core of a metallo-dendrimer was pursued by the group of Van Leeuwen, who prepared a ferrocenyldiphosphine (DPPF) core functionalized with different generations of carbosilane dendrons (**23**, Fig. 19) [37]. The resulting dendritic ligands were used for the in situ complexation of $PdCl_2$ from a suitable Pd(II) precursor to yield $PdCl_2$-dendrimer complexes. These complexes were used as catalysts for the allylic alkylation of 3-phenyl-acetate with diethyl 2-sodio-2-methylmalonate. For this reaction, a decrease in catalyst activity with increasing generation number of the carbosilane dendrons was found. In addition, the selectivity for the *trans*-product slightly decreased from 90% for a DPPF model compound to 76% for a G_3 carbosilane dendron ligand.

Dendritic phthalocyanines were prepared and studied by Kimura et al. [38]. Cobalt complexes of these phthalocyanines (**24**, Fig. 20) were applied as catalysts for the oxidation of 2-mercaptoethanol. The catalytic activity of the dendrimer catalyst was 20% less than that of a non-dendritic phthalocyanine. However, the stability of the dendritic catalyst was higher than that of the non-dendritic species, most likely due to encapsulation of the metallo-phthalocyanine in the dendritic structure. The dendritic structure also prevented molecular aggegration of the phthalocyanines in polar solvents and thin films. The authors suggest that these dendritic phthalocyanines can be used as shape-selective catalysts.

Recently the same authors reported a poly(propylene imine) dendrimer that was functionalized with poly(*N*-isopropylacrylamide) (PIPAAm) (**25**, Fig. 20) [39]. This dendrimer was applied as a dendritic host for modified, anionic cobalt(II) phthalocyanine complexes (**26**, **27**, Fig. 20), which bind via electrostatic and hydrophobic interactions. These dendritic complexes were applied as homogeneous catalysts in the thiol oxidation described above and showed an interesting temperature dependency; above 34 °C the reaction rate increases sharply. The authors propose that above the lower critical solubility temperature (LCST) the PIPAAm arms phase-separate and contract. At that point, the phthalocyanine complexes are better accessible for substrates and the reaction rate increases.



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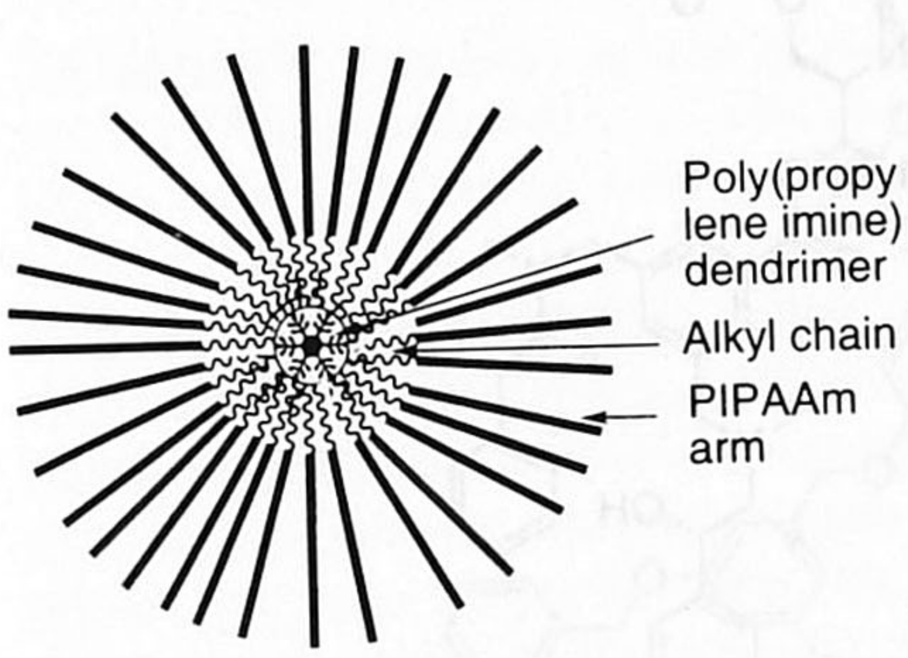

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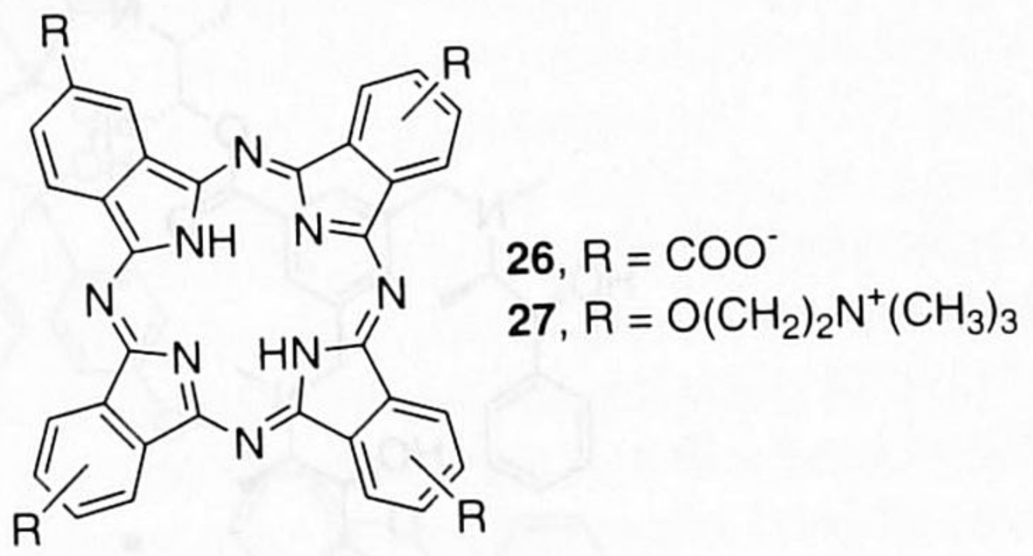
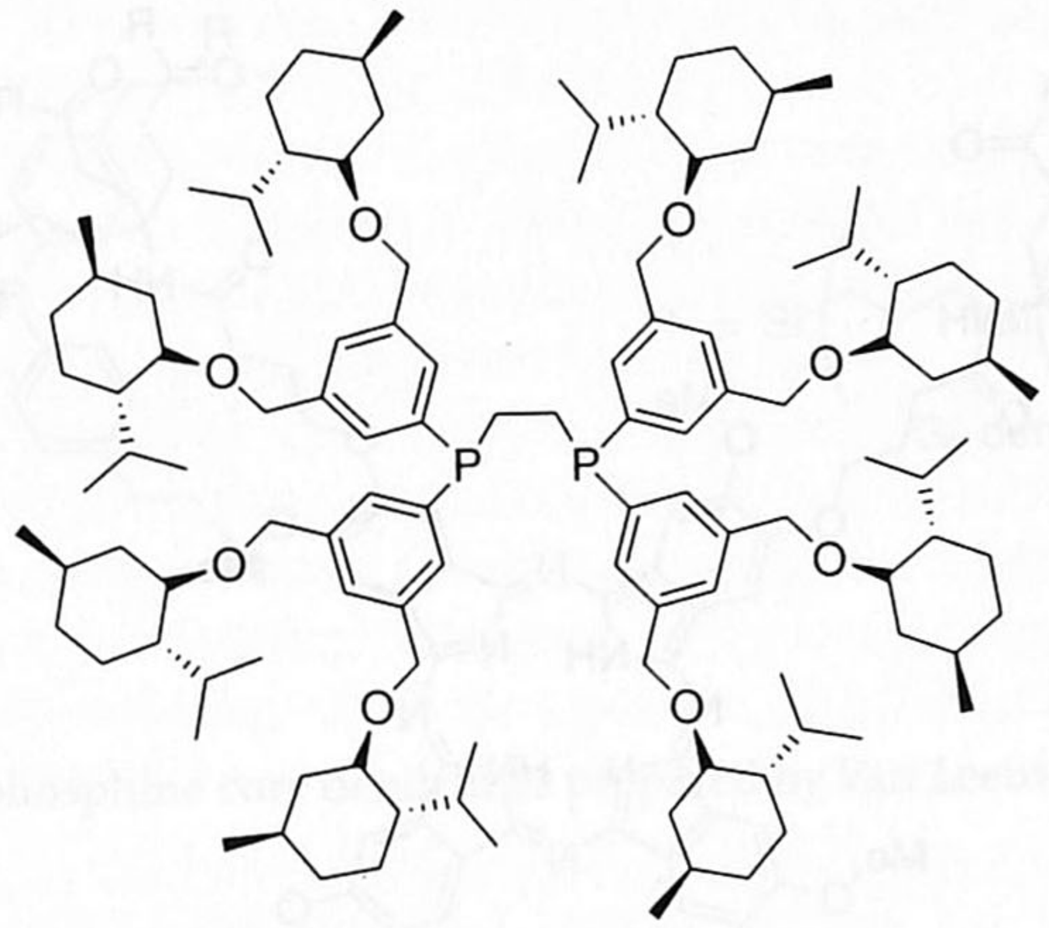


26, R = COO^-
27, R = $O(CH_2)_2N^+(CH_3)_3$

Fig. 20. Dendritic phthalocyanine and host-guest system reported by Kimura et al.

3.2 Enantioselective Catalysis in the Core of a Metallo-Dendrimer

Brunner et al. synthesized and applied metal complexes with a shell of dendrons, which he called *dendrizymes*, in enantioselective catalysis [40]. These catalysts are based on core phosphine donor atoms, which are complexed to transition metal salts. The phosphines carry dendrons that are functionalized with chiral groups like menthol or borneol ligands (see **28**, Fig. 21). The core phosphine donor-atoms can be complexed to (transition) metals salts, like rhodium, resulting in a dendron-enlarged 1,2-bis(diphosphino)ethane Rh(I) complex that was used as catalyst in the hydrogenation of acetamidocinnamic acid to yield



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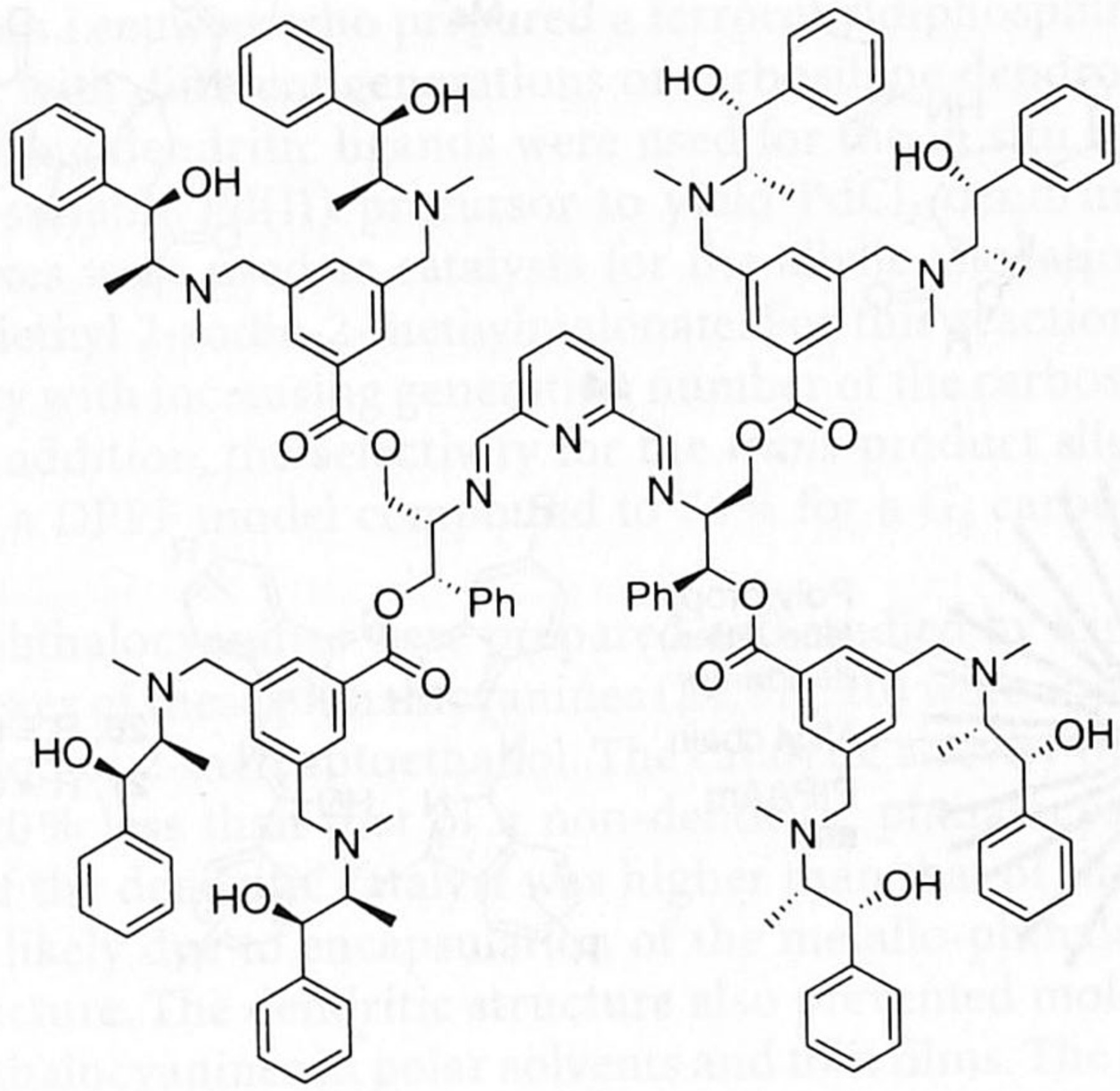

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Fig. 21. Dendron-enlarged 1,2-bis(diphospino)ethane and 2,6-pyridinediimine derivatives reported by Brunner et al.

N-acetylphenylalanine. A small retardation of the hydrogenation of the substrate was encountered, which was ascribed to the *meta*-positioned dendron substituents. No products that were significantly enantiomerically enriched were isolated. However, using different dendritic species based on a 2,6-pyridinediimine CuOTf complex as the core (see, e.g., **29**, Fig. 21), a low enantioselectivity, up to 10–11% ee, was observed in the cyclopropanation of styrene with ethyl diazoacetate [41].

An elegant example of dendrimer catalysts having a chiral metal complex as core is found in the work of Seebach et al., who applied $\alpha,\alpha,\alpha',\alpha'$-tetraaryl-1,3-dioxolane-4,5-dimethanols (TADDOLS) as core for dendritic ligands [42, 43].

Different dendrons were attached to these core complexes: classical Fréchet dendrons (e.g., **30**, Fig. 22), chiral dendrons (derived from 3-hydroxybutanoic acid), and Fréchet dendrons with peripheral octyl groups. TitaniumTADDOL dendritic complexes with either non-chiral or chiral dendrons were applied as homogeneous catalysts in the asymmetric reductive alkylation of benzaldehyde with diethylzinc, yielding the secondary alcohol with ees up to 96%. These results are almost identical to the results obtained for model TADDOL complexes in this type of catalysis. The dendritic TADDOLates show high catalytic activities that slightly decrease from G_3 upwards. The authors assume that this effect is due to the accessibility of the catalytic site. Furthermore, the enantioselectivity was not influenced by the presence or absence of chirality in the dendrons, due to the distance between the metal center and the additional chiral building blocks.

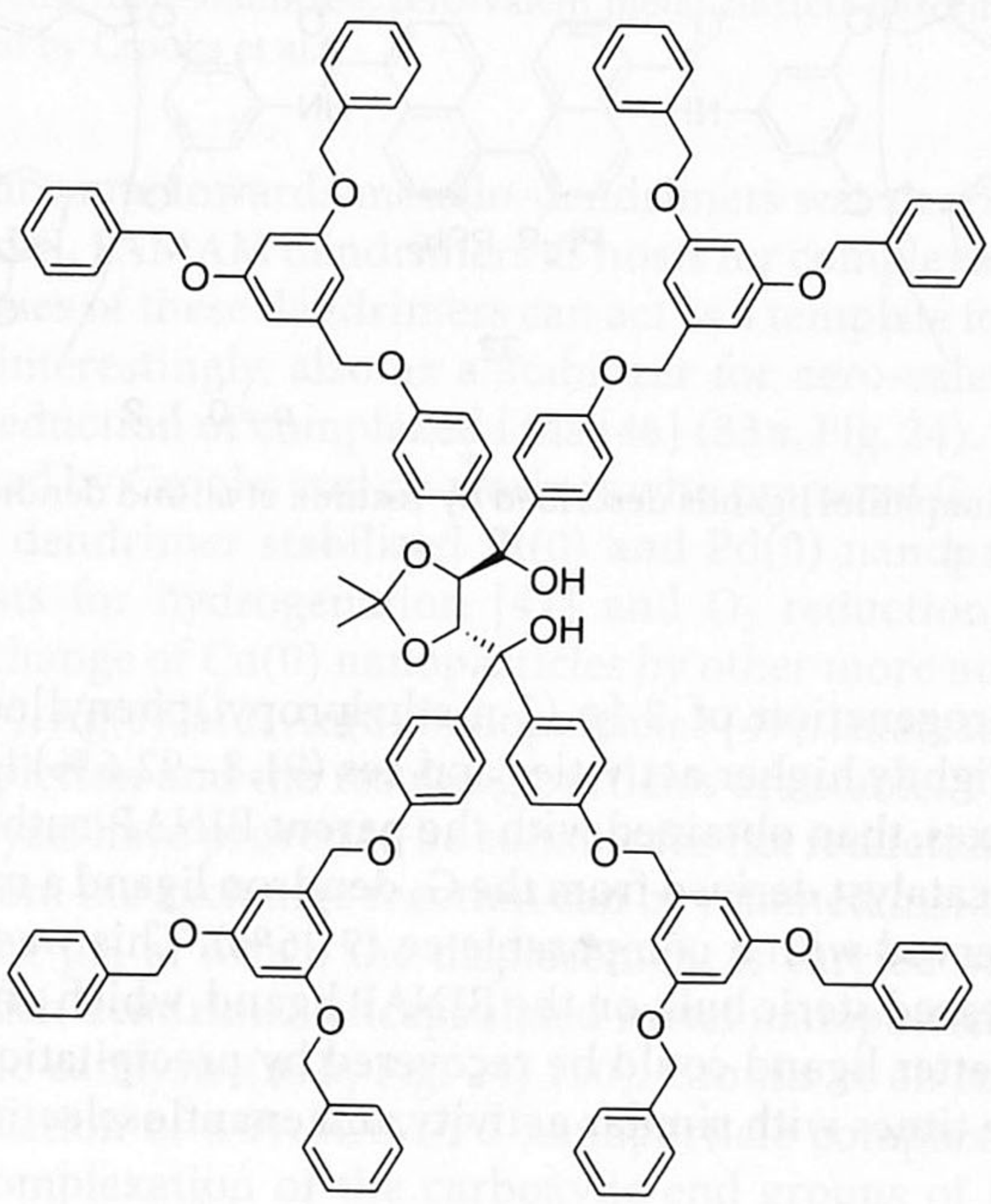

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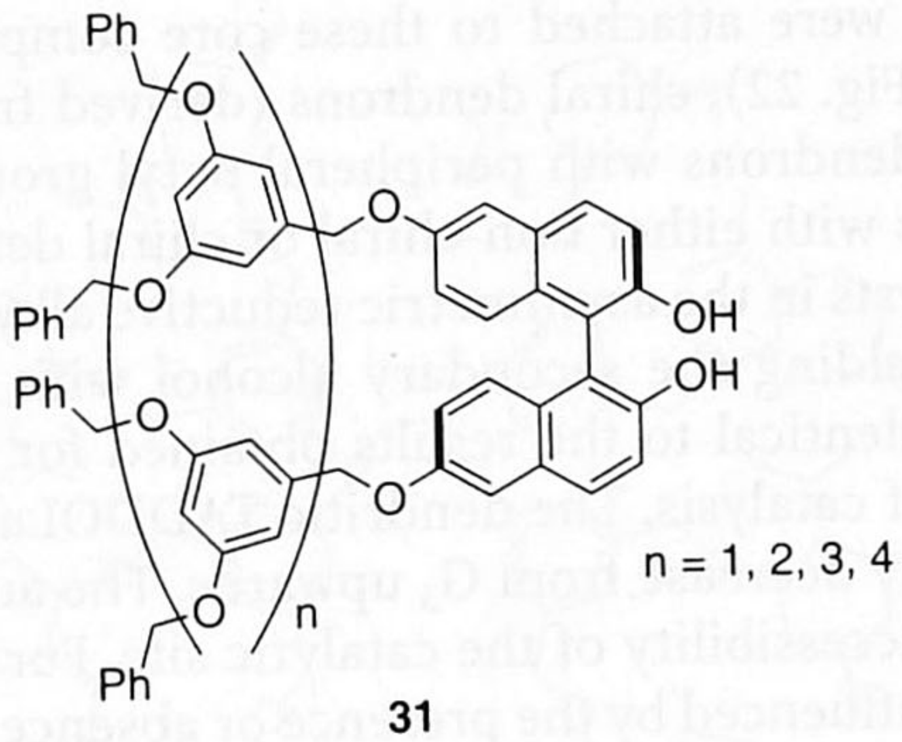
Fig. 22. Enantioselective dendritic TADDOL ligand prepared by Seebach et al.

Binaphthol (BINOL) ligands modified with Fréchet-type dendrons of different generations (**31**, Fig. 23) were applied as homogeneous catalysts in the allylation of benzaldehyde with allylstannane by Yoshida et al. [44]. Compared to a parent binaphthol ligand, these ligands show similar activities and ees, indicating that comparable titanium complexes are formed in situ.

Similar dendritic ligands, BINAP ligands equipped with Fréchet-type dendrons of different generations (**32**, Fig. 23), were applied by Chan et al. [45]. In situ prepared ruthenium(II) complexes were tested for their activity in the



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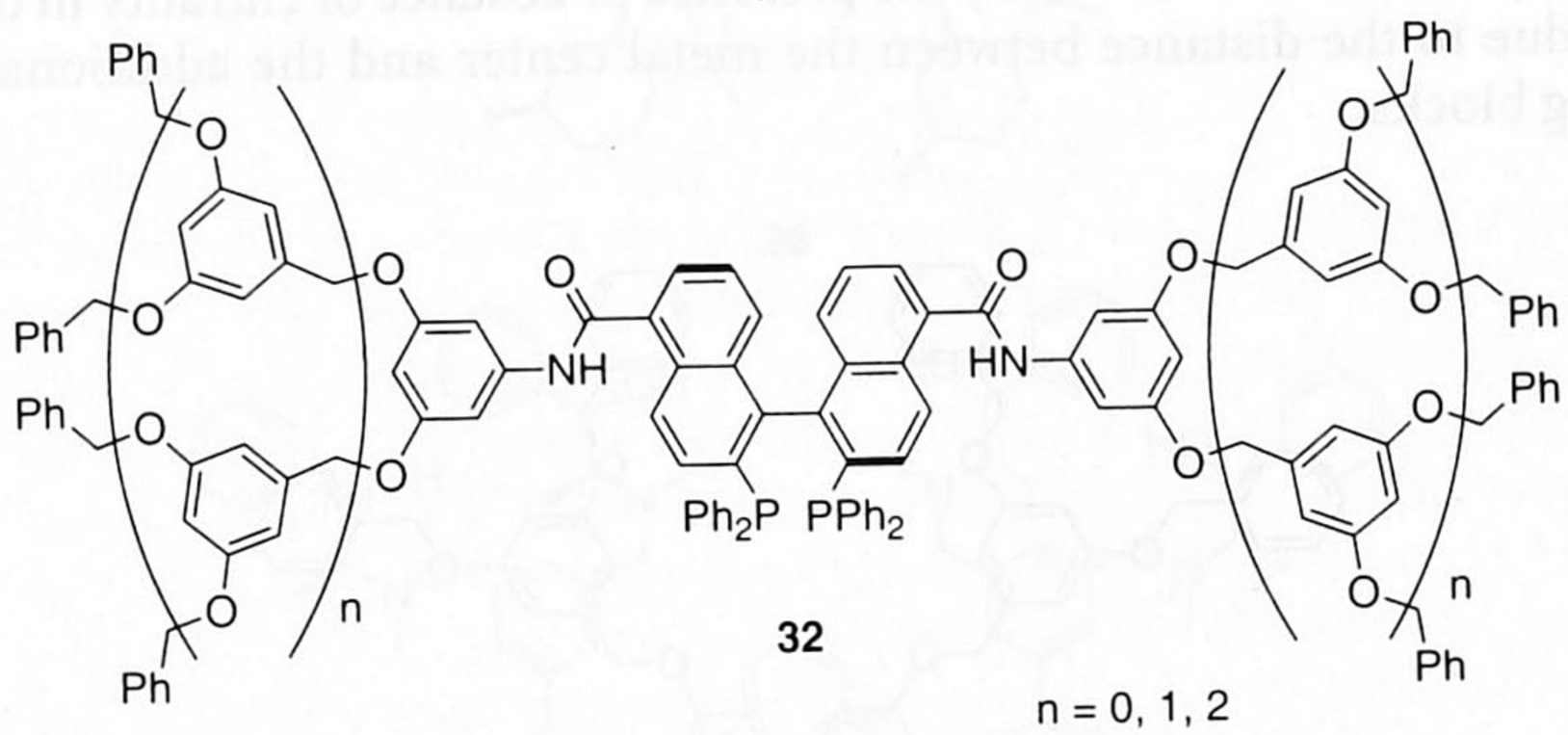

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Fig. 23. Dendritic binaphthol ligands described by Yoshida et al. and dendritic BINAP ligands reported by Chan et al.

asymmetric hydrogenation of 2-[*p*-(2-methylpropyl)phenyl]acrylic acid. The authors report slightly higher activities and ees (91.8–92.6%) for the G_0 and G_1 dendron complexes, than obtained with the parent BINAP-ruthenium complex. However, for the catalyst derived from the G_2 dendron ligand a much higher conversion was observed with a comparable ee (91.6%). This was ascribed to the presence of increased steric bulk on the BINAP ligand, which affects the ligand's bite-angle. The latter ligand could be recovered by precipitation and filtration, and reused three times with similar activity and enantioselectivity.

4 Metal Complexes Throughout the Dendritic Structure

Besides metallo-dendrimers having metal complexes at either the periphery or at the core, some examples exist of dendrimers with ligating sites in the backbone itself to which metal ions can be complexed. Apart from the striking fact that for this kind of dendrimers the backbone is at the same time the "ligating site", an advantage is found in the fact that the ratio of metal-to-support (i.e., the dendrimer) is much higher than for periphery- or core-functionalized dendrimers. Examples of this kind of metallo-dendrimers are described below: dendrimer-stabilized, zero-valent metal-nanoparticles and dendrimer backbone-complexed metal-ions.

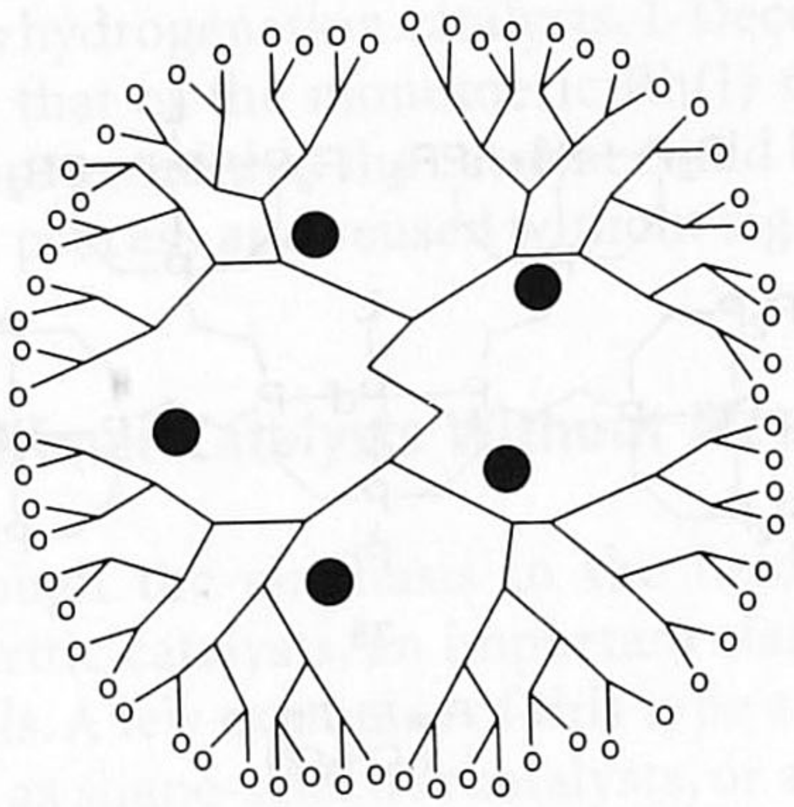

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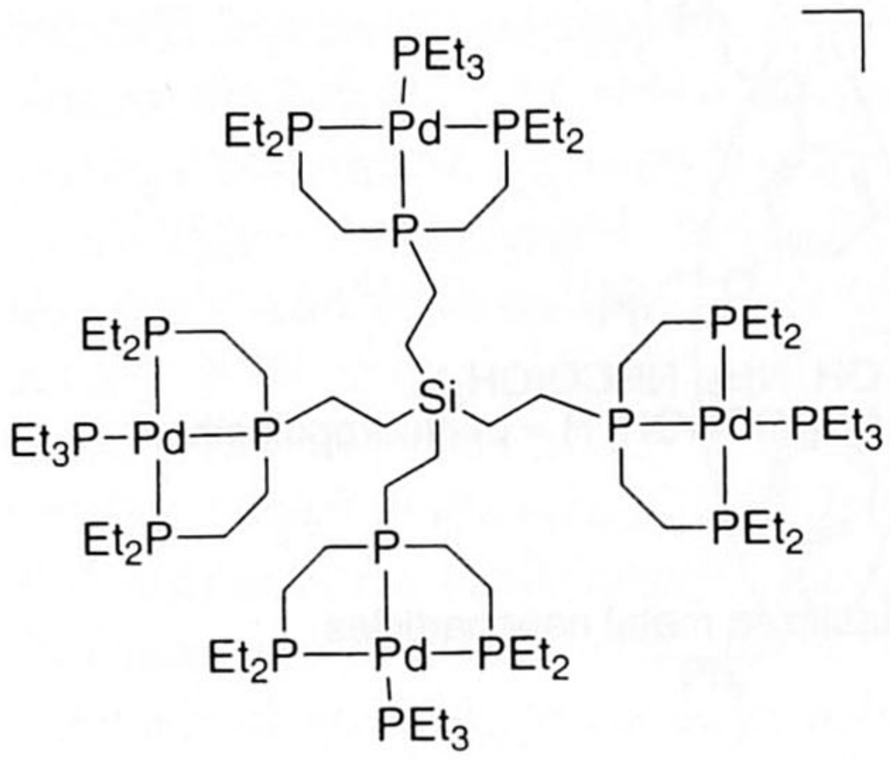
Fig. 24. PAMAM dendrimer-stabilized, zero-valent metal clusters described by Tomalia et al. and further applied by Crooks et al.

A very elegant route towards metallo-dendrimers was described by Tomalia, who used G_4 and G_5 PAMAM dendrimers as hosts for complexation of Cu(II) ion guests. The cavities of these dendrimers can act as a template for metal ion complexation and, interestingly, also as a stabilizer for zero-valent metal clusters obtained after reduction of complexed ions [46] (**33 a**, Fig. 24). This concept was further elaborated by Crooks and co-workers who prepared G_4 and higher generation PAMAM dendrimer stabilized Pt(0) and Pd(0) nanoparticles and used these as catalysts for hydrogenation [47] and O_2 reduction [48]. They also reported the exchange of Cu(0) nanoparticles by other more noble metal ions to form Pt(0), Pd(0), Ag(0), and Au(0) nanoparticles [49]. Interestingly, these reactions go to completion and the resulting particles are stable. These noble metal dendrimer catalysts have proven to be suitable for the reduction of O_2. The Cu^{2+} ions resulting from the exchange reaction can be retained inside the dendrimer, depending on the pH at which the displacement is carried out. A very recent application of such dendrimer-encapsulated metal nanoparticles is their use in fluorous biphasic catalysis (**33 b**, Fig. 24) [50]. Crooks et al. reported the non-covalent modification of a PAMAM-Pd nanoparticle complex with perfluoropolyethers by complexation of the carboxylic end groups of these polyethers with the terminal amine groups of the dendrimer. This modification afforded dendrimers that dissolved exclusively in the fluorous phase of a THF/FC-75 (fluorous solvent) mixture. A biphasic Pd(0)-dendrimer system was successfully applied in the reduction of alkenes and the catalyst could be recycled for 12 times without appreciable loss of activity.

Homogeneous organophosphine dendrimers containing metal sites throughout the structure were reported by Dubois et al. [51]. The authors prepared different small dendritic structures with phosphorus branching points, which can serve as binding sites for metals. The resulting terdentate (P,P,P)-ligating sites were palladated using a Pd(II) salt in the presence of PEt_3. The resultant cationic complexes (e.g., **34**, **35**, Fig. 25) were successfully applied as homogeneous catalysts for the electrochemical reduction of CO_2 to CO. The observed reaction rates



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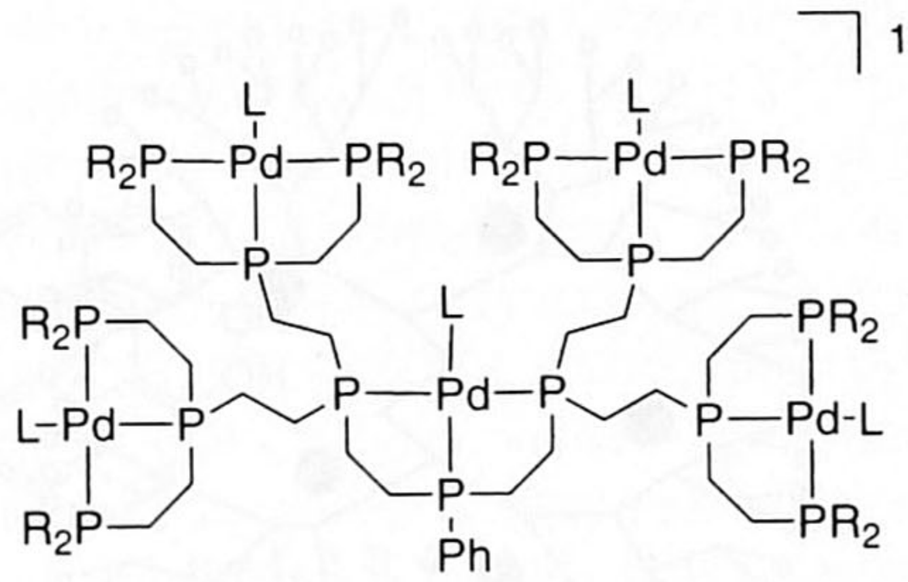

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R = Et, Ph
L = CH_3CN

Fig. 25. Phosphorus-based dendrimer-Pd complexes having ligating sites throughout the structure reported by Dubois et al.

and selectivities were comparable to those found for an analogous monomeric palladium complex, indicating that no cooperative effects between the different metal sites are present.

Another phosphorus-based example of dendrimers containing ligating sites throughout the structure was prepared by Kakkar et al. [52]. They succeeded in the synthesis of various generations of metallophosphino dendrimers by acid-base hydrolysis of aminosilanes with molecules possessing terminal OH-groups. Each phosphorus branching point could serve as a ligating site for Rh(I) centers. These Rh-complexes (e.g., **36**, Fig. 26) were successfully applied as homoge-

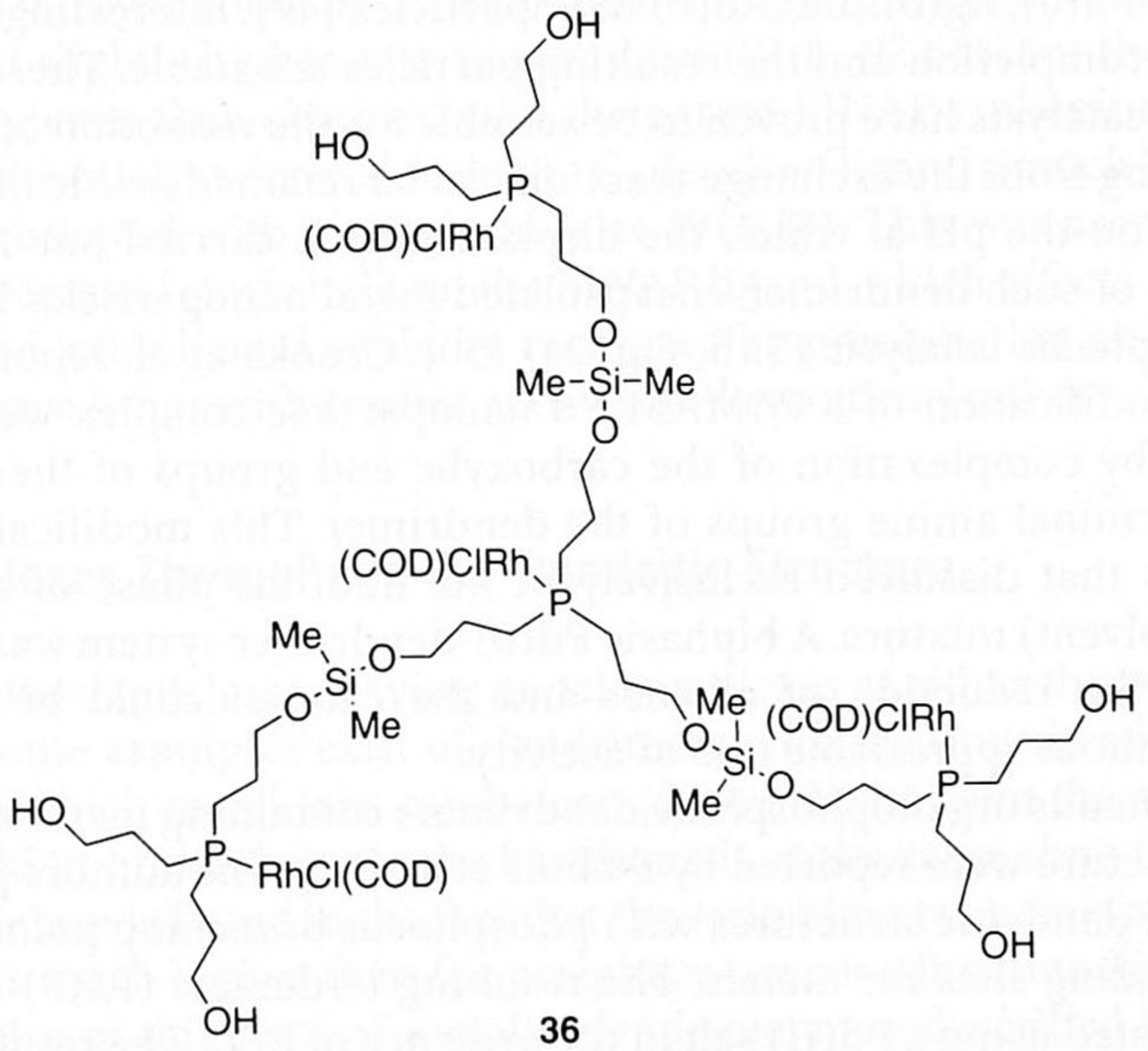

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Fig. 26. Phosphorus-based dendrimers containing P-Rh sites throughout the structure as reported by Kakkar et al.

neous hydrogenation catalysts. 1-Decene was hydrogenated with activities similar to that of the monomeric Rh(I) model complex. Furthermore, the authors demonstrated that the catalyst could be recovered by a simple precipitation in a batch process and reused without significant loss of activity.

5 Dendrimer Catalysts Without Metals

Although the emphasis in the field of dendrimer catalysis lies on metallodendritic catalysts, an important class is formed by dendritic catalysts without metals. A few examples of this type are described, which can act as stabilizer for ions, as shape-selective catalysts, or as chiral auxiliaries.

The first example of the use of a non-metal containing dendrimer for catalysis was provided by the work of Ford et al. [53], who made use of polyether dendrimers that were functionalized at the periphery with quaternary ammonium ions (**37**, Fig. 27). These dendrimers were used in the unimolecular decarboxylation of 6-nitrobenzisoxazole-3-carboxylate and the bimolecular hydrolysis of *p*-nitrophenyl diphenyl phosphate catalyzed by *o*-iodobenzoate. In aqueous media, these reactions are accelerated by the polycationic dendrimer through stabilization of the organic anions, which presumably bind in high concentration to the polycationic periphery of the dendrimer. The pseudo micellar environment of the dendrimer promotes the formation of organic anions. In the same group poly(propylene imine) dendrimer complexes with Cu(II), Zn(II), and Co(III) ions were investigated as catalysts in the reaction described above [54]. Reaction rates were found to be 1.3–6.3 times faster than in the absence of metal ions.

Recently, the same authors reported DAB-based dendrimers fuctionalized with triethyleneoxy methyl ether (TEO) and octyl chains at each amine [55]. These dendrimers could be quaternarized using methyl iodide (**38**, Fig. 28) after which chloride ions were introduced via ion exchange. The resulting quaternary

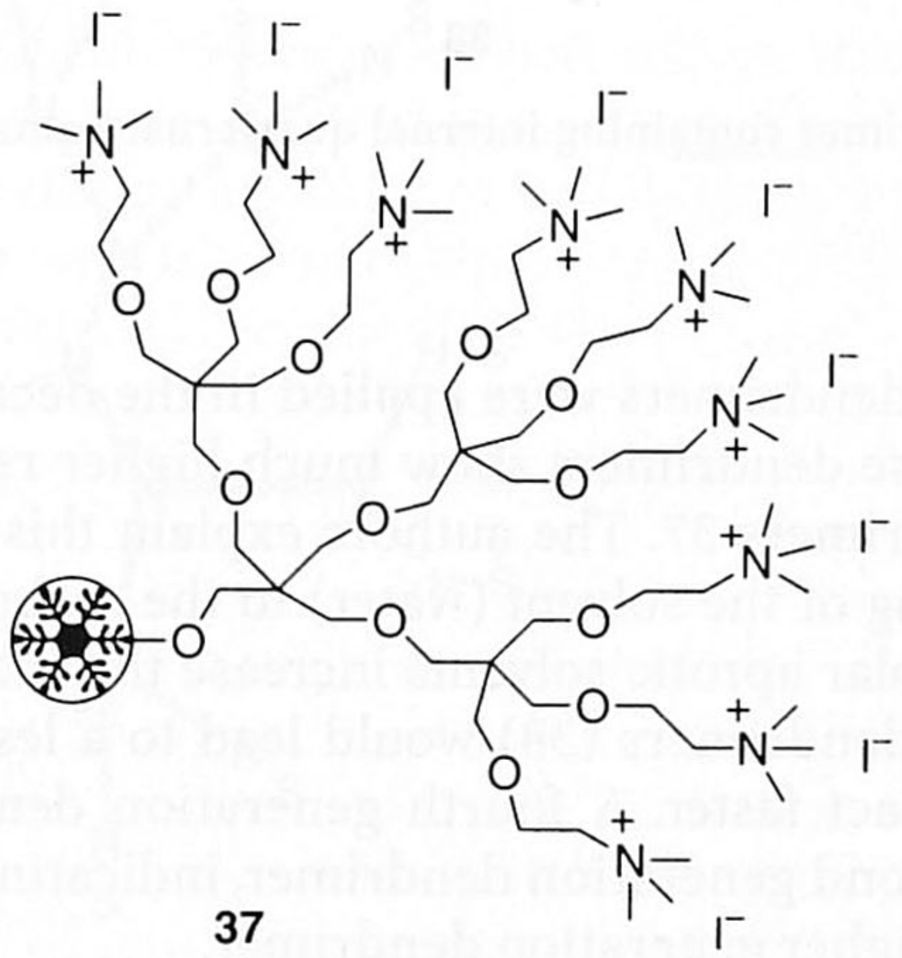

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Fig. 27. Polyether dendrimer functionalized with peripheral quaternary ammonium groups reported by Ford et al.

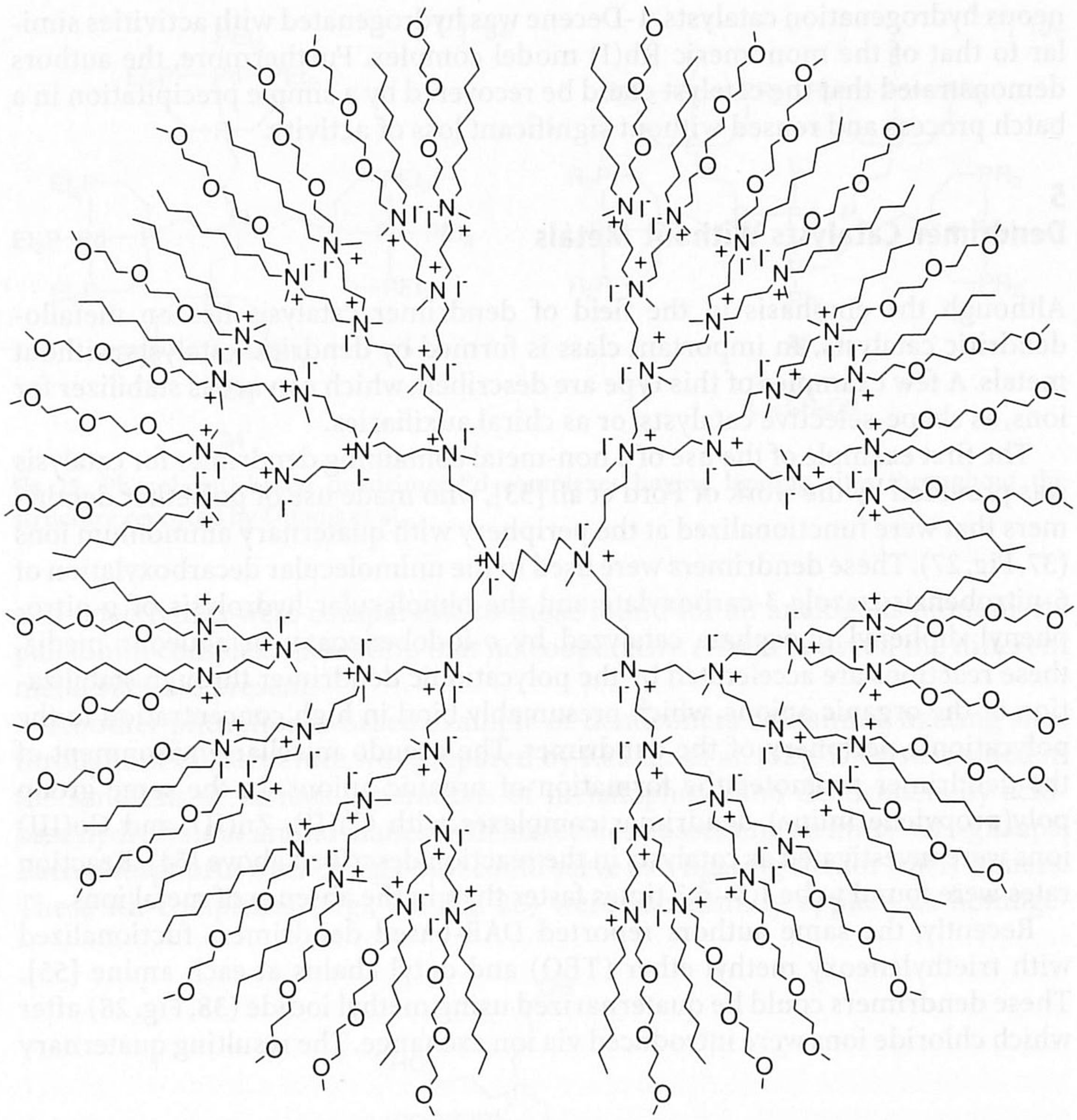

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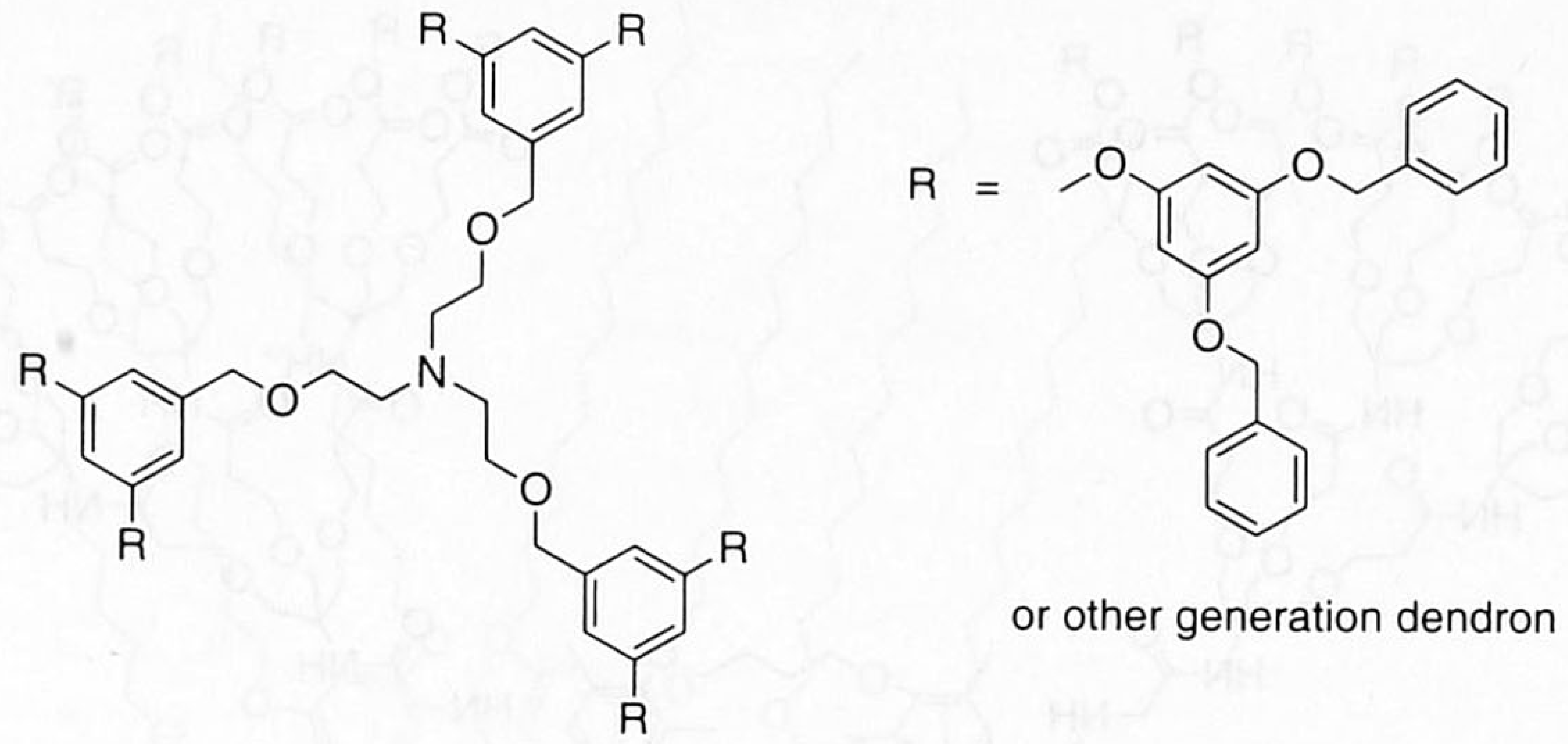
Fig. 28. DAB-based dendrimer containing internal quarternary ammonium groups reported by Ford et al.

ammonium chloride dendrimers were applied in the decarboxylation reaction described above. These dendrimers show much higher rates than the external ammonium ion dendrimers **37**. The authors explain this difference by stating that hydrogen bonding of the solvent (water) to the carboxylate anion reduces the rate, whereas dipolar aprotic solvents increase the rate of decarboxylation. Use of the modified dendrimers (**38**) would lead to a less hydrated substrate, which then would react faster. A fourth generation dendrimer resulted in a higher rate than a second generation dendrimer, indicating that the substrate is less hydrated in the higher generation dendrimer.

Another example of a non-metal containing dendrimer in catalysis is the use of a single amine core, functionalized with Fréchet-type polyether dendrons

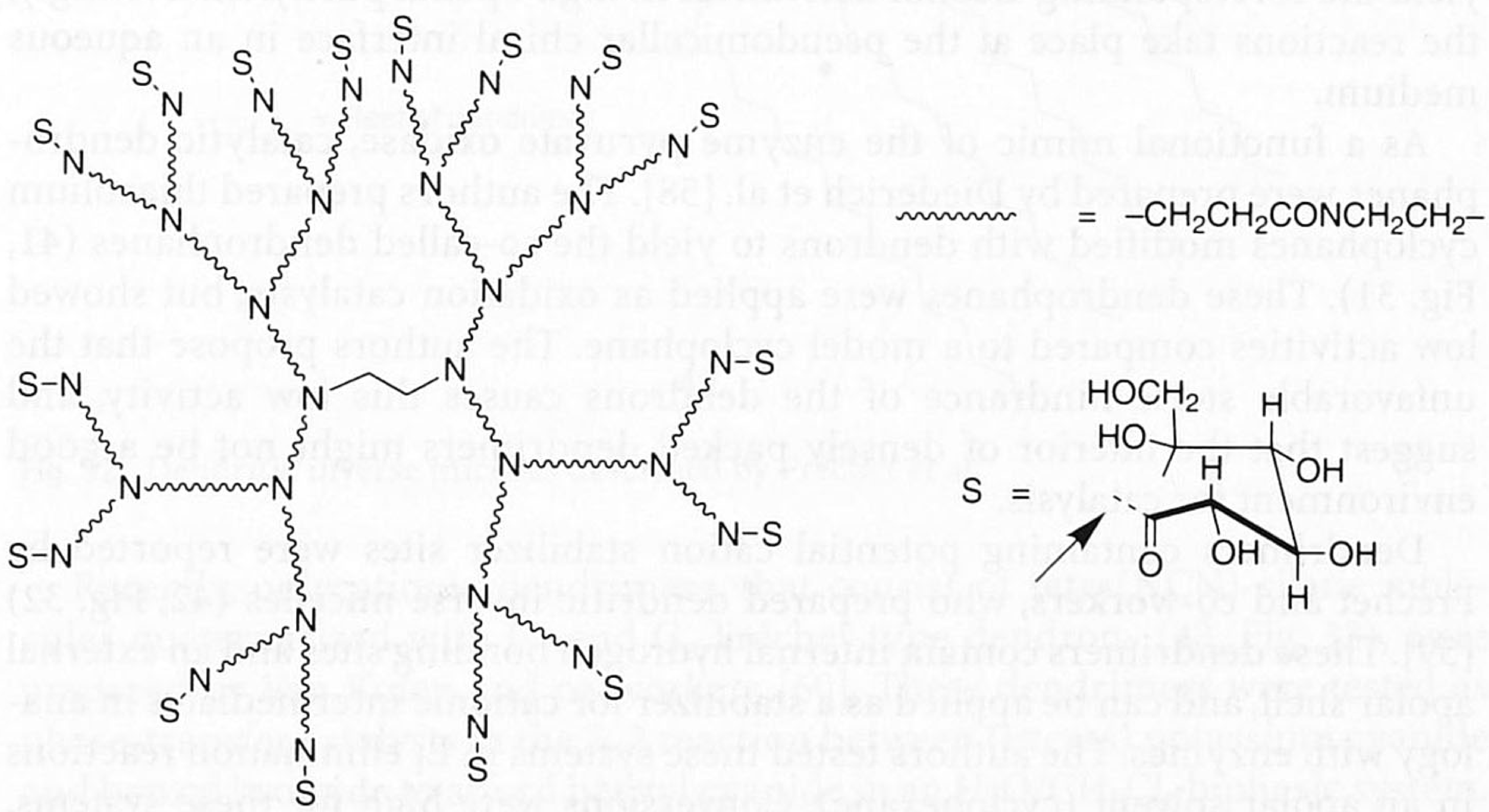


39

Fig. 29. Dendron-enlarged single amine core reported by Morao and Cossío

(39, Fig. 29) [56]. These amines can catalyze the nitroaldol or Henry reaction between aromatic aldehydes and nitroalkanes. Molecular modeling studies indicate that the cavities around the amine core should be able to accommodate the reactants, although in the higher generation dendrimers the core is more shielded by the dendrons. Catalyst activity is found to decrease with increasing generation number, suggesting that shielding of the center by the dendrons indeed takes place.

Chiral amphiphilic dendrimers were applied by Rico-Lattes and co-workers [57]. These water-soluble, but-THF insoluble, dendrimers consist of amine-based dendrimers functionalized with glucose derivatives (e.g., 40, Fig. 30) and can be used in the homogeneously (water) and heterogeneously (THF) catalyzed reduction of prochiral aromatic ketones by sodium borohydride to



40

Fig. 30. Chiral water-soluble dendritic catalysts reported by Rico-Lattes et al.

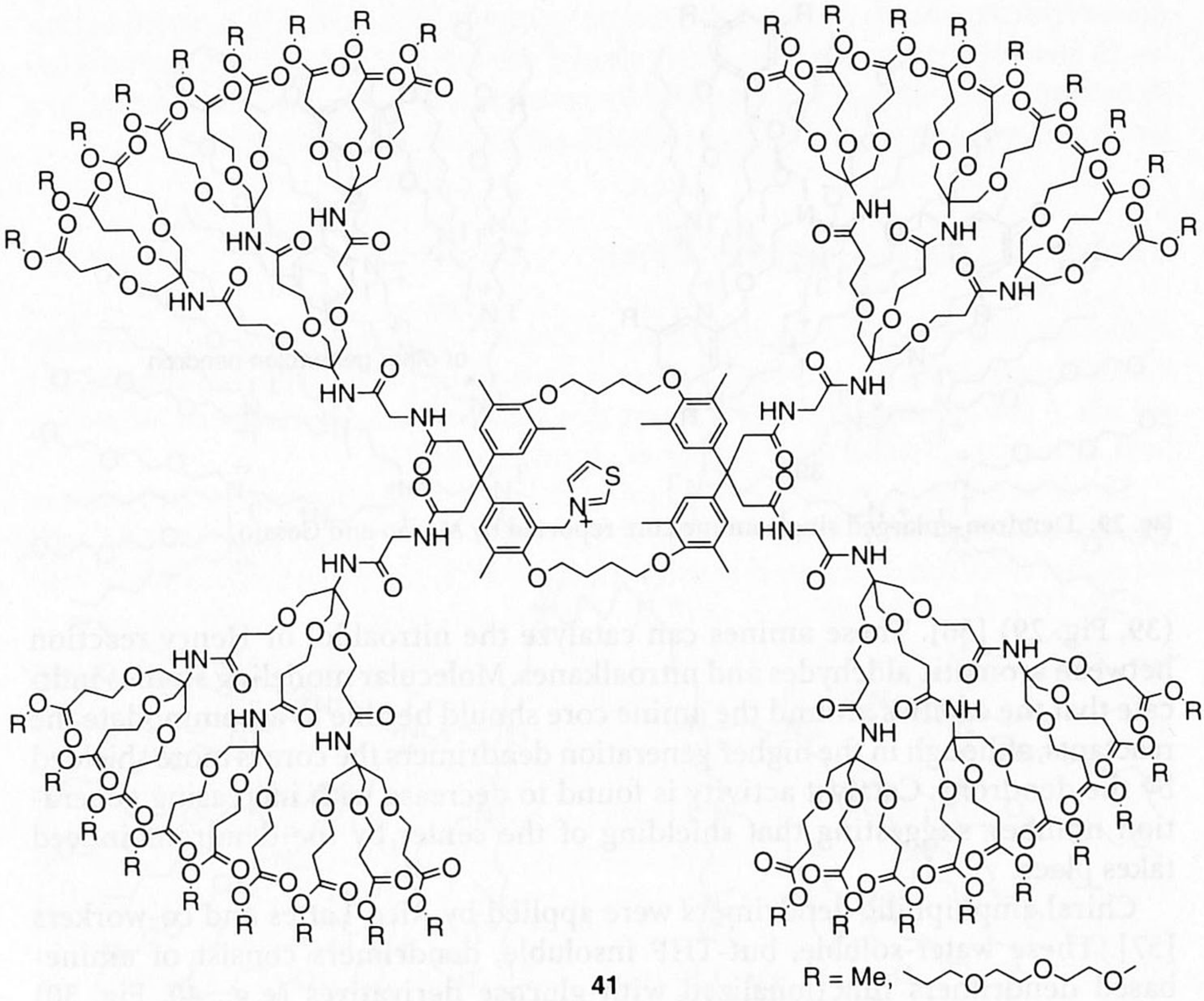
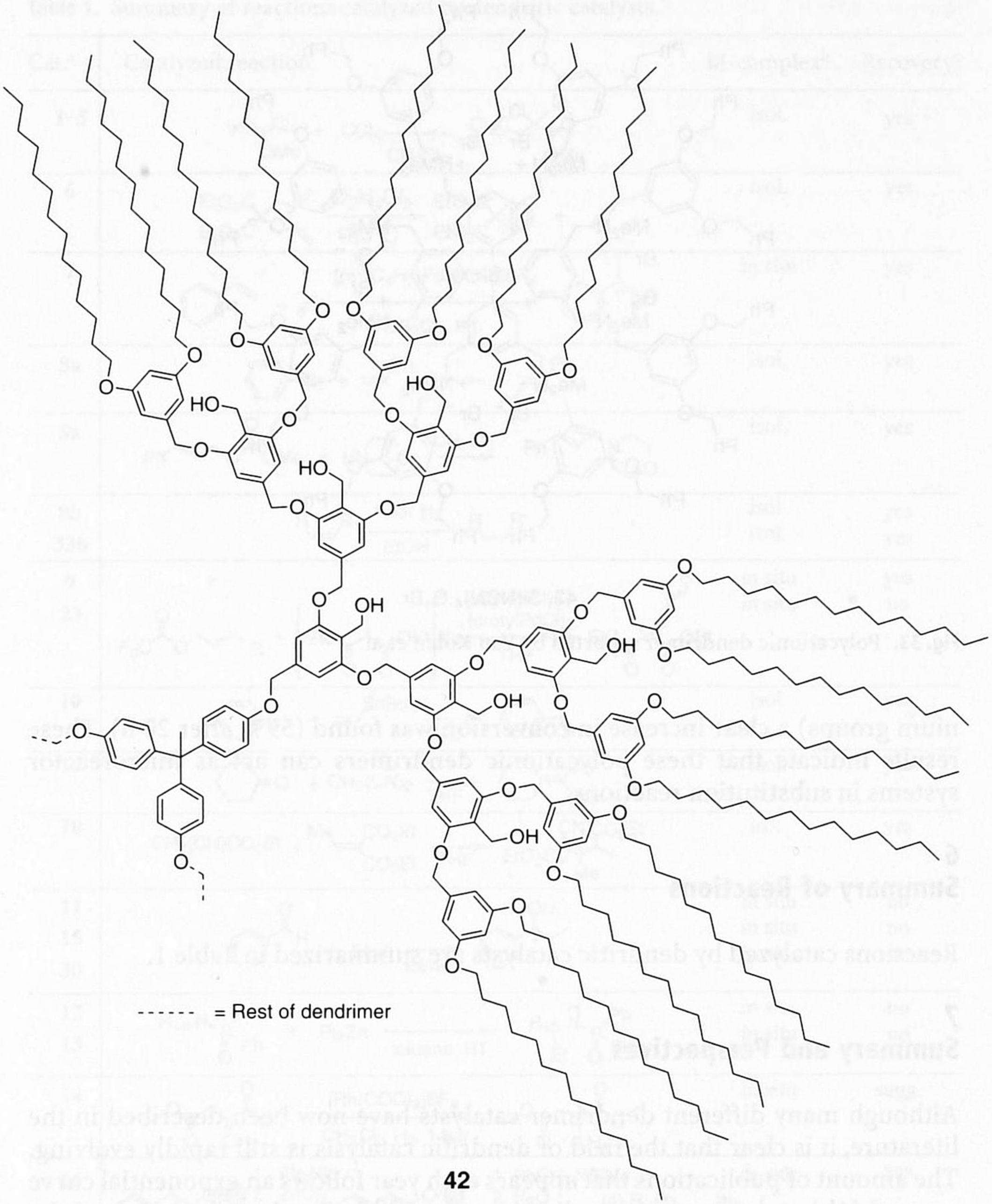


Fig. 31. Dendrophane structure reported by Diederich et al.

yield the corresponding alcohol derivatives in high optical purity. Interestingly, the reactions take place at the pseudomicellar chiral interface in an aqueous medium.

As a functional mimic of the enzyme pyruvate oxidase, catalytic dendrophanes were prepared by Diederich et al. [58]. The authors prepared thiazolium cyclophanes modified with dendrons to yield the so-called dendrophanes (**41**, Fig. 31). These dendrophanes were applied as oxidation catalysts, but showed low activities compared to a model cyclophane. The authors propose that the unfavorable steric hindrance of the dendrons causes this low activity, and suggest that the interior of densely packed dendrimers might not be a good environment for catalysis.

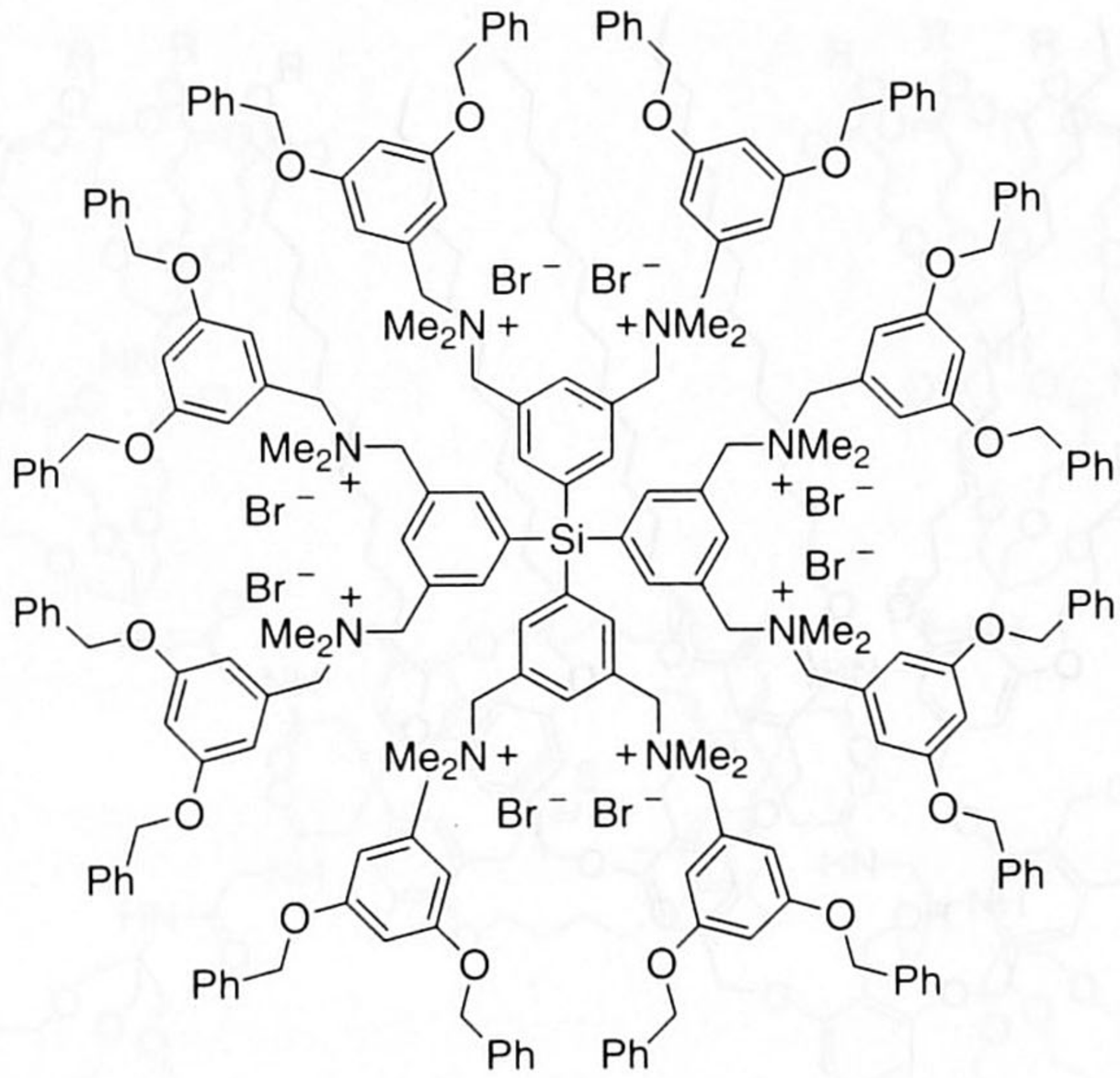
Dendrimers containing potential cation stabilizer sites were reported by Fréchet and co-workers, who prepared dendritic inverse micelles (**42**, Fig. 32) [59]. These dendrimers contain internal hydrogen bonding sites and an external apolar shell, and can be applied as a stabilizer for cationic intermediates in analogy with enzymes. The authors tested these systems in E_1 elimination reactions in an apolar solvent (cyclohexane). Conversions were high for these systems. The authors claim that the polar interior of the dendrimer provides an ideal nanoenvironment for reactions that involve polar transition states.



42

Fig. 32. Dendritic inverse micelles described by Fréchet et al.

Recently, polycationic dendrimers, that consist of tetra(NCN)-silane molecules quaternarized with G_1 and G_2 Fréchet-type dendrons (**43**, Fig. 33), were prepared by Van Koten and co-workers [60]. These dendrimers were tested as phase-transfer catalysts in the S_N2 reaction between (excess) potassium cyanide and benzyl bromide to afford benzyl cyanide in an H_2O/CH_2Cl_2 biphasic system. In the absence of catalyst only minor amounts of benzyl cyanide (= 6% after 20 h) were formed, whereas in the presence of **43** (0.01 mol % catalytic ammo-



43, $Si(NCN)_4.G_1Br$

Fig. 33. Polycationic dendrimer reported by Van Koten et al.

nium groups) a clear increase in conversion was found (59% after 20 h). These results indicate that these polycationic dendrimers can act as microreactor systems in substitution reactions.

6 Summary of Reactions

Reactions catalyzed by dendritic catalysts are summarized in Table 1.

7 Summary and Perspectives

Although many different dendrimer catalysts have now been described in the literature, it is clear that the field of dendritic catalysis is still rapidly evolving. The amount of publications that appears each year follows an exponential curve upward [1b] and many new applications are still being described. One of the latest developments in dendrimer catalysis is the recovery of the catalyst by means of nanomembrane filtration techniques. After pioneering work by Kragl and co-workers [61, 62], using polymer-enlarged oxazaborolidines, some interesting dendritic examples were reported as described above [3, 10, 12, 13, 17]. However, we are still quite far from a stable dendrimer catalyst system that can be applied in a continuous membrane reactor system, without loss of activity. We believe that a great challenge lies in this field, in particular when more suitable membrane systems are developed. The stability of metal complexes depends very much on the way of metal binding. From the results presented

Table 1. Summary of reactions catalyzed by dendritic catalysts.

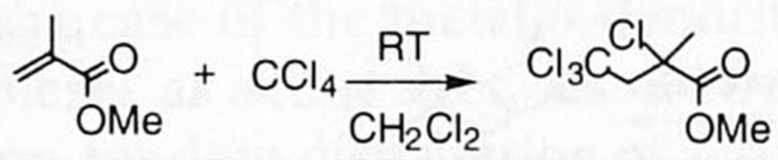
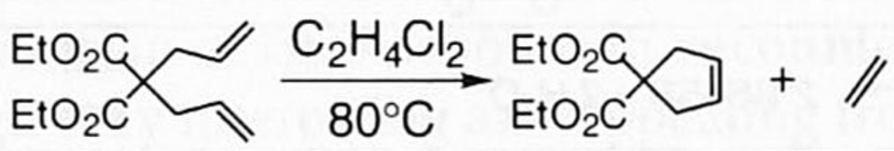
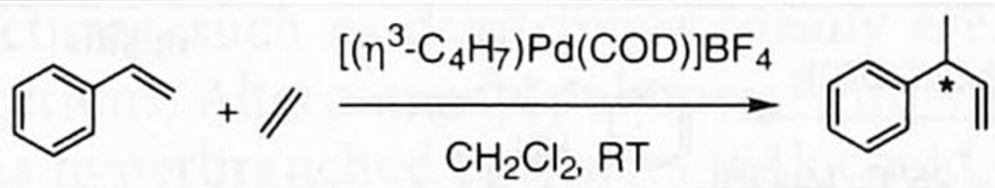
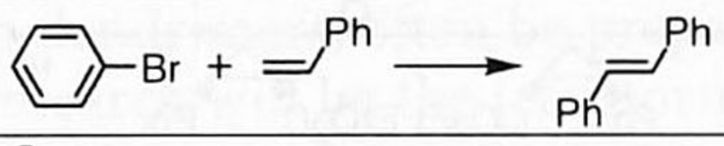
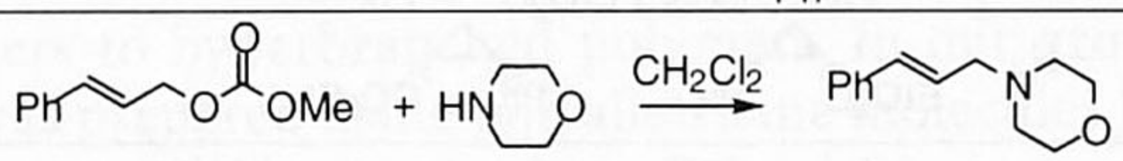
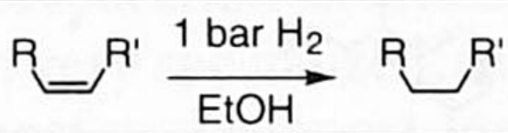
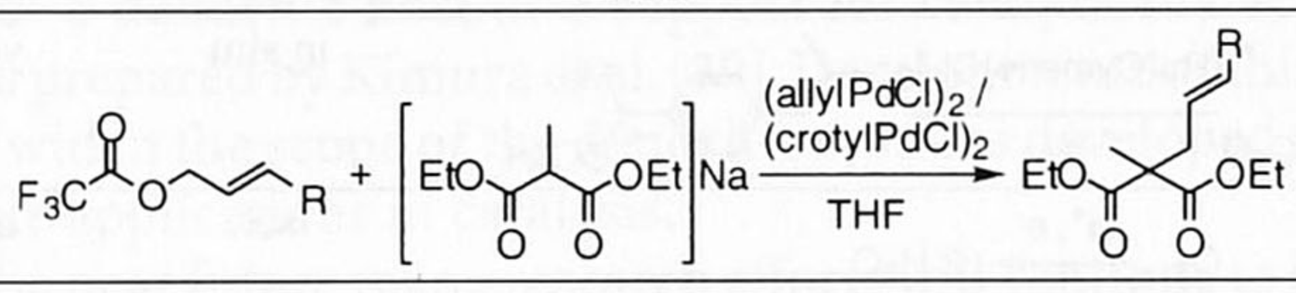
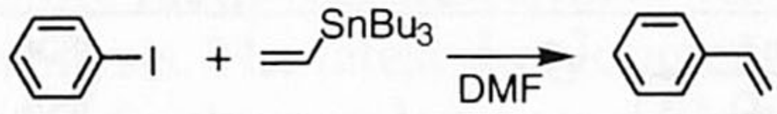
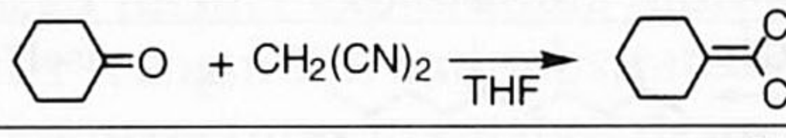
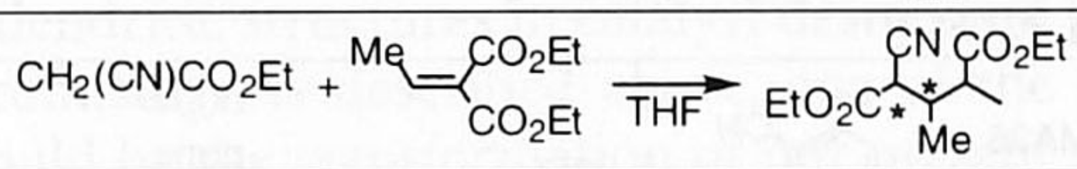
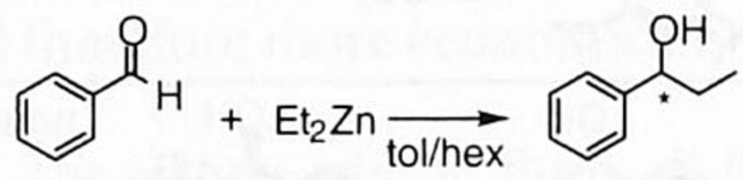
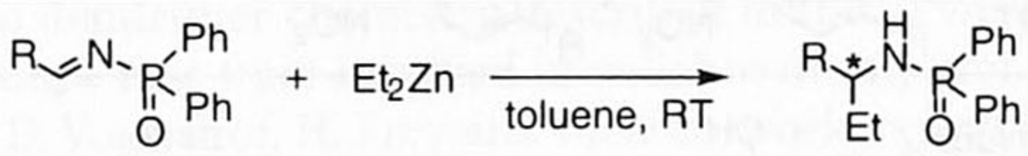
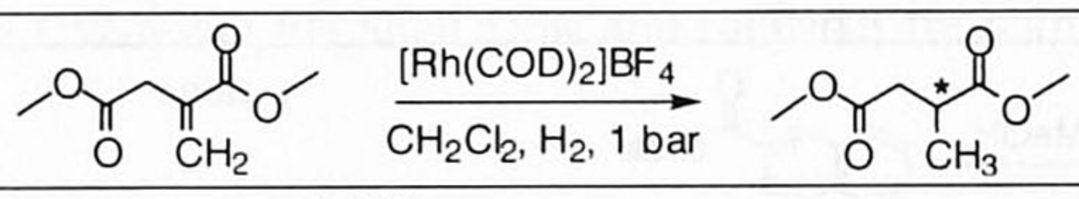
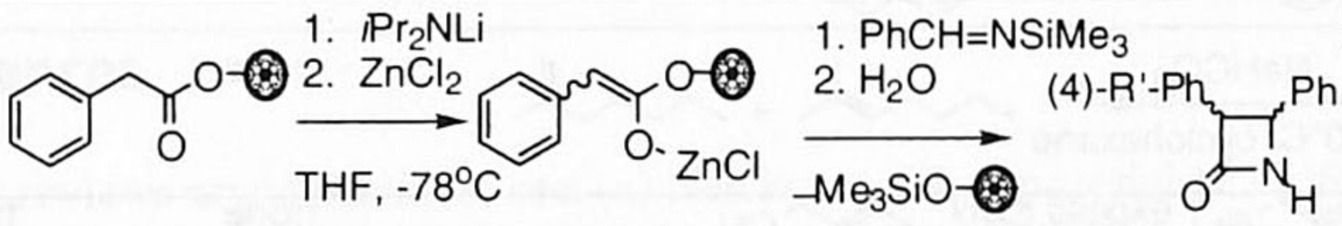
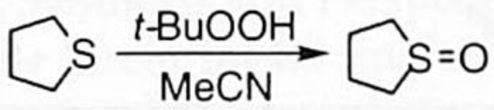
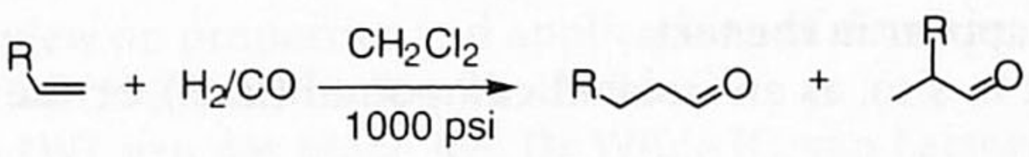
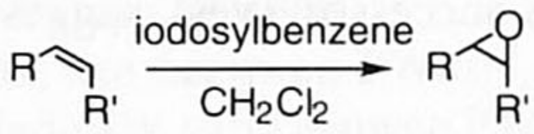
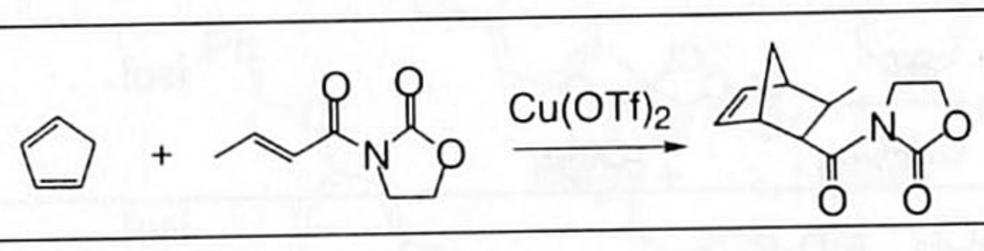
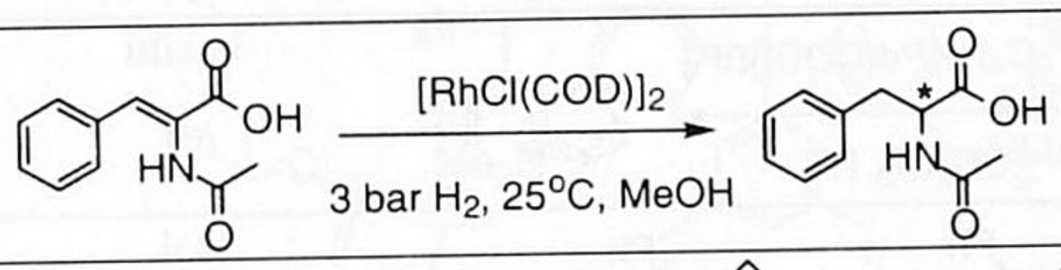
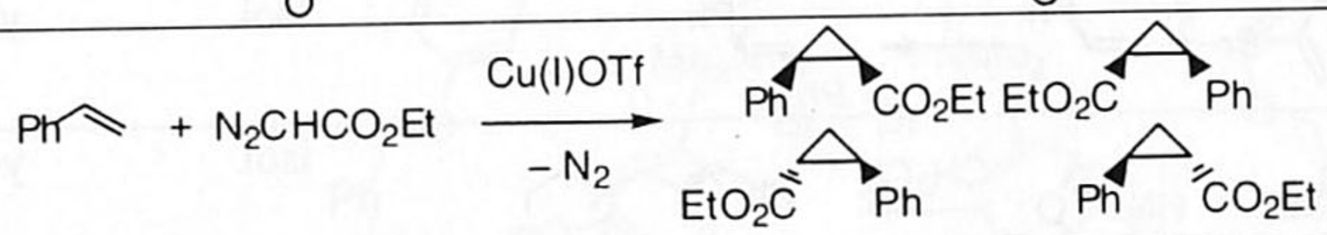
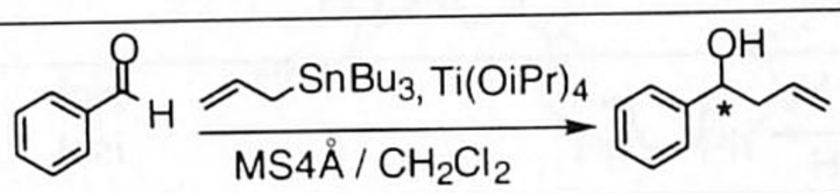
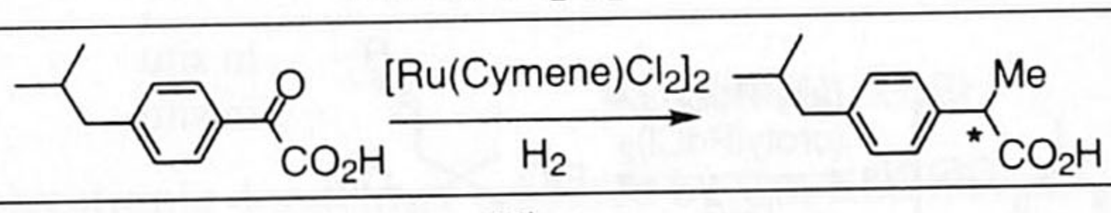
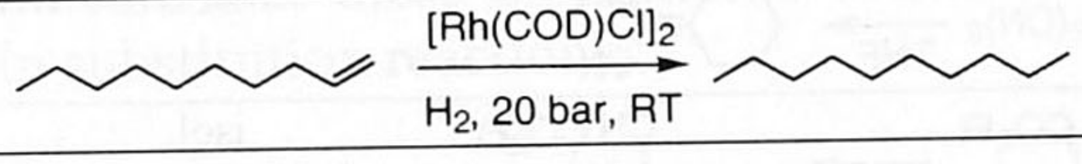
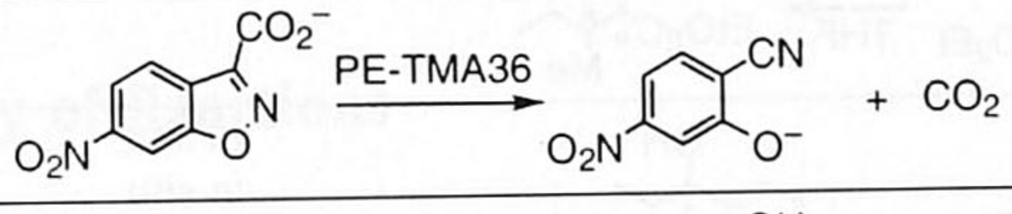
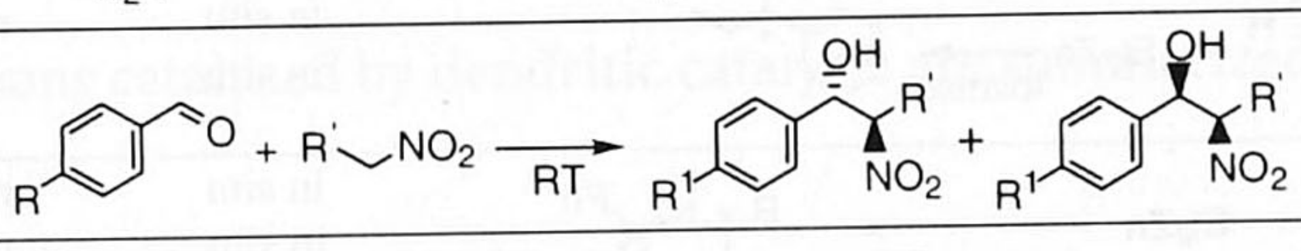
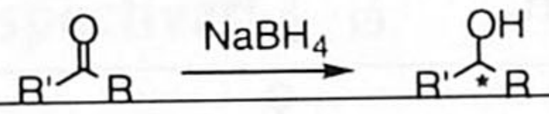
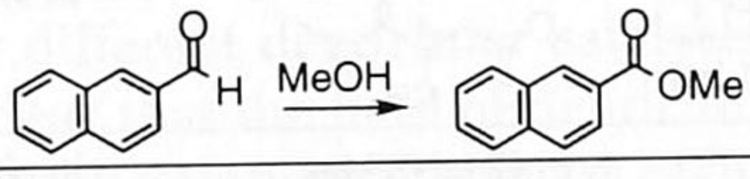
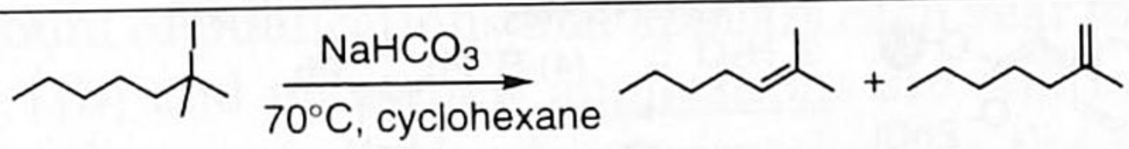
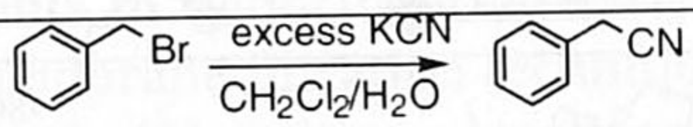
Cat.[a]	Catalyzed reaction	M-complex[b]	Recovery[c]
1–5		isol.	yes
6		isol.	yes
7		in situ	yes
8a		isol.	yes
8a		isol.	yes
8b **33b**		isol. isol.	yes yes
9 **23**		in situ in situ	yes no
10		isol.	yes
10		isol.	yes
10		isol.	yes
11 **15** **30**		in situ in situ in situ	no no no
12 **13**		in situ in situ	no no
14		in situ	sugg.
16		in situ	yes
18		isol.	yes
9 **19** **20**		in situ isol. isol.	yes sugg. sugg.
21		isol.	no

Table 1 *(Continued)*

Cat.[a]	Catalyzed reaction	M-complex[b]	Recovery[c]
22		in situ	no
24	$4\ RSH + O_2 \longrightarrow 2\ RS{-}SR + 2\ H_2O$	isol.	no
25		isol.	no
28		in situ	no
29		in situ	no
31		in situ	no
32		in situ	yes
33a	$O_2 \xrightarrow{H^+,\ e^-} 2\ H_2O$	isol.	no
34	$CO_2 + H^+ \xrightarrow[-H_2O]{e^-} CO$	isol.	no
35		isol.	no
36		isol.	yes
37		none	no
38		none	no
39		none	no
40		none	no
41		none	no
42		none	no
43		none	no

[a] Catalysts are numbered as they appear in the text.
[b] Preparation of a metal complex in situ, as an isolated compound (isol.), or the absence of metal (none).
[c] Recovery of the dendritic catalyst that was successful (yes), suggested as possible (sugg.), and not performed (no).

above it can also be concluded that binding of the metal via a metal-carbon σ-bond results in metallo-dendritic catalysts with more stable metal sites. Consequently, these catalyst systems do not suffer from the leaching problems encountered in the case of the metallo-dendritic catalysts with peripheral coordination complexes as active sites. Another unsolved problem in dendrimer catalysis is the non-random distribution of active sites, in contrast to the homogeneous distribution of sites in solution encountered for monomeric catalysts.

Even though very interesting and appealing from an academic point of view, perfect structures, such as dendrimers ideally are, are not a prerequisite for many applications. Alternatively, polymers with very narrow weight distributions, such as hyperbranched polymers [63], could be applied. These polymers can, in contrast to dendrimers, often be prepared in one step. One of the challenges in future research will be the transformation of principles designed for dendrimers to hyperbranched polymers. In our group an example of such a system was prepared using polyallylsilane molecules [64].

Furthermore, the preparation of dendritic systems that are more versatile than the current, often very specialized, catalysts could be of interest. One could think of a dendritic host as a support for catalytically active guest molecules, such as prepared by Kimura et al. [39]. Developments of this type of host systems would widen the scope of the dendritic systems developed so far, and allow more versatile applications in catalysis.

In the near future many research efforts will continue to be devoted to the field of dendrimer catalysis. The latest developments in this area show very attractive concepts that need further exploration. Although we are still far from using the level of molecular recognition and substrate selectivity exemplified by enzymes, usage of dendritic structures in catalyst design and biomimicry continues to be highly promising. As described above, one of the greatest challenges for the future would be the transformation of our present systems into more versatile and flexible, and therefore more economically attractive, and applicable systems.

Acknowledgements. The authors wish to thank all their co-workers, who have made contributions to dendrimer chemistry described in this review. We would also like to thank the different groups that were involved in collaborations, Prof. P. W. N. M. Van Leeuwen, Prof. U. Kragl, Prof. D. Vogt, Prof. H. Frey and their co-workers and Dr. J. Verweij (DSM-GB). Furthermore, STW, CW-NWO, EU, Shell, Dow, and DSM-GB are acknowledged for financial support.

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