Imprinting Chiral Information into Rigidified Dendrimers

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Chiral, polymerizable P_2Pt(*S*-BINOL) metallodendrimers constructed of flexible benzyl ether repeat units were cross-linked/imprinted into highly porous and rigid organic polymers (methacrylate-based). Two *meta*-Cl substituents on the P−Ar portion of the metallomonomer reduced BINOL loss during polymer formation to levels that enabled site accessibility to be measured by the quantitation of *S*-BINOL cleavage (HCl) and BINOL/Br_2BINOL exchange reactions. In general, the total site accessibility decreased as the generation number or steric bulk of the dendritic arms increased, which was offset by an increased effectiveness of the chiral imprint as the size of the dendritic arms increased. Thus polymerizable dendritic metallomonomers can be copolymerized into highly cross-linked organic polymers, and a memory for the absolute stereochemistry of the imprint ligand retained and used to affect the stereochemistry of reactions at the metal in the core.

Introduction

The heterogenization of "homogeneous" catalysts onto solid supports[1] (silica,[2] alumina,[3] polymers,[4,5] etc.) has long been seen as a methodology for combining the most beneficial aspects of each catalyst type into a single formulation. As a result, the primary focus of these efforts has been on the development of highly selective and/or stable catalysts with physical properties that enable phase discrimination between the product and catalyst. Strategies encompassing solid/liquid, solid/gas, and liquid/liquid[6,7] differentiation of products and catalysts are the rule,[8] although many recent sophisticated approaches to reversible phase switching have been developed.[9] Much less effort has emerged, however, in combining the properties of homo- and heterogeneous catalysis to obtain catalysts with wholly new properties, not available in either a purely homogeneous or heterogeneous catalyst formulation.

It was with the significant technical challenges embroiled in this caveat that we began to explore strategies to synthesize "homogeneous" catalysts that operated within the confines of an artificial, "well-defined" active site that was composed of a solid phase material. In particular we desired active site structures that contained structural elements reminiscent of biological active sites for the purpose of achieving chemical reactivity not obtainable from a "normally" solvated transition metal catalyst.

Molecular imprinting[10] seemed like an ideal platform for the synthesis of transition metal catalysts located within the interior of a polymer-imprinted active site. The imprinting process consists of the copolymerization of organic or inorganic templates into highly cross-linked organic polymers, their modification or excision providing molecularly imprinted polymers (MIPs) that retain chemical information (shape, functional group display, etc.) related to the original template. While most of the MIP efforts have been directed to analytical applications, these techniques have more recently been applied to problems in synthesis[11] and catalysis.[12]

With regard to the synthesis of chiral active sites for applications in asymmetric catalysis, we have previously

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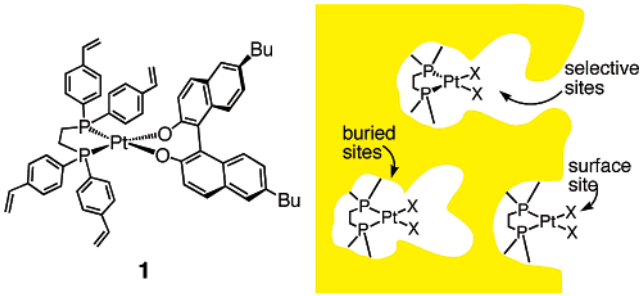
Scheme 1



shown that copolymerizing chiral metallomonomers such as **1** into highly cross-linked porous polymers (~95% cross-linking monomer) leads, after BINOL removal, to P_2Pt- sites capable of enantiomer recognition in BINOL rebinding.[13] The chiral cavity generated by BINOL removal enabled an otherwise achiral metal to recognize the BINOL enantiomer that was originally used to imprint the associated chiral cavity.[14]

Enantiomer ratios for BINOL recognition experiments depended on several factors but reached as high as 97:3 in favor of the imprinted enantiomer. Obtaining such high selectivities, however, required that many less selective sites be poisoned, taking advantage of the fact that *the less selective sites were more reactive*. The obvious conclusion was that these MIPs were composed of a complex distribution of sites that ranged from completely encapsulated and inaccessible to entirely solvent exposed (no chiral cavity), with every imaginable combination in between. Scheme 1 depicts such a MIP emphasizing the polydispersity of sites.

Although site heterogeneity[15] is not necessarily detrimental to analytical applications,[10] it seriously undermines the goal of synthesizing well-defined (and controllable) catalytic sites with associated shape and functionality,[16,17] since unselective hyperactive sites will disproportionately contribute to product output or selectivity (for example the surface site in Scheme 1 would be unselective). Thus the goal of multi-turnover catalysis puts a premium on eliminating heterogeneity in general and surface sites in particular.[18]

Polymer matrix formation is a complex process that begins with a 1:1 ratio of the monomer(s) to the porogenic solvent and ends with a biphasic monolith: a solvent-filled three-dimensional pore phase microscopically intermixed with a cross-linked polymer.[19] Unfortunately, given the complexity of this process, we considered it unlikely that tweaking the polymerization conditions would significantly overcome the problem of microscopic site heterogeneity.

A possible solution presented itself when we considered that only the interface between the cavity and the bulk polymer might be consequential to site structure and fidelity. By providing the metallomonomer with its own interface to bulk polymer we hypothesized that tailorable active sites with significantly enhanced structural and compositional homogeneity would be possible.

We imagined that a metallomonomer with polymerizable dendritic arms of relatively short length would provide the means to such a controllable interface.[20] Since each active site would contain the same degree of dendritic foliage, they should be more chemically and compositionally similar, at least in comparison to those in normal MIPs. This protocol would differ from a traditional MIP since the imprinting media would actually be the rigidified dendrimer[21] instead of the cross-linked bulk polymer matrix.

This approach is conceptually similar to and was stimulated by Zimmerman's early work on cored, shell-cross-linked dendrimers.[22] More recently he has demonstrated a significant advance to molecular imprinting in that core removal leads to *soluble* "monomolecular" imprinted dendrimers capable of molecular recognition.[23,24] In the latter case, porphyrin core-based dendrimers with peripheral alkene groups were subjected to the Grubbs metathesis catalyst under high dilution conditions, which provides the intramolecular cross-links needed to zip-up the surface of the dendritic sphere. Core removal provides soluble, monomolecular imprints with eight carboxy groups converging at the core of the dendrimer host, the organization of which provides the means to differentiate pyridine-functionalized porphyrins of various sizes and shapes.

Although Zimmerman's work has convincingly shown that size and functionality can be imprinted into soluble dendrimers, our adaptation of the dendrimer imprinting approach to asymmetric catalysis/molecular recognition by metal-containing species required that *chiral* information be *imprinted* into dendrimers, an accomplishment that, to our knowledge, has not been reported.[25] Thus, we report herein experiments designed to test the hypothesis that dendrimers can be rigidified to imprint chiral information and that this information can be used to affect the stereochemical outcome of reactions at metals located in the core.

As a first step to implementing our strategy for new catalyst design, we synthesized metallomonomers with polymerizable dendrons and examined the imprint fidelity as a function of the generation number and substitution pattern of the dendrimer arm. The arms

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(14) For related case studies utilizing transition state analogues to imprint cavities for metal catalysis see: (a) Polborn, K.; Severin, K. *Chem. Commun.* **1999**, 2481−2482. (b) Polborn, K.; Severin, K. *Eur. J. Inorg. Chem.* **2000**, 1687−1692.
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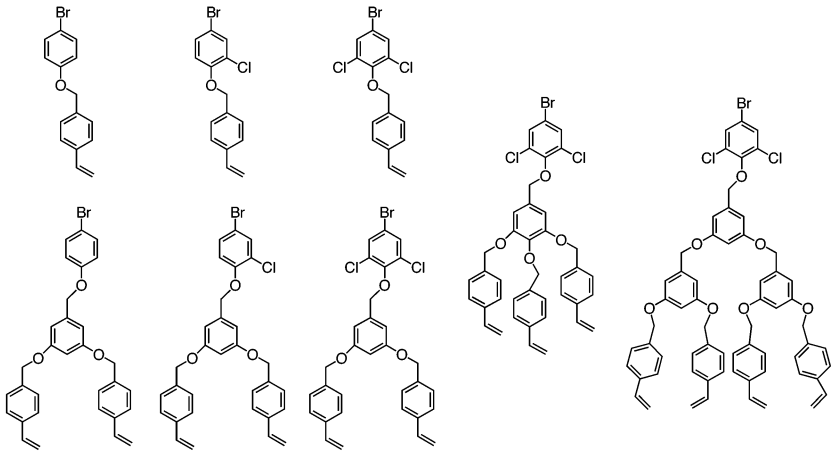
Scheme 2



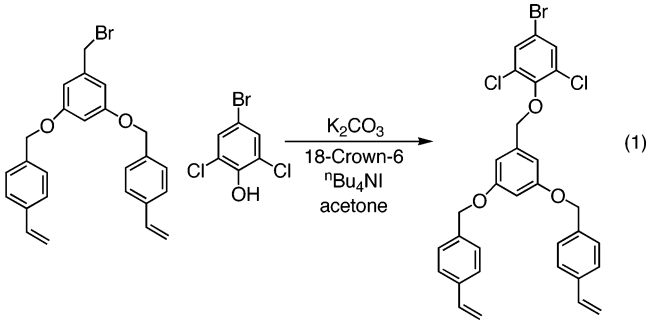
were designed to emanate from the rear of the molecule to the front reactive quadrants, and thus define an active site.

Although literature precedence suggested that the metallomonomers would be readily available, we had concerns that the dendrimer arms would be entirely too flexible to effectively imprint (and retain) subtle chiral information. On the other hand, dendron rigidification by copolymerization into a stiff polymer matrix should provide a significant force to the arms; the balance of those forces, flexible versus rigid, was not a priori predictable. The results reported herein show that chiral information can indeed be imprinted into these environments and this information utilized to affect the stereochemistry of chemical reactions occurring at the metal core of the active site.

Directly relevant to our current work are the benzyl ether dendritic diphosphine ligands synthesized by Tsuji[26] and the polymerizable TADDOL-[27] and BINOL-based[28] dendrimers of Seebach, which were copolymerized and utilized in multi-recycle asymmetric catalysis. Seebach's polymerizable dendrimers seemed like the perfect starting point and are based on the benzyl ether repeat unit developed by Fréchet.[29]

Results and Discussion

Dendron Synthesis. The polymerizable dendrons used for metallomonomer synthesis were available through standard convergent methods starting with 4-vinylbenzyl chloride, Seebach's polymerizable generation one (G1) and generation two (G2) benzyl bromides, or the tri-styryl-derivatized pyrogallols previously reported by Kumar.[30] The benzyl halides were coupled, in good yields, to 4-bromophenol, 4-bromo-2-chlorophenol, and 4-bromo-2,6-dichlorophenol (e.g., eq 1), with Fréchet's optimized coupling conditions[29] (K_2CO_3 and 18-crown-6 ether in refluxing acetone). The polymerizable dendrons synthesized in this manner are collected in Scheme 2.



Platinum Complex Synthesis. Coupling of these dendrons to bis(dichlorophosphino)ethane was accomplished with a modified procedure of Tsuji.[26] Activation by metal/halogen exchange of the aryl bromides by *n*BuLi (−78 °C, THF) followed by addition of CuCl and bis(dichlorophosphino)ethane produced extremely oxygen sensitive diphosphines (at least in the non-chlorinated cases) that could never be isolated without extensive oxidation. Standard phosphine reduction and protection protocols were incompatible with the peripheral vinyl groups, so the diphosphines were quenched with $(COD)PtCl_2$ prior to workup to produce the corresponding P_2PtCl_2 precursors as foamy solids (Scheme 3). Although the exact role of CuCl in the P−C coupling is unclear, its absence leads to numerous unidentifiable minor phosphine species in the reaction mixture.[31] By ^1H NMR the main impurity present in the crude P_2PtCl_2 reaction mixture was debrominated dendron, which could be removed with successive Et_2O washes. The P_2PtCl_2 were first converted to P_2PtCO_3 intermediates with Ag_2CO_3 and then directly to the desired enantiopure P_2Pt(*S*-BINOL) metallomonomers by the methods of Andrews[32] (Scheme 3); each of the metallomonomers was a foamy, amorphous solid. The P_2Pt(BINOL) metallomonomers were purified from traces of excess BINOL by washing with Et_2O or precipitating with Et_2O

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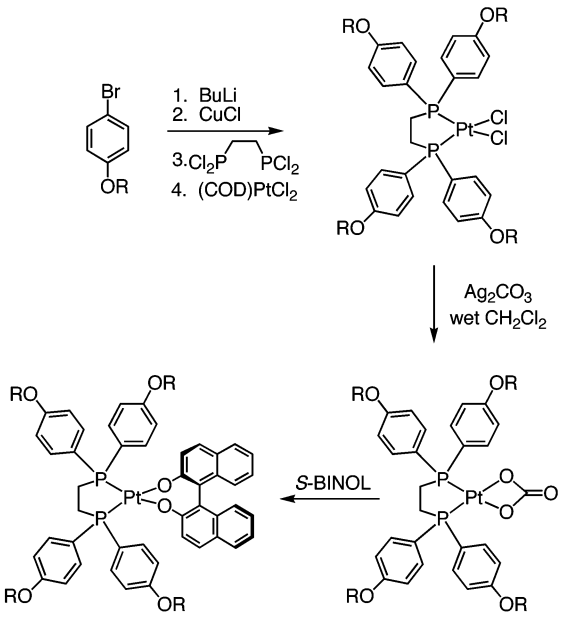
Scheme 3

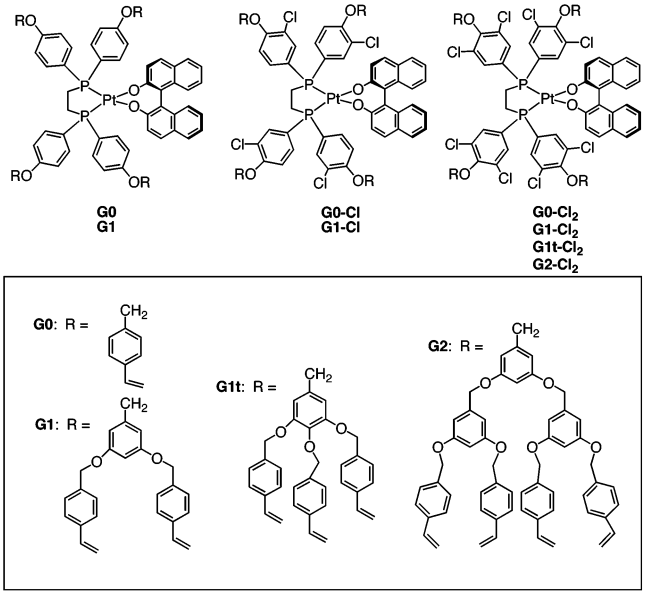


from a CH_2Cl_2 solution, which led to prepolymerization materials that were free of unreacted dendron and BINOL, although all traces of solvent could never be removed from the foams.

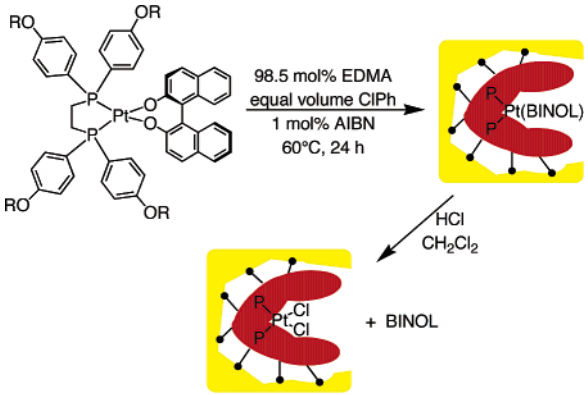
The ^{31}P NMR spectra of all metallomonomers display a single resonance at ~25 ppm(s) with couplings to platinum of 3620−3690 Hz. The ^{1}H NMR spectra are generally broad (the higher the generation, the broader the peaks) and are not diagnostic except for the vinyl and benzyl regions (4.92−5.87 ppm). The *meta*-chloro substituents significantly sharpen the ^{1}H NMR spectra of the metallomonomers, with the dichloro-substituted dendrimers providing the sharpest spectra. The reduced C_2-symmetry of the BINOLates is observed as a splitting of the peaks in the diagnostic vinyl and benzyl regions. Although sections of the ^{1}H NMR spectra are broad, free BINOL and unreacted dendron can be clearly observed, when present, providing additional confidence in the purity of the metallomonomers used for polymer synthesis.

Test Polymerizations. The first polymers to be made employed the "zero" (G0) and first-generation (G1) non-chlorinated metallomonomers **G0** and **G1** (Scheme 4). The two polymers were synthesized using a standard imprinting protocol (62 μmol Pt, ~98 mol % ethylene dimethacrylate (EDMA),[33] 1:1 by weight with ClPh, 1 mol % AIBN, 60 °C, 24 h), providing brown monolithic polymers with a permanent pore structure and high surface areas[34] (Scheme 5). The product polymers were manually broken into small pieces, Soxhlet extracted with CH_2Cl_2 for 6 h to remove any residual high-boiling chlorobenzene, and dried in vacuo for 12 h at 50 °C. Quantitative HPLC analysis unexpectedly showed 20% (**G0**) and 36% (**G1**) of the polymer's BINOL content being washed out prior to deliberate cleavage from the metal. Since BINOL quantification is the indirect tool

Scheme 4



Scheme 5



used to measure site accessibility and fidelity (vide infra), BINOL loss at this stage was intolerable.[35]

Numerous control experiments indicated that a simple generation-dependent decomposition was not operative, as thermolysis of **G0** and **G1** in chlorobenzene and ClPh/EDMA mixtures showed them to be thermally stable (by ^{31}P NMR) to 120 °C. Hypothesizing that BINOL loss was caused by or was accompanied by P_2PtCl_2 formation during the polymerization, we also examined non-chlorinated porogens. Using **G0** as the test metallomonomer, polymers were made with toluene and *o*-difluorobenzene porogens; however, significant BINOL loss was still observed (toluene, 21%; *o*-difluorobenzene, 19%). Moreover, a nonpolymerizable version of these compounds, (tetra-4-methoxydppe)Pt(BINOL), **2**, was subjected to identical polymerization and Soxhlet extraction conditions and was recovered intact after polymer formation, suggesting that BINOL extrusion is somehow related to the physical forces on the molecule generated by the growth and rigidification of the polymer around the complex as it is incorporated into the matrix. Apparently larger dendrimers are more sensitive to these forces.

(33) This value varies with the MW of the dendritic comonomer. The Pt-loading is constant in each experiment, however.

(34) Santora, B. P.; Gagné, M. R.; Moloy, K. G.; Radu, N. S. *Macromolecules* **2001**, *34*, 658−661.

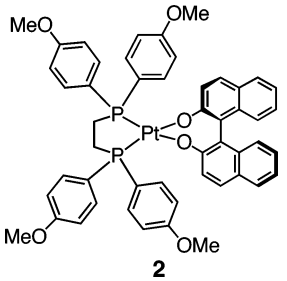
(35) In contrast, polymers made with dppe **1** lost <1% of the Bu_2-BINOL prior to cleavage (see ref 13).

Table 1. %BINOL Loss during Polymerization[a]

entry	polymer	%BINOL loss	$\Sigma(\sigma_p + \sigma_m)$[38]
1	**P-(G0)**	20	−0.27
2	**P-(G1)**	36	−0.27
3	**P-(G0-Cl)**	9	0.10
4	**P-(G1-Cl)**	22	0.10
5	**P-(G0-Cl_2)**	1	0.47
6	**P-(G1-Cl_2)**	7	0.47
7	**P-(G2-Cl_2)**	2	0.47
8	**P-(G1t-Cl_2)**	2	0.47

[a] Determined after 6 h Soxhlet wash with CH_2Cl_2.

Chloro-Based Dendrimers. To test a second hypothesis that the higher electron density of the 4-benzyloxy-substituted diphosphines (cf. **1**) was contributing to BINOL lability during polymer formation (also supported by the observation that these diphosphines are extremely prone to oxidation), metallomonomers with one and two *meta*-chloro substituents on each of the P−Ar rings were prepared (Schemes 2−4). Polymer formation with EDMA provided six new yellow polymers.[36]



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As Table 1 summarizes, two trends emerge, the first being that BINOL loss is again generation dependent, but more importantly that electron-withdrawing groups provide enhancements in template stability. For example in G1 metallomonomers, zero, one, and two *meta* substituents lead to 36, 22, and 7% loss, respectively, upon polymer formation (entries 2, 4, and 6). The trend is identical in G0 metallomonomers, although the absolute BINOL loss is lower. Unexpectedly, the single G2 metallomonomer that was made loses less BINOL than G1 (entries 6 and 7). In the *meta,meta*-Cl_2 systems, where BINOL loss is diminished [1, 7, 2, and 2% for **P-(G0-Cl_2)**, **P-(G1-Cl_2)**, **P-(G2-Cl_2)**, and **P-(G1t-Cl_2)**, respectively], only the G1 has >2% BINOL loss. Although the reason(s) for BINOL loss is not known, it is clear that both the local steric hindrance (generation number) and phosphine basicity combine to create instability during the polymerization process.[37] Nevertheless, the enhanced stabilities provided by the *meta*, *meta*-Cl_2-modified templates solved a critical problem and enabled careful studies to assess the recognition properties of these imprinted polymers.

Site Accessibility. The adopted standard for measuring the absolute active site accessibility was the amount of the BINOL imprinting ligand that could be protonatively removed from the polymer. Treating the yellow to brown BINOLate polymers with HCl liberated the BINOL from the Pt site and presumably converted the imprinted site to the yellow to colorless P_2PtCl_2 forms.[39] The free BINOL was then removed from the polymer matrix (Soxhlet washing with CH_2Cl_2 for 12 h) and quantified by HPLC.

Table 2. HCl Cleavage and Rebinding Data for Cl_2-Substituted Dendrimers

entry	polymer	% BINOL HCl cleavage[a]	% Br_2BINOL[b] (% of BINOL sites)[c]	% ee Br_2BINOL[d]
1	**P-(G0-Cl_2)**	87	47 (54)	35
2	**P-(G1-Cl_2)**	68	36 (53)	39
3	**P-(G2-Cl_2)**	63	32 (51)	41
4	**P-(G1t-Cl_2)**	67	31 (46)	44

[a] % of the total BINOL sites present in the polymer, uncorrected for BINOL loss occurring prior to cleavage. [b] Percentage of total Pt sites that exchange BINOL for Br_2BINOL. [c] Percentage of sites capable of egressing BINOL (by HCl cleavage) that also exchange BINOL for Br_2BINOL. [d] % enantiomeric excess of the exchanged Br_2BINOL.

Total active site accessibility was not surprisingly generation dependent, as **P-(G0-Cl_2)** showed a relatively high accessibility (87% BINOL cleavage), whereas BINOL cleavage occurred at only 68, 63, and 67% of the platinum sites in **P-(G1-Cl_2)**, **P-(G2-Cl_2)**, and **P-(G1t-Cl_2)**, respectively (Table 2). Since bleaching of the polymers suggested complete reaction of the P_2Pt-(BINOL) unit with HCl (strong thermodynamic driving force), the reduced recovery of BINOL was interpreted as hindered egress of the large BINOL ligand either directly from the active site or indirectly via constrictions in the solvent channels not allowing passage of the large ligands.[40] The significant drop in accessibility between G0 and the relatively similar G1 and G2 polymers hinted at a genuine difference in the physical structure of these sites; the G0 systems were not expected to be very "dendritic" in character.

Several attempts to modify the rigidity of the matrix to enable better access to the site and still maintain BINOL memory were made. Replacing the EDMA component of the monomers with a 75:25 mass ratio of EDMA and MMA or a 1:1 mixture of EDMA and the more flexible butyl-linked dimethacrylate (BDMA),[41] in **P-(G1-Cl_2)**, did not provide any accessibility differences. The EDMA/MMA and EDMA/BDMA matrixes each led to 5 and 9% BINOL loss during polymer formation and HCl cleavages of 69 and 67%, respectively. Thus these apparently more flexible supports do not provide the anticipated higher accessibility, suggesting that site accessibility may be more a function of the dendritic interface to bulk polymer than the bulk matrix itself (vide infra).

Since the weight percent of metallomonomer (constant loading of 62 μmol Pt/g dry polymer) increased significantly on progressing from G0 to G2, the accessible

(36) Metallomonomers with two, one, and zero chlorine substituents are yellow, yellow-brown, and brown, respectively.

(37) Consistent with a significant electronic contribution is the observation that the **G1** metallomonomer containing the less basic 6,6′-Br_2BINOL ligand loses only 20% Br_2BINOL during polymer formation (cf. 36%, entry 2). The pK_a's of 6-Br-2-naphthol and 2-naphthol are 16.2 and 17.1, respectively. Bordwell, F. G.; Cheng, J.-P. *J. Am. Chem. Soc.* **1991**, *113*, 1736−1743.

(38) Sigma for −OMe was used to simulate a benzyloxy substituent. Harisch, C.; Leo, A.; Unger, S. H.; Kim, K. H.; Nikaitami, D.; Lien, E. J. *J. Med. Chem.* **1973**, *16*, 1207−1216.

(39) P_2PtCl_2 complexes with two, one, and zero chlorine substituents are off-white, pale yellow, and yellow-brown, respectively.

(40) Unpublished studies have shown that variations in ligand size correlate in the expected way for ligand egress (larger = more hindered escape).

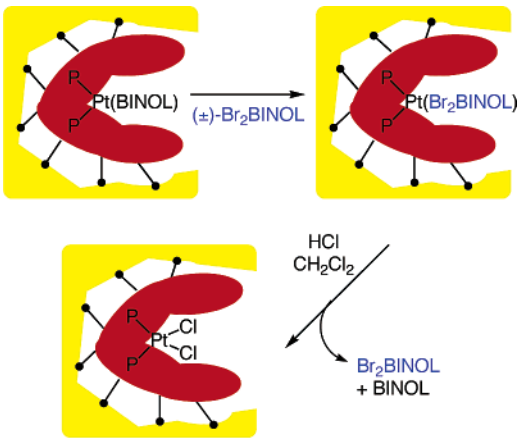
(41) Wulff, G. In *Polymeric Reagents and Catalysis*; Ford, W. T., Ed.; American Chemical Society: Washington, DC, 1986; pp 186−230.

Table 3. Accessible Surface Area (SA, N_2 BET) as a Function of Generation Number at a Metallomonomer Loading of 62 μmol Pt/g of Polymer

sample[a]	SA (m^2/g)	wt % comonomer	comonomer MW
pEDMA	460		
P-(3)	403	6.7	1038.1
P-(G0-Cl_2)	301	10.1	1682.4
P-(G1-Cl_2)	255	17.0	2633.5
P-(G2-Cl_2)	198	29.1	4537.5
P-(G1t-Cl_2)	245	19.3	3165.4
P-(G1-Cl_2)[b]	260	15.8	2633.5
P-(G1-Cl_2)[c]	157	15.6	2633.5

[a] Surface area analyses were carried out after HCl cleavage (Scheme 5). [b] 75:25 EDMA/MMA. [c] 1:1 EDMA/BDMA.

Scheme 6



surface area of each polymer was measured by N_2 BET. These data are collected in Table 3 and show that the bulk properties of the polymer indeed respond to the change in cross-link density and/or the weight percent of metallomonomer, with the higher generation metallomonomers leading to diminished surface areas. Although the differences are numerically significant, the absolute surface areas are still relatively high, and it does not seem likely that this drop is the source of the change in site accessibility.

Site Fidelity. To assess the chiral memory of the imprinted dendrimer, an (*S*)-BINOL/(±)-6,6′-Br_2BINOL (Br_2BINOL) exchange reaction was developed (Scheme 6). This method proved capable of quantifying the extent and selectivity of a ligand exchange reaction and thus the ability of the dendrimer to recognize the originally imprinted enantiomer of BINOL. Thermolysis of the polymer with excess Br_2BINOL exchanged those platinum sites able to accommodate the (presumably associative) ligand exchange. Removing the unreacted Br_2BINOL and excised BINOL, followed by HCl cleavage of all BINOL species present in the polymer and quantification by chiral HPLC, provides a direct measure of the number of sites able to ligand exchange (%Br_2BINOL) along with their selectivity (% ee Br_2-BINOL) (Scheme 6). This procedure probes the efficiency of the chiral imprint in addition to providing information on site distribution and selectivity in the imprinted dendrimer.

The initial exchange reactions were carried out at 60 °C in chlorobenzene (similar to the initial polymerization conditions). In each rebinding experiment, the polymer was suspended in a chlorobenzene solution containing 20 equiv of (±)-Br_2BINOL and 15 vol % H_2O at 60 °C for 12 h. Excess Br_2BINOL and excised BINOL were washed from the polymer by Soxhlet extraction (CH_2Cl_2, 12 h). The polymer was then treated with HCl to release the rebound Br_2BINOL, which was collected by Soxhlet extraction, and analyzed by chiral HPLC to quantify the extent and the selectivity of the rebinding reaction.

As Table 2 summarizes, the dendrimer-based metallomonomers indeed lead to active sites capable of recognizing the absolute sense of the originally imprinted BINOL enantiomer; *that is, otherwise achiral dendrimers can be rigidified into supramolecular conformations that retain chiral information*. Thus, **P-(G0-Cl_2)**, **P-(G1-Cl_2)**, **P−(G2-Cl_2)**, and **P-(G1t-Cl_2)** exchange the BINOL in 47, 36, 32, and 31% of their total platinum sites for Br_2BINOL, with enantioselectivities of 35, 39, 41, and 44%, respectively (Table 2). This ability to recognize the same absolute sense of a chiral imprinting ligand represents the first reported case of asymmetric dendrimer imprinting.

Taken together the data show that as the size (generation) of the dendritic metallomonomers increases, fewer sites liberate BINOL for both HCl cleavage and Br_2BINOL exchange. However, when the number of sites exchanging BINOL for Br_2BINOL is normalized by the number of sites fundamentally capable of egressing BINOL (as assessed by HCl cleavage), the exchange percentages are remarkably constant from G0 to G2 (54, 53, and 51%, respectively), Table 2.

With regard to enantiomer recognition, the enantioselectivity for Br_2BINOL recognition gradually increases from G0 to G1 to G2 (35 → 39 → 41% ee), although just as importantly, the absolute sense of recognition is the same as that of the imprinting ligand (*S*). Thus the arms of the dendrimer can indeed be rigidified by copolymerization into highly cross-linked polymers and chiral information cast into the dendritic structure.

From a synthetic perspective the observation that the tris-styryl-terminated G1 metallomonomer (**G1t-Cl_2**) functioned slightly better (accessibility and selectivity) than the G2-bis-styryl-terminated case is noteworthy, since the synthetic difficulty on progressing from G1 to G2 is significant, the G2 having a MW of ∼4500.[42] A three-dimensional model of the G1 pyrogallol metallomonomer with *S*-BINOL is shown in Figure 1.

Site Homogeneity. As a tool to measure site homogeneity in MIPs, a comparison of BINOL/Br_2BINOL exchange reactions at 60 and 120 °C was performed. Table 4 collects the data for the exchange reactions at the two temperatures, organized to compare changes in the number of sites to react and their respective selectivities for the different dendritic metallomonomers (entries 1−4). Not surprisingly the number of sites to exchange the BINOL ligands increased at the higher temperature, although the magnitude of the increase was less than expected based on prior studies.[13] The increase in reactive sites on going from 60 to 120 °C was only 1% for G0 and 6 and 7% for G1 and G2, respectively. This similarity in site accessibility was not observed in earlier phenol/BINOL exchange reactions.[13]

(42) Only the largest of the dendrimers likely approach bona fide dendritic properties, see: Bosman, A. W.; Janssen, H. M.; Meijer, W. W. *Chem. Rev.* **1999**, *99*, 1665−1688.

Table 4. BINOL/Br_2BINOL Exchange Data

entry	polymer	% Pt (60 °C)	% ee (60 °C)	% Pt (120 °C)	% ee (120 °C)	Δ% Pt (120−60 °C)	Δ% ee (120−60 °C)	$\Delta(\Delta\Delta G^{\ddagger})^a$
1	**P-(G0-Cl_2)**	47	35	48	44	1	9	0.25
2	**P-(G1-Cl_2)**	36	39	42	41	6	2	0.14
3	**P-(G2-Cl_2)**	32	41	39	50	7	9	0.28
4	**P-(G1t-Cl_2)**	31	44	37	50	6	6	0.23
5	**P-(3)**[b]	33	51	51	71	18	20	0.64

[a] $\Delta\Delta G^{\ddagger}$ of k_S/k_R at s120 °C − $\Delta\Delta G^{\ddagger}$ of k_S/k_R at 60 °C. [b] BINOL cleavage with HCl liberates 89% of available BINOL.

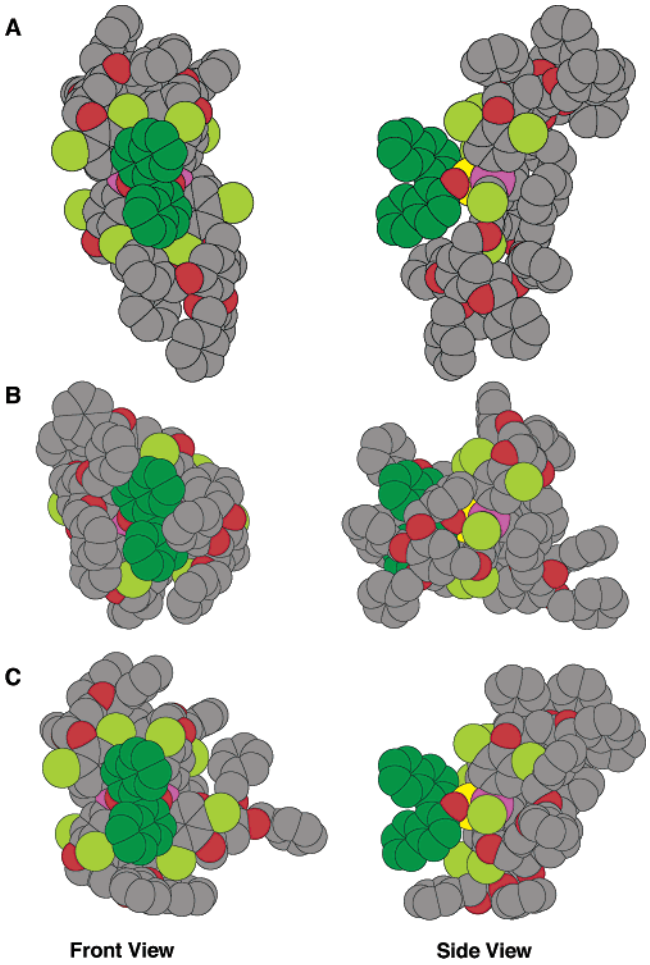
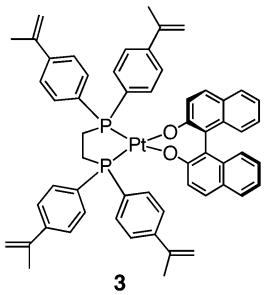


Figure 1. Space-filling representations (H atoms removed for simplification) of the three representative local minima from the Spartan MMFF94 Monte Carlo conformer analysis of the non-styryl version of **G1t-Cl_2**. A is the lowest energy structure, while B and C are randomly chosen local minima of nearly equal relative energy (see text). Light green, Cl; dark green, BINOL carbons; red, O; pink, P; yellow, Pt.

Like these other studies, however, the enantioselectivities do *increase* at the higher temperatures, a phenomenon that was previously interpreted as resulting from the accessibility of more hindered, more selective sites at the higher temperatures. Apparently some slightly more selective dendritic sites are accessible at 120 °C, although the overall selectivity increases are modest (2−9%, 0.14−0.28 kcal mol^{-1}). In regard to changes in site accessibility and selectivity, the pyrogallol-terminated metallodendrimer again performs nearly identical to the more "expensive" G2 metallomonomer.

To provide a point of comparison to previously investigated nondendritic metallomonomers, the (tetraisopropenyldppe)Pt(*S*-BINOL) metallomonomer **3** was tested under the identical BINOL/Br_2BINOL exchange conditions. At 60 °C, 33% of the total sites exchange BINOL for Br_2BINOL (the same as the G1-pyrogallol), with an enantioselectivity of 51% (cf. 44% for **G1t-Cl_2**), similar to the best performing dendrimer. The biggest difference between **P-(3)** and the dendritic polymer sites came at 120 °C. At this temperature the number of sites to undergo ligand exchange and the enantioselectivity increased significantly (+18% and +20% ee) compared to the 60 °C results. In units of activation energy differences, the change is even more noteworthy ($\Delta(\Delta\Delta G^{\ddagger})$ = 0.64 kcal mol^{-1}). Thus it appears that *additional superselective sites are accessible at high temperature in* ***P-(3)*** *but not in the dendritic polymers*. These superselective sites provide the large boost in selectivity for BINOL recognition at 120 °C; their selectivity is consistent with the kinetic selectivity of the most selective phenol/BINOL exchange previously measured.[13]

These large changes in site reactivity and selectivity suggest a broader diversity of *reactive* sites in the traditional MIP experiment, highly selective sites being accessible at high, but not moderate temperatures. In contrast, the attenuated temperature-dependent changes in reactivity/selectivity of the dendritic metallomonomers point to a significantly narrowed distribution in the *reactive* sites. This higher uniformity, however, comes at the expense of a subset of most selective sites that is accessible/populated at high temperatures in **P-(3)**.



3

Further complicating the overall picture of site accessibility is the increase with dendrimer generation in the number of inaccessible sites (from HCl cleavage), even though these higher generations have relatively homogeneous reactive site distributions. Apparently two types of sites are obtained from the imprinting of a dendritic metallomonomer, one class that inadvertently buries the template (makes it inaccessible) and another class that is open, reactive, and homogeneous in nature but only moderately selective. Increasing the size of the dendritic periphery shifts the distribution of these sites in an intuitively reasonable fashion (i.e., bulkier = more

buried sites), but only subtly changes the selectivity of the reactive sites. In the dendritic systems a site could become buried either by complete encapsulation of the core by the polymer or by a single dendrimer arm blocking the egress of BINOL (vide infra). In contrast, the more traditional metallomonomer leads to fewer completely buried sites but, because of the site construction material (bulk amorphous polymer), generates a continuous distribution of reactive sites, including the selective high-temperature ones.

Our working hypothesis on the unusual behavior of the metallodendrimers currently focuses on the many conformational degrees of freedom available to the flexible $-CH_2-O-$ linkage (C−O bond rotation is also rapid).[43] Depending on the solvent, these dendrimers can adopt highly compact (arms folded in) or extended structures.[44] Polymerization of the former conformers could easily lead to a subset of active sites with blocked BINOL egress (by our definition an inaccessible site), the folded in arm blocking the escape pathway for the ligand. These notions of conformational-dependent behavior stimulated the computational studies detailed below.

Monte Carlo Simulations. To model/visualize the accessible minimized structures available to these flexible materials, a Monte Carlo simulation was carried out on the dendritic portion of a non-styryl derivative of **G1t-Cl$_2$** using Spartan MMFF94. The terminal tribenzylated pyrrogallol unit was preminimized (after conformational searching) and was not systematically varied during the simulation, although it was allowed to respond to minimization. The central metal fragment was constrained to be square planar with 90° P−Pt−P, P−Pt−O, and O−Pt−O bond angles. A total of ∼2300 different initial starting points were minimized and examined with an eye to assessing the conformation degrees of freedom accessible to a prepolymerization complex. Because of the admittedly low-level calculation, the bottom 10 kcal mol^{-1} structures (∼65) were each kept and inspected.

Figure 1 contains three of these structures, chosen to represent the diversity of this set. Figure 1A (front and side view) represents the lowest energy-minimized structure. The dendritic arms adopt a gross C_2 symmetric arrangement that is compact and contains interligand π-stacks. The relevance of this lowest energy structure to a complex process that involves the cross-linking of this solvated structure into the matrix of a highly rigidified polymer is dubious; however it provides an informative visualization of the structure.

Equally revealing are several of the other structures present in the set of local minima (Figures 1B and 1C). In the set of 65, the most compact was 1B, which completely encapsulates the BINOL fragment from behind and above and if polymerized with a similar geometry would lead to a completely encapsulated structure (no doubt a highly selective one). Figure 1C, on the other hand, was more typical in that the dendritic arms tended to be less compact, with arms jutting out in seemingly random directions. In this case one of the arms reaches below the BINOL fragment, while the remainder stay pulled back (a fourth structure is shown in the table of contents graphic of this issue).

Viewed as an ensemble of local minima, the display of structural variability at a nearly isoenergetic point is as impressive as it is sobering, especially considering that imprinting into this array of structures is what leads to the observed enantiomer selective rebinding results. Clearly this media, while capable of rigidification and imprinting, has its own unique challenges to obtaining high-quality homogeneous imprints.

On the basis of this analysis, we hypothesize that more rigid metallodendrimers, along with decreasing the degrees of freedom accessible to the dendrimer arm and providing a more uniform conformational ensemble, should also adopt more extended structures that will limit the number of buried sites; that is, stiffer dendrons should keep the polymerizable ends on the exterior of the metallomonomer. Future experiments aimed at examining the response of reactivity/selectivity to increases in the dendron chain rigidity will help to address the issue of dendron conformations on site accessibility and fidelity.

Summary

Polymerizable metallodendrimers constructed of a flexible repeat unit can be cross-linked into highly porous and rigid organic polymers to imprint chiral information. This chiral information, temporally trapped in the supramolecular conformations of the rigidified dendritic arms, modifies the stereochemistry of reactions occurring at the core of the dendrimers.

The effectiveness of the chiral imprint is dependent on a number of factors. As the generation number (steric bulk) increases, the total active site accessibility for imprinting ligand removal and BINOL/Br_2BINOL exchange reactions decrease, but the ability of the dendrimer to imprint and retain chiral information increases slightly. The number of *reactive* Pt sites only slightly decreased from generation 1 to 2, and the selectivities were remarkably constant (small Δ% ee) over the range of accessible sites, at least when compared to the more traditional **P-3** metallomonomer system (large Δ% ee).

Substitution patterns of the dendron were also important; chlorine substituents are necessary on the P−Ar portion of the dendron to stabilize the complexes to BINOL loss during polymer formation. Substitution patterns at the periphery of the dendron also have an affect on reactivity/selectivity; the first-generation pyrogallol (tris-styryl-terminated) dendrimer has an accessibility and selectivity similar to those of the G2 bis-styryl-terminated dendrimer.

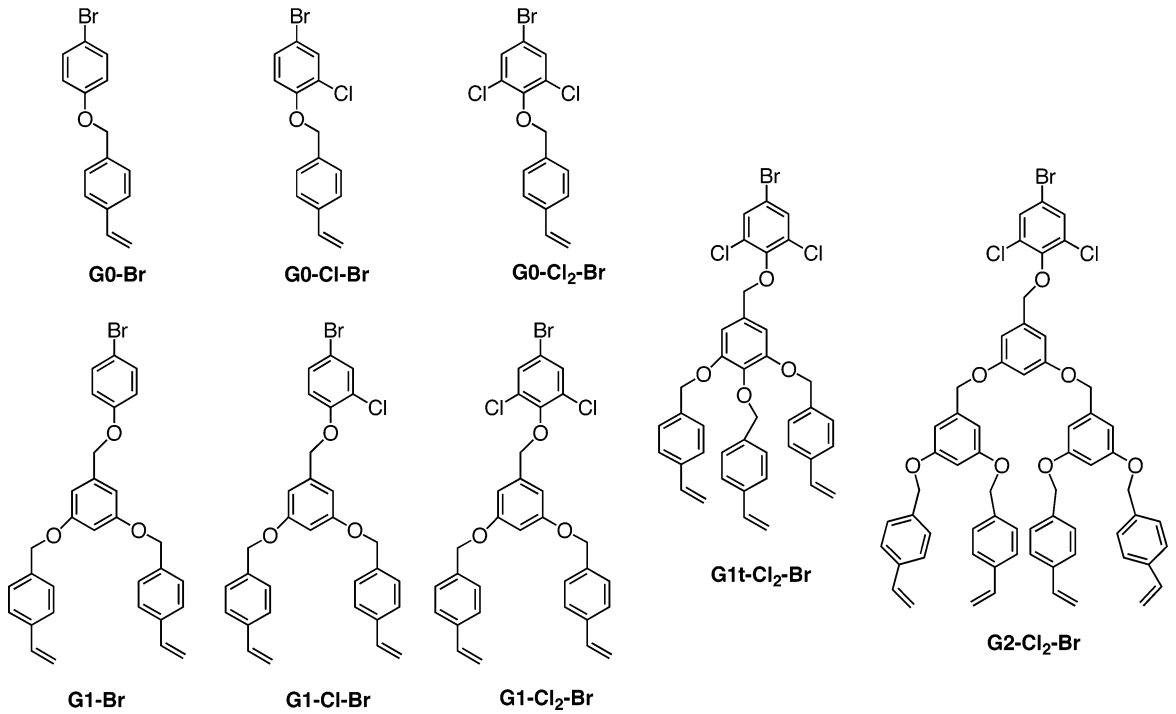
Experimental Section

General Methods. Racemic Br_2BINOL,[45] isopropenyldppe,[46] (COD)$PtCl_2$,[47] 4-bromo-2,6-dichlorophenol,[48] and benzyl

(43) Eliel, E. L.; Wilen, S. H.; Mander, L. N. *Stereochemistry of Organic Compounds*; John Wiley & Sons: New York, 1994.
(44) For a summary of extensive discussions on dendrimer end localization, see ref 42.

(45) Cram, D. J.; Sogah, G. D. Y. *J. Am. Chem. Soc.* **1979**, *101*, 3035−3042.
(46) Taylor, R. A.; Santora, B. P.; Gagné, M. R. *Org. Lett.* **2000**, *2*, 1781−1783.
(47) McDermott, J. X.; White, J. F.; Whitesides, G. M. *J. Am. Chem. Soc.* **1976**, *98*, 6521−6527.
(48) Kısakürek, D.; Aslan, A.; Işçi, H. *Polymer* **2000**, *41*, 5149−5155.

Chart 1



bromides[28] were synthesized according to literature procedures. All chemicals were purchased from Aldrich except 1,2-bis(dichlorophosphino)ethane (Strem) and *S*-BINOL (Kankyo Kagaku Center Co., Ltd., Japan). The platinum complexes P_2PtCl_2, P_2PtCO_3, and $P_2PtBINOL$ were synthesized by procedures similar to those published for dppe analogues.[32,49] Chlorobenzene was distilled from P_2O_5 and freeze−pump−thaw degassed before use as a porogen, but was used as received in rebinding experiments. 2,2′-Azobis(isobutyro)nitrile (AIBN) was recrystallized from MeOH, dried in vacuo, and stored under N_2 at −35 °C. EDMA was washed twice with aqueous 1 M NaOH and once with brine to remove inhibitor, dried over $MgSO_4$, filtered, distilled (105 °C/1 mmHg), freeze−pump−thaw degassed, and stored under N_2 at −35 °C. CuCl was used as received and stored under N_2. Polymerizations were performed in an MBraun LabMaster 100 glovebox. Reactions performed under Ar were carried out using standard Schlenk techniques.

NMR spectra were recorded on either a Bruker Avance 300 or a Bruker Avance 400 spectrometer. Chemical shifts are reported in ppm and referenced to residual solvent peaks (^{1}H and ^{13}C NMR) or to an external standard (85% H_3PO_4, ^{31}P NMR). Microanalysis data are reported for those complexes that were well-behaved solids. Most of the dendritic compounds were foamy solids or of a honey-like consistency that precluded complete solvent removal.

HPLC analysis was performed on a Hewlett-Packard Series 1100 instrument, using a Daicel Chiralcel OD-H column (95% hexanes/5% EtOH, 0.8 mL/min flow rate). HPLC chromatograms were recorded at wavelengths of 254, 278, 289, and 333 nm and compared to calibration curves to determine analyte concentration. **G0-Br.**[50] 4-Vinylbenzyl chloride (3.26 mL, 23.1 mmol), 4-bromophenol (4.00 g, 23.1 mmol), K_2CO_3 (3.83 mg, 27.71 mmol), 18-crown-6 ether (581.8 mg, 2.20 mmol), and tetrabutylammonium iodide (474.0 mg, 1.28 mmol) were combined in 66 mL of dry THF and heated to reflux for 16 h. The reaction mixture was cooled to room temperature and filtered through Celite, eluting with THF. The solvent was evaporated to an off-white solid and precipitated from EtOAc/petroleum ether to yield 6.01 g (90%) of a waxy solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37 (m, 6 H), 6.84 (m, 2 H), 6.72 (dd, J = 10.8, 17.6 Hz, 1 H), 5.76 (d, J = 17.6 Hz, 1 H), 5.26 (d, J = 10.8 Hz, 1 H), 5.01 (s, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.6, 137.4, 136.3, 136.0, 132.3, 127.6, 126.4, 116.7, 114.2, 113.1, 69.9. Anal. Calcd for $C_{15}H_{13}BrO$: C, 62.30; H, 4.53. Found: C, 62.38; H, 4.41.

(G0)PtCl$_2$. G0-Br (993.4 mg, 3.44 mmol) was dissolved in 30 mL of THF. The solution was cooled to −78 °C, and a freshly titrated 2.5 M solution of ^{n}BuLi in hexanes (1.37 mL, 3.43 mmol) was added dropwise. After stirring at −78 °C for 1 h, CuCl (372.0 mg, 3.76 mmol) was added, and the reaction mixture was stirred for an additional 15 min, followed by addition of 1,2-bis(dichlorophosphino)ethane (1.42 mL of a 0.6024 M solution in THF, 0.855 mmol). The resulting reaction mixture was stirred at −78 °C under Ar for 24 h. The solution was then transferred via cannula to a solution of 321.3 mg (0.859 mmol) of $(COD)PtCl_2$ in 20 mL of CH_2Cl_2. After stirring for 1 h at room temperature, the volatiles were removed in vacuo. The dark yellow residue was taken up in CH_2Cl_2 and filtered through Celite to remove any salts. Evaporation of the solvent followed by Et_2O wash of the residue, to remove any uncoupled dendron, resulted in **(G0)PtCl$_2$.** ^{31}P NMR (162 MHz, CD_2Cl_2): δ 40.4 (J_{P-Pt} = 3650 Hz). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.56 (dd, J = 8.8, 11.6 Hz, 8 H), 7.43 (dd, J = 8.0, 21.2 Hz, 16 H), 7.07 (d, J = 7.2 Hz, 8 H), 6.74 (dd, J = 10.8, 17.6 Hz, 4 H), 5.78 (d, J = 18.0 Hz, 4 H), 5.27 (d, J = 11.2 Hz, 4 H), 5.11 (s, 8 H), 2.22 (m, 4 H).

(G0)PtCO$_3$. (G0)PtCl$_2$ (1.0248 g, 0.859 mmol) was dissolved in 50 mL of wet CH_2Cl_2. Ag_2CO_3 (867.3 mg, 3.146 mmol) was added and the reaction mixture stirred at room temperature, protected from light. After 8 h, the reaction was complete by ^{31}P NMR, and the reaction mixture was filtered through Celite to remove AgCl. The solvent was removed in vacuo to afford 732.2 mg (72%) of a dark brown powder, which was taken on without further purification to the next step. ^{31}P NMR (162 MHz, CD_2Cl_2): δ 30.1 (J_{P-Pt} = 3522 Hz). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.75 (dd, J = 8.8, 11.6 Hz, 8 H), 7.39 (m, 16 H), 7.01 (d, J = 7.2 Hz, 8 H), 6.71 (dd, J = 10.4, 17.6 Hz, 4 H),

(49) (a) Gugger, P.; Limmer, S. O.; Watson, A. A.; Willis, A. C.; Wild, S. B. *Inorg. Chem.* **1993**, *32*, 5692−5696. (b) Brunkan, N. M.; White, P. S.; Gagné, M. R. *Angew. Chem., Int. Ed.* **1998**, *37*, 1579−1582.

(50) Cramer, E.; Percec, V. *J. Poly Sci., A: Polym. Chem.* **1990**, *28*, 3029−46.

5.77 (dd, J = 0.4, 17.6 Hz, 4 H), 5.26 (dd, J = 0.4, 10.4 Hz, 4 H), 5.04 (s, 8 H), 2.38 (m, 4 H).

(G0)Pt(*S*-BINOL). (G0)PtCO$_3$ (732.2 mg, 0.619 mmol) and *S*-BINOL (187.4 mg, 0.655 mmol) were dissolved in 40 mL of CH_2Cl_2. After 4 h the reaction was complete by ^{31}P NMR, and the solvent was removed in vacuo. The brown solid was washed three times with Et_2O to remove free BINOL. After drying in vacuo the brown product was obtained in 94% yield (822.4 mg). ^{31}P NMR (121.5 MHz, CD_2Cl_2): δ 26.3 (J_{P-Pt} = 3660 Hz). ^{1}H NMR (300 MHz, CD_2Cl_2): δ 7.88 (m, 4 H), 7.75 (m, 4 H), 7.46 (m, 20 H), 7.29 (t, J = 9.3 Hz, 2 H), 7.15 (t, J = 14.7 Hz, 2 H), 7.02 (m, 8 H), 6.82 (m, 6 H), 6.58 (d, J = 8.7 Hz, 2 H), 5.84 (dd, J = 18.0, 19.8 Hz, 4 H), 5.33 (m, 4 H), 5.15 (s, 4 H), 4.98 (s, 4 H), 2.12 (m, 4 H). ^{13}C NMR (75.5 MHz, CD_2Cl_2): δ 162.5, 161.9, 153.8, 138.0, 137.8, 136.7, 136.4, 136.3, 135.8, 135.7, 135.2, 134.5, 129.2, 128.9, 128.2, 128.1, 127.6, 126.8, 126.7, 126.1, 125.4, 125.0, 124.7, 121.4, 120.5, 118.2, 115.8, 115.6, 114.5, 114.4, 70.2, 70.1, 27.5.

P-(G0). Metallomonomer **(G0)Pt(*S*-BINOL)** (137.4 mg, 97.69 μmol), AIBN (12.9 mg, 78.56 μmol), EDMA (1368.5 mg, 6904 μmol), and chlorobenzene (1497.4 mg) were combined in a 20 mL scintillation vial under N_2 and sealed with a Teflon-lined cap. The vial was heated to 60 °C for 24 h, yielding a hard, transparent, brown polymer. After Soxhlet extraction with CH_2Cl_2 for 6 h and drying in vacuo at 50 °C for 12 h, 1.4772 g of **P-(G0)** (62.56 μmol of Pt/g of polymer) was obtained.

G1-Br. G1-benzyl bromide (3.0017 g, 6.88 mmol),[28] 4-bromophenol (1.2549 g, 7.25 mmol), K_2CO_3 (1.9999 g, 14.46 mmol), 18-crown-6 ether (387.4 mg, 1.46 mmol), and tetrabutylammonium iodide (138.8 mg, 0.376 mmol) were combined in 50 mL of dry acetone and heated to reflux for 17 h. The reaction mixture was cooled to room temperature and filtered. The filtrate was evaporated and the resulting residue taken up in Et_2O, extracted twice with H_2O, dried over $MgSO_4$, filtered, and evaporated to a yellow oil. After purification by column chromatography (silica gel, 5:1 hexanes/EtOAc) 3.374 g (93%) of an extremely viscous oil was obtained. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39 (m, 10 H), 6.80 (m, 2 H), 6.72 (dd, J = 10.8, 17.6 Hz, 2 H), 6.63 (d, J = 2.0 Hz, 2 H), 6.54 (t, J = 2.4 Hz, 1 H), 5.76 (dd, J = 0.4, 17.6 Hz, 2 H), 5.26 (d, J = 10.8, 2 H), 5.01 (s, 4 H), 4.95 (s, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.1, 157.7, 139.0, 137.4, 136.4, 136.2, 132.2, 127.7, 126.4, 116.7, 114.1, 113.1, 106.2, 101.6, 70.0, 69.8.

(G1)PtCl$_2$. G1-Br (1.5227 g, 2.88 mmol) was dissolved in 30 mL of THF. The solution was cooled to −78 °C, and a freshly titrated 2.5 M solution of ^{n}BuLi in hexanes (1.15 mL, 2.875 mmol) was added dropwise. After stirring at −78 °C for 1 h, CuCl (320.0 mg, 3.23 mmol) was added, and the reaction mixture was stirred for an additional 15 min, followed by addition of 1,2-bis(dichlorophosphino)ethane (1.18 mL of a 0.6024 M solution in THF, 0.7108 mmol). The resulting reaction mixture was stirred at −78 °C under Ar for 24 h. The solution was then transferred via cannula to a solution of 266.3 mg (0.7117 mmol) of (COD)$PtCl_2$ in 20 mL of CH_2Cl_2. After stirring for 1 h at room temperature, the volatiles were removed in vacuo. The brown residue was taken up in CH_2Cl_2 and filtered through Celite to remove any salts. Evaporation of the solvent followed by Et_2O wash of the residue, to remove any uncoupled dendron, resulted in 1.5281 g (98%) of **(G1)-PtCl$_2$**. ^{31}P NMR (162 MHz, CD_2Cl_2): δ 40.4 (J_{P-Pt} = 3665 Hz). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.75 (dd, J = 8.8, 11.6 Hz, 4 H), 7.44−6.56 (series of multiplets, 64 H), 5.77 (m, 8 H), 5.26 (m, 8 H), 5.08−4.98 (overlapping singlets, 24 H), 2.48 (m, 4 H).

(G1)PtCO$_3$. (G1)PtCl$_2$ (1.5281 g, 0.712 mmol) was dissolved in 50 mL of wet CH_2Cl_2. Ag_2CO_3 (710.5 mg, 2.577 mmol) was added and the reaction mixture stirred at room temperature, protected from light. After 8 h, the reaction was complete by ^{31}P NMR, and the reaction mixture was filtered through Celite to remove AgCl. The solvent was removed in vacuo to afford 1.3114 g (86%) of a dark brown powder, which was taken on without further purification to the next step. ^{31}P NMR (162 MHz, CD_2Cl_2): δ 30.4 (J_{P-Pt} = 3532 Hz). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.74 (dd, J = 8.4, 11.2 Hz, 4 H), 7.45−6.55 (series of multiplets, 64 H), 5.78 (m, 8 H), 5.26 (m, 8 H), 5.04−4.95 (overlapping singlets, 24 H), 2.25 (m, 4 H).

(G1)Pt(*S*-BINOL). (G1)PtCO$_3$ (1.3114 g, 0.614 mmol) and *S*-BINOL (176.8 mg, 0.617 mmol) were dissolved in 40 mL of CH_2Cl_2. After 3 h the reaction was complete by ^{31}P NMR, and the solvent was removed in vacuo. The dark brown solid was washed three times with Et_2O to remove free BINOL. After drying in vacuo the dark brown product was obtained in 79% yield (1.1492 g). ^{31}P NMR (121.5 MHz, CD_2Cl_2): δ 26.7 (J_{P-Pt} = 3687 Hz). ^{1}H NMR (300 MHz, CD_2Cl_2): δ 7.89−7.67 (m, 8 H), 7.56−6.56 (series of multiplets, 72 H), 5.80 (m, 8 H), 5.29 (m, 8 H), 5.11−4.94 (overlapping singlets, 24 H), 2.12 (m, 4 H). ^{13}C NMR (75.5 MHz, CD_2Cl_2): δ 162.3, 161.9, 160.6, 160.5, 153.6, 139.3, 139.2, 137.8, 137.7, 136.8, 136.7, 135.8, 135.7, 135.2, 134.3, 132.6, 130.5, 129.4, 129.0, 128.7, 128.2, 128.1, 126.7, 136.6, 124.9, 123.5, 121.4, 120.5, 118.8, 118.1, 115.8, 115.6, 114.3, 114.2, 113.4, 106.8, 106.7, 101.9, 70.3, 70.2, 70.1, 27.6.

P-(G1). Metallomonomer **(G1)Pt(*S*-BINOL)** (229.4 mg, 97.22 μmol), AIBN (11.8 mg, 71.95 μmol), EDMA (1267.2 mg, 6393 μmol), and chlorobenzene (1.4996 g) were combined in a 20 mL scintillation vial under N_2 and sealed with a Teflon-lined cap. The vial was heated to 60 °C for 24 h, yielding a hard, transparent, dark brown polymer. After Soxhlet extraction with CH_2Cl_2 for 6 h and drying in vacuo at 50 °C for 12 h, 1.4748 g of **P-(G1)** (62.67 μmol of Pt/g of polymer) was obtained.

G0-Cl-Br. 4-Vinylbenzyl chloride (580 μL, 4.12 mmol), 4-bromo-2-chlorophenol (867.0 mg, 4.15 mmol), K_2CO_3 (874.9 mg, 6.33 mmol), 18-crown-6 ether (222.1 mg, 0.840 mmol), and tetrabutylammonium iodide (78.3 mg, 0.212 mmol) were combined in 30 mL of dry acetone and heated to reflux for 16 h. The reaction mixture was cooled to room temperature and filtered. The filtrate was evaporated and the resulting residue taken up in Et_2O, extracted twice with H_2O, dried over $MgSO_4$, filtered, and evaporated to a white solid. After purification through a plug of silica gel (1:1 hexanes/EtOAc) 1.1876 g (89%) of a waxy white solid was obtained. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51 (d, J = 2.5 Hz, 1 H), 7.40 (m, 4 H), 7.26 (dd, J = 2.4, 8.7 Hz, 1 H), 6.79 (d, J = 8.8 Hz, 1 H), 6.72 (dd, J = 10.8, 17.6 Hz, 1 H), 5.76 (d, J = 17.6 Hz, 1 H), 5.27 (d, J = 10.8, 1 H), 5.09 (s, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.3, 137.4, 136.3, 135.4, 132.7, 130.4, 127.3, 126.4, 124.3, 115.2, 114.2, 112.9, 70.7. Anal. Calcd for $C_{15}H_{12}BrClO$: C, 55.67; H, 3.74. Found: C, 55.70; H, 3.69.

(G0-Cl)PtCl$_2$. G0-Cl-Br (493.7 mg, 1.526 mmol) was dissolved in 20 mL of THF. The solution was cooled to −78 °C, and a freshly titrated 2.5 M solution of ^{n}BuLi in hexanes (600 μL, 1.500 mmol) was added dropwise. After stirring at −78 °C for 1 h, CuCl (193.6 mg, 1.956 mmol) was added and the reaction mixture was stirred for an additional 15 min, followed by addition of 1,2-bis(dichlorophosphino)ethane (630 μL of a 0.6024 M solution in THF, 0.3795 mmol). The resulting reaction mixture was stirred at −78 °C under Ar for 24 h. The solution was then transferred via cannula to a solution of 142.5 mg (0.381 mmol) of (COD)$PtCl_2$ in 20 mL of CH_2Cl_2. After stirring for 1 h at room temperature, the volatiles were removed in vacuo. The yellow residue was taken up in CH_2Cl_2 and filtered through Celite to remove any salts. Evaporation of the solvent followed by Et_2O wash of the residue, to remove any uncoupled dendron, resulted in 564.1 mg (99%) of **(G0-Cl)PtCl$_2$.** ^{31}P NMR (162 MHz, CD_2Cl_2): δ 39.1 (J_{P-Pt} = 3633 Hz). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.80 (m, 4 H), 7.71 (dd, J = 2.0, 11.6 Hz, 4 H), 7.43 (m, 16 H), 7.12 (dd, J = 2.0, 11.6 Hz, 4 H), 6.75 (dd, J = 10.8, 17.6 Hz, 4 H), 5.79 (d, J = 17.6 Hz, 4 H), 5.28 (d, J = 10.8 Hz, 4 H), 5.20 (s, 8 H), 2.28 (m, 4 H).

(G0-Cl)PtCO$_3$. (G0-Cl)PtCl$_2$ (564.1 mg, 0.4238 mmol) was dissolved in 20 mL of wet CH_2Cl_2. Ag_2CO_3 (463.2 mg, 1.679 mmol) was added and the reaction mixture stirred at room temperature, protected from light. After 4 h, the reaction was complete by ^{31}P NMR, and the reaction mixture was filtered through Celite to remove AgCl. The solvent was removed in vacuo to afford 475.6 mg (85%) of a dark yellow powder, which was taken on without further purification to the next step. ^{31}P NMR (162 MHz, CD_2Cl_2): δ 31.1 (J_{P-Pt} = 3528 Hz). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.80 (m, 4 H), 7.71 (dd, J = 1.6, 11.2 Hz, 4 H), 7.43 (m, 16 H), 7.05 (dd, J = 2.0, 8.8 Hz, 4 H), 6.72 (dd, J = 8.0, 11.2 Hz, 4 H), 5.77 (dd, J = 0.4, 17.6 Hz, 4 H), 5.27 (d, J = 10.8 Hz, 4 H), 5.12 (s, 8 H), 2.45 (m, 4 H).

(G0-Cl)Pt(*S*-BINOL). (G0-Cl)PtCO$_3$ (475.6 mg, 0.360 mmol) and *S*-BINOL (103.4 mg, 0.362 mmol) were dissolved in 20 mL of CH_2Cl_2. After 4 h the reaction was complete by ^{31}P NMR, and the solvent was removed in vacuo. The dark yellow solid was washed three times with Et_2O to remove free BINOL. After drying in vacuo the dark yellow product was obtained in 91% yield (504.5 mg). ^{31}P NMR (121.5 MHz, CD_2Cl_2): δ 25.1 (J_{P-Pt} = 3644 Hz). ^{1}H NMR (300 MHz, CD_2Cl_2): δ 8.01 (m, 2 H), 7.75 (m, 8 H), 7.55 (m, 10 H), 7.42 (m, 8 H), 7.16 (t, J = 6.9 Hz, 2 H), 6.99 (m, 6 H), 6.88 (d, J = 9.6 Hz, 2 H), 6.77 (m, 6 H), 5.83 (m, 4 H), 5.33 (m, 4 H), 5.23 (s, 4 H), 5.04 (s, 4 H), 2.13 (m, 4 H). ^{13}C NMR (75.5 MHz, CD_2Cl_2): δ 162.0, 157.5, 157.4, 138.1, 138.0, 136.6, 135.8, 135.6, 135.0, 134.9, 134.5, 134.4, 132.9, 129.2, 129.1, 128.4, 128.0, 127.9, 127.8, 127.1, 126.9, 126.7, 125.9, 125.4, 124.9, 124.3, 124.0, 121.6, 120.9, 119.0, 114.7, 114.6, 114.5, 114.1, 71.1, 71.0, 27.1.

P-(G0-Cl). Metallomonomer **(G0-Cl)Pt(*S*-BINOL)** (76.2 mg, 49.30 μmol), AIBN (5.7 mg, 34.7 μmol), EDMA (677.5 mg, 3418 μmol), and chlorobenzene (768.5 mg) were combined in a 20 mL scintillation vial under N_2 and sealed with a Teflon-lined cap. The vial was heated to 60 °C for 24 h, yielding a hard, transparent, yellow polymer. After Soxhlet extraction with CH_2Cl_2 for 6 h and drying in vacuo at 50 °C for 12 h, 724.9 mg of **P-(G0-Cl)** (63.09 μmol of Pt/g of polymer) was obtained.

G1-Cl-Br. G1-benzyl bromide (1.7400 g, 3.99 mmol),[28] 4-bromo-2-chlorophenol (844.7 mg, 4.07 mmol), K_2CO_3 (860.5 mg, 6.23 mmol), 18-crown-6 ether (220.9 mg, 0.836 mmol), and tetrabutylammonium iodide (90.1 mg, 0.244 mmol) were combined in 40 mL of dry acetone and heated to reflux for 21 h. The reaction mixture was cooled to room temperature and filtered. The filtrate was evaporated and the resulting residue taken up in Et_2O, extracted twice with H_2O, dried over $MgSO_4$, filtered, and evaporated to a pale yellow oil. After purification by column chromatography (silica gel, 2:1 hexanes/EtOAc) 1.8939 g (85%) of an extremely viscous oil was obtained. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.49 (d, J = 2.4 Hz, 1 H), 7.36 (m, 8 H), 7.21 (d, J = 2.0 Hz, 2 H), 6.72 (m, 2 H), 6.64 (d, J = 1.6 Hz, 2 H), 6.54 (br s, 1 H), 5.75 (d, J = 17.6 Hz, 2 H), 5.25 (d, J = 10.8 Hz, 2 H), 5.04 (s, 2 H), 5.01 (s, 4 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.1, 153.3, 138.5, 137.3, 136.4, 136.2, 132.7, 130.4, 127.7, 126.4, 124.3, 115.2, 114.1, 112.9, 105.8, 101.7, 70.7, 69.8.

(G1-Cl)PtCl$_2$. G1-Cl-Br (1.0993 g, 1.958 mmol) was dissolved in 25 mL of THF. The solution was cooled to −78 °C, and a freshly titrated 2.33 M solution of ^{n}BuLi in hexanes (850 μL, 1.981 mmol) was added dropwise. After stirring at −78 °C for 1 h, CuCl (215.8 mg, 2.180 mmol) was added and the reaction mixture was stirred for an additional 15 min, followed by addition of 1,2-bis(dichlorophosphino)ethane (800 μL of a 0.6024 M solution in THF, 0.4819 mmol). The resulting reaction mixture was stirred at −78 °C under Ar for 24 h. The solution was then transferred via cannula to a solution of 181.3 mg (0.4845 mmol) of (COD)PtCl$_2$ in 20 mL of CH_2Cl_2. After stirring for 1 h at room temperature, the volatiles were removed in vacuo. The yellow residue was taken up in CH_2Cl_2 and filtered through Celite to remove any salts. Evaporation of the solvent followed by Et_2O wash of the residue, to remove any uncoupled dendron, resulted in 929.1 mg (83%) of **(G1-Cl)PtCl$_2$.** ^{31}P NMR (162 MHz, CD_2Cl_2): δ 39.8 (J_{P-Pt} = 3631 Hz). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.79 (m, 8 H), 7.45−7.14 (m, 32 H), 7.10 (d, J = 8.4 Hz, 4 H), 6.77−6.59 (m, 20 H), 5.78 (d, J = 17.6 Hz, 8 H), 5.25 (d, J = 10.8 Hz, 8 H), 5.13 (s, 8 H), 5.09 (s, 16 H), 2.31 (m, 4 H).

(G1-Cl)PtCO$_3$. (G1-Cl)PtCl$_2$ (929.1 mg, 0.407 mmol) was dissolved in 30 mL of wet CH_2Cl_2. Ag_2CO_3 (425.2 mg, 1.542 mmol) was added and the reaction mixture stirred at room temperature, protected from light. After 4 h, the reaction was complete by ^{31}P NMR, and the reaction mixture was filtered through Celite to remove AgCl. The solvent was removed in vacuo to afford 877.2 mg (95%) of a dark yellow powder, which was taken on without further purification to the next step. ^{31}P NMR (162 MHz, CD_2Cl_2): δ 31.2 (J_{P-Pt} = 3531 Hz). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.79 (t, J = 11.2 Hz, 4 H), 7.69 (d, J = 9.6 Hz, 4 H), 7.40 (m, 32 H), 7.06 (d, J = 8.0 Hz, 4 H), 6.76−6.56 (m, 20 H), 5.77 (d, J = 17.6 Hz, 8 H), 5.26 (d, J = 10.8 Hz, 8 H), 5.10 (s, 8 H), 5.01 (s, 16 H), 2.39 (m, 4 H).

(G1-Cl)Pt(*S*-BINOL). (G1-Cl)PtCO$_3$ (877.2 mg, 0.386 mmol) and *S*-BINOL (112.6 mg, 0.394 mmol) were dissolved in 30 mL of CH_2Cl_2. After 4 h the reaction was complete by ^{31}P NMR, and the solvent was removed in vacuo. The dark yellow solid was washed three times with Et_2O to remove free BINOL. After drying in vacuo the dark yellow product was obtained in 93% yield (900.6 mg). ^{31}P NMR (121.5 MHz, CD_2Cl_2): δ 25.5 (J_{P-Pt} = 3666 Hz). ^{1}H NMR (300 MHz, CD_2Cl_2): δ 8.08 (m, 2 H), 7.80−7.60 (m, 8 H), 7.44−7.17 (m, 38 H), 7.02 (m, 6 H), 6.79−6.57 (m, 22 H), 5.81 (d, J = 14.4 Hz, 8 H), 5.30 (m, 8 H), 5.18−5.02 (overlapping singlets, 24 H), 2.19 (m, 4 H). ^{13}C NMR (75.5 MHz, CD_2Cl_2): δ 161.7, 160.5, 160.4, 157.3, 157.2, 153.6, 138.6, 138.5, 137.8, 137.7, 136.7, 135.8, 135.3, 134.9, 134.6, 134.4, 132.8, 130.6, 130.4, 129.3, 129.1, 128.5, 128.2, 128.1, 127.9, 126.7, 126.6, 125.8, 125.4, 124.9, 124.4, 124.0, 123.4, 121.7, 120.8, 118.9, 114.3, 114.2, 113.6, 106.5, 106.4, 102.1, 71.1, 70.9, 70.1, 70.0, 27.2.

P-(G1-Cl). Metallomonomer **(G1-Cl)Pt(*S*-BINOL)** (163.0 mg, 65.33 μmol), AIBN (7.0 mg, 42.6 μmol), EDMA (837.3 mg, 4224 μmol), and chlorobenzene (999.5 mg) were combined in a 20 mL scintillation vial under N_2 and sealed with a Teflon-lined cap. The vial was heated to 60 °C for 24 h, yielding a hard, transparent, dark yellow polymer. After Soxhlet extraction with CH_2Cl_2 for 6 h and drying in vacuo at 50 °C for 12 h, 947.4 mg of **P-(G1-Cl)** (63.04 μmol of Pt/g of polymer) was obtained.

G0-Cl$_2$-Br. 4-Vinylbenzyl chloride (600 μL, 4.26 mmol), 4-bromo-2,6-dichlorophenol (1.0429 g, 4.29 mmol), K_2CO_3 (890.3 mg, 6.44 mmol), 18-crown-6 ether (234.7 mg, 0.888 mmol), and tetrabutylammonium iodide (80.8 mg, 0.219 mmol) were combined in 30 mL of dry acetone and heated to reflux for 16 h. The reaction mixture was cooled to room temperature and filtered. The filtrate was evaporated and the resulting residue taken up in Et_2O, extracted twice with H_2O, dried over $MgSO_4$, filtered, and evaporated to a white solid. After purification through a plug of silica gel (1:1 hexanes/EtOAc) 1.3471 g (88%) of a waxy white solid was obtained. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44 (m, 6 H), 6.72 (dd, J = 10.8, 17.6 Hz, 1 H), 5.77 (dd, J = 0.8, 17.6 Hz, 1 H), 5.27 (dd, J = 0.4, 10.8, 1 H), 5.00 (s, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.5, 137.8, 136.4, 135.3, 131.6, 130.6, 128.7, 126.3, 116.6, 114.3, 74.8. Anal. Calcd for $C_{15}H_{11}BrCl_2O$: C, 50.32; H, 3.10. Found: C, 50.36; H, 2.94.

(G0-Cl$_2$)PtCl$_2$. G0-Cl$_2$-Br (494.2 mg, 1.377 mmol) was dissolved in 20 mL of THF. The solution was cooled to −78 °C, and a freshly titrated 2.5 M solution of ^{n}BuLi in hexanes (550 μL, 1.375 mmol) was added dropwise. After stirring at −78 °C for 1 h, CuCl (162.5 mg, 1.642 mmol) was added and the reaction mixture was stirred for an additional 15 min, followed by addition of 1,2-bis(dichlorophosphino)ethane (570 μL of a 0.6024 M solution in THF, 0.3434 mmol). The resulting reaction mixture was stirred at −78 °C under Ar for 24 h. The

solution was then transferred via cannula to a solution of 128.7 mg (0.344 mmol) of $(COD)PtCl_2$ in 20 mL of CH_2Cl_2. After stirring for 1 h at room temperature, the volatiles were removed in vacuo. The yellow residue was taken up in CH_2Cl_2 and filtered through Celite to remove any salts. Evaporation of the solvent followed by Et_2O wash of the residue, to remove any uncoupled dendron, resulted in 488.0 mg (97%) of **(G0-Cl$_2$)PtCl$_2$.** ^{31}P NMR (162 MHz, CD_2Cl_2): δ 40.0 (J_{P-Pt} = 3605 Hz). ^1H NMR (400 MHz, CD_2Cl_2): δ 7.82 (d, J = 12.0 Hz, 8 H), 7.49 (m, 16 H), 6.75 (dd, J = 10.8, 17.6 Hz, 4 H), 5.80 (dd, J = 0.4, 17.6 Hz, 4 H), 5.29 (dd, J = 0.4, 10.8 Hz, 4 H), 5.13 (s, 8 H), 2.39 (m, 4 H).

(G0-Cl$_2$)PtCO$_3$. (G0-Cl$_2$)PtCl$_2$ (488.0 mg, 0.332 mmol) was dissolved in 20 mL of wet CH_2Cl_2. Ag_2CO_3 (384.5 mg, 1.395 mmol) was added and the reaction mixture stirred at room temperature, protected from light. After 4 h, the reaction was complete by ^{31}P NMR, and the reaction mixture was filtered through Celite to remove AgCl. The solvent was removed in vacuo to afford 460.7 mg (95%) of a dark yellow powder, which was taken on without further purification to the next step. ^{31}P NMR (162 MHz, CD_2Cl_2): δ 33.3 (J_{P-Pt} = 3530 Hz). ^1H NMR (400 MHz, CD_2Cl_2): δ 7.86 (d, J = 12.4 Hz, 8 H), 7.44 (m, 16 H), 6.73 (dd, J = 10.8, 17.6 Hz, 4 H), 5.78 (d, J = 17.6 Hz, 4 H), 5.27 (d, J = 10.8 Hz, 4 H), 5.05 (s, 8 H), 2.66 (m, 4 H).

(G0-Cl$_2$)Pt(*S*-BINOL). (G0-Cl$_2$)PtCO$_3$ (460.7 mg, 0.316 mmol) and *S*-BINOL (91.0 mg, 0.318 mmol) were dissolved in 20 mL of CH_2Cl_2. After 8 h the reaction was complete by ^{31}P NMR, and the solvent was removed in vacuo. The yellow solid was washed three times with Et_2O to remove free BINOL. After drying in vacuo the yellow product was obtained in 85% yield (450.6 mg). ^{31}P NMR (121.5 MHz, CD_2Cl_2): δ 25.0 (J_{P-Pt} = 3611 Hz). ^1H NMR (300 MHz, CD_2Cl_2): δ 7.89 (dd, J = 4.8, 12.0 Hz, 8 H), 7.80 (d, J = 8.0 Hz, 2 H), 7.72 (d, J = 8.8 Hz, 2 H), 7.55 (m, 8 H), 7.44 (m, 8 H), 7.18 (t, J = 6.8 Hz, 2 H), 7.06 (t, J = 8.4 Hz, 2 H), 6.98 (d, J = 8.8 Hz, 2 H), 6.92 (d, J = 8.4 Hz, 2 H), 6.77 (m, 4 H), 5.81 (dd, J = 17.6, 25.6 Hz, 4 H), 5.25 (dd, J = 10.8, 21.6 Hz, 4 H), 5.22 (s, 4 H), 5.03 (d, J = 2.0 Hz, 4 H), 2.45 (m, 2 H), 2.10 (m, 2 H). ^{13}C NMR (75.5 MHz, CD_2Cl_2): δ 161.1, 155.2, 154.9, 138.5, 138.3, 136.7, 135.9, 135.7, 135.6, 134.6, 133.2, 131.5, 131.4, 129.4, 129.2, 128.2, 128.1, 126.7, 126.6, 125.4, 125.3, 125.2, 124.8, 124.0, 122.0, 114.8, 114.6, 75.7, 75.5, 26.7.[51]

P-(G0-Cl$_2$). Metallomonomer **(G0-Cl$_2$)Pt(*S*-BINOL)** (84.9 mg, 50.46 μmol), AIBN (5.5 mg, 33.49 μmol), EDMA (669.1 mg, 3376 μmol), and chlorobenzene (752.9 mg) were combined in a 20 mL scintillation vial under N_2 and sealed with a Teflon-lined cap. The vial was heated to 60 °C for 24 h, yielding a hard, transparent, yellow polymer. After Soxhlet extraction with CH_2Cl_2 for 6 h and drying in vacuo at 50 °C for 12 h, 726.7 mg of **P-(G0-Cl$_2$)** (64.66 μmol of Pt/g of polymer) was obtained.

G1-Cl$_2$-Br. G1-benzyl bromide (1.7870 g, 4.10 mmol),[28] 4-bromo-2,6-dichlorophenol (1.0167 g, 4.18 mmol), K_2CO_3 (926.1 mg, 6.70 mmol), 18-crown-6 ether (223.1 mg, 0.844 mmol), and tetrabutylammonium iodide (94.6 mg, 0.256 mmol) were combined in 40 mL of dry acetone and heated to reflux for 21 h. The reaction mixture was cooled to room temperature and filtered. The filtrate was evaporated and the resulting residue taken up in Et_2O, extracted twice with H_2O, dried over $MgSO_4$, filtered, and evaporated to a white solid. After purification by column chromatography (silica gel, 2:1 hexanes/EtOAc) 2.4114 g (98%) of a waxy white powder was obtained. ^1H NMR (400 MHz, $CDCl_3$): δ 7.44 (m, 10 H), 6.83 (d, J = 2.0 Hz, 2 H), 6.76 (dd, J = 10.8, 17.6 Hz, 1 H), 6.64 (t, J = 2.0 Hz, 2 H), 5.80 (dd, J = 0.4, 17.6 Hz, 2 H), 5.30 (d, J = 10.8 Hz, 2 H), 5.06 (s, 4 H), 4.97 (s, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.9, 150.3, 138.1, 137.2, 136.3, 136.2, 131.5, 130.5, 127.6, 126.3, 116.6, 114.0, 107.2, 102.1, 74.6, 69.7. Anal. Calcd for $C_{31}H_{25}BrCl_2O_3$: C, 62.44; H, 4.23. Found: C, 62.49; H, 4.24.

(G1-Cl$_2$)PtCl$_2$. G1-Cl$_2$-Br (1.0054 g, 1.687 mmol) was dissolved in 20 mL of THF. The solution was cooled to −78 °C, and a freshly titrated 2.33 M solution of ^{n}BuLi in hexanes (725 μL, 1.689 mmol) was added dropwise. After stirring at −78 °C for 1 h, CuCl (196.1 mg, 1.981 mmol) was added and the reaction mixture was stirred for an additional 15 min, followed by addition of 1,2-bis(dichlorophosphino)ethane (700 μL of a 0.6024 M solution in THF, 0.4217 mmol). The resulting reaction mixture was stirred at −78 °C under Ar for 24 h. The solution was then transferred via cannula to a solution of 158.8 mg (0.4244 mmol) of $(COD)PtCl_2$ in 20 mL of CH_2Cl_2. After stirring for 1 h at room temperature, the volatiles were removed in vacuo. The yellow residue was taken up in CH_2Cl_2 and filtered through Celite to remove any salts. Evaporation of the solvent followed by Et_2O wash of the residue, to remove any uncoupled dendron, resulted in 876.4 mg (86%) of **(G1-Cl$_2$)PtCl$_2$.** ^{31}P NMR (162 MHz, CD_2Cl_2): δ 40.7 (J_{P-Pt} = 3616 Hz). ^1H NMR (400 MHz, CD_2Cl_2): δ 7.88 (d, J = 12.0 Hz, 8 H), 7.43 (m, 32 H), 6.82 (d, J = 2.0 Hz, 8 H), 6.76 (dd, J = 11.2, 17.6 Hz, 8 H), 6.64 (s, 4 H), 5.80 (d, J = 17.6 Hz, 8 H), 5.28 (d, J = 10.8 Hz, 8 H), 5.07 (br s, 24 H), 2.42 (m, 4 H).

(G1-Cl$_2$)PtCO$_3$. (G1-Cl$_2$)PtCl$_2$ (876.4 mg, 0.362 mmol) was dissolved in 30 mL of wet CH_2Cl_2. Ag_2CO_3 (380.3 mg, 1.379 mmol) was added and the reaction mixture stirred at room temperature, protected from light. After 4 h, the reaction was complete by ^{31}P NMR, and the reaction mixture was filtered through Celite to remove AgCl. The solvent was removed in vacuo to afford 779.8 mg (89%) of a dark yellow powder, which was taken on without further purification to the next step. ^{31}P NMR (162 MHz, CD_2Cl_2): δ 33.3 (J_{P-Pt} = 3523 Hz). ^1H NMR (400 MHz, CD_2Cl_2): δ 7.86 (d, J = 12.0 Hz, 8 H), 7.42 (m, 32 H), 6.77 (d, J = 2.4 Hz, 8 H), 6.72 (m, 8 H), 6.59 (t, J = 2.0 Hz, 4 H), 5.78 (dd, J = 0.8, 17.6 Hz, 8 H), 5.26 (dd, J = 0.8, 10.8 Hz, 8 H), 5.03 (br s, 24 H), 2.60 (m, 4 H).

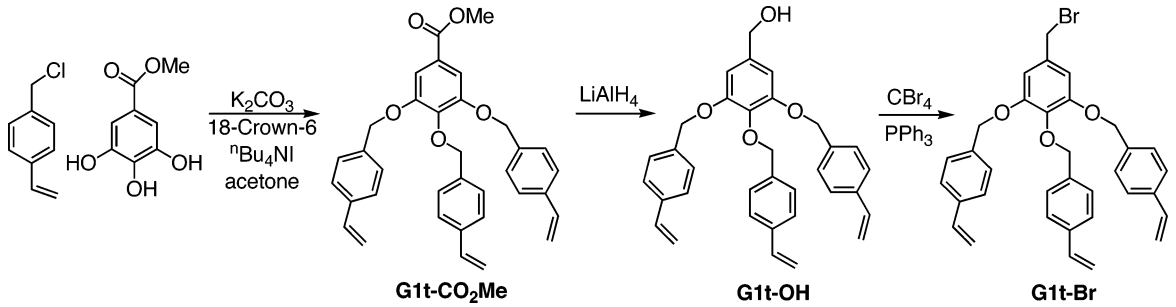
(G1-Cl$_2$)Pt(*S*-BINOL). (G1-Cl$_2$)PtCO$_3$ (779.8 mg, 0.324 mmol) and *S*-BINOL (94.0 mg, 0.329 mmol) were dissolved in 30 mL of CH_2Cl_2. After 8 h the reaction was complete by ^{31}P NMR, and the solvent was removed in vacuo. The dark yellow solid was washed three times with Et_2O to remove free BINOL. After drying in vacuo the dark yellow product was obtained in 95% yield (791.0 mg). ^{31}P NMR (121.5 MHz, CD_2Cl_2): δ 25.0 (J_{P-Pt} = 3613 Hz). ^1H NMR (300 MHz, CD_2Cl_2): δ 7.94 (dd, J = 6.4, 11.6 Hz, 8 H), 7.79 (dd, J = 8.0, 22.8 Hz, 4 H), 7.43 (m, 32 H), 7.20 (t, J = 7.2 Hz, 4 H), 7.08 (t, J = 7.2 Hz, 2 H), 7.03 (d, J = 8.8 Hz, 2 H), 6.96 (d, J = 8.8 Hz, 2 H), 6.89 (d, J = 2.0 Hz, 2 H), 6.74 (m, 14 H), 6.60 (br s, 2 H), 5.80 (dd, J = 8.4, 17.6 Hz, 8 H), 5.29 (dd, J = 6.8, 10.8 Hz, 8 H), 5.17 (s, 4 H), 5.12 (s, 8 H), 5.04 (s, 8 H), 4.97 (s, 4 H), 2.45 (m, 2 H), 2.11 (br s, 2 H). ^{13}C NMR (75.5 MHz, CD_2Cl_2): δ 161.0, 160.3, 160.2, 155.1, 154.8, 138.4, 138.3, 137.6, 137.5, 136.7, 136.6, 125.8, 134.5, 133.1, 131.4, 131.3, 129.6, 129.3, 128.6, 128.1, 128.0, 127.8, 127.2, 126.6, 126.5, 125.3, 125.1, 124.8, 124.7, 123.9, 122.0, 114.2, 114.1, 107.8, 107.6, 102.5, 102.4, 75.6, 75.4, 10.2, 70.1, 26.6.[51]

P-(G1-Cl$_2$). Metallomonomer **(G1-Cl$_2$)Pt(*S*-BINOL)** (170.8 mg, 64.87 μmol), AIBN (7.8 mg, 47.50 μmol), EDMA (831.3 mg, 4194 μmol), and chlorobenzene (1.0065 g) were combined in a 20 mL scintillation vial under N_2 and sealed with a Teflon-lined cap. The vial was heated to 60 °C for 24 h, yielding a hard, transparent, dark yellow polymer. After Soxhlet extraction with CH_2Cl_2 for 6 h and drying in vacuo at 50 °C for 12 h, 971.4 mg of **P-(G1-Cl$_2$)** (62.49 μmol of Pt/g of polymer) was obtained.

G2-Cl$_2$-Br. G2-benzyl bromide (2.6155 g, 2.87 mmol),[28] 4-bromo-2,6-dichlorophenol (714.0 mg, 2.94 mmol), K_2CO_3 (729.9 mg, 5.28 mmol), 18-crown-6 ether (154.8 mg, 0.586 mmol), and tetrabutylammonium iodide (57.9 mg, 0.157 mmol) were combined in 60 mL of dry acetone and heated to reflux for 21 h. The reaction mixture was cooled to room temperature

(51) Not all aromatic ^{13}C resonances were observed.

Chart 2



and filtered. The filtrate was evaporated and the resulting residue taken up in CH_2Cl_2, extracted twice with H_2O, dried over $MgSO_4$, filtered, and evaporated to a white foamy solid. After purification by column chromatography (silica gel, 2:1 CH_2Cl_2/hexanes) 2.885 g (94%) of a white foam was obtained. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41 (m, 18 H), 6.78 (m, 10 H), 6.64 (t, J = 2.1 Hz, 1 H), 6.61 (t, J = 2.1 Hz, 2 H), 5.80 (d, J = 17.7 Hz, 4 H), 5.30 (d, J = 11.1 Hz, 4 H), 5.04 (s, 8 H), 5.03 (s, 4 H), 4.97 (s, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.2, 160.0, 150.5, 139.4, 138.3, 137.4, 136.5, 136.4, 131.7, 130.7, 127.7, 126.5, 116.8, 114.2, 107.4, 106.4, 102.3, 101.7, 75.0, 70.1, 69.9.

(G2-Cl$_2$)PtCl$_2$. G2-Cl$_2$-Br (2.6348 g, 2.46 mmol) was dissolved in 50 mL of THF. The solution was cooled to −78 °C and a freshly titrated 2.5 M solution of ^{n}BuLi in hexanes (985 μL, 2.46 mmol) was added dropwise. After stirring at −78 °C for 1 h, CuCl (286.4 mg, 2.89 mmol) was added and the reaction mixture was stirred for an additional 15 min, followed by addition of 1,2-bis(dichlorophosphino)ethane (1019 μL of a 0.6024 M solution in THF, 0.6138 mmol). The resulting reaction mixture was stirred at −78 °C under Ar for 24 h. The solution was then transferred via cannula to a solution of 231.9 mg (0.6198 mmol) of (COD)$PtCl_2$ in 40 mL of CH_2Cl_2. After stirring for 1 h at room temperature, the volatiles were removed in vacuo. The yellow-brown residue was taken up in CH_2Cl_2 and filtered through Celite to remove any salts. Evaporation of the solvent resulted in 2.6972 g (102%) of crude **(G2-Cl$_2$)PtCl$_2$**, which was carried on without purification. ^{1}H NMR analysis showed product along with uncoupled G2-dendron; however only one phosphorus-containing species was present. ^{31}P NMR (162 MHz, CD_2Cl_2): δ 40.6 (J_{P-Pt} = 3600 Hz). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.84 (d, J = 12.0 Hz, 8 H), 7.39 (m, 64 H), 6.81−6.56 (series of multiplets, 52 H), 5.77 (d, J = 17.6 Hz, 16 H), 5.26 (d, J = 10.8 Hz, 16 H), 5.02 (m, 56 H), 2.35 (m, 4 H).

(G2-Cl$_2$)PtCO$_3$. (G2-Cl$_2$)PtCl$_2$ (2.6972 g, 0.6238 mmol) was dissolved in 30 mL of wet CH_2Cl_2. Ag_2CO_3 (633.5 mg, 2.298 mmol) was added and the reaction mixture stirred at room temperature, protected from light. After 7 h, the reaction was complete by ^{31}P NMR, and the reaction mixture was filtered through Celite to remove AgCl. The solvent was removed in vacuo to afford 2.4355 g (91%) of a yellow-brown powder, which was taken on without further purification to the next step. ^{31}P NMR (162 MHz, CD_2Cl_2): δ 33.0 (J_{P-Pt} = 3526 Hz). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.80 (d, J = 12.0 Hz, 8 H), 7.39 (m, 64 H), 6.82−6.66 (series of multiplets, 36 H), 6.60−6.55 (m, 16 H), 5.76 (d, J = 17.6 Hz, 16 H), 5.25 (d, J = 10.8 Hz, 16 H), 5.01 (m, 56 H), 2.37 (m, 4 H).

(G2-Cl$_2$)Pt(*S*-BINOL). (G2-Cl$_2$)PtCO$_3$ (2.4355 mg, 0.5647 mmol) and *S*-BINOL (164.5 mg, 0.5752 mmol) were dissolved in 40 mL of CH_2Cl_2. After 6 h the reaction was complete by ^{31}P NMR, and the solvent was removed in vacuo. The yellow-brown solid was taken up in CH_2Cl_2 and precipitated with Et_2O three times to remove free BINOL and uncoupled G2-dendron. After drying in vacuo the yellow-brown product was obtained in 75% yield (1.9324 g). ^{31}P NMR (121.5 MHz, CD_2Cl_2): δ 25.0 (J_{P-Pt} = 3628 Hz). ^{1}H NMR (300 MHz, CD_2Cl_2): δ 7.90 (dd, J = 12.0, 13.8 Hz, 8 H), 7.74 (t, J = 9.3 Hz, 4 H), 7.38 (m, 70 H), 7.01 (d, J = 8.7 Hz, 2 H), 6.87 (m, 4 H), 6.82−6.64 (series of multiplets, 36 H), 6.54 (m, 12 H), 5.76 (d, J = 17.7 Hz, 16 H), 5.25 (d, J = 10.8 Hz, 16 H), 5.01 (m, 56 H), 2.34 (m, 2 H), 2.02 (m, 2 H). ^{13}C NMR (75.5 MHz, CD_2Cl_2): δ 161.1, 160.5, 160.4, 160.3, 160.2, 158.7, 158.1, 155.2, 154.8, 141.2, 139.8, 138.5, 138.4, 137.6, 136.8, 136.7, 136.2, 135.9, 135.5, 134.7, 133.1, 131.6, 131.4, 129.4, 128.8, 128.7, 128.5, 128.1, 127.8, 127.4, 126.7, 125.7, 125.3, 125.0, 124.8, 124.0, 122.1, 120.7, 114.3, 107.9, 107.7, 106.7, 106.6, 102.5, 101.8, 100.7, 75.7, 75.5, 70.3, 70.2, 70.1, 66.0, 26.6.

P-(G2-Cl$_2$). Metallomonomer **(G2-Cl$_2$)Pt(*S*-BINOL)** (295.9 mg, 65.21 μmol), AIBN (5.6 mg, 34.10 μmol), EDMA (714.2 mg, 3603 μmol), and chlorobenzene (1.0063 g) were combined in a 20 mL scintillation vial under N_2 and sealed with a Teflon-lined cap. The vial was heated to 60 °C for 24 h, yielding a hard, transparent, yellow-brown polymer. After Soxhlet extraction with CH_2Cl_2 for 6 h and drying in vacuo at 50 °C for 12 h, 975.9 mg of **P-(G2-Cl$_2$)** (62.41 μmol of Pt/g of polymer) was obtained. **G1t-CO$_2$Me.** 4-Vinylbenzyl chloride (12.0 mL, 85.15 mmol), methyl 3,4,5-trihydroxybenzoate (5.0067 g, 27.19 mmol), K_2CO_3 (15.76 g, 113.60 mmol), 18-crown-6 ether (2.1707 g, 8.21 mmol), and tetrabutylammonium iodide (1.0185 g, 2.76 mmol) were combined in 200 mL of dry acetone and heated to reflux for 42 h. The reaction mixture was cooled to room temperature and filtered. The filtrate was evaporated and the resulting residue taken up in CH_2Cl_2, extracted twice with H_2O, dried over $MgSO_4$, and filtered; the solvent evaporated to a pale pink solid to produce 12.93 g of **G1t-CO$_2$Me** (89%), which was carried on without purification to the next step. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41−7.24 (m, 14 H), 6.70 (m, 3 H), 5.73 (m, 3 H), 5.24 (m, 3 H), 5.09 (s, 4 H), 5.08 (s, 2 H), 3.86 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.5, 152.4, 142.1, 137.3, 137.2, 136.9, 136.5, 136.3, 136.0, 128.7, 127.7, 126.3, 125.9, 125.3, 114.0, 113.8, 108.9, 70.8, 70.5, 52.2.

G1t-OH. G1t-CO$_2$Me (14.02 g, 26.37 mmol) was dissolved in 200 mL of THF and slowly added to 1.54 g (40.58 mmol) of $LiAlH_4$ in 60 mL of THF at 0 °C. After warming to room temperature and stirring overnight the reaction was quenched with H_2O and extracted with Et_2O. The organic layer was dried over $MgSO_4$, filtered, and evaporated to a pink solid. After precipitation from CH_2Cl_2/hexanes, 8.07 g (61%) of **G1t-OH**, which was carried on without purification to the next step, was obtained. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40−7.24 (m, 12 H), 6.75−6.53 (m, 5 H), 5.74 (m, 3 H), 5.23 (m, 3 H), 5.06 (s, 4 H), 5.02 (s, 2 H), 5.54 (d, J = 4.8 Hz, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.8, 137.5, 137.4, 137.2, 137.0, 136.6, 136.5, 136.4, 128.8, 127.6, 126.3, 126.0, 114.0, 113.7, 106.2, 74.9, 70.8, 65.3.[51]

G1t-Br. G1t-OH (8.07 g, 16.01 mmol) was dissolved in 30 mL of THF and cooled to 0 °C. CBr_4 (8.02 g, 24.18 mmol) was added followed by 6.31 g (24.06 mmol) of PPh_3. The reaction was stirred at 0 °C for 30 min and then warmed to room temperature and stirred overnight. H_2O was added and the reaction mixture extracted with Et_2O. The organic layer was dried over $MgSO_4$, filtered, and evaporated to a yellow solid. After purification by column chromatography (silica gel, 2:1

CH_2Cl_2/hexanes → 1:1 CH_2Cl_2/hexanes) 4.03 g (33%) of a waxy white solid was obtained. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41−7.24 (m, 12 H), 6.76−6.66 (m, 5 H), 5.75 (m, 3 H), 5.25 (m, 3 H), 5.07 (s, 4 H), 5.02 (s, 2 H), 4.39 (s, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.8, 138.5, 137.3, 137.2, 137.1, 136.6, 136.4, 136.3, 133.1, 128.37, 127.6, 126.3, 136.0, 114.1, 113.7, 108.7, 74.9, 71.0, 34.2.

G1t-Cl_2-Br. G1t-Br (1.9965 g, 3.52 mmol), 4-bromo-2,6-dichlorophenol (873.9 mg, 3.60 mmol), K_2CO_3 (1.0724 g, 7.76 mmol), 18-crown-6 ether (191.4 mg, 0.724 mmol), and tetrabutylammonium iodide (67.1 mg, 0.182 mmol) were combined in 50 mL of dry acetone and heated to reflux for 21 h. The reaction mixture was cooled to room temperature and filtered. The filtrate was evaporated and the resulting residue taken up in CH_2Cl_2, extracted twice with H_2O, dried over $MgSO_4$, filtered, and evaporated to a white solid. After purification by column chromatography (silica gel, 3:1 CH_2Cl_2/hexanes) 2.3923 g (93%) of a foamy white solid was obtained. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43−7.24 (m, 14 H), 6.78−6.66 (m, 5 H), 5.74 (m, 3 H), 5.24 (m, 3 H), 5.09 (s, 4 H), 5.04 (s, 2 H), 4.88 (s, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.8, 150.3, 138.5, 137.3, 137.2, 137.1, 136.7, 136.5, 136.4, 131.6, 131.3, 130.6, 128.8, 127.6, 126.3, 126.0, 116.6, 114.0, 113.7, 108.2, 75.1, 74.9, 71.0. Anal. Calcd for $C_{40}H_{33}BrCl_2O_4$: C, 65.95; H, 4.57. Found: C, 65.71; H, 4.54.

(G1t-Cl_2)PtCl_2. G1t-Cl_2-Br (951.3 mg, 1.31 mmol) was dissolved in 25 mL of THF. The solution was cooled to −78 °C, and a freshly titrated 2.5 M solution of ^{n}BuLi in hexanes (522.5 μL, 1.31 mmol) was added dropwise. After stirring at −78 °C for 1 h, CuCl (160.0 mg, 1.62 mmol) was added and the reaction mixture was stirred for an additional 15 min, followed by addition of 1,2-bis(dichlorophosphino)ethane (540 μL of a 0.6024 M solution in THF, 0.3253 mmol). The resulting reaction mixture was stirred at −78 °C under Ar for 24 h. The solution was then transferred via cannula to a solution of 121.7 mg (0.3253 mmol) of (COD)PtCl_2 in 40 mL of CH_2Cl_2. After stirring for 1 h at room temperature, the volatiles were removed in vacuo. The yellow-brown residue was taken up in CH_2Cl_2 and filtered through Celite to remove any salts. Evaporation of the solvent resulted in 887.8 mg (92%) of crude **(G1t-Cl_2)PtCl_2**, which was carried on without purification. ^{31}P NMR (162 MHz, CD_2Cl_2): δ 41.0 (J_{P-Pt} = 3609 Hz). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.96 (d, J = 16.0 Hz, 4 H), 7.55−7.38 (m, 52 H), 6.96 (s, 8 H), 6.81 (m, 12 H), 5.85 (m, 12 H), 5.33 (m, 12 H), 5.16 (s, 16 H), 5.13−5.01 (m, 16 H), 2.53 (m, 4 H).

(G1t-Cl_2)PtCO_3. (G1t-Cl_2)PtCl_2 (877.8 mg, 0.301 mmol) was dissolved in 30 mL of wet CH_2Cl_2. Ag_2CO_3 (450.0 mg, 1.63 mmol) was added and the reaction mixture stirred at room temperature, protected from light. After 4 h, the reaction was complete by ^{31}P NMR, and the reaction mixture was filtered through Celite to remove AgCl. The solvent was removed in vacuo to afford 714.1 mg (81%) of a yellow-brown powder, which was taken on without further purification to the next step. ^{31}P NMR (162 MHz, CD_2Cl_2): δ 34.7 (J_{P-Pt} = 3526 Hz). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 8.16 (d, J = 11.2 Hz, 4 H), 7.63−7.54 (m, 52 H), 7.09 (d, J = 16.0 Hz, 8 H), 6.96 (m, 12 H), 6.00 (m, 12 H), 5.48 (br s, 12 H), 5.33−5.19 (m, 32 H), 2.91 (m, 4 H).

(G1t-Cl_2)Pt(*S*-BINOL). (G1t-Cl_2)PtCO_3 (714.1 mg, 0.2428 mmol) and *S*-BINOL (71.4 mg, 0.2497 mmol) were dissolved in 40 mL of CH_2Cl_2. After 4.5 h the reaction was complete by ^{31}P NMR, and the solvent was removed in vacuo. The yellow-brown solid was taken up in CH_2Cl_2 and precipitated with Et_2O three times to remove free BINOL and uncoupled G2-dendron. After drying in vacuo the yellow-brown product was obtained in 73% yield (562.1 mg). ^{31}P NMR (121.5 MHz, CD_2Cl_2): δ 25.2 (J_{P-Pt} = 3619 Hz). ^{1}H NMR (300 MHz, CD_2Cl_2): δ 7.97 (dd, J = 4.2, 11.7 Hz, 6 H), 7.83 (dd, J = 7.8, 15.6 Hz, 4 H), 7.52−7.37 (m, 52 H), 7.15−6.71 (series of multiplets, 26 H), 5.81 (m, 12 H), 5.31 (m, 12 H), 5.21−4.92 (overlapping singlets, 32 H), 2.51 (m, 2 H), 2.18 (m, 2 H). ^{13}C NMR (75.5 MHz, CD_2Cl_2): δ 161.1, 155.2, 154.9, 153.3, 153.1, 138.8, 138.6, 137.9, 137.8, 137.7, 137.6, 137.5, 137.0, 136.8, 125.9, 134.7, 133.2, 132.3, 131.8, 131.7, 131.6, 131.4, 130.0, 129.4, 129.3, 129.1, 129.0, 128.2, 128.1, 127.3, 126.7, 126.6, 126.4, 126.3, 125.8, 125.5, 125.4, 125.0, 124.9, 124.0, 122.2, 114.3, 114.2, 114.0, 113.9, 108.3, 108.2, 76.0, 75.9, 75.2, 75.1, 71.3, 71.2, 26.8.[51]

P-(G1t-Cl_2). Metallomonomer **(G1t-Cl_2)Pt(*S*-BINOL)** (158.0 mg, 49.91 μmol), AIBN (6.5 mg, 39.6 μmol), EDMA (662.0 mg, 3340 μmol), and chlorobenzene (819.5 mg) were combined in a 20 mL scintillation vial under N_2 and sealed with a Teflon-lined cap. The vial was heated to 60 °C for 24 h, yielding a hard, transparent, yellow-brown polymer. After Soxhlet extraction with CH_2Cl_2 for 6 h and drying in vacuo at 50 °C for 12 h, 791.4 mg of **P-(G1t-Cl_2)** (58.73 μmol of Pt/g of polymer) was obtained.

(Isopropenyldppe)PtCl_2. Isopropenyldppe (1.0446 g, 1.87 mmol) in 20 mL of CH_2Cl_2 was slowly added to a solution of (COD)PtCl_2 (703.6 mg, 1.88 mmol) in 25 mL of CH_2Cl_2. After stirring for 30 min the volatiles were removed in vacuo, and the white solid was recrystallized from CH_2Cl_2/hexanes to afford 638.3 mg (41%) of (isopropenyldppe)PtCl_2. ^{31}P NMR (121.5 MHz, $CDCl_3$): δ 40.4 (J_{P-Pt} = 3622 Hz). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.80 (dd, J = 8.1, 12.0 Hz, 8 H), 7.52 (dd, J = 2.1, 8.4 Hz, 8 H), 5.43 (s, 4 H), 5.18 (s, 4 H), 2.31 (m, 4 H), 2.13 (m, 12 H).

(Isopropenyldppe)Pt(*S*-BINOL) (3). *S*-BINOL (104.2 mg, 0.364 mmol) and NaO^{t}Bu (71.5 mg, 0.744 mmol) were dissolved in 5 mL of 1:1 THF and toluene. After stirring for 30 min the solution was transferred via cannula to a suspension of 299.8 mg (0.364 mmol) of (isopropenyldppe)PtCl_2 in 60 mL of chlorobenzene. The reaction mixture immediately turned yellow and after 1 h of stirring became homogeneous. The volatiles were removed in vacuo and the yellow solid triterated three times with 20 mL of dry toluene to remove residual *tert*-butyl alcohol. CH_2Cl_2 (50 mL) was added and filtered to remove the NaCl byproduct. Recrystallization from CH_2Cl_2/Et_2O afforded 256.9 mg (68%) of yellow crystals. ^{31}P NMR (121.5 MHz, CD_2Cl_2): δ 26.9 (J_{P-Pt} = 3638 Hz); ^{1}H NMR (300 MHz, CD_2Cl_2): δ 7.90 (dd, J = 8.4, 11.1 Hz, 4 H), 7.77 (m, 6 H), 7.55 (m, 10 H), 7.10 (m, 2 H), 6.96 (m, 2 H), 6.81 (d, J = 8.4 Hz, 2 H), 6.63 (d, J = 8.7 Hz, 2 H), 6.54 (br. s, 2 H), 5.42 (br s, 2 H), 5.28 (br s, 2 H), 5.16 (br s, 2 H), 2.20 (m, 10 H), 2.10 (s, 6 H). ^{13}C NMR (75.5 MHz, CD_2Cl_2): δ 162.6, 145.2, 144.9, 142.8, 135.8, 134.2, 133.2, 128.9, 127.9, 127.7, 127.5, 126.4, 126.2, 126.1, 125.7, 125.3, 125.0, 124.7, 121.4, 115.0, 114.7, 27.2, 21.8, 21.6.[51] Anal. Calcd for $C_{58}H_{52}O_2P_2Pt$: C, 67.11; H, 5.05. Found: C, 67.04; H, 5.05.

dppe Polymer (P-3). Metallomonomer **3** (100.5 mg, 96.81 μmol), AIBN (12.0 mg, 73.08 μmol), EDMA (1397.4 mg, 7050 μmol), and chlorobenzene (1.5033 g) were combined in a 20 mL scintillation vial under N_2 and sealed with a Teflon-lined cap. The vial was heated to 60 °C for 24 h, yielding a hard, transparent, yellow polymer. After Soxhlet extraction with CH_2Cl_2 for 6 h and drying in vacuo at 50 °C for 12 h, 1.49 g of **P-3** (62.34 μmol of Pt/g of polymer) was obtained.

Typical HCl Cleavage Experiment. P-(G1-Cl_2) (245.5 mg, 15.34 μmol of Pt) was suspended in 20 mL of CH_2Cl_2, and 10 drops of concentrated HCl(aq) was added. After 6 h of stirring at room temperature, the polymer was filtered from solution through a glass Soxhlet thimble. The filtrate was used for Soxhlet extraction for 12 h. The solvent was removed in vacuo, and the residue was dissolved in 1.931 mL of ^{i}PrOH. Quantitative HPLC analysis revealed that *S*-BINOL was removed from 67% of the Pt sites (22.4 min (*S*-BINOL)).

Typical Rebinding Experiment. P-(G1-Cl_2) (309.4 mg, 19.33 μmol of Pt), *rac*-Br_2BINOL (149.2 mg, 336.0 μmol), 3 mL of chlorobenzene, and 0.5 mL of water were added to a Schlenk tube under argon. The tube was sealed and placed in a 60 °C oil bath. After stirring at 60 °C for 12 h, the polymer was filtered from the hot solution through a glass Soxhlet thimble and extracted with the filtrate and additional CH_2Cl_2 for 12

h. The polymer was dried for 1 h under vacuum, then suspended in 20 mL of CH_2Cl_2, and 10 drops of concentrated HCl(aq) was added. After 6 h of stirring at room temperature, the polymer was again filtered from solution through a glass Soxhlet thimble. The filtrate was used for Soxhlet extraction for 16 h. The solvent was removed in vacuo and the residue was dissolved in a known amount of ^{i}PrOH for quantitative chiral HPLC analysis (22.4 min (*S*-BINOL), 27.7 min (*S*-Br_2-BINOL), 38.6 min (*R*-Br_2BINOL)).

Surface Area. Dinitrogen adsorption/desorption measurements were performed at 77.3 K on a Quantrachrome model Autosorb-1 porosimiter. Samples were degassed at 26 °C for 8 or 16 h prior to data collection. Surface area measurements utilized a six-point adsorption isotherm collected over 0.05−0.30 p/p_0 and were analyzed via the BET method.[52] Reported surface area values are reported on the adsorption isotherm.

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Supporting Information Available: HCl cleavage and rebinding data for the non-chlorinated and mono-chlorinated metallodendrimers. This material is available free of charge via the Internet at http://pubs.acs.org.

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