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Shape-Persistent Nanosize Organometallic Complexes: Synthesis and Application in a Nanofiltration Membrane Reactor

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Shape-persistent multi(NCN−palladium and/or −platinum) complexes having one- (**5** and **6**), two- (**1** and **2**), and three-dimensional (**3** and **4**) geometries were prepared in moderate to good yields. Two different approaches were used to construct the multimetallic materials: (i) the construction of the multisite ligands followed by the permetalation step and (ii) selective and mild one-pot coupling of monometallic buiding blocks to a multifunctional shape-persistent organic core molecule. The first approach was used to prepare the palladated and/or platinated tris- (**2**) and bis(NCN−pincer) (**5**) complexes, while the second approach afforded the palladated and platinated octakis- (**3**) and dodecakis(NCN−pincer) (**4**) complexes. Complexes **1**−**6** were subjected to nanofiltration (NF) experiments in order to investigate the influence of rigidity and geometry on the retention of these molecules by NF membranes. For this purpose, the corresponding $(NCN-Pt-X)_n$ complexes (**1c**−**4c**, **5**, and **6**) were used since exposing these complexes to sulfur dioxide in solution resulted in the formation of bright orange complexes, allowing the use of UV/vis spectroscopy to accurately determine the concentrations of **1**−**6** in both retentate and permeate. Using the MPF-60 (MWCO = 400) NF-membrane, retention rates of 82.4 (**6**), 93.9 (**1c**), 98.7 (**2c**), 99.5 (**3c**), 99.6 (**5**), and >99.9% (**4c**) were found, while **2c** and **4c** in combination with the MPF-50 (MWCO = 700) NF-membrane were retained in 97.6 and 99.9%, respectively. A clear relationship is observed between the dimensions calculated by molecular modeling and the retention rates of **1**−**6**. The one-dimensional bis(pincer−platinum) complex **5**, however, shows an unexpectedly high retention rate (99.6%) that can be due to precipitation of the complex in the membrane (clogging of the membrane) and/or to the formation of larger aggregates near the membrane. In addition, comparison of **2** and **4** with flexible nickelated G0- and G1-dendrimers with similar dimensions proved that a high degree of rigidity in the backbone of macromolecular complexes indeed leads to more efficient retentions of these multimetallic materials by NF-membranes.

Introduction

A recent, promising development in the area of catalyst recovery and reuse (recycling) is the incorporation of homogeneous catalysts on large organic frameworks. In this way, macromolecular catalysts are created that can be separated from the product-containing solution by ultra- or nanofiltration techniques.[1,2] By these methods, several advantages of homogeneous (high selectivity/activity, good catalyst description, and reproducibility) and heterogeneous catalysis (easy catalyst recovery, high turnover numbers, and small amounts of catalyst needed) can be combined. For this purpose, dendrimer-bound homogeneous catalysts have been investigated extensively in recent years.[3]

The prevention of rapid washout of the catalyst and/or loss of activity are absolute prerequisites for any possible industrial application of nanosize homogeneous catalysts in a continuous catalytic process.[4] However, a good understanding of how macromolecular catalysts can

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(1) For an overview on homogeneous catalyst recycling using ultra- or nanofiltration techniques, see: Dijkstra, H. P.; van Klink, G. P. M.; van Koten, G. *Acc. Chem. Res.* **2002**, ASAP (AR0100778).

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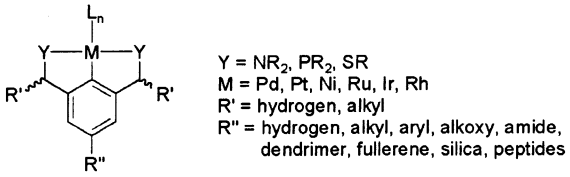

FIGURE 1. Metalated pincer complexes: a versatile catalyst.

be designed to avoid these pitfalls is still lacking. In recent studies, it was shown that the combination of a monoanionic, terdentate coordinating YCY−pincer ligand system (Figure 1) and an appropriate metal resulted in catalytic systems[5] that do not suffer from catalyst deactivation or decomposition.[6] The strong, covalent metal−carbon bond is maintained during catalysis. Furthermore, we demonstrated that the aryl-C4 position (R″) is an excellent branching point for anchoring these pincer complexes to support materials such as dendrimers,[7] fullerenes,[8] polymers,[9] solid supports,[10] and peptides.[11] These features make the pincer moiety suitable for attachment to a soluble nanosize support in order to create a homogeneous catalyst that is stable under continuous operating conditions.

Very efficient retentions (>99%) of the homogeneous macromolecular catalysts by nanofiltration membranes are required in order to prevent a fast washout of the catalysts (R = 99.9% means a washout of 10% after 100 reactor volume exchanges). From previous explorative homogeneous catalysis studies in nanofiltration membrane reactors, predominantly the higher generation metallodendrimers (G2 or higher, M_w > 2000 Da) are applicable in continuous processes.[1] This is rather surprising since the reported cutoff masses of the nanofiltration membranes are normally lower than 1000 Da. This contradiction is due to a number of features: (i) the imperfect structure of the membranes used (vide infra), (ii) the solvent used, since the structure of the membrane alters upon changing solvents, (iii) the flexibility of the dendrimer backbones, and (iv) the nature of the *surface* groups of the macromolecular catalysts.

Since the first two features are determined by the membrane and the reaction conditions, we concentrated mainly on the third issue; the construction of more rigid (i.e., shape-persistent) catalyst structures. So far, mainly metallodendrimers have been used in this research field, because of their well-defined structure, which allows easy comparison with the monometallic analogues in terms of selectivity and activity. However, dendritic materials often possess flexible backbones and are thus able to undergo shape-changes in solution.[12] This behavior can affect their retention rates by nanofiltration membranes. A detailed investigation on the influences of flexibility, size, and geometry of nanosize catalysts on their retention rates by a given type of nanofiltration membrane has never been performed. This important aspect of nanomembrane filtration is investigated in this paper. In the future, this will enable predictions of the minimal size and optimal geometry needed for the macromolecular catalysts. In addition, knowledge about the influence of these features on retention rates is likewise important to design nanosize catalytic materials that can be synthesized in a minimal number of synthetic steps.

Nanosize molecules with shape-persistent cores of types **1**,[13b] **2**, **3**, and **4** and the rodlike bispincer complex **5** (Figure 2) were synthesized in order to investigate the influence of size and geometry on the retention rates of these macromolecules by the MPF-60 and MPF-50 nanofiltration membranes.[14] As reference, we also decided to test the mononuclear NCN−Pt−Br complex **6** in a nanomembrane reactor.[15] All of these molecules do not

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(14) SelRo-nanofiltration membranes (MPF-60, MWCO = 400 Da; MPF-50, MWCO = 700 Da) were purchased from Koch Membrane Systems, Inc., Düsseldorf, Germany; further product information can be found at http://www.kochmembrane.com.

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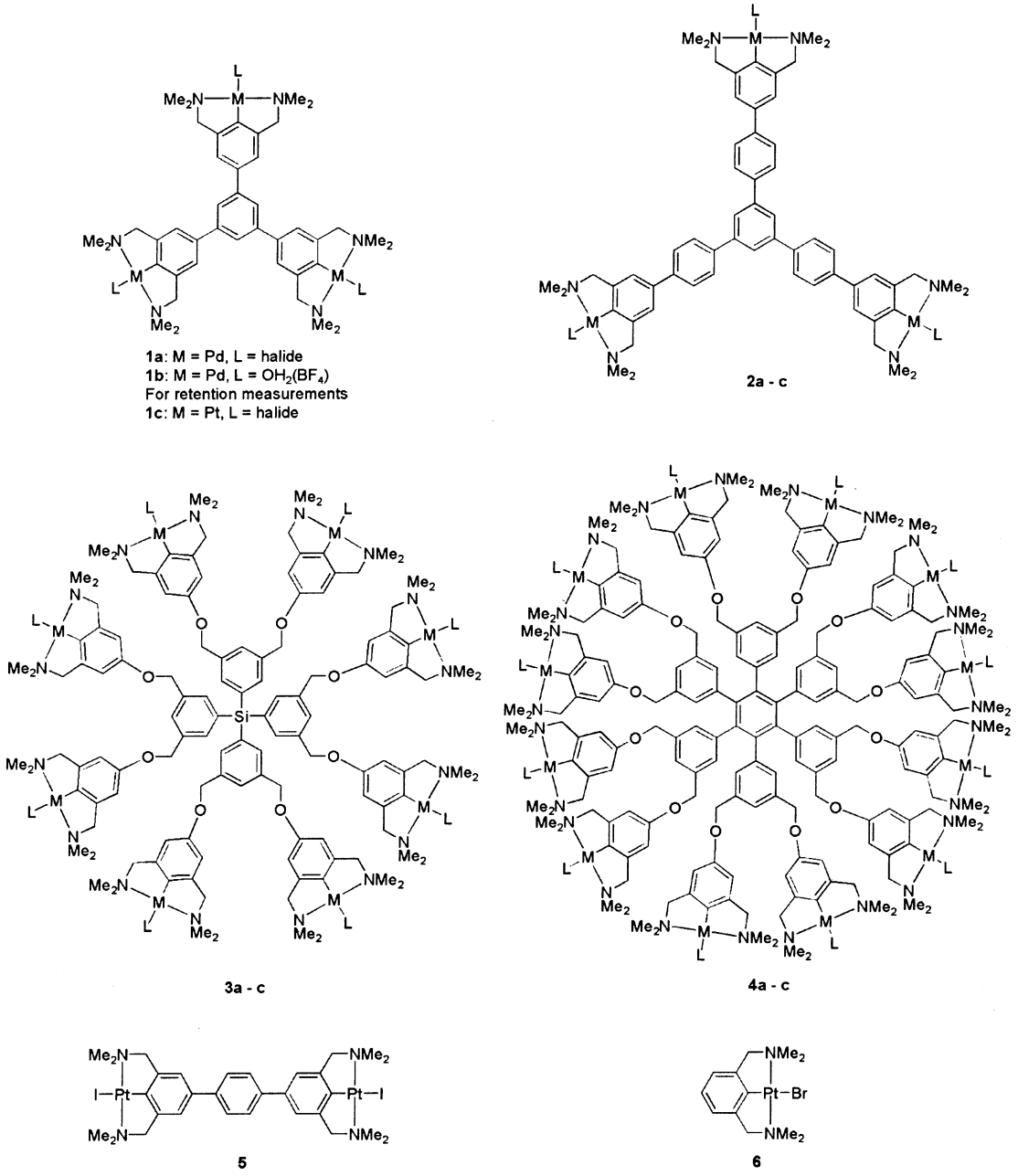


FIGURE 2. Shape-persistent nanosize complexes.

undergo significant shape changes in solution due to their rigid backbones. While in complexes **1**, **2**, and **5** the organometallic sites are part of the shape-persistent cores, **3** and **4** possess a more flexible organometallic shell around a rigid core. Compounds **1**, **2**, **5**, and **6** are rather flat, two-dimensional structures, while **3** possesses a spherically shaped, three-dimensional geometry. Despite the rigid two-dimensional core, **4** exerts a three-dimensional structure due to the more flexible organometallic shell at its periphery, affording this molecule its flattened-spherical geometry. The use of complexes **1**−**6** in a nanofiltration membrane reactor should provide direct information about the influence of size and geometry on the retention rates of these molecules by this type of organic polymeric nanofiltration membranes.

Results and Discussion

To obtain an impression of the size and molecular structure of complexes **1**−**6**, we have performed molecular modeling[16] studies on the platinum complexes **1c**−**4c**, **5**, and **6** (Figure 3). In addition, the X-ray crystal structure of **1a** (L = Br)[13b] was determined and was compared to the structure of **1a** obtained by molecular modeling. The modeled shape and geometry of **1a** are in good agreement with the structure found for **1a**. Furthermore, changing the metal from palladium to platinum (**1a** vs **1c**) and/or changing the metal-bound halide (L) did not influence the molecular geometry and size of

(16) For molecular modeling the Spartan 5.1.1 (SGI) program was used with MMFF94 as the force field.

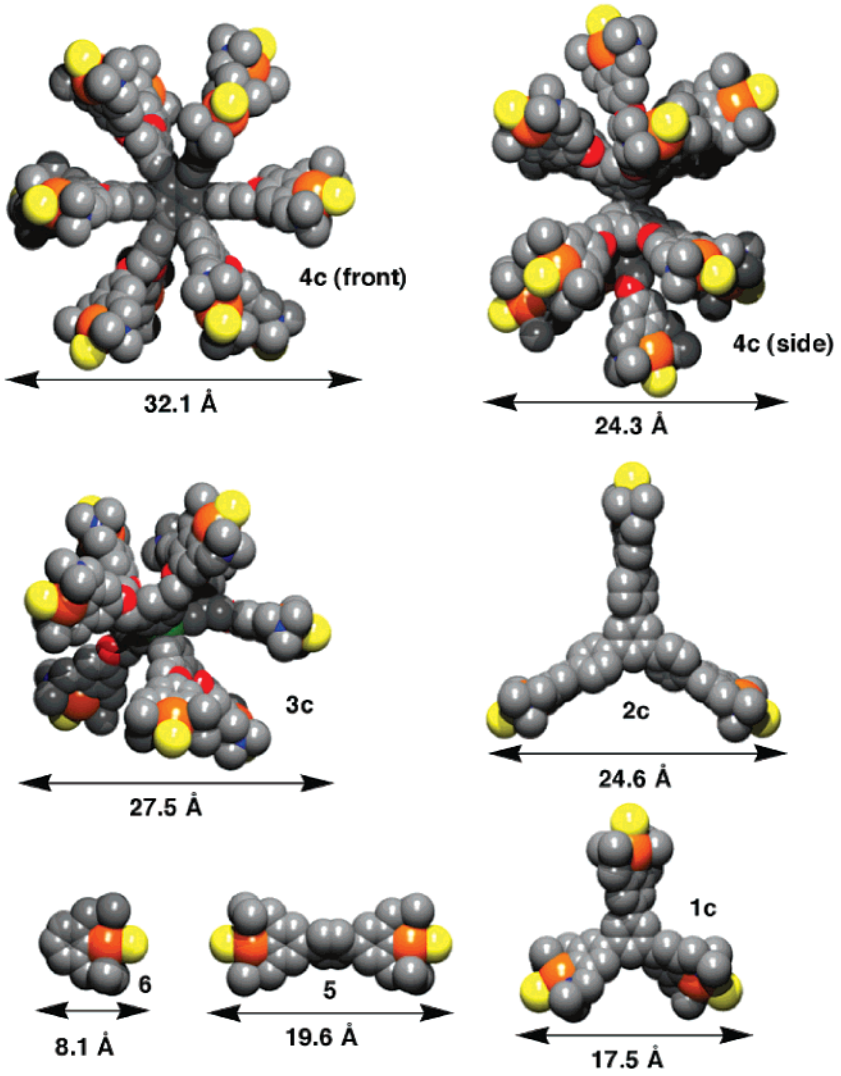


FIGURE 3. Space-filling molecular structures of **1**−**6**.

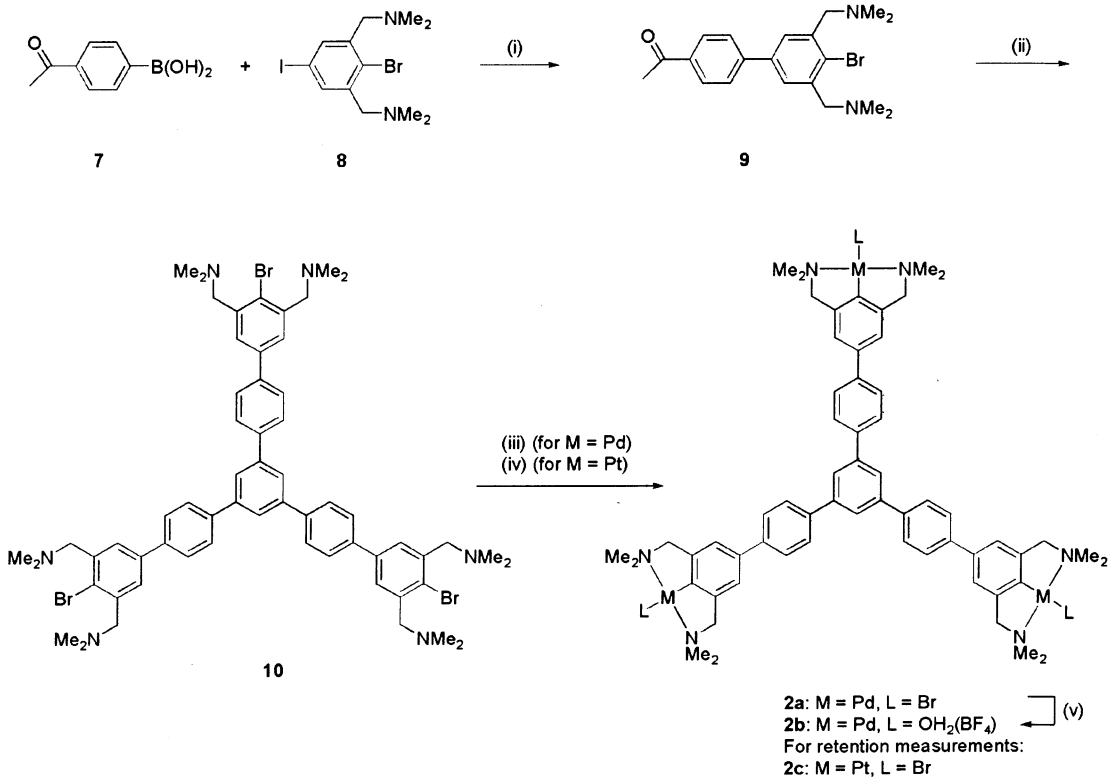
1. This means that molecular modeling gives an accurate representation of the molecular structures of **1**−**6** and allows a direct comparison between the palladium complexes (**1a**−**4a**) and their platinum analogues (**1c**−**4c**). The molecular modeling structure of **1c** (L = Br) shows a disklike molecule with a bromine−bromine distance of 17.5 Å and a disk thickness of ∼6 Å, which emphasizes the two-dimensional form of **1c**. The molecular modeling structure of **2c** (L = Br) also showed a two-dimensional structure with a bromine−bromine distance of 24.6 Å and a thickness of ∼6 Å. The calculated structures of **3c** (L = I) and **4c** (L = Br), on the other hand, display three-dimensional structures, with **3** having a tetrahedral sphere-like structure with a diameter of 27.5 Å, while **4** has a structure that resembles a flattened sphere with a diametrically opposed iodine−iodine distance of 32.1 Å and a thickness of 24.3 Å. Bispincer **5** shows also a rather one-dimensional, rodlike structure with an iodine−iodine distance of 19.6 Å, while monopincer **6** possesses a maximum diameter of 8.1 Å.

Different routes were developed for the synthesis of the shape-persistent pincer−metal complexes **1**−**5**. Recently, we reported the synthesis of fully metalated tris(pincer) cartwheel complexes **1** and its catalytic behavior as a Lewis acid catalyst in a double-Michael reaction.[13b] In the present study, the preparation of metalated NCN−pincer complexes **2**−**5** was carried out as well as retention measurements of **1**−**6** using the MPF-60 and/or MPF-50 nanofiltration membranes in a nanofiltration membrane reactor.

Synthesis of Tris(pincer) Complexes 2. The synthesis of the phenylene extended tris(pincer) complexes **2** is outlined in Scheme 1. The synthesis commences with the palladium-catalyzed Suzuki coupling of boronic acid **7** and iodo-pincer **8**,[10c] affording substituted acetophenone **9** in 53% yield. In this reaction, the carbon−iodine bond is selectively converted without affecting the carbon−bromine bond.[17] In the next step, a triple condensation reaction of **9** using tetrachlorosilane in dry ethanol resulted in the formation of tris(NCN)−benzene **10** in 70% yield.[18] Palladation of this tris(pincer) ligand is achieved via a 3-fold oxidative addition reaction with $Pd(dba)_2$, affording palladated tris(pincer) complex **2a** in 73% yield. The neutral trispalladium(II) complex **2a** was

(17) Rodríguez, G.; Albrecht, M.; Schoenmaker, J.; Ford, A.; Lutz, M.; Spek, A. L.; van Koten, G. *J. Am. Chem. Soc.* **2002**, *124*, 5127.
(18) Modification of a reported method was used: Elmorsy, S. S.; Pelter, A.; Smith, K. *Tetrahedron Lett.* **1991**, *32*, 4175.

SCHEME 1. Synthesis of Enlarged Tris(pincer) Complexes[a]



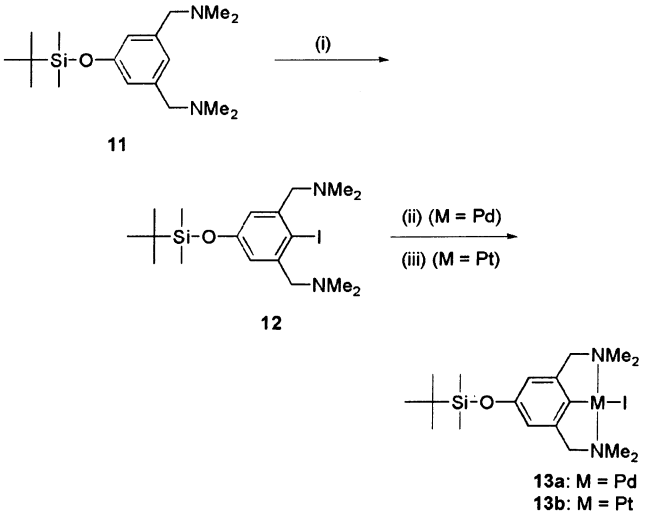
[a] Reagents and conditions: (i) $Pd(PPh_3)_4$, DME, 2 M Na_2CO_3 (aq), reflux, 18 h; (ii) $SiCl_4$, dry EtOH, reflux, 18 h; (iii) $Pd(dba)_2$, C_6H_6, rt, 18 h; (iv) $[Pt(p\text{-tol})_2SEt_2]_2$, C_6H_6, reflux, 3 h; (v) $AgBF_4$, wet acetone, rt, 1 h.

readily converted into the corresponding tri-ionic complex **2b** by treatment with silver tetrafluoroborate in wet acetone. The trisplatinum(II) compound **2c** was obtained in 78% yield by reaction of **10** with $[Pt(p\text{-tol})_2SEt_2]_2$.[19]

Synthesis of Multi(pincer) Complexes 3 and 4. For the synthesis of octakis- and dodecakis(pincer) complexes **3** and **4**, organometallic building blocks **13a** and **13b** were initially prepared (Scheme 2). The synthesis began with the iodination of **11** using a lithiation/iodination reaction sequence, resulting in ligand precursor **12** in 66% yield. Treatment of **12** with $Pd(dba)_2$ resulted in the formation of palladium(II) pincer **13a** (72%), while the corresponding platinum(II) compound **13b** was prepared in 83% yield by reaction of **12** with $[Pt(p\text{-tol})_2SEt_2]_2$.

Synthesis of Octakis(pincer) Complexes 3. The synthesis of octakis(pincer) complexes **3** started with the lithiation of iodoarene **14**. The in situ prepared aryllithium compound was reacted with tetrachlorosilane, thereby obtaining tetraarylsilane **15** in 90% yield (Scheme 3). Subsequently, the methoxy groups of **15** were converted into bromines by treatment with acetyl bromide and trifluoroborane·etherate, resulting in the formation of octabromide **16** in 52% yield. Reaction of this octabromide with 8 equiv of palladium(II) building block **13a** in the presence of tetrabutylammonium fluoride gave the corresponding octakis(pincer−palladium(II)) complex **3a**, which was converted to the corresponding ionic complex **3b** by treatment with silver tetrafluoroborate in wet acetone. The octakis(pincer−platinum(II)) complex **3c** was analogously obtained by reaction of **16** with 8 equiv of platinum(II) building block **13b** in 44% yield.

SCHEME 2. Synthesis of Monometallic Building Blocks[a]

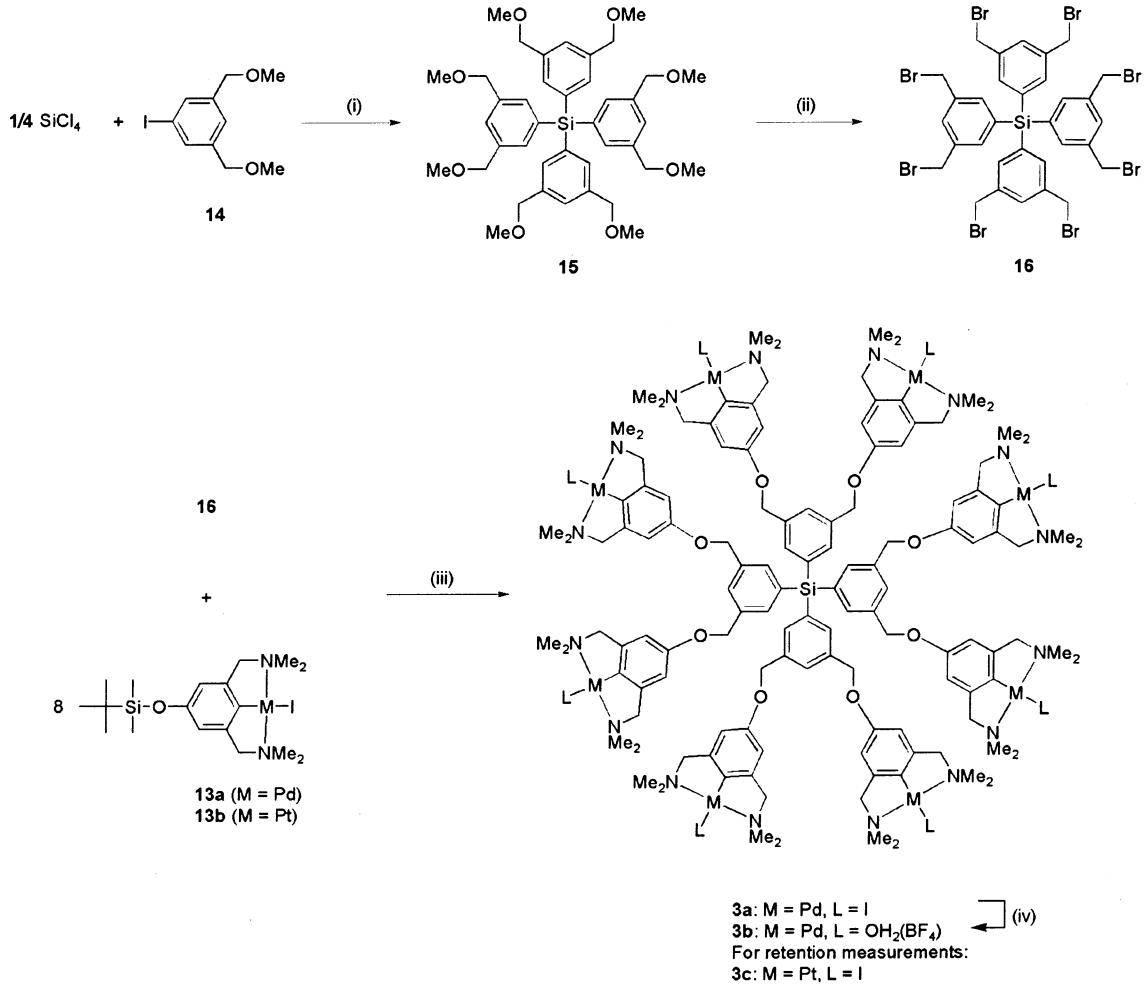


[a] Reagents and conditions: (i) *n*-BuLi, hexanes, −80 °C → rt, 4 h, followed by I_2, THF, rt, 3 h; (ii) $Pd(dba)_2$, C_6H_6, rt, 6 h; (iii) $[Pt(p\text{-tol})_2SEt_2]_2$, C_6H_6, reflux, 3 h.

Synthesis of Dodecakis(pincer) Complexes 4. The synthesis of dodecakis(pincer) complexes **4** is outlined in Scheme 4. Reaction of 12 equiv of organometallic building block **13a** with dodecabenzylic bromide **17**[13b] in the presence of tetrabutylammonium fluoride resulted in the formation of dodecakis(pincer−palladium(II)) complex **4a**.

(19) Procedure reported by: Canty, A. J.; Patel, J.; Skelton, B. W.; White, A. H. *J. Organomet. Chem.* **2000**, *599*, 195.

SCHEME 3. Synthesis of Octakis(pincer−metal) Complexes[a]



[a] Reagents and conditions: (i) 2 equiv of *t*-BuLi, Et_2O, −80 °C, 20 min followed by 0.25 equiv $SiCl_4$, −80 °C → rt, 22 h; (ii) AcBr, $BF_3{\cdot}OEt_2$, CH_2Cl_2, reflux, 20 h; (iii) Bu_4NF, K_2CO_3, 18-crown-6, acetone, rt, 20 h; (iv) $AgBF_4$, wet acetone, rt, 1 h.

The neutral complex **4a** can easily be converted into the corresponding ionic complex **4b** with silver tetrafluoroborate in wet acetone (Scheme 4). The analogous dodecaplatinum(II) complex **4c** was obtained by reaction of 12 equiv of **13b** with dodecabromide **17**.

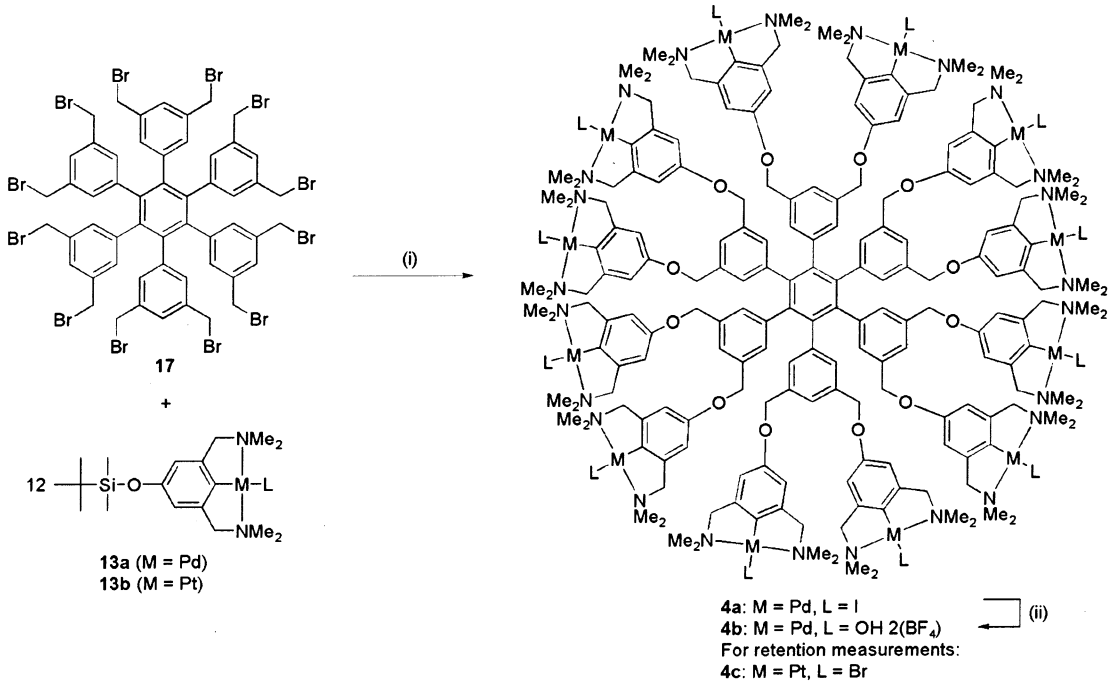
It is noteworthy that in the synthesis of **3** and **4** 8 or 12 metal centers, respectively, are introduced into the multimetallic material in a one-pot reaction under very mild reaction conditions. With the metal already present in the pincer moiety in the final construction step of the multimetallic material, this route results in the quantitative formation of fully metalated materials. The alternative route—preparation of the octakis- or dodecakis(pincer) ligands followed by permetalation—is a method that can lead to incomplete metalations and decomposition because more severe reaction conditions are required.

Synthesis of Bis(pincer) Complex 5. The bis(pincer−platinum(II)) complex **5** was prepared in four steps as depicted in Scheme 5. In the first step, bromopincer ligand **18** was, via a lithiation/boronation step, converted into boronic acid **19**, which was subsequently reacted with 1,4-diiodobenzene under Suzuki-coupling conditions to yield bis(pincer)benzene **20**. Via a double lithiation/iodination step, iodine was introduced resulting in the formation of ligand precursor **21** in 87% yield. Treatment of **21** with 2 equiv of $[Pt(p\text{-tol})_2SEt_2]_2$ gave the corresponding bis(pincer)−platinum(II) complex **5** in 86% yield.

Nanofiltration Studies. Nanofiltration is a relatively new method to address the separation problems of metal-containing homogeneous catalysts from product-containing solutions.[1] Therefore, the question is raised whether the MPF-membranes, the most widely used nanofiltration membranes in this research area, only discriminate on size or also on the flexibility and the molecular shape (geometry) of the molecules. To obtain more insight in this issue, we performed membrane filtration experiments with complexes **1**−**6**.

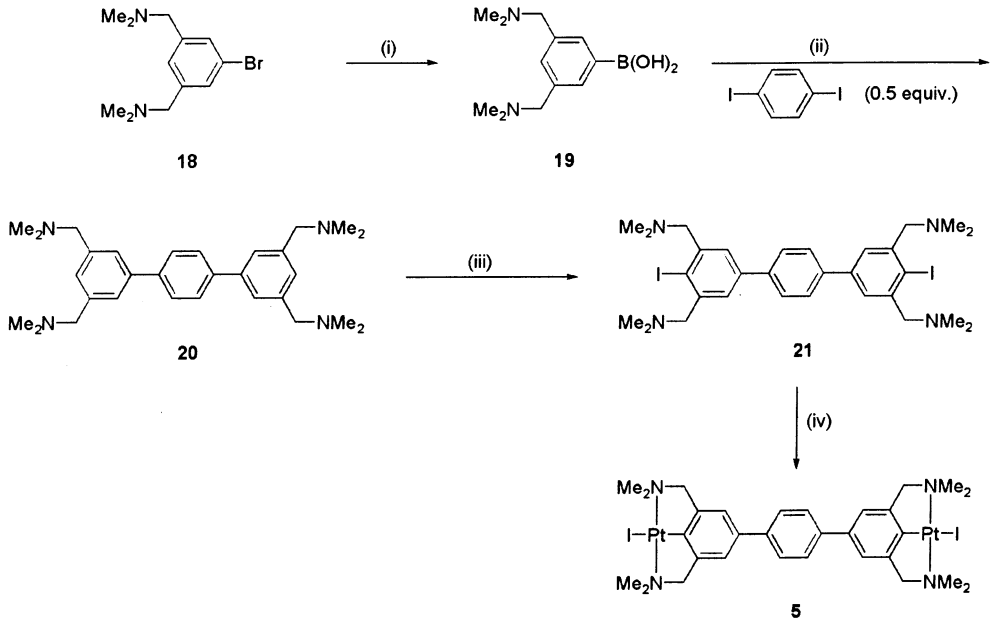
A prerequisite to determine the retention rates of the nanosize materials by nanofiltration membranes is having a sensitive analysis technique, since very small variations in the retention rates can already have large influences in continuous catalytic processes.[1] Therefore, we decided to use the neutral multi(NCN−platinum(II)) complexes **1c**,[13b] **2c**, **3c**, **4c**, **5**, and **6** for the retention rate determinations. Previously, it was found that square-planar neutral $[NCNPt^{II}X]$ complexes reversibly bind sulfur dioxide (Scheme 6), leading to five-coordinate SO_2 adducts that are deep orange in color and thus have

SCHEME 4. Synthesis of Dodecakis(pincer) Complexes[a]



[a] Reagents and conditions: (i) Bu_4NF, K_2CO_3, 18-crown-6, acetone, rt, 20 h (for **4c**, the reaction was performed in the presence of LiBr); (ii) $AgBF_4$, wet acetone, rt, 1 h.

SCHEME 5. Synthesis of Bis(pincer) Complex 5[a]



[a] Reagents and conditions: (i) 2 equiv of *t*-BuLi, Et_2O, −80 °C, 1 h followed by B(O-*i*-Pr)$_3$, −80 °C → rt, 18 h followed by NH_4OH (aq); (ii) $Pd(PPh_3)_4$, Na_2CO_3, DME/H_2O, 90 °C, 48 h; (iii) 2 equiv of *n*-BuLi, C_6H_6, rt, 18 h, followed by I_2, THF, rt, 1 h; (iv) $[Pt(p\text{-tol})_2SEt_2]_2$, C_6H_6, 55 °C, 3 h.

strong absorptions in the UV/vis region (300−450 nm).[20] These absorptions originate from two Pt → S metal-to-ligand charge-transfer bands.[21] Extinction coefficients (ϵ) were found to be between 6000 and 16 000 M^{-1} cm^{-1} (depending on R, Scheme 6),[7f] indicating that even concentrations of approximately 10^{-7}−10^{-6} M can be determined. In addition, since molecular-modeling studies indicated that the dimensions of the multipincer systems are independent of the metal, the retention rates determined for **1c**, **2c**, **3c**, **4c**, **5**, and **6** can be directly

(20) See 7f and: (a) Terheijden, J.; Mul, P. W.; van Koten, G.; Muller, F.; Stam, H. C. *Organometallics* **1986**, *5*, 519. (b) Albrecht, M.; Gossage, R. A.; Spek, A. L.; van Koten, G. *Chem. Commun.* **1998**, 1003. (c) Albrecht, M.; van Koten, G. *Adv. Mater.* **1999**, *11*, 171. (c) Albrecht, M.; Lutz, M.; Spek, A. L.; van Koten, G. *Nature* **2000**, *406*, 970.

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SCHEME 6. [PtX(NCN)] as SO_2 Sensor

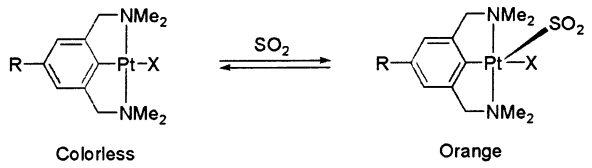

TABLE 1. Extinction Coefficients and Retention Rates of the Various Platinated NCN−Pincer Complexes

compd	extinction coeff (ϵ) ($\times 10^3$ M^{-1} cm^{-1})	R[a] (%) (MPF-60)	R[a] (%) (MPF-50)
1d	9.8	93.9	n.d
2d	11.7	98.7	97.6
3d	8.1	99.5	n.d.
4d	7.7	>99.9	99.9
22	10.8	99.6	n.d.
23	9.2	82.4	n.d.

[a] The following formula was used for determining the retention rates: $R = 1 + (V_t/V_r) \ln(C_f/C_0)$, V_t = total volume flushed through membrane, V_r = reactor volume, C_f = concentration in filtrate, C_0 = initial concentration in reactor. For the nanofiltration experiments, complexes **1c**−**4c**, **22**, and **6** were dissolved in CH_2Cl_2 and injected into the reactor. The corresponding SO_2 adducts **1d**−**4d**, **22**, and **23** were used for analysis with UV/vis spectroscopy.

translated to the catalytically active derivatives (i.e., palladium analogues) of **1**−**6**.

Treatment of **1c**−**4c**, **5**, and **6** in methylene chloride with sulfur dioxide afforded the corresponding SO_2 adducts **1d**−**4d**, **22**, and **23**, respectively (eq 1). The observed maxima of **1d**−**4d**, **22**, and **23** in the UV/vis spectrum are positioned at approximately 359 nm with a broad shoulder at longer wavelengths. The extinction coefficients (ϵ) per platinum center at 359 nm are summarized in Table 1. The sometimes large differences in the extinction coefficients of the various complexes can be ascribed to the variable absorptive abilities of the aromatic systems of these materials in the UV/vis region. Complexes **2c** and **5** in particular are already strongly colored without subjection to sulfur dioxide.

$$\mathbf{1c-4c, 5, 6} \overset{SO_2}{\rightleftharpoons} \mathbf{1d-4d, 22, 23} \qquad (1)$$

The nanofiltration experiments were performed in a continuously operating high-pressure-membrane reactor equipped with the MPF-60 or MPF-50 nanofiltration membrane. The concentrations of **1d**−**4d**, **22**, and **23** in the permeate and in the retentate were determined by UV/vis spectroscopy, and the obtained retention rates of the complexes **1**−**6** are summarized in Table 1. With the MPF-60 membrane, the concentration of **4d** in the permeate was below the detection limit of UV/vis spectroscopy, i.e., a retention rate higher than 99.9%. Surprisingly, the one-dimensional rodlike pincer **5** is retained in 99.6% by the MPF-60 membrane, which is considerably higher than the retention rates obtained for the two-dimensional tris(pincer) systems **1c** and **2c** (93.9 and 98.7%, respectively). For the membrane filtration tests, however, **5** was first converted into **22** in order to obtain a sufficiently soluble bis(pincer) complex for retention rate determination. Since the sulfur dioxide coordination is a reversible process, it is likely that at elongated residence times **22** is completely converted into **5**, which subsequently can precipitate and clog the membrane. As a result, higher retention rates will be observed. A second possibility is the formation of aggregates in solution at higher concentrations, preventing leaching of the unimolecular complexes. With the filtration setup (dead-end-filtration) used, it is known that molecules can accumulate on the membrane surface, possibly inducing aggregate formation. These aspects are currently under investigation. With the mononuclear NCN-pincer **6**, a retention rate of 82.4% was found, which is already rather efficient for such a small molecule. It has to be noted, however, that 82.4% retention means that the catalyst is completely washed out of the reactor within 30 cycles, which is far from being sufficient for continuous catalysis.

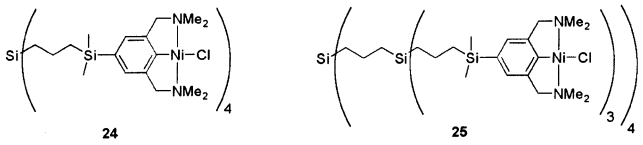

FIGURE 4. Nickelated G0- and G1-carbosilane dendrimers.

Complexes **2c** and **4c** were also tested in combination with the MPF-50 membrane; the observed retention rates were only slightly lower than with the MPF-60 membranes (Table 1). Thus, although the MWCO (defined as the molecular weight at which 90% of the solutes are retained by the membrane) of the MPF-50 membrane is considerably higher as compared to the MPF-60 membrane (700 vs 400 Da), no significant influence on the retention rates of these macromolecular materials was found.

To further investigate the concept of shape persistence in the core of the macromolecular catalysts for attaining optimal retentions, we related the retention rates of **2c** and **4c** to the calculated molecular volumes of these complexes. The same procedure was performed with recently prepared flexible G0-Ni_4, **24**, and G1-Ni_{12}, **25**, carbosilane dendrimers (Figure 4).[2h] For **2c** and **4c**, molecular modeling gave molecular volumes of 1.2×10^3 and 4.4×10^3 Å^3, respectively, while the G0-Ni_4 and the G1-Ni_{12} dendrimers **24** and **25** possess volumes of 1.7×10^3 and 5.3×10^3 Å^3, respectively. Earlier studies with the MPF-50 membrane revealed a retention rate of 97.4% for **24** and 99.8% for **25**.[2h] Thus, although **2c** (R = 97.7%) and **4c** (R = 99.9%) possess smaller molecular volumes as compared to G0- **24** and G1-dendrimer **25**, respectively, the shape-persistent materials **2c** and **4c** are retained more efficiently by the nanofiltration membranes than the more flexible dendritic systems. Although these differences in retention seem rather small, under continuously operating reaction conditions, such small differences (between 0.1 and 0.5%) can already have a significant impact.[1]

It can be concluded that for future development and application in the area of homogeneous catalyst recycling by means of nanofiltration membranes, it is advisable to use macromolecular catalysts with a high degree of shape-persistence in the backbone. Currently, we are exploring the use of such materials as homogeneous catalysts. We are also developing a continuous process in a nanofiltration membrane reactor for a catalyst of type **4**, since this system is completely retained by the MPF-60 and MPF-50 nanofiltration membranes.

Experimental Section

General Methods. All reactions were carried out using standard Schlenk techniques under an inert nitrogen atmosphere unless stated otherwise. Et_2O, THF, and hexanes were carefully dried and distilled from Na/benzophenone prior to use. CH_2Cl_2 was distilled from CaH_2. All standard reagents were used as purchased. Compounds **8**,[10c] **11**,[22] **14**,[23] **17**,[13b,23] **18**,[24] $Pd(dba)_2$,[25] and $[Pt(p\text{-tol})_2SEt_2]_2$[19] were prepared according to literature procedures. The nanofiltration experiments were carried out in a stainless steel membrane reactor under elevated pressures. For MALDI-TOF measurements, the matrix (3,5-dihydroxybenzoic acid) and the sample were dissolved in THF or CH_2Cl_2 (~30 mg/mL), and 0.2 μL of both solutions were mixed and placed on a gold MALDI target and analyzed after evaporation of the solvent. Elemental microanalyses were performed by Dornis und Kolbe, Mikroanalytisches Laboratorium, Müllheim a.d. Ruhr, Germany.

Synthesis of 9-Acetyl-3,5-bis(dimethylaminomethyl)-4-bromobiphenyl (9). A degassed solution of 4-acetophenoneboronic acid **7** (1.90 g, 11.6 mmol), 4-bromo-3,5-bis(dimethylaminomethyl)iodobenzene **8** (2.42 g, 6.1 mmol), and $Pd(PPh_3)_4$ (176.1 mg, 0.15 mmol) in dimethoxyethane (DME) (50 mL) was mixed with a degassed solution of Na_2CO_3 (aq) (2 M, 15 mL). The resulting mixture was heated to reflux for 15 h. After the mixture was cooled to room temperature, all volatiles were evaporated in vacuo and CH_2Cl_2 (100 mL) and H_2O (100 mL) were added. The organic layer was collected, and the aqueous layer was extracted with CH_2Cl_2. The organic layers were combined and concentrated to 100 mL, and the product was extracted with 1 M HCl (aq). The acidic aqueous layers were combined and treated with 6 M K_2CO_3 (aq) until pH 10−11 was reached. The product was extracted with CH_2Cl_2, and the organic fractions were combined, dried over $MgSO_4$, filtered, and concentrated in vacuo, leaving a yellow oil that solidified upon standing at room temperature. The product was washed with cold hexanes (−20 °C) and dried in vacuo. Yield: 1.2 g (53%). ^{1}H NMR (acetone-d_6, 300 MHz): δ 8.12 (d, $^3J_{H-H}$ = 4.2 Hz, 2H, Ar-H), 7.82 (d, $^3J_{H-H}$ = 4.2 Hz, 2H, Ar-H), 7.78 (s, 2H, Ar-H), 3.62 (s, 4H, CH_2), 2.63 (s, 3H, $CH_3C(O)$), 2.32 (s, 12H, CH_3). ^{13}C NMR (acetone-d_6, 75 MHz): δ 196.8, 144.6, 139.9, 138.5, 136.6, 129.2, 127.9, 127.2, 126.6, 63.2, 45.2, 26.1. Anal. Calcd. for $C_{20}H_{26}BrN_2O$: C, 61.70; H, 6.47; N, 7.20. Found: C, 61.58; H, 6.42; N, 7.12.

Synthesis of 1,3,5-Tris(4-(4-bromo-3,5-bis(dimethylaminomethyl)phenyl)phenylene)benzene (10). $SiCl_4$ (5 mL, 43.6 mmol) was added dropwise to a solution of **9** (0.9 g, 2.3 mmol) in dry ethanol (20 mL) at 0 °C. A white precipitate was formed immediately and the solution turned from orange to dark red. The reaction mixture was kept at reflux temperatures for 16 h, whereby the color of the solution changed from dark red to yellow. After the mixture was cooled to room temperature, 1 M HCl (aq) (50 mL) was added, and stirring was continued for 15 min. The acidic suspension was washed with ether and treated with 4 M NaOH (aq) until pH 13−14 was reached. The product was extracted with CH_2Cl_2, dried over $MgSO_4$, filtered, and concentrated in vacuo, affording a orange/yellow solid. The solid was washed with cold hexane (−20 °C) and dried in vacuo. Yield: 0.6 g (70%). ^{1}H NMR (acetone-d_6, 200 MHz): δ 8.06 (s, 3H, Ar-H), 8.01 (d, $^3J_{H-H}$ = 4.2 Hz, 6H, Ar-H), 7.85 (d, $^3J_{H-H}$ = 4.2 Hz, 6H, Ar-H), 7.81 (s, 6H, Ar-H), 3.63 (s, 12H, CH_2), 2.34 (s, 36H, CH_3). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 142.3, 140.5, 139.7, 139.3, 128.2, 128.0, 127.9, 126.5, 125.3, 64.3, 45.9. Anal. Calcd for $C_{60}H_{69}Br_3N_6$: C, 64.69; H, 6.25; N, 7.54. Found: C, 64.78; H, 6.25; N, 7.46.

Synthesis of 1,3,5-Tris(4-(4-(bromopalladium)-3,5-bis(dimethylaminomethyl)phenyl)phenylene)benzene (2a). A solution of **10** (0.25 g, 0.23 mmol) and $Pd(dba)_2$ (0.43 g, 0.74 mmol) in dry benzene (30 mL) was stirred overnight at room temperature. The solvent was removed in vacuo, THF (30 mL) was added, and stirring was continued for 20 h, affording a black precipitate. The solvent was evaporated, and the residue was dissolved in CH_2Cl_2 and filtered through Celite. The filtrate was concentrated, and the remaining solid was washed with Et_2O. The crude product was dissolved in CH_2Cl_2 (2 mL), and slow addition of Et_2O (4 mL) resulted in the precipitation of a yellow solid. This last two-step sequence was repeated once. The solid was collected and dried in vacuo. Yield: 0.24 g (73%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.87 (s, 3H, Ar−H), 7.77 (d, $^3J_{H-H}$ = 4.2 Hz, 6H, Ar-H), 7.63 (d, $^3J_{H-H}$ = 4.2 Hz, 6H, Ar-H), 7.09 (s, 6H, Ar-H), 4.10 (s, 12H, CH_2), 3.03 (s, 36H, CH_3). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 157.41, 145.9, 142.2, 141.1, 139.9, 137.9, 127.9, 127.6, 125.1, 118.9, 74.9, 54.1. Anal. Calcd for $C_{60}H_{69}Br_3N_6Pd_3$: C, 50.28; H, 4.86; N, 5.86. Found: C, 50.18; H, 4.74; N, 5.78.

Synthesis of 1,3,5-Tris(4-(4-(aquapalladium)-3,5-bis(dimethylaminomethyl)phenyl)phenylene)benzene Tris(tetrafluoroborate) (2b). $AgBF_4$ (45.0 mg, 77.0 μmol) was added to a suspension of **2a** (0.11 g, 77.2 μmol) in wet acetone (5 mL) and stirred for 30 min. The suspension was filtered through Celite, and the solvents were evaporated in vacuo. The solid residue was extracted with acetone (5 mL), and the acetone layer was filtered again through Celite. The filtrate was concentrated to 2 mL, and slow addition of Et_2O resulted in the precipitation of an off-white solid. The solid was collected and dried in vacuo. Yield: 88.5 mg (76%). ^{1}H NMR (acetone-d_6, 200 MHz): δ 8.01 (s, 3H, Ar-H), 7.97 (d, $^3J_{H-H}$ = 4.4 Hz, 6H, Ar-H), 7.76 (d, $^3J_{H-H}$ = 4.4 Hz, 6H, Ar-H), 7.30 (s, 6H, Ar-H), 4.29 (s, 12H, CH_2), 2.91 (s, 36H, CH_3). ^{13}C NMR (acetone-d_6, 75 MHz): δ 146.3, 142.1, 139.7, 138.2, 127.9, 127.4, 124.6, 119.0, 73.6, 51.8.

Synthesis of 1,3,5-Tris(4-(3,5-bis(dimethylaminomethyl)-4-(bromoplatinum)phenyl)phenylene)benzene (2c). Ligand **10** (0.15 g, 0.12 mmol) and $[Pt(p\text{-tol})_2SEt_2]_2$ (0.18 g, 0.19 mmol) were dissolved in dry benzene (20 mL) and heated at reflux for 3 h. The reaction mixture was cooled to room temperature, and all volatiles were evaporated in vacuo. The residue was washed with Et_2O, and the remaining solid was dissolved in CH_2Cl_2 (10 mL). The mixture was filtered through Celite, and the filtrate was concentrated to 2 mL. Slow addition of Et_2O (3 mL) resulted in the precipitation of a yellow solid. The solid was collected and dried in vacuo. Yield: 0.16 g (78%). ^{1}H NMR (CD_2Cl_2, 200 MHz): δ 7.93 (s, Ar-H), 7.82 and 7.48 (d, AB, $^3J_{H,H}$ = 4.2 Hz, 6H, Ar-H), 7.17, (s, 6H, Ar-H), 4.13 (s, $^3J_{Pt,H}$ = 20.6 Hz, 12H, CH_2N), 3.31 (s, $^3J_{Pt,H}$ = 17.2 Hz, 36H, CH_3N). ^{13}C NMR (CD_2Cl_2, 75 MHz): δ 149.6, 144.6, 142.2, 141.8, 139.4, 136.3, 127.9, 127.2, 124.7, 118.4, 77.1, 56.4. Anal. Calcd for $C_{60}H_{69}Br_3N_6Pt_3$: C, 42.41; H, 4.09; N, 4.95. Found: C, 41.99; H, 4.23; N, 4.62.

Synthesis of 4-*tert*-Butyldimethylsiloxyl-2,6-bis(dimethylaminomethyl)-1-iodobenzene (12). *n*-BuLi (11.3 mL, 18.0 mmol) was added to a solution of **11** (5.0 g, 15.5 mmol) in hexanes (50 mL) at −70 °C. After complete addition, the temperature was allowed to rise to room temperature, and stirring was continued for 4 h. Subsequently, iodine (5.1 g, 20.0 mmol) in THF (15 mL) was added, and stirring was continued at room temperature for 3 h. The reaction mixture was poured into 2 M $NaHSO_3$ (aq) (100 mL), and the organic layer was collected. The aqueous layer was extracted with Et_2O, and the combined organic layer was washed with brine, dried over $MgSO_4$, and filtered. After evaporation of all volatiles a brown oil remained, which was flame-distilled to yield a yellow oil. Yield: 4.6 g (66%). This product was used without further purification. ^{1}H NMR ($CDCl_3$, 200 MHz): δ 6.86 (s, 2H, Ar−H), 3.47 (s, 4H, CH_2), 2.30 (s, 12H, CH_3N), 0.97 (s, 9H, CH_3C), 0.19 (s, 6H, CH_3Si).

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Synthesis of 4-*tert*-Butyldimethylsiloxyl-2,6-bis(dimethylaminomethyl)-1-(iodopalladium)benzene (13a). A solution of **12** (2.35 g, 5.23 mmol) and $Pd(dba)_2$ (2.85 g, 5.23 mmol) in benzene (30 mL) was stirred at room temperature for 6 h. Subsequently, this mixture was filtered over Celite, and all volatiles were evaporated. The product was extracted with CH_2Cl_2 (10 mL) and pentane was added dropwise to this solution, resulting in the formation of a yellowish solid. The procedure was repeated until a white solid was obtained. This solid was collected and dried in vacuo. Yield: 2.1 g (72%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 6.39 (s, 2H, Ar-H), 3.94 (s, 4H, CH_2N), 3.01 (s, 12H, CH_3N), 0.96 (s, 9H, CH_3C), 0.16 (s, 6H, CH_3Si). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 153.68, 150.57, 145.98, 112.01, 74.21, 55.20, 25.86, 18.30, −4.20. Anal. Calcd for $C_{18}H_{33}IN_2PdOSi$: C, 38.96; H, 6.00; N, 5.05. Found: C, 38.88; H, 5.93; N, 4.95.

Synthesis of 4-*tert*-Butyldimethylsiloxyl-2,6-bis(dimethylaminomethyl)-1-(iodoplatinum)benzene (13b). A mixture of **12** (1.03 g, 2.30 mmol) and $[Pt(p\text{-tol})_2SEt_2]_2$ (1.07 g, 1.15 mmol) in benzene (20 mL) was heated at reflux for 3 h. After the solution was cooled to room temperature, all volatiles were evaporated. The light-yellow solid was washed with Et_2O, and the remaining white solid was dissolved in CH_2Cl_2 (5 mL). Upon dropwise addition of hexanes (20 mL), the product precipitated as a white solid. This solid was collected and dried in vacuo. Yield: 0.1.2 g (83%). ^{1}H NMR (C_6D_6, 300 MHz): δ 6.34 (s, 2H, Ar-H), 3.19 (s, $^3J_{Pt,H}$ = 21.9 Hz, CH_2N), 2.75 (s, $^3J_{Pt,H}$ = 19.2 Hz, CH_3N), 1.06 (s, 9H, CH_3C), 0.19 (s, 6H, CH_3Si). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 152.67, 144.62, 142.94, 111.46, 76.59, 55.93, 25.79, 18.27, −4.36. Anal. Calcd for $C_{18}H_{33}IN_2PtOSi$: C, 33.59; H, 5.17; N, 4.35. Found: C, 33.68; H, 5.08; N, 4.26.

Synthesis of Tetrakis(3,5-bis(methoxymethyl)phenyl)-silane (15). To a solution of **14** (4.91 g, 16.8 mmol) in Et_2O (60 mL) was added *t*-BuLi (20 mL, 30 mmol) at −90 °C. After the white suspension was stirred for ca. 20 min, $SiCl_4$ (0.4 mL, 3.49 mmol) was added, and the resultant red-brown suspension was allowed to reach room temperature and was stirred for an additional 22 h. An extra amount of *t*-BuLi (5 mL, 7.50 mmol)) was added, followed by H_2O (100 mL) to hydrolyze the excess of *t*-BuLi. The organic layer was separated, and the aqueous layer was extracted with Et_2O. The combined organic layers were dried over Na_2SO_4, filtered, and concentrated in vacuo. The free 3,5-di(methoxymethyl)benzene was removed by bulb-to-bulb distillation (140−160 °C, 0.1−0.2 mmHg) to yield a yellow, viscous oil. Yield: 8.7 g (90%). ^{1}H NMR (C_6D_6, 200 MHz): δ 7.87 (s, 8H, Ar-H), 7.55 (s, 4H, Ar-H), 4.18 (s, 12H, CH_2O), 3.07 (s, 48H, OCH_3). ^{13}C NMR (C_6D_6, 75 MHz): δ 139.0, 135.1, 134.7, 128.9 (Ar), 74.5 (CH_2O), 57.8 (OMe). ^{29}Si NMR (C_6D_6, 59 MHz): δ −13.2 (SiAr).

Synthesis of Tetrakis(3,5-bis(bromomethyl)phenyl)-silane (16). To a solution of **15** (2.16 g, 3.14 mmol) in CH_2Cl_2 (500 mL) was added dropwise a solution of $BF_3{\cdot}Et_2O$ (13 mL, 0.10 mol) and acetyl bromide (8 mL, 0.10 mol) in CH_2Cl_2 (60 mL) at 0 °C. The slightly brown solution was heated to reflux for 20 h, whereupon the reaction mixture was allowed to cool to rt. Aqueous Na_2CO_3 (5%, 450 mL) was added slowly to hydrolyze the excess of $BF_3{\cdot}Et_2O$. Next, the organic layer was separated, washed with water, dried over Na_2SO_4, filtered, and concentrated in vacuo. The product was purified by crystallization from a CH_2Cl_2/pentane mixture (v/v 5:1) at − 25 °C, to yield a white powder (52%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.56 (s, 4H, Ar-H), 7.45 (s, 8H, Ar-H), 4.46 (s, 16H, CH_2Br). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 138.75, 136.86, 134.10, 131.92, 32.88. Anal. Calcd for $C_{32}H_{28}Br_8Si$: C, 35.59; H, 2.61; Si, 2.61. Found: C, 35.74; H, 2.65; Si, 2.64.

Synthesis of 3a. Bu_4NF (1 M in THF, 1.05 mL, 1.05 mmol) was added to a mixture of **16** (0.14 g, 0.13 mmol), **13a** (0.58 g, 1.05 mmol), K_2CO_3 (0.73 g, 5.25 mmol), and 18-crown-6 (20 mg, 76 μmol) in acetone (15 mL), and this mixture was stirred at room temperature for 20 h. Subsequently, all volatiles were evaporated, and the product was extracted with CH_2Cl_2 (10 mL). Upon dropwise addition of Et_2O (20 mL), an off-white solid precipitated, which was collected. This procedure was repeated twice, and the product was dried in vacuo. Yield: 0.34 g (67%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.65 (s, 4H, Ar-H), 7.50 (s, 8H, Ar-H), 6.44 (s, 16H, Ar−H), 4.92 (s, 16H, CH_2O), 3.92 (s, 32H, CH_2N), 2.95 (s, 96H, CH_3N). ^{13}C NMR (CD_2Cl_2, 75 MHz): δ 156.65, 144.66, 144.38, 137.69, 135.01, 134.22, 128.56, 107.07, 77.44, 70.83, 55.38. Anal. Calcd for $C_{128}H_{172}I_8N_{16}Pd_8O_8Si$: C, 38.85; H, 4.38; N, 5.66. Found: C, 39.03; H, 4.46; N, 5.64.

Synthesis of 3b. A solution of $AgBF_4$ (19.2 mg, 98.8 μmol) in water (0.5 mL) was added to a suspension of **3a** (48.9 mg, 12.4 μmol) in acetone (10 mL), and the resulting mixture was stirred at room temperature in the absence of light for 1 h. The reaction mixture was filtered through Celite, and the Celite was washed with acetone. The filtrate was concentrated to 3 mL, and dropwise addition of Et_2O (10 mL) resulted in an off-white precipitate, which was collected and dried in vacuo. Yield: 39.4 mg (84%). ^{1}H NMR (acetone-d_6, 200 MHz): δ 7.73 (m, 12H, Ar-H), 6.58 (s, 16H, Ar-H), 5.07 (s, 16H, CH_2O), 4.00 (s, 24H, CH_2N), 2.76 (s, 96H, CH_3N). ^{13}C NMR (acetone-d_6, 75 MHz): δ 158.10, 146.24, 141.23, 137.96, 134.73, 134.24, 128.38, 107.96, 73.49, 70.14, 51.88.

Synthesis of 3c. Bu_4NF (1 M in THF, 0.75 mL, 0.75 mmol) was added to a mixture of **16** (0.10 g, 93 μmol), **13b** (0.48 g, 0.75 mmol), K_2CO_3 (0.52 g, 3.76 mmol), and 18-crown-6 (20 mg, 76 μmol) in acetone (15 mL), and this mixture was stirred at room temperature for 20 h. Subsequently, all volatiles were evaporated, and the product was extracted with CH_2Cl_2 (10 mL). Upon dropwise addition of Et_2O (20 mL), a white solid precipitated, which was collected. This procedure was repeated twice, and the product was dried in vacuo. Yield: 0.19 g (44%). ^{1}H NMR (CD_2Cl_2, 300 MHz): δ 7.66 (s, 4H, Ar-H), 7.61 (s, 8H, Ar-H), 6.49 (s, 16H, Ar-H), 4.98 (s, 16H, CH_2O), 3.94 (s, $^3J_{Pt,H}$ = not resolved, 32H, CH_2N), 3.05 (s, $^3J_{Pt,H}$ = not resolved, 96H, CH_3N). ^{13}C NMR (CD_2Cl_2, 75 MHz): δ 156.65, 144.69, 144.40, 137.88, 134.92, 134.25, 128.45, 106.98, 77.93, 70.72, 55.13. MALDI-TOF-MS: m/z 4542.75 ($[M - I]^+$, calcd 4540.00). Anal. Calcd for $C_{128}H_{172}I_8N_{16}Pt_8O_8Si$: C, 32.94; H, 3.72; N, 4.80. Found: C, 33.16; H, 3.81; N, 4.69.

Synthesis of 4a. Bu_4NF (1 M in THF, 0.97 mL, 0.97 mmol) was added to a mixture of **17** (0.12 g, 79 μmol), **13a** (0.53 g, 0.95 mmol), K_2CO_3 (0.66 g, 4.80 mmol), and 18-crown-6 (25 mg, 95 μmol) in acetone (20 mL), and the resulting mixture was stirred at room temperature for 20 h. Subsequently, all volatiles were evaporated, and the product was extracted with CH_2Cl_2 (10 mL). Upon dropwise addition of acetone (20 mL) a white solid precipitated, which was collected. This procedure was repeated twice, and the product was dried in vacuo. Yield: 0.25 g (53%). ^{1}H NMR (CD_2Cl_2, 300 MHz): δ 6.96 (br s, 18H, Ar-H), 6.26 (br s, 24H, Ar-H), 4.69 (br s, 24H, CH_2O), 3.83 (br s, 48H, CH_2N), 2.96 (br s, 144H, CH_3N). ^{13}C NMR (CD_2Cl_2, 75 MHz): δ 157.30, 150.78, 148.99, 146.48, 140.24, 136.79, 129.36, 122.15, 106.89, 74.22, 70.20, 55.16. Anal. Calcd for $C_{198}H_{258}I_{12}N_{24}Pd_{12}O_{12}$: C, 39.86; H, 4.36; N, 5.63. Found: C, 40.08; H, 4.28; N, 5.73.

Synthesis of 4b. A solution of $AgBF_4$ (75 mg, 0.38 mmol) in water (1 mL) was added to a suspension of **4a** (0.19 g, 32.0 μmol) in acetone (10 mL), and the resulting mixture was stirred at room temperature in the absence of light for 1 h. The reaction mixture was filtered through Celite, and the Celite was washed with acetone. The filtrate was concentrated to 3 mL, and dropwise addition of Et_2O (10 mL) resulted in an off-white precipitate, which was collected and dried in vacuo. Yield: 0.17 g (91%). ^{1}H NMR (acetone-d_6, 200 MHz): δ 7.07 (s, 12H, Ar-H), 7.05 (s, 6H, Ar-H), 6.45 (s, 24H, Ar-H), 4.75 (s, 24H, CH_2O), 4.00 (s, 48H, CH_2N), 2.80 (s, 144H, CH_3N). ^{13}C NMR (acetone-d_6, 75 MHz): δ 158.30, 146.17, 140.96, 140.36, 136.67, 129.66, 122.54, 107.88, 73.51, 69.90, 52.04.

Synthesis of 4c. Bu_4NF (1 M in THF, 0.97 mL, 0.97 mmol) was added to a mixture of **17** (0.12 g, 79 μmol), **13a** (0.61 g, 0.95 mmol), LiBr (0.83 g, 9.6 mmol), K_2CO_3 (0.66 g, 4.80 mmol).

and 18-crown-6 (25 mg, 95 μmol) in acetone (20 mL), and the resulting mixture was stirred at room temperature for 20 h. Subsequently, all volatiles were evaporated. and the product was extracted with CH_2Cl_2 (10 mL) and filtered. Upon dropwise addition of ethyl acetate (20 mL), a white solid precipitated, which was collected. This procedure was repeated twice. and the product was dried in vacuo. Yield: 0.34 g (67%). ^{1}H NMR (CD_2Cl_2, 300 MHz): δ 7.00 (br s, 18H, Ar-H), 6.29 (br s, 24H, Ar-H), 4.69 (br s, 24H, CH_2O), 3.84 (br s, $^3J_{Pt,H}$ = not resolved, 48H, CH_2N), 3.03 (br s, $^3J_{Pt,H}$ = not resolved, 144H, CH_3N). ^{13}C NMR (CD_2Cl_2, 75 MHz): most relevant peaks δ 143.60, 136.57, 107.92, 76.10, 70.60, 54.64. MALDI-TOF-MS: *m*/*z* 6381.64 ([M − Br]$^+$, calcd 6386.48). Anal. Calcd for $C_{198}H_{258}Br_{12}N_{24}Pt_{12}O_{12}$: C, 36.78; H, 4.02; N, 5.20. Found: C, 36.94; H, 4.20; N, 5.11.

Synthesis of 3,5-Bis(dimethylaminomethyl)phenylboronic Acid (19). To a solution of 3,5-bis(dimethylaminomethyl)-1-bromobenzene **18**[24] (2.71 g, 10 mmol) in dry Et_2O (50 mL) at −78 °C was added *t*-BuLi (13.0 mL, 19.5 mmol). After the mixture was stirred for 1 h at that temperature, B(O-*i*-Pr)$_3$ (4.48 g, 20 mmol) was added. After complete addition, the temperature was allowed to rise to room temperature, and stirring was continued overnight. A solution of saturated NH_4OH (aq) (40 mL) was added to the reaction mixture, and the organic layer was separated. The aqueous layer was evaporated under reduced pressure to give boronic acid **19** as a white solid. The inorganic salts were removed by column chromatography using silica gel and ethanol/saturated NH_4OH (aq) (1:1) as the eluent. Yield: 2.10 g (89%). ^{1}H NMR (D_2O, 200 MHz): δ 7.40 (s, 2H, ArH), 7.07 (s, 1H, ArH), 3.52 (s, 4H, CH_2), 2.22 (s, 12H, NCH_3). ^{13}C NMR (CD_3OD, 75 MHz): δ 136.15, 135.95, 132.25, 64.8, 45.05.

Synthesis of 1,4-Bis(3,5-(dimethylaminomethyl)phenyl)benzene (20). To a solution of boronic acid derivative **19** (2.48 g, 10.5 mmol) in a degassed mixture of dimethoxyethane (150 mL) and water (80 mL) at −25 °C was added 1,4-diiodobenzene (1.65 g, 5 mmol). After 10 min, Pd(PPh$_3$)$_4$ (0.27 g, 0.5 mmol) and Na_2CO_3 (6.36 g, 60 mmol) were subsequently added. The resulting mixture was stirred at 90 °C for 48 h. Then, the mixture was cooled to 25 °C, and HCl (4 M) was added until pH <2. The aqueous layer was washed with CH_2Cl_2 and subsequently treated with powdered K_2CO_3 until pH >12. The basic aqueous layer was extracted with CH_2Cl_2, and the organic layer was dried over $MgSO_4$ and concentrated to give pure **20** as a yellow solid. Yield: 4.50 g (98%). Mp: 112−114 °C. ^{1}H NMR ($CDCl_3$, 200 MHz): δ 7.68 (s, 4H, ArH), 7.49 (s, 4H, ArH), 7.24 (s, 2H, ArH), 3.49 (s, 8H, CH_2), 2.26 (s, 24H, NCH_3). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 140.6, 139.8, 139.2, 128.8, 127.35, 126.4, 64.25, 45.35. Anal. Calcd for $C_{30}H_{42}N_4 \cdot {}^1/_4CH_2Cl_2$: C, 75.71; H, 8.93; N, 11.67. Found: C, 75.91; H, 8.46; N, 11.26.

Synthesis of 1,4-Bis(3,5-(dimethylaminomethyl)-4-iodophenyl)benzene (21). To a solution of corresponding terphenyl derivative **20** (0.46 g, 1.0 mmol) in dry benzene (10 mL) at 25 °C was added a solution of *n*-BuLi (1.63 mL, 2.6 mmol). After the mixture was stirred overnight, iodine (0.66 g, 2.6 mmol) in THF (20 mL) was added to the deep pink suspension. After being stirred for 1 h, the reaction mixture was quenched with saturated $Na_2S_2O_3$ (aq) (50 mL), and the resulting mixture was extracted with CH_2Cl_2. The combined organic layer was dried over $MgSO_4$ and concentrated to give **21** as a yellow solid. Elemental-analysis pure **21** was obtained by column chromatography using silica and EtOH/saturated NH_4OH (aq) (9:1) as the eluent. Yield: 0.62 g (87%). Mp: 198−200 °C. ^{1}H NMR ($CDCl_3$, 200 MHz): δ 7.72 (s, 4H, ArH), 7.58 (s, 4H, ArH), 3.59 (s, 8H, CH_2), 2.36 (s, 24H, NCH_3). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 142.2, 139.7, 139.2, 127.4, 127.35, 106.15, 69.0, 45.55. MALDI-TOF-MS (*m*/*z*): 710.54 (M$^+$, calcd 710.13). Anal. Calcd for $C_{30}H_{40}I_2N_4$: C, 50.72; H, 5.67; N, 7.89. Found: C, 50.89; H, 5.61; N, 7.76.

Synthesis of 1,4-Bis(3,5-(dimethylaminomethyl)-4-(iodoplatinum)phenyl)benzene (5). A mixture of **21** (0.71 g, 1.0 mmol) and [Pt(*p*-tol)$_2$SEt$_2$]$_2$ (0.93 g, 1.0 mmol) in dry benzene (50 mL) was stirred at 55 °C for 3 h. The mixture was cooled to room temperature, and all volatiles were removed in vacuo. The yellow solid was washed with Et_2O, and the very poorly soluble crude diplatinum compound **5** was suspended in CH_2Cl_2 (20 mL). Subsequently, sulfur dioxide was bubbled through this mixture, resulting in a clear deep orange solution. Upon addition of Et_2O, an orange solid precipitated. This solid was collected and washed with Et_2O. The orange solid was redissolved in CH_2Cl_2, and this mixture was evaporated to dryness under reduced pressure, to liberate the diplatinum complex from sulfur dioxide. This resulted in pure **5** as a yellow solid. Yield: 0.95 g (86%). ^{1}H NMR (CD_2Cl_2, 200 MHz): δ 7.59 (s, 4H, ArH), 7.21 (s, 4H, ArH), 4.11 (s, $^3J_{Pt,H}$ = 49.8 Hz, 8H, CH_2), 3.20 (s, $^3J_{Pt,H}$ = 41.4 Hz, 24H, NCH_3). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 144.15, 140.25, 136.7, 127.25, 126.05, 125.95, 118.4, 77.7, 55.35. MALDI-TOF-MS (*m*/*z*): 973.98 ([M − I]$^+$, calcd 973.13). Anal. Calcd for $C_{30}H_{40}I_2N_4Pt_2$: C, 32.74; H, 3.66; N, 5.09. Found: C, 32.96; H, 3.78; N, 5.13.

Retention Measurements. The retention measurements were perfomed in methylene chloride at room temperature in a nanofiltration membrane cell with a flow-rate of 20 mL h^{-1} using a SelRo MPF-60 or MPF-50 flat-membrane.[14] Prior to the filtration experiments, the membranes were first stored overnight in a methanol bath, followed by 1 h in a CH_2Cl_2 bath, and finally CH_2Cl_2 was flushed through the membrane in the membrane reactor in order to remove residual traces of methanol. Typically, 70 μmol of **1c**−**4c** and **6** was dissolved in 3 mL of CH_2Cl_2 and injected into the reactor. For solubility reasons, **5** was first converted into **22** by treating a suspension of **5** in CH_2Cl_2 (3 mL) with sulfur dioxide, resulting in a bright orange solution that was injected into the reactor. After the filtration experiments, the concentration of the macromolecular materials **1**−**6** in the permeate and the retentate were determined by UV/vis spectroscopy: an exact volume of the retentate/permeate was mixed with an exact volume of a saturated solution of sulfur dioxide in CH_2Cl_2, and the resulting solution was analyzed with UV/vis spectroscopy.

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