Multiple Use of Soluble Metallodendritic Materials as Catalysts and Dyes

Martin Albrecht, Neldes J. Hovestad, Jaap Boersma, and Gerard van Koten*[a]

Abstract: Different sizes of core-functionalized metallodendritic wedges were prepared by anchoring sensor-active arylplatinum(II) sites at the focal point of Fréchet-type polyether dendritic wedges of various generations. The strong color of these metallodendrimers in the presence of SO_2 was used to assess the permeability of nanofiltration membranes (molecular weight cut-off of 400 dalton) at ambient pressure. A primary result of these studies is that dendrimers do not have to be exceptionally large for successful retention. Hence, nanofiltration, membrane-capped, immersion vials were developed, which operate as sensor devices when loaded with metallodendrimers with good retention properties. Appropriate substitution of the dye site at the focal point of these metallodendritic wedges by a catalytically active group afforded dendritic catalysts that exhibit essentially the same physical properties (shape, retention) as the corresponding dye-functionalized dendritic wedges. When this homogeneous catalyst is compartmentalized in membrane-capped vials, a unique and convenient method for its retrieval from product solutions is available. Moreover, such immobilized metallodendritic catalysts can be regenerated and stored for months without losing their activity; this provides access for the development of novel sustainable homogeneous catalysts.

Keywords: dendrimers · homogeneous catalysis · metallodendrimers · nanofiltration · nickel · platinum · sensors

Introduction

Metallodendrimers,[1] that is, dendrimers that are functionalized with transition metal centers, have attracted widespread interest for various applications such as ion detection, gas sensoring, light harvesting, or redox-active switches.[2] Particularly intriguing is their use as homogeneous (multisite) catalysts,[3] since they combine many advantages of heterogeneous and homogeneous catalysts (convenient separation of catalyst and product solution paired with high and well-defined selectivity). Nanofiltration techniques with appropriate membranes have been suggested for efficient catalyst removal and recovery for multiple use.[4] It is evident that the availability of nanofiltration membranes[5] with suitable permeability characteristics is critical for the success of such dendritic applications. Whilst several techniques for the measurement of the porosity (*pore size*) of various types of membranes have been developed,[6] a fast and reliable assessment of the *permeability* of nanofiltration membranes still presents a major issue, in particular for the application of metallodendritic catalysts in membrane reactors.[7]

Our concept to assess the permeability of membranes relies on the use of macromolecular supports of known size[8] that are functionalized with (pertinent) dyes as markers.[9] We have chosen for a new, "serial" approach, which involves first the functionalization of a series of suitable dendritic supports of increasing molecular weight and size with a dye to assess the permeability of a given membrane. Subsequently the dye in the dendritic support of choice is substituted by a catalytically active center, thus providing a macromolecular catalyst system with well-defined permeability properties. Evidently, these modifications should not affect the structure and/or shape of the macromolecular support. Moreover, the dye and catalytically active site should exert a similar (ideally the same) influence on the properties of the support (polarity, size, etc.).

A system that fulfills these prerequisites is based on a series of polyether dendritic wedges,[10] the core of which is functionalized with a pincer ligand that is known to complex a variety of different metal centers. Depending on the metal site, such pincer–metal complexes can be used as catalysts (e.g., Ru^{II}, Rh^{I}, Ir^{I}, Pd^{II})[3a, 11] in a number of organic transformations or as dyes (Pt^{II}).

The working principle of the platinum dye is the instantaneous detection of SO_2 gas by formation of a reversible η^1-Pt–S bond between SO_2 and the platinum center in [PtX(NCN–R)] complexes (where NCN–R is the *N*,*C*,*N′* terdentate-bonding "pincer"-type ligand $[2,6\text{-}(CH_2NMe_2)_2\text{-}4\text{-}(R)\text{-}C_6H_2]^-$ and R is a linker, e.g., to a dendritic wedge).[12] Bonding of SO_2 gas is accompanied by characteristic spectroscopic changes, as these initially colorless [PtX(NCN–R)] complexes turn bright orange on SO_2 coordination. Hence,

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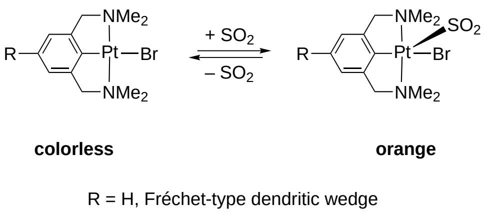
the diagnostic color in SO_2-saturated solutions can be used as a probe to assess the permeation of (sensor-functionalized) dendrimers through nanofiltration membranes.

Results and Discussion

Fréchet-type polyether dendritic wedges of zeroth to third generation[10] were functionalized at their focal points with the sensor-active organoplatinum(II) site. A covalent linkage between sensor unit and dendritic support was achieved by etherification of the phenolic hydroxyl group of the pincer ligand in the complex [PtBr(NCN–OH)] (**1**) with benzylic bromides present in the dendritic wedges. This gave the metallodendrimers **2**–**5** in good yields (Scheme 1). Spectroscopic analyses are in good accordance with the formation of these platinum-functionalized dendrimers and, hence, provide evidence that the organometallic sites are resistent to the applied reaction conditions, as no decomposition products originating from Pt–N or Pt–C bond cleavage were observed. The ^1H NMR spectra of the metallodendrimers in the $\delta = 4.5-5.1$ region are illustrative: the signals due to the benzylic $ArCH_2Br$ protons of the dendritic wedges of the starting materials (located at $\delta_H \approx 4.6$) disappeared completely upon coupling and instead, new resonance signals appeared around $\delta = 5.0$, which were assigned to the benzylic protons from the newly formed benzyl aryl ether.

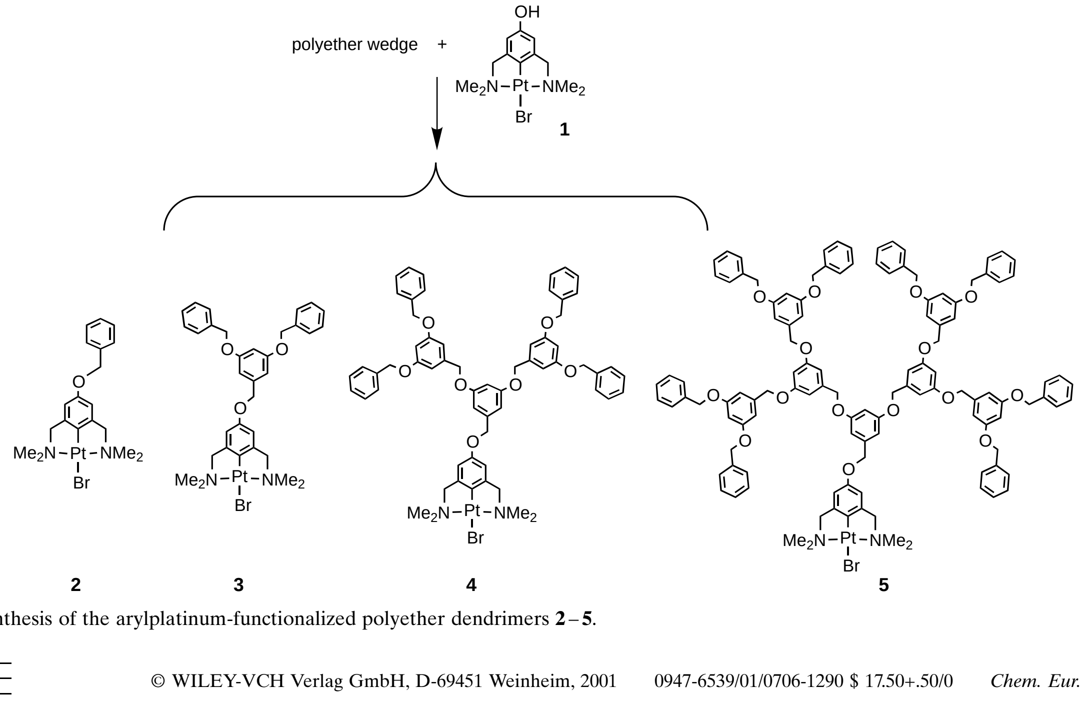
The size of these metallodendrimers correlates with increasing generation number. Theoretical and experimental investigations on the second- and higher generations suggested that the dendritic wedges adopt a partly backfolded conformation with a hydrodynamic radius r_h of 0.8 nm (for second-generation wedge) and 1.0 nm (for third generation).[13] The first-generation dendritic molecule **3** was calculated to possess a radius of not more than 0.6 nm (fully extended structure, molecular mechanics, mm2 level). Due to the additional presence of the organoplatinum unit in **4** and **5**, these values represent only the lower limits.

Similar to the original detector systems, which are composed of platinum complexes that contain the pincer ligand without dendritic support (e.g., **1**),[12] the novel metallodendrimers **2**–**5** display a high sensitivity towards low concentrations of SO_2. Selective SO_2 recognition by these organoplatinum materials was established to occur through reversible η^1-Pt–S bond formation (Scheme 2), which is indicated by various spectroscopic changes and which is most prominently reflected by two characteristic metal-to-ligand charge transfer bands in the UV/vis spectrum (λ_{max} around 420 and 350 nm). Similarly, the metallodendrimers **2**–**5** instantly turn from colorless to bright orange when exposed to an SO_2-enriched solution.[14] From UV-visible spectroscopic measurements, no indication was obtained for a generation-dependent solvatochromism (in CH_2Cl_2, $CHCl_3$, or C_6H_6).[15] Therefore, these arylplatinum-functionalized dendrimers **2**–**5** can have a dual function as i) sensors for reversible SO_2 gas detection and ii) as dyes, provided that excess of SO_2 is present.



Scheme 2. Reversible bonding of SO_2 on platinum(II) complexes containing the NCN pincer ligand induces a diagnostic color change of the material.

We have used the dye characteristics to probe the suitability of these macromolecules for nanofiltration membrane applications in homogeneous systems.[16] In SO_2-saturated solutions, leaching of any dendritic material through a membrane is instantly indicated by colorization of the solution at the



Scheme 1. Synthesis of the arylplatinum-functionalized polyether dendrimers **2**–**5**.

other side of the membrane. In a typical experiment, a solution of the metallodendrimers **3**–**5** was separated by a nanofiltration membrane (SelRO-MPF-60; claimed molecular weight cut-off: 400 dalton)[17] from pure CH_2Cl_2 under a static SO_2 atmosphere (1 atm). The diffusion of the metallodendrimer through this membrane was subsequently monitored on-line by UV-visible spectroscopy and related to the elapsed time. A plot is shown in Figure 1, which clearly reveals a correlation of the diffusion properties of the metallodendrimers **3**–**5** with the molecular weight and size of the corresponding macromolecules (Figure 1). A moderate retention performance was established for **3** ($t_{1/2} = 108$ h), whereas the retention time of the higher generation dendrimers is acceptable ($t_{1/2}$ for **4** = ca. 300 h) to excellent (extrapolated $t_{1/2}$ for **5** > 60 days). A direct conclusion from these results is that *dendrimers do not need to be exceedingly large* for successful membrane applications.

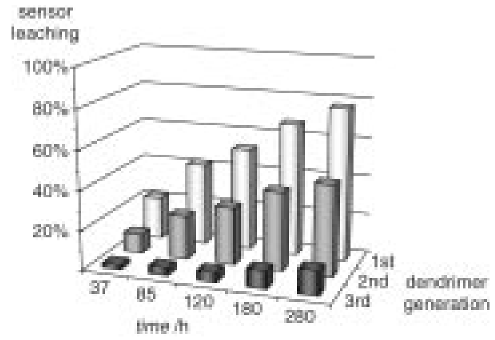


Figure 1. Generation-dependent retention behavior of metallodendrimers by nanofiltration membranes, measured as relative absorbance of the detector sites outside the immersion vial (UV-visible spectroscopy).

This was demonstrated by loading a nanofiltration, membrane-capped, glass vial (Figure 2) with a solution of **5** in CH_2Cl_2 (colorless). When such a vial was placed in CH_2Cl_2 that was pre-treated with SO_2, a rapid and diagnostic color change to orange was observed within the vial only. Notably, such vials allow for the qualitative *and* quantitative on-line SO_2 gas detection owing to the solubility and well-defined connectivity in **5**. When using other supports, these applications are limited because of an undefined number of active sites (e.g., in polymers) or because of difficulties associated with the homogeneity of the system (solid-phase supports).

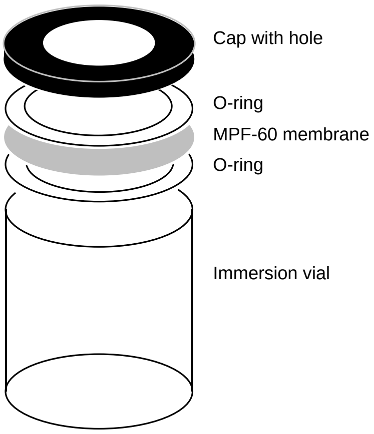
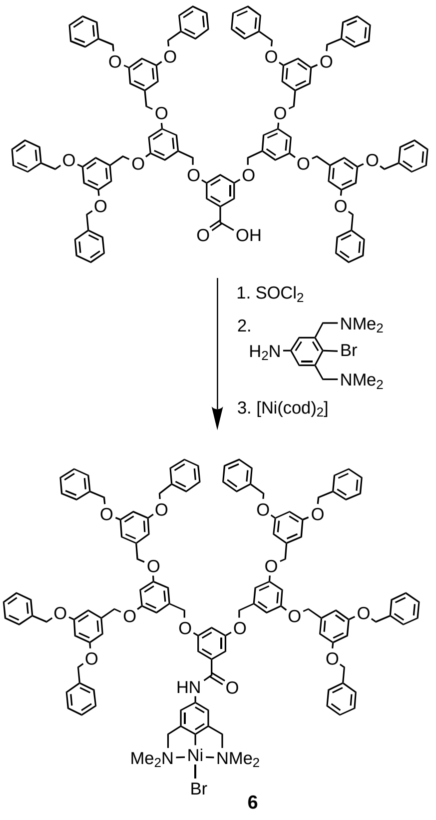


Figure 2. Schematic representation of the nanofiltration, membrane-capped, immersion vials fabricated for dendrimer compartmentalization.

The compartmentalized sensor device was conveniently regenerated by removal of the orange vial from the SO_2-containing environment and subsequent washing with pure CH_2Cl_2. Proper storage of such vials did not lead to any notable loss of activity.[18, 19]

This concept is readily extended to the fabrication of a multiple use metallodendritic device: substitution of the arylplatinum unit in **5** by a catalytically active site affords a metallodendritic catalyst with well-defined retention properties for applications with a specific membrane.[20] This approach was exemplified by using substituted [NiCl(NCN)] units as catalysts for the Kharasch addition of polyhalogenated alkanes to alkenes (C–C bond formation).[21] To this end, the NCN-type ligand precursor 2,6-$(CH_2NMe_2)_2$-4-NH_2-BrC_6H_2 was connected to a third-generation dendritic wedge, by applying an amidation protocol, and was subsequently treated with $[Ni(cod)_2]$ which afforded the metallodendrimer **6** (Scheme 3). The catalytic activity of **6** was preliminarily tested in the Kharasch addition of CCl_4 to methyl methacrylate (MMA) under standard conditions.[21] Comparison of these results with unsupported catalysts (i.e., of [NiCl(NCN)]) reveals similar reaction rates and turnover numbers (TON = 310).[11b] This is in contrast to the earlier observations with periphery-functionalized, polynickelated dendrimers, which



Scheme 3. Synthetic protocol for the preparation of the dendritic nickel(II) catalyst **6**.

suffer from (negative) dendritic effects during catalysis.[22] This dendritic effect relies on the fact that the Kharasch addition reaction involves the formation of a persistent arylnickel(III) radical and a reactive $^{\bullet}CCl_3$ radical, which adds to the alkene under formation of a product radical.[23] Product formation involves a single electron transfer and nickel reduction from Ni^{III} again to Ni^{II}. When the nickel sites are located in too close proximity (i.e., non-random distribution in solution), as in periphery-functionalized metallodendrimers of higher generations, recombination of $^{\bullet}CCl_3$ and/or product radicals at the dendrimer periphery becomes a competitive process due to the high local radical concentration. This process prevents the reduction of the catalytically inactive Ni^{III} center, thereby quenching the Kharasch addition reaction.[22] Evidently, these undesired effects cannot occur in the present core-functionalized mononickelated dendrimers.

Since the organonickel dendrimer **6** combines the catalytic activity of the model catalyst with the permeability properties established for the dye macromolecule **5**, it was compartmentalized in a nanofiltration, membrane-capped, immersion vial. When such a vial was exposed to substrate-containing solutions (CCl_4 and MMA), a catalytic reaction inside the vial took place, which was essentially complete within 48 hours (conversion >99%, Figure 3). The relatively long reaction time required for this process (cf. 4 h reaction time with noncompartmentalized catalyst **6**) presumably originates from a restricted mass transfer of substrates into the immersion vial. These (technical) problems can be solved by increasing the overall percentage of the membrane-covered surface of the immersion vial. Note that in the setup used here, this surface is very small and does not exceed 5% of the total surface of the vial (Figure 2).

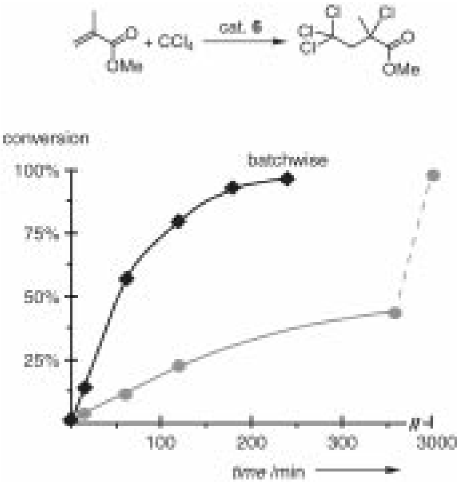


Figure 3. Kharasch addition reaction using a membrane-capped vial loaded with a solution of the third-generation nickel dendrimer **6** as catalyst (circles). After 36 h, the conversion has reached virtually 100%. For comparison, an identical reaction has been carried out without having compartmentalized the catalyst (batchwise; squares), which required a work-up procedure involving separation of the product from residual catalyst traces. The reaction delay with catalyst **6** is attributed to limited mass transfer caused by the relatively small membrane surface area.

Separation of the dendrimer-bound nickel catalyst from product solution is conveniently accomplished by removing the vial. Catalyst recycling and separation from residual substrate occurred analogously to sensor regeneration (vide supra), and is efficiently achieved by washing the catalyst-containing immersion vial in pure solvents.

This technique provides a unique solution for keeping the soluble metal catalyst continuously compartmentalized during homogeneous catalysis, also at ambient pressure. Moreover, this method warrants a nondestructive yet efficient catalyst recovery[24] and may provide access to sustainable catalysts that can be stored for several weeks without significant loss of catalyst activity.

Conclusion

In the work presented here, we have demonstrated the potential of metallodendritic wedges as multiple use devices: when functionalized at the focal point with dyes these well-defined macromolecules can be used for the assessment of the permeability properties of (nano)porous materials at ambient pressure. In this way, dendritic wedges with excellent retention characteristics for a given nanofiltration membrane were identified. Modification of the *chemical* properties of these dendritic wedges was accomplished by substitution of the core unit without significantly affecting its *physical* characteristics, for example, shape and retention properties. This is a consequence of the unique molecular architecture of core-functionalized dendritic wedges, which is characterized by a highly regular and well-defined structure at the periphery and a well-defined active site that is located at its focal point. In a serial approach, substitution of the dye in the core of these wedges with a catalytically active center afforded metallodendritic catalysts with known retention properties. Immersion of these catalytically active metallodendrimers as solutions in membrane-capped vials provided novel and simple catalyst systems, which successfully combine the benefits of homogeneous and heterogeneous catalysts: they operate in a fully dissolved (homogeneous) mode (cf. high selectivity, random distribution of the catalytic sites within the vial), are conveniently removed from product mixtures, and can be fully regenerated and stored for prolonged time.

Experimental Section

General: All reagents and solvents were obtained commercially and used without further purification unless stated. Reactions involving nickel derivatives were carried out by using standard Schlenk techniques under an inert atmosphere of dry, oxygen-free nitrogen. Et_2O, THF, and hexane were distilled from Na/benzophenone, and CH_2Cl_2 was distilled from CaH_2 prior to use. The retention measurements were carried out according to literature procedures by using carefully activated MPF-60 nanofiltration membranes.[5] All spectra were recorded at 300 MHz (^1H) and 75 MHz ($^{13}C\{^1H\}$). Spectra were obtained in $CDCl_3$ solution at 25 °C, unless stated otherwise, and are referenced to $SiMe_4$ ($\delta = 0.00$). Mass spectra were carried out under electron ionization (EI) conditions (70 eV). Elemental analyses were obtained from Kolbe, Mikroanalytisches Laboratorium (Mülheim, Germany). Matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectra were acquired by using a nitrogen laser emitting at 337 nm (accelerating voltage: 23000–25000 V; external calibration: bovine insuline; matrix: 3,5-dihydroxy-benzoic acid).

The platinum complex $[PtBr\{2,6\text{-}(CH_2NMe_2)_2\text{-}4\text{-}(OSiMe_2t\text{Bu})\text{-}C_6H_2\}]$,[12b] $[Ni(cod)_2]$ (cod = cycloocta-1,5-diene),[25] 4-amino-2,6-bis[(dimethylamino)methyl]bromobenzene,[26] and the dendritic wedges (containing either a carboxylic acid or a benzyl bromide functionality at the core)[10] were prepared according to described procedures.

$[PtBr\{2,6\text{-}(CH_2NMe_2)_2\text{-}4\text{-}(OH)\text{-}C_6H_2\}]$ (1): Bu_4NF (1 mL, 1 M in THF) was added to a solution of $[PtBr\{2,6\text{-}(CH_2NMe_2)_2\text{-}4\text{-}(OSiMe_2t\text{Bu})\text{-}C_6H_2\}]$ (0.60 g, 1.0 mmol) in THF (15 mL). After 0.5 h, H_2O was added (1 mL, excess), and the reaction mixture stirred for 16 h. During this period, a white precipitate gradually formed, which was subsequently collected by filtration. The solid was washed with THF (2 × 5 mL) and dried in vacuo to afford **1** as a white solid (0.39 g, 81 %); elemental analysis calcd (%) for $C_{12}H_{19}BrN_2OPt$: C 29.88, H 3.97, N 5.81; found C 29.71, H 3.89, N 5.78; ^{1}H NMR: $\delta = 6.39$ (s, 2H; Ar*H*), 4.45 (brs, 1H; OH), 3.98 (s, $^3J(Pt,H) = 45.0$ Hz, 4H; $ArCH_2N$), 3.12 (s, $^3J(Pt,H) = 39.3$ Hz, 12H; NCH_3); $^{13}C\{^1H\}$ NMR: $\delta = 152.9$ (C-*para*), 144.1 (C-*ortho*), 137.0 (C-*ipso*), 106.9 (C-*meta*), 77.2 ($ArCH_2N$), 55.1 (NCH_3).

General procedure for the coupling of 1 with dendritic benzyl bromides (platinum metallodendrimers): A suspension containing equimolar amounts of $BrCH_2{-}G_x$ ($x = 0-3$), **1**, and excess of K_2CO_3 (2–4 mol equiv) in acetone was heated to reflux temperature in the presence of [18]crown-6 (0.2 mol %) for 20 h. The mixture was poured on water and extracted three times with CH_2Cl_2. This afforded the crude product, which was redissolved in a small amount of CH_2Cl_2 and precipitated by adding pentane (ca. 20 volume equiv). Subsequent purification by column chromatography (SiO_2; CH_2Cl_2/acetone 4:1) afforded the organometallic dendrimers as analytically pure, white solids.

$[PtBr\{2,6\text{-}(CH_2NMe_2)_2\text{-}4\text{-}(OCH_2\text{-}G_0)\text{-}C_6H_2\}]$ (2): From $BrCH_2\text{-}G_0$ (0.55 g, 3.2 mmol), **1** (388 mg, 0.80 mmol), and K_2CO_3 (0.14 g, 1 mmol) in acetone (10 mL). Analytically pure **2** was obtained by liquid–liquid diffusion of Et_2O into a solution of **2** in CH_2Cl_2. Elemental analysis calcd (%) for $C_{19}H_{25}BrN_2OPt$ (572.42): C 39.87, H 4.40, N 4.89; found C 39.75, H 4.53, N 4.82; ^{1}H NMR: $\delta = 7.42-7.34$ (m, 5H; Ar*H*), 6.53 (s, 2H; Ar*H*), 4.98 (s, 2H; $ArCH_2O$), 3.99 (s, $^3J(Pt,H) = 46.4$ Hz, 4H; $ArCH_2N$), 3.12 (s, $^3J(Pt,H) = 38.2$ Hz, 12H; NCH_3); $^{13}C\{^1H\}$ NMR: $\delta = 156.6$ (C-*para*), 143.9 (C-*ortho*), 137.5 (C-*ipso*), 137.3 (Ar*C*), 128.5 (Ar*C*), 127.9 (Ar*C*), 127.4 (Ar*C*), 106.8 (C-*meta*), 77.6 ($ArCH_2N$), 70.6 ($ArCH_2O$), 55.1 (NCH_3); FAB-MS: *m*/*z*: 491.2 $[M - Br]^+$, 572.2 $[M]^+$.

$[PtBr\{2,6\text{-}(CH_2NMe_2)_2\text{-}4\text{-}(OCH_2\text{-}G_1)\text{-}C_6H_2\}]$ (3): From $BrCH_2\text{-}G_1$ (183 mg, 0.48 mmol), **1** (233 mg, 0.48 mmol), and K_2CO_3 (0.27 g, 2 mmol) in acetone (15 mL). Slow diffusion of Et_2O into a concentrated solution of crude **3** in CH_2Cl_2 afforded pure **3** as microcrystalline, white solid. Yield: 352 mg (94 %); elemental analysis calcd (%) for $C_{33}H_{37}BrN_2O_3Pt$ (784.67): C 50.51, H 4.75, N 3.57; found C 50.38, H 4.67, N 3.49; ^{1}H NMR: $\delta = 7.43-7.31$ (m, 10H; Ar*H*), 6.66–6.56 (m, 3H; Ar*H*), 6.50 (s, 2H; Ar*H*), 5.02 (s, 4H; $ArCH_2O$), 4.91 (s, 2H; $ArCH_2O$), 3.97 (s, $^3J(Pt,H) = 40.2$ Hz, 4H; $ArCH_2N$), 3.10 (s, $^3J(Pt,H) = 35.7$ Hz, 12H; NCH_3); $^{13}C\{^1H\}$ NMR: $\delta = 160.1$ (Ar*C*), 156.5 (C-*para*), 143.9 (C-*ortho*), 139.8 (Ar*C*), 137.5 (*C*-ipso), 136.7 (Ar*C*), 128.6 (Ar*C*), 128.0 (Ar*C*), 127.5 (Ar*C*), 106.8 (C-*meta*), 106.2 (Ar*C*), 101.2 (Ar*C*), 77.5 ($ArCH_2N$), 70.4 ($ArCH_2O$), 70.1 ($ArCH_2O$), 55.1 (NCH_3); FAB-MS: *m*/*z*: 704.3 $[M - Br]^+$, 784.3 $[M]^+$.

$[PtBr\{2,6\text{-}(CH_2NMe_2)_2\text{-}4\text{-}(OCH_2\text{-}G_2)\text{-}C_6H_2\}]$ (4): From $BrCH_2\text{-}G_2$ (202 mg, 0.25 mmol), **1** (127 mg, 0.26 mmol), and K_2CO_3 (0.11 g, 0,8 mmol) in acetone (10 mL). Yield: 260 mg (86 %); elemental analysis calcd (%) for $C_{61}H_{61}BrN_2O_7Pt$ (1209.17): C 60.59, H 5.09, N 2.32; found C 61.58, H 5.29, N 1.96; ^{1}H NMR: $\delta = 7.44-7.31$ (m, 20H; Ar*H*), 6.68–6.54 (m, 9H; Ar*H*), 6.50 (s, 2H; Ar*H*), 5.03 (s, 8H; $ArCH_2O$), 4.98 (s, 4H; $ArCH_2O$), 4.91 (s, 2H; $ArCH_2O$), 3.96 (s, $^3J(Pt,H) = 39.3$ Hz, 4H; $ArCH_2N$), 3.10 (s, $^3J(Pt,H) = 35.7$ Hz, 12H; NCH_3); $^{13}C\{^1H\}$ NMR: $\delta = 160.1$ (Ar*C*), 160.0 (Ar*C*), 156.5 (C-*para*), 143.9 (C-*ortho*), 139.9 (Ar*C*), 139.2 (Ar*C*), 137.5 (C-*ipso*), 136.7 (Ar*C*), 128.6 (Ar*C*), 128.0 (Ar*C*), 127.5 (Ar*C*), 106.8 (C-*meta*), 106.4 (Ar*C*), 106.3 (Ar*C*), 101.5 (Ar*C*), 101.3 (Ar*C*), 77.5 ($ArCH_2N$), 70.4 ($ArCH_2O$), 70.1 ($ArCH_2O$), 70.0 ($ArCH_2O$), 55.1 (NCH_3); MALDI-TOF: *m*/*z*: 1130.5 $[M - Br]^+$, 1233.1 $[M{+}Na]^+$.

$[PtBr\{2,6\text{-}(CH_2NMe_2)_2\text{-}4\text{-}(OCH_2\text{-}G_3)\text{-}C_6H_2\}]$ (5): From $BrCH_2\text{-}G_3$ (340 mg, 0.021 mmol), **1** (27 mg, 0.06 mmol), and K_2CO_3 (0.11 g, 0,8 mmol) in acetone (10 mL). Yield: 325 mg (77 %); elemental analysis calcd (%) for $C_{117}H_{109}BrN_2O_{15}Pt \cdot 3\,CH_2Cl_2$ (2312.96): C 62.31, H 5.01, N 1.21; found C 62.38, H 5.31, N 1.42; ^{1}H NMR: $\delta = 7.44-7.33$ (m, 40H; Ar*H*), 6.70–6.58 (m, 21H; Ar*H*), 6.51 (s, 2H; Ar*H*), 5.03 (s, 16H; $ArCH_2O$), 5.01 (s, 2H; $ArCH_2O$), 4.98 (s, 8H; $ArCH_2O$), 4.91 (s, 4H; $ArCH_2O$), 3.93 (brs, $^3J(Pt,H)$ not resolved, 4H; $ArCH_2N$), 3.09 (s, $^3J(Pt,H)$ not resolved, 12H; NCH_3); $^{13}C\{^1H\}$ NMR: $\delta = 160.1$ (Ar*C*), 160.0 (Ar*C*), 158.6 (Ar*C*), 156.5 (C-*para*), 143.9 (C-*ortho*), 139.9 (Ar*C*), 139.2 (Ar*C*), 139.1 (Ar*C*), 138.7 (Ar*C*), 137.5 (C-*ipso*), 136.7 (Ar*C*), 128.6 (Ar*C*), 127.9 (Ar*C*), 127.5 (Ar*C*), 106.8 (C-*meta*), 106.3 (Ar*C*), 101.5 (Ar*C*), 101.3 (Ar*C*), 77.2 ($ArCH_2N$), 71.0 ($ArCH_2O$), 70.4 ($ArCH_2O$), 70.0 ($ArCH_2O$), 69.9 ($ArCH_2O$), 55.0 (NCH_3), two quaternary carbons not resolved; MALDI-TOF: *m*/*z*: 1978.1 $[M - Br]^+$, 2058.0 $[M]^+$.

$Br\{2,6\text{-}(CH_2NMe_2)_2\text{-}4\text{-}\{OC(O)\text{-}G_3\}\text{-}C_6H_2\}$: A solution of $SOCl_2$ (0.40 mL, 0.5 M solution in Et_2O, 0.20 mmol) was added dropwise to a solution of $HOC(O)\text{-}G_3$ (0.24 g, 0.15 mmol) in THF (10 mL) over 15 min. The reaction mixture was stirred for 2 h, followed by in vacuo removal of the organic solvents. The residue was redissolved in CH_2Cl_2 (3 mL) and added dropwise to a solution of 4-amino-2,6-bis[(dimethylamino)methyl]bromobenzene (57.2 mg, 0.20 mmol) in CH_2Cl_2 (5 mL). The reaction mixture was heated at reflux temperature for 16 h. Subsequently, this mixture was washed with aqueous K_2CO_3 (1 M, 3 × 15 mL), and the organic layers dried over Na_2SO_4. After removal of all volatiles in vacuo, the dendrimer-supported ligand precursor was obtained as a yellowish solid. Yield: 0.26 g (93 %); elemental analysis calcd (%) for $C_{117}H_{108}BrN_3O_{15}$ (1876.08): C 74.91, H 5.80, N 2.24; found C 75.10, H 5.91, N 2.15; ^{1}H NMR: $\delta = 8.17$ (brs, 1H; NH), 7.77 (s, 2H; Ar*H*), 7.40 (m, 40H; Ar*H*), 7.13 (s, 2H; Ar*H*), 6.77 (s, 1H; Ar*H*), 6.65 (m, 18H; Ar*H*), 5.02 (m, 28H; $ArCH_2O$), 3.60 (s, 4H; $ArCH_2N$), 2.35 (s, 12H; NCH_3); $^{13}C\{^1H\}$ NMR: $\delta = 165.5$ (C=O), 160.7 (Ar*C*), 160.5 (Ar*C*), 160.3 (Ar*C*), 139.4 (C-*ortho*), 139.1 (Ar*C*), 137.2 (C-*para*), 137.2 (Ar*C*), 137.0 (Ar*C*), 131.4 (Ar*C*), 128.8 (Ar*C*), 128.3 (Ar*C*), 127.8 (Ar*C*), 121.7 (C-*ipso*), 121.5 (C-*meta*), 106.7 (Ar*C*), 106.4 (Ar*C*), 106.0 (Ar*C*), 105.8 (Ar*C*), 102.0 (Ar*C*), 101.9 (Ar*C*), 70.3 ($ArCH_2O$), 64.0 ($ArCH_2N$), 45.8 (NCH_3), one $ArCH_2O$ signal not resolved; FAB-MS: *m*/*z*: 1876.5 $[M{+}H]^+$.

$[NiBr\{2,6\text{-}(CH_2NMe_2)_2\text{-}4\text{-}\{OC(O)\text{-}G_3\}\text{-}C_6H_2\}]$ (6): To a stirred solution of $Ni(cod)_2$ (50.0 mg, 0.182 mmol) in THF (10 mL) at −78 °C was added dropwise a solution of the dendritic ligand precursor (0.20 g, 0.11 mmol) in THF (5 mL). After the addition was complete, the temperature was allowed to warm to room temperature over 2 h and stirring was continued for another 2 h. The suspension was filtered, and the filtrate evaporated in vacuo. The residue was washed with cold hexane (2 × 5 mL), then redissolved in CH_2Cl_2 (5 mL), and precipitated by adding hexane (40 mL). This yielded 0.18 g of **6** as a yellow solid (87 %). ^{1}H NMR (CD_2Cl_2): $\delta = 7.72$ (brs, 1H; NH), 7.35 (m, 42H; Ar*H*), 6.65 (m, 21H; Ar*H*), 5.00 (m, 28H; $ArCH_2O$), 3.95 (s, 4H; $ArCH_2$), 3.11 (s, 12H; NCH_3); $^{13}C\{^1H\}$ NMR (CD_2Cl_2): $\delta = 165.5$ (C=O), 160.2 (Ar*C*), 160.1 (C-*ipso*), 158.6 (Ar*C*), 156.5 (Ar*C*), 143.9 (C-*ortho*), 139.9 (Ar*C*), 139.2 (C-*para*), 139.2 (Ar*C*), 138.7 (Ar*C*), 136.8 (Ar*C*), 128.6 (Ar*C*), 128.0 (Ar*C*), 127.5 (Ar*C*), 121.5 (Ar*C*), 110.9 (C-*meta*), 108.2 (Ar*C*), 106.9 (Ar*C*), 106.2 (Ar*C*), 104.9 (Ar*C*), 101.6 (Ar*C*), 101.3 (Ar*C*), 70.1 ($ArCH_2N$ and $ArCH_2O$), 65.8 ($ArCH_2O$), 55.1 (NCH_3); MALDI-TOF-MS *m*/*z*: 1959.0 $[M{+}Na]^+$.

Permeability measurements: An immersion vial (2 mL volume) was charged with a solution of the appropriate metallodendrimer (typically 20 μmol in 2 mL CH_2Cl_2) and closed with a membrane-covered cap. This vial was then placed into a flask containing CH_2Cl_2 (60 mL), which was previously saturated with SO_2. The change of the color of this outer solution was monitored through a cuvette, which was directly connected to the flask containing the CH_2Cl_2, and related to the elapsed time.

Standard catalysis: Prior to use, a solution of methyl methacrylate (28 mmol), CCl_4 (104 mmol), and dodecane (internal standard, 8.9 mmol) was degassed thoroughly by using standard freeze-pump-thaw methods. Subsequently, the catalyst (9.1×10^{-5} mol) in CH_2Cl_2 (10 mL) was added under an inert atmosphere at room temperature. The reaction was monitored by regular collection of samples (0.2 mL) which were subjected to GC analysis.

Acknowledgement

This work was supported in part (NJH) by the Council for Chemical Sciences of the Netherlands Organization for Scientific Research (CW-NWO) and the Dutch Technology Foundation (STW) with financial aid from DSM/Gist-brocades.

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Received: July 10, 2000 [F2592]