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Periphery-functionalized organometallic dendrimers for homogeneous catalysis

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Abstract

The use of carbosilane based dendrimers as molecular scaffolds for the attachment of organomettallic Ni "pincer" complexes that are active as a catalyst in the Kharasch addition reaction is described. It is shown that increasing steric crowding at the dendrimer periphery results in decreased catalyst activity, most likely as a consequence of an intramolecular redox process. Furthermore, preliminary investigations have shown that the application of this catalyst system in a continous process using a membrane reactor is possible. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Periphery; Organometallic dendrimer; Catalysis

1. Introduction

To overcome the problem of the separation of products and homogeneous catalysts, much effort has been spent on developing catalytically active systems that combine the advantages of homogeneous (high selectivity) and heterogeneous catalyses (easy separation of product and catalyst). The immobilisation of homogeneous catalysts on solid supports such as metal oxides (e.g., SiO_2 or Al_2O_3) or polymers is one of the first approaches that have been explored. Already in 1971, the first attempts were reported to immobilise diphenylphosphino units on cross-linked and thus insoluble polymers [1]. Disadvantages of these immobilized catalysts are that the catalytic sites on the polymer are not equally accessible. Some are buried inside the polymeric structure and solvents have a strong influence on the supported catalyst properties because of the solvent-dependent swell of the polymeric structure. Consequently, the reactions are mass transport-controlled which often results in reduced catalytic activity. The use of soluble polymers for the immobilization of homogeneous catalysts provides equal accessibility to all catalytic sites but, like in the case of the cross-linked polymer supports, these sites are distributed in a random fashion, causing mutual deactivation (e.g., by dimer formation) and reduced catalytic activity. Moreover, these soluble polymers have a non-persistent microscopic size which makes ultrafiltration difficult, in particular, as reptation of the polymer through the membrane filters occurs.

Some years ago, we set out to explore the use of dendritic polymers as supports for homoge-

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neous catalysts [2]. Dendrimers are highly branched macromolecules (for an overview, see Refs. [3,4] and references cited therein), with low polydispersity, i.e., in principle, they have a persistent microscopic size which makes ultrafiltration easy. As dendrimers have a well-defined molecular structure, they are constructed starting from a core entity by a repetition of discrete synthetic operations. Also, the catalytic entities can be attached in a controlled way to the dendritic structure. As a result, the location as well as the distribution of the catalytic sites is well-defined and the local stereochemistry of these sites can be designed. For example, the dendritic surface can be decorated with catalytic sites, the spatiation and the mutual distance of catalytic sites can be modelled and they can be attached to the interior rather than the surface of the dendrimer. In this way, the local environment of the catalytic sites can be controlled and varied. In our studies, we mainly use carbosilane (Cs) dendrimers [5–7]. These have a silicon atom or atom-assembly as a core and silicon centers as branching points. The connections are made by alkanediyl links (see Fig. 1). In this case, the links are C_3 entities, but they can be varied in length and rigidity.

We have chosen these carbosilanes because they are chemically inert and compatible with most organometallic reagents. As catalysts, we are currently using the 'pincer'–metal compounds developed in our laboratory [8,9] (see Fig. 2).

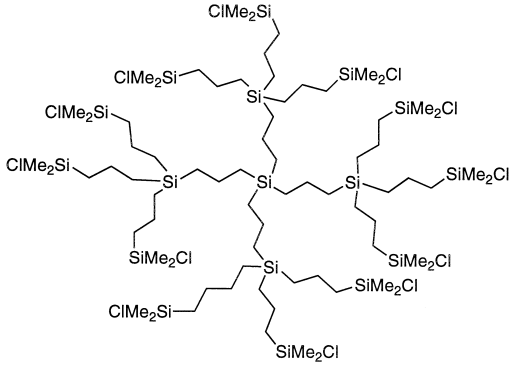


Fig. 1. Example of a G_1-carbosilane dendrimer.

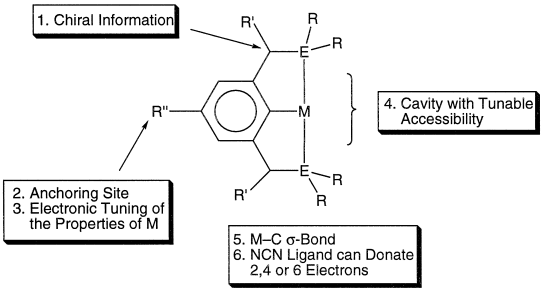
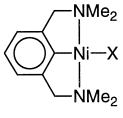
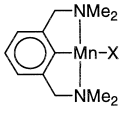
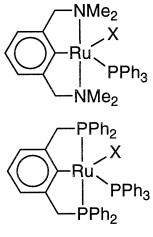


Fig. 2. The catalytic site.

The 'pincer'-skeleton comprises an aryl anion which can be connected to a metal center via a metal–carbon σ-bond. This is an essential feature for the performance of the supported metal catalyst as this covalent, rather than coordinate, linking of the metal site prevents metal leaching to a large extent if not completely. Through the design of the 'pincer' ligand, the *ortho*-substituents are held in a fixed spatial position and can coordinate to the metal site either via S, N or P donor atoms. The accessibility of the metal site may be influenced by the size of the heteroatom substituents. Stereochemical information may be introduced at the benzylic carbons as well as the heteroatom substituents. Finally, the pincer ligand may be im-

Table 1
Some examples of processes catalyzed by pincer–metal complexes (see Refs. [12,17,18])

	Kharash Addition [12] Controlled Atom Transfer Radical Polymerisation [12]
	Conjugate Additions [17] C–C Cross coupling reactions [17]
	Hydrogen Transfer [18]

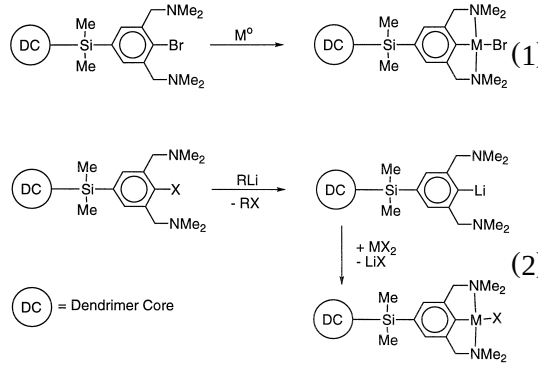
mobilised via a tether at the *para*-position of the aryl ring. It must be noted that the reactivity of the metal center can be influenced by variations of the electronic properties of this *para*-substituent. Most likely, this is due to the coplanarity of the π-aryl system with the principal coordination planes of the metal center. The organometallic chemistry of the 'pincer'–metal compounds, based on the use of the *ortho*-diaminoarylpincer $[C_6H_3(CH(R')NR_2)_2\text{-}2,6]^-$ (NCN), has been reviewed [8,9]. Table 1 lists reactions catalysed by NCN–metal compounds.

2. Synthesis of the carbosilane dendrimer

The first synthesis of carbosilane dendrimers has been reported by van der Made and van Leeuwen [5]. It starts with $SiCl_4$ and builds-up the dendrimer in a series of synthetic steps involving a reaction with allylmagnesium chloride followed by a hydrosilation reaction with trichlorosilane. Variations of the connecting chain (e.g., using vinylmagnesium halide) as well as of the branching point (e.g., using Me_2SiClH) are possible. In our initial studies, we chose a $SiMe_2Cl$ group as the terminal point to which our catalyst was to be connected. This ensured that the catalytic sites at the dendrimer surface are well-separated. Furthermore, initially, a relatively long linker between the Si-center and the *para*-position of the NCN–metal catalyst was chosen. This places the catalytic site even further away from the dendrimer surface [2]. Recently, we also studied the direct attachment of the catalytic site to the silicon surface-branching points. A comparison of the reactivities of these two different designs is given below.

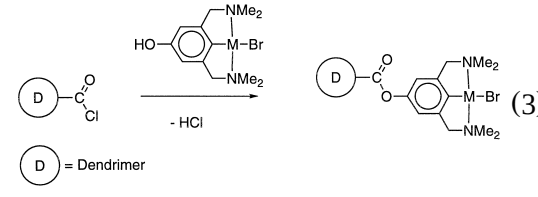
3. Fixation of the NCN catalyst to the dendrimer surface

It is obvious that each of the steps during the dendrimer synthesis has to be quantitative and selective to prevent faults in the dendritic structure which will have a detrimental effect on the microscopic regularity of the resulting dendritic species. These prerequisites also apply to the attachment of the catalytic sites to the dendrimer. So far, two approaches have been used. The first involves the use of a NCN–Br precursor. Via an oxidative-addition reaction to a zero- or low-valent metal species, the NCN–metal catalyst can be made, (see Eq. (1)). The second approach uses a transmetalation route as shown in Eq. (2).



The nickel-containing metallodendrimer can be made via both routes; for the Pd^{II} and Pt^{II} analogs, only the route in Eq. (2) is possible. The synthetic protocols for these routes have been optimised and dendrimers with up to 36 Ni centers have been synthesised [11].

A third route in which the metal site is already in place is shown schematically in Eq. (3) (see Ref. [10] for examples). In this way, the intermediate synthesis of highly reactive dendritic organolithium species can be avoided.



Two different metallodendrimers containing the NCNNiX catalyst have been made, i.e., type

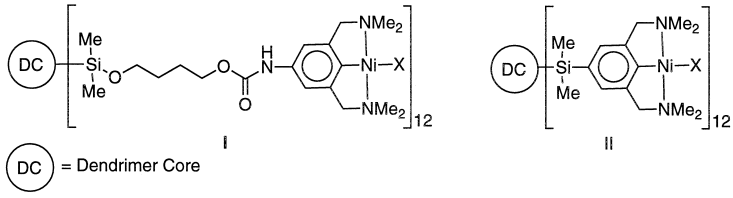


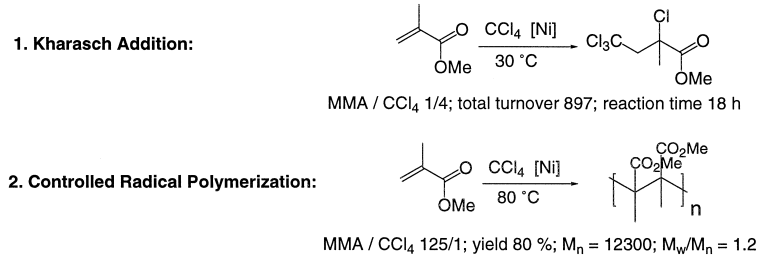
Fig. 3. Type I and type II dendrimers.

I with the dendritic surface and the NCNNiX catalyst well-separated by a $OCH_2CH_2CH_2$-NHC(O) tether [2] and type II with the NCNNiX catalyst directly attached [11] to the dendritic surface, see Fig. 3.

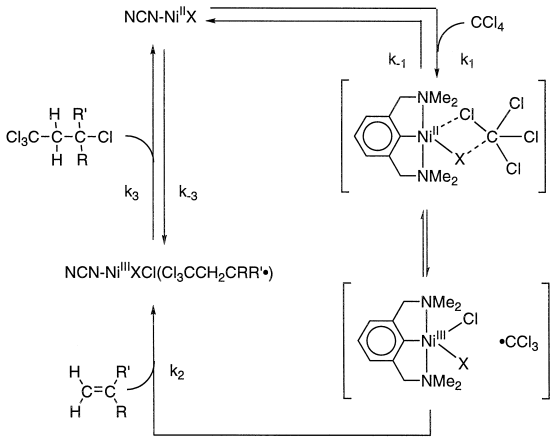
4. The NCNNiX catalyst

In recent years, the mononuclear NCN–Ni catalyst (NCN= $[C_6H_3(CH(R')NR_2)_2\text{-}2,6]^-$) has been successfully used for the 1:1 addition of polyhaloalkanes to carbon–carbon double bonds (Kharasch addition) [12,13] as well as for the controlled atom transfer radical polymerisation (ATRP) of methyl methacrylate and styrenes [14] (see Scheme 1).

This catalysis is based on the unique feature of the NCNNiX catalyst of having a low Ni^{II}/Ni^{III} redox potential ($E_{1/2} = 0.14$ V vs. SCE). In fact, the one-electron oxidation of NCNNiX (diamagnetic, d^8 Ni^{II}) yields the very stable organonickel(III) species $NCNNiX_2$ (paramagnetic, d^7 Ni^{III}). Note that this redox reaction is reversible and occurs with retention of the Ni–C σ-bond. $NCNNiX_2$ has been fully characterized by single crystal X-ray diffraction and electron spin resonance (ESR) spectroscopy [15,16]. This arylnickel(III) species can be seen as a *persistent radical* and it is this property that drives both the Kharasch addition as well as the ATRP reaction. This so-called persistent radical effect has recently been formulated by Fischer [19]. Scheme 2 shows the catalytic cycle. Key-feature in this cycle is the formation of a persistent radical and a CCl_3-radical. The selectivity of both reactions shown in Scheme 2 is driven by special kinetics when one of the radical partners is a persistent radical. As the persistent radical is exclusively involved in the backward reaction (electron- and halide transfer) while this reaction is also fast as compared with the forward reaction between NCNNiX and CCl_4, radical dimerization reactions (formation of, e.g., C_2Cl_6) are kinetically suppressed. The same applies for the product radical which is efficiently quenched by the Ni^{III} persistent radical to prevent oligomer formation by reaction with another alkene molecule or another radical. Any diversion of the CCl_3-radical results in the formation of an equivalent amount of the persistent radical, i.e., of the organo-



Scheme 1.



Scheme 2.

metallic radical, $NCNNiX_2$, which eventually contributes to an enhanced selectivity of the reaction.

The catalytic activity of the NCNNiX catalyst increases with increasing electron-donating properties of the *para*-substituent, R″: NMe_2 > OMe > H > Cl > MeC(O) (see Fig. 2), and this order holds also for increasing $E_{1/2}$ of the *para*-substituted NCNNiX catalysts which varies 123 mV going from a *para*-NMe_2 to a *para*-MeC(O) substituent. The view, that in an encounter complex between NCNNiX and CCl_4 the single electron transfer (inner-sphere SET) occurs, is corroborated by the observation that the rate of the reaction is dependent on the steric requirements of the NR_2 substituent, i.e., the activity increases in the order NMe_2 > 2-methylpiperidine > NEt_2 > N(Me)*i*-Pr. The applicability of the 1:1 addition reaction is rather large with catalyst concentrations amounting to values as low as 0.007 mol%.

5. The Ni-carbosilane dendrimers I and II as catalysts

The catalytic activity of the dendritic catalysts of type I is compared in Table 2. It is obvious that the calculated catalytic activity per Ni site decreases, going from the parent mononuclear catalyst to G_1–Ni_{12}. However, these calculations are based on perfect materials and it is clear that it is impossible to synthesize structurally perfect dendritic materials [3,4]. In the present case, the somewhat lower reactivity of G_1–Ni_{12} points to the presence per dendrimer of an average of 11 nickel centers instead of 12. Currently, we are studying the reactivity of the dendritic catalysts of type II where the Ni-sites are close to the dendrimer surface. The results we have gathered so far point to a large difference in the properties of the G_0–Ni_4 and G_1–Ni_{12}. The latter dendritic catalyst gives only a conversion of 17% after 2 h vs. 91% after 2 h for the corresponding 4-Me_3Si-substituted NCNNiX catalyst. Detailed investigations are underway to establish the origin of this low activity. It seems likely that as the Ni^{II} sites are closely together in the type II metallodendrimer, electron transfer among Ni^{II} and Ni^{III} sites at the dendritic surface is beginning to compete with electron transfer between persistent radicals ($NCNNiX_2$) present at the

Table 2
Comparison of the catalytic activity of the type I dendritic catalysts

Compound	Number of Ni sites (mol × 10^{-5})	Reaction time (h)	Conversion[a] (%)	Initial reaction rate[b]
NCN–NiBr	10.06	0.25	21	234
	10.06	2	80	–
G_0-(NCN–NiBr)$_4$	10.01	0.25	17	190
	10.01	2	74	–
G_1-(NCN–NiBr)$_{12}$	9.4	0.25	14	167
	9.4	2	63	–

[a]Selectivity for the formation of the 1:1 adduct of methyl methacrylate with CCl_4 is 100%.
[b]Turnovers per Ni site per hour during the first 15 min.

dendrimer surface and radicals in solution. In that case, the *retro* electron transfer between the persistent radical and initial or product radicals will be negatively affected.

6. The membrane filtration

The application of abovementioned 'dendritic'-catalysts in a membrane reactor as described earlier [20,21] allows, in principle, a continuous process. It should be noted that the catalytic reactions outlined before usually are carried out as a batch process. In contrast to its application in biotechnology [22,23], the use of membrane reactors in organic and organometallic chemistry is still in its infancy. Recently, the first example of such an application, i.e., the enantioselective addition of Et_2Zn to benzaldehyde with the aid of a polymer-immobilized aminoalcohol catalyst precursor in a membrane reactor has been reported [24].

Preliminary investigations of our dendritic systems in a membrane reactor, carried out by Kleij et al. [11], have shown that already G_0 can be retained quite efficiently. For the type II catalyst, endurance tests showed that after 100 cycles, still 80% of G_1–Ni_{12} is retained. A detailed study is current. In conclusion, these experiments have shown that the combination of a membrane reactor with a catalyst immobilised on well-defined carbosilane dendrimers is feasible. However, this technique needs much improvements. New membranes which are compatible with organic solvents and organometallic reagents are required to develop this area of supported catalysts to its full potential.

So far, dendritic systems containing a catalytic active center at each periferic site have been discussed. As a consequence, with increasing generation of the dendrimer, the number of catalytic sites per dendrimer will increase according to an exponential function. A preliminary conclusion of the investigations outlined above is that this results in a dramatic decrease of catalytic activity per nickel site, vide supra.

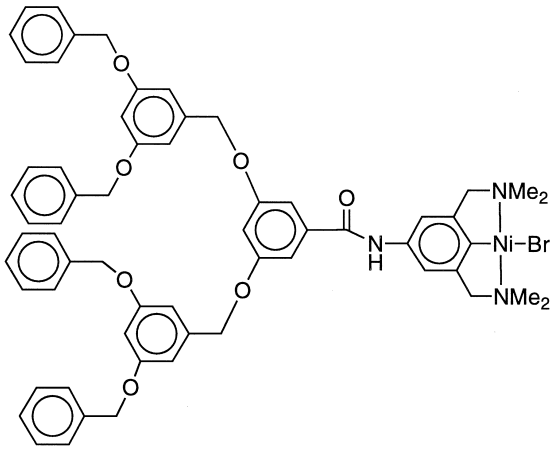


Fig. 4. Example of dendritic system with one catalytically active center per dendrimer molecule.

Therefore, we are now investigating the synthesis, characterization and catalytic activity of dendritic systems that contain only one catalytically active center per dendrimer molecule (see Fig. 4), thus preventing intramolecular redox processes.

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References

[1] R.H. Grubbs, L.C. Kroll, J. Am. Chem. Soc. 93 (1971) 3062.
[2] J.W.J. Knapen, A.W. van der Made, J.C. de Wilde, P.W.N.M. van Leeuwen, P. Wijkens, D.M. Grove, G. van Koten, Nature 372 (1994) 659.
[3] G.R. Newkome, C.N. Moorefield, F. Vögtle, Dendritic Molecules, VCH, Weinheim, 1996.
[4] F. Vögtle (Ed.), Topics in Current Chemistry, Dendrimers, Vol. 197, Springer-Verlag, Berlin, 1998.
[5] A.W. van der Made, P.W.N.M. van Leeuwen, J. Chem. Soc., Chem. Commun. (1992) 1400.
[6] A.W. van der Made, P.W.N.M. van Leeuwen, J.C. de Wilde, R.A.C. Brandes, Adv. Mater. 5 (1993) 466.

[7] D. Seyferth, D.Y. Son, A.L. Rheingold, R.L. Ostrader, Organometallics 3 (1994) 2682.
[8] M.H.P. Rietveld, D.M. Grove, G. van Koten, New J. Chem. 21 (1997) 751.
[9] G. van Koten, Pure Appl. Chem. 61 (1989) 1681.
[10] M. Albrecht, R.A. Gossage, A.L. Spek, G. van Koten, Chem. Commun. (1998) 1003.
[11] A.W. Kleij, R.A. Gossage, I. Eijgendaal, U. Kragl, J.T.B.H. Jastrzebski, G. van Koten, manuscript in preparation.
[12] R.A. Gossage, L.A. van de Kuil, G. van Koten, Acc. Chem. Res. 31 (1998) 423.
[13] L.A. van de Kuil, D.M. Grove, R.A. Gossage, J.W. Zwikker, L.W. Jenneskens, W. Drenth, G. van Koten, Organometallics 16 (1997) 4985.
[14] C. Granel, Ph. Dubois, R. Jérôme, Ph. Teyssié, Macromolecules 29 (1996) 8576.
[15] D.M. Grove, G. van Koten, P. Mul, A.A.H. van der Zeijden, J. Terheijden, M.C. Zoutberg, C.H. Stam, Organometallics 5 (1986) 322.
[16] D.M. Grove, G. van Koten, P. Mul, R. Zoet, J.G.M. van der Linden, J. Legters, J.E.J. Schmitz, N.W. Murral, A.J. Welch, Inorg. Chem. 27 (1988) 2466.
[17] J.G. Donkervoort, J.L. Vicario, J.T.B.H. Jastrzebski, G. Cahiez, G. van Koten, J. Organomet. Chem. 558 (1998) 61.
[18] P. Dani, T. Karlen, R.A. Gossage, W.J.J. Smeets, A.L. Spek, G. van Koten, J. Am. Chem. Soc. 119 (1997) 11317.
[19] H. Fischer, J. Am. Chem. Soc. 108 (1986) 3925.
[20] U. Kragl, D. Gygax, O. Ghisalba, C. Wandrey, Angew. Chem. Int. Ed. Engl. 30 (1991) 827.
[21] G.F. Herrmann, U. Kragl, C. Wandrey, Angew. Chem. Int. Ed. Engl. 32 (1993) 1342.
[22] A.S. Bommarius, Biotechnology, in: H.-J. Rehm, G. Reed, A. Pühler, P. Stadler, G. Stephanopoulos (Eds.), Bioprocessing, Vol. 3, VCH, Weinheim, 1993, p. 427.
[23] U. Kragl, in: T. Godfrey, S. West (Eds.), Industrial Enzymology, 2nd edn., Macmillan, New York, 1996.
[24] U. Kragl, C. Dreisbach, Angew. Chem. Int. Ed. Engl. 35 (1996) 642.