Rigidified Dendritic Structures for Imprinting Chiral Information

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Chiral, polymerizable P_2Pt(*S*-BINOL) metallodendrimers constructed with a rigid phenyl benzoate ester linkage were copolymerized into highly porous and cross-linked methacrylate-based polymers. The performance of these polymers with respect to BINOL exchange reaction enantioselectivities was compared to similar metallodendrimers constructed of more flexible benzyl ether repeat units. The increased rigidity of the ester linkage resulted in higher enantioselectivities for a BINOL/Br_2BINOL exchange reaction, though exact structure/selectivity relationships are difficult to establish. At elevated temperatures, BINOL loss is observed leading to the inactivation of sites, though it is the less selective, and therefore less hindered sites, that are preferentially deactivated. Enantiomeric ratios of up to 84:16 were observed for the substitution of P_2Pt(*S*-BINOL) with (±)-Br_2BINOL within the imprinted polymer site, which equals the best yet achieved.

Introduction

In recent years, chemists have attempted to synthesize functional polymers that rival the sophistication of the chemical systems found in nature. Molecularly imprinted polymers (MIPs)[1] are particularly suited to the task of imparting to traditional metal catalysts the outer-sphere control elements observed in a metalloenzyme. A molecularly imprinted polymer is formed when a template molecule is copolymerized into a highly cross-linked polymer matrix with a cross-linking monomer in the presence of a porogen. When the template is removed, a three-dimensional cavity is formed that is complementary to the template molecule in size, shape, and chemical functionality. The guiding notion is thus that this man-made cavity can be made similar to the active site in a metalloenzyme. The molecular recognition properties of these cavities have been utilized most successfully as chromatographic stationary phases,[2] but applications in sensors,[3] synthesis,[4] and catalysis[5,6] have also been demonstrated.

Because enzymes are unique molecular structures, built up of specific interactions between amino acids, the active site is spatially oriented in the protein cavity and each site is identical. This contrasts the case of molecularly imprinted active sites since each active site is constructed of a seemingly random collection of monomers under conditions that are heavily dependent on complex phase separations and heterogeneous reaction kinetics.[7] The ill-defined nature of matrix formation necessarily leads to a diversity of sites, each differing in the degree of encapsulation by the polymer matrix.[8] Some of the sites are situated on the surface with no surrounding polymer matrix, while other sites are formed with well-defined polymer cavities. Finally, some sites are completely surrounded by polymer and, thus, are prevented from interacting with substrate. Although good activities and selectivities are possible with MIP catalysts, this problem of site heterogeneity prevents MIPs from displaying the desirably high structure−activity correlation that one observes in metalloenzymes.[9] Another approach to achieving metalloenzyme-like active sites has been monomolecular imprinting where the active site is contained within an organic nanoparticle synthesized by the intramolecular cross-linking of a dendrimer.[10]

(1) (a) Whitcombe, M. J.; Vulfson, E. N. *Adv. Mater.* **2001**, *13*, 467−478. (b) Wulff, G. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1812−1833. (c) Sellergren, B.; Hall, A. J. In *Molecularly Imprinted Polymers*; Sellergren, B., Ed.; Elsevier: Amsterdam, 2001; pp 21−55.

(2) (a) Sellergren, B. *J. Chromatogr., A* **2001**, *906*, 227−252. (b) Andersson, L. I. *J. Chromatogr,. B* **2000**, *745*, 3−13. (c) Andersson, L. I.; Mosbach, K. *J. Chromatogr., A* **1990**, *516*, 323−331. (d) Buchmeiser, M. R. *J. Chromatogr., A* **2001**, *918*, 233−266.

(3) *Molecularly Imprinted Materials−Sensors and Other Devices*; Shea, K. J., Yan, M., Roberts, M. J., Eds.; Material Research Society Symposium Proceedings 723; Materials Research Society: Warrendale, PA, 2002.

(4) (a) Whitcombe, M. J.; Alexander, C.; Vulfson, E. N. *Synlett* **2000**, *6*, 911−923. (b) Brüggeman, O.; Haupt, K.; Ye, L.; Yilmaz, E.; Mosbach, K. *J. Chromatogr., A* **2000**, *889*, 15−24.

(5) For reviews see: (a) Wulff, G. *Chem. Rev.* **2002**, *102*, 1−27. (b) Tada, M.; Iwasawa, Y. *J. Mol. Catal.* **2003**, *199*, 115−137. (c) Alexander, C.; Davidson, L.; Hayes, W. *Tetrahedron* **2003**, *59*, 2025−2057. (d) Severin, K. *Curr. Opin. Chem. Biol.* **2000**, *4*, 710−714.

(6) (a) Liu, J.; Wulff, G. *J. Am. Chem. Soc.* **2004**, *126*, 7452−7453. (b) Svenson, J.; Zheng, N.; Nicholls, I. A. *J. Am. Chem. Soc.* **2004**, *126*, 8554−8560. (c) Visnjevski, A.; Yilmaz, E.; Brüggeman, O. *Appl, Catal., A* **2004**, *260*, 169−174. (d) Wendicke, S. B.; Burri, E.; Scopelliti, R.; Severin, K. *Organometallics* **2003**, *22*, 1894−1897. (e) Nestler, N.; Severin, K. *Org. Lett.* **2001**, *3*, 3907−3909. (f) Polborn, K.; Severin, K. *Chem. Eur. J.* **2000**, *6*, 4604−4611. (g) Cammidge, A. N.; Baines, N. J.; Bellingham, R. K. *Chem. Commun.* **1999**, *24*, 2588−2589. (h) Aït-Haddou, H.; Leeder, S. M.; Gagné, M. R. *Inorg. Chim. Acta* **2004**, *357*, 3854−3864. (i) Viton. F.; White, P. S.; Gagné, M. R. *Chem. Commun.* **2003**, *24*, 3040−3041. (j) Koh, J. H.; Larsen. A. O.; White, P. S.; Gagné, M. R. *Organometallics* **2002**, *21*, 7−9.

(7) Sherrington, D. C. *Chem. Commun.* **1998**, *21*, 2275−2286.

(8) Brunkan, N. M.; Gagné, M. R. *J. Am. Chem. Soc.* **2000**, *122*, 6217−6225.

(9) Carey, J. R.; Ma, S. K.; Pfister, T. D.; Garner, D. K.; Kim, H. K.; Abramite, J. A.; Wang, Z.; Guo, Z.; Lu, Y. *J. Am. Chem. Soc.* **2004**, *126*, 10812−10813.

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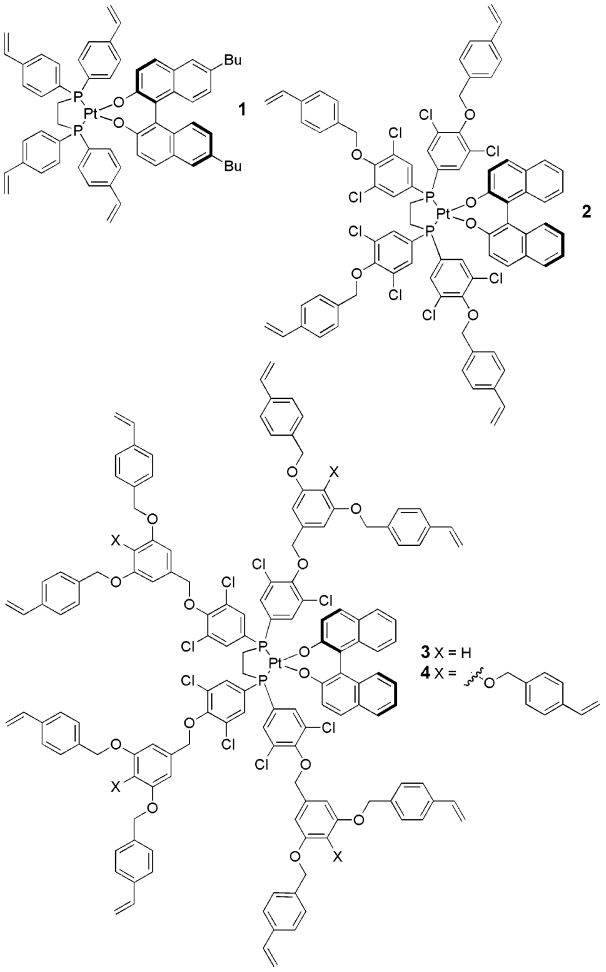
Scheme 1



MIPs previously produced in our lab from metallomonomer **1** (Scheme 1) contained a complex distribution of platinum active sites. The overall enantioselectivity of the polymer for the imprinted enantiomer of BINOL was 82:18, with some sites achieving selectivities of up to 97:3.[8] To achieve a polymer in which each site is similarly encapsulated by the polymer matrix, the environment directly surrounding the template molecule must be better controlled. To this end, our laboratory developed polymerizable, dendritic diphosphine ligands[11] with the expectation that the dendritic arms of the phosphine ligand would provide an interface to the bulk polymer that would be similar for each platinum atom.[12]

This strategy with metallodendrimers **2**, **3**, and **4** (Scheme 1) showed less variability in reactivity and selectivity as a function of temperature (cf. **1**), indicative of a more homogeneous distribution of sites; however, the overall selectivity of the dendritic MIP systems was lower than that of the nondendritic MIP. The source of the lower selectivity was thought to be the flexibility of the benzyl ether arms of the dendritic phosphine ligand,

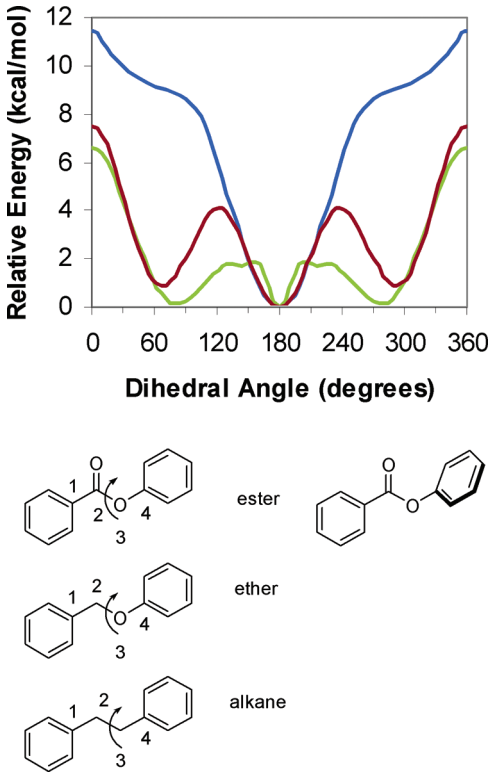


Figure 1. Bond rotation energy profiles for phenyl benzoate (blue), benzyl phenyl ether (green), and diphenylethane (red) vs $\phi_{1,2,3,4}$, along with the lowest energy conformation of phenyl benzoate (RHF-6-31G* as implemented in MacSpartan02).

which are consequently capable of adopting a large number of conformations during the imprinting process. This was postulated to lead to sites that, although constitutionally similar, were less selective by virtue of *conformational heterogeneity*. We hypothesized that increasing the rigidity of the dendritic arms might improve the fidelity of the imprint while retaining the site homogeneity and, thus, improve the observed drop in selectivity.

Results and Discussion

Conformational Analysis. An approach to achieving a more rigid template was arrived at by an analysis of rotational barriers. In alkanes and ethers, the barrier to rotation around a C−C or C−O bond is less than 5 kcal/mol, and there is only a slight preference for the anti conformer. In contrast, the C−O bond of an ester possesses partial double-bond character, which increases the barrier to rotation around the C−O bond (10−13 kcal/mol).[13] Figure 1 shows the rotational profiles of 1,2-diphenylethane, benzyl phenyl ether, and phenyl benzoate as a function of the dihedral angle defined by atoms 1, 2, 3, and 4 ($\phi_{1,2,3,4}$).[14] The barrier to rotation around the C−O bond in the ester is 11 kcal/mol, and at room temperature, the thermodynamic preference for the anti conformer is significant. In

(10) (a) Mertz, E.; Elmer, S. L.; Balija, A. M.; Zimmerman, S. C. *Tetrahedron* **2004**, *60*, 11191−11204. (b) Zimmerman, S. C.; Zharov, I.; Wendland, M. S.; Rakow, N. A.; Suslick, K. S. *J. Am. Chem. Soc.* **2004**, *125*, 13504−13518. (c) Zimmerman, S. C.; Lemcoff, N. G. *Chem. Commun.* **2004**, *1*, 5−14.

(11) Balaji, B. S.; Obora, Y.; Ohara, D.; Koide, S.; Tsuji, Y. *Organometallics* **2001**, *20*, 5342−5350.

(12) Becker, J. J.; Gagné, M. R. *Organometallics* **2003**, *22*, 4984−4998.

(13) Eliel, E. L.; Wilen, S. H.; Mahler, L. N. Conformation of Acyclic Molecules. *Stereochemistry of Organic Compounds*; John Wiley & Sons: New York, 1994; pp 597−624.

(14) The data were generated by driving the relevant dihedral angle in 10° increments with full optimization at each step (RHF-6-31G*) as implemented in Macspartan 2002.

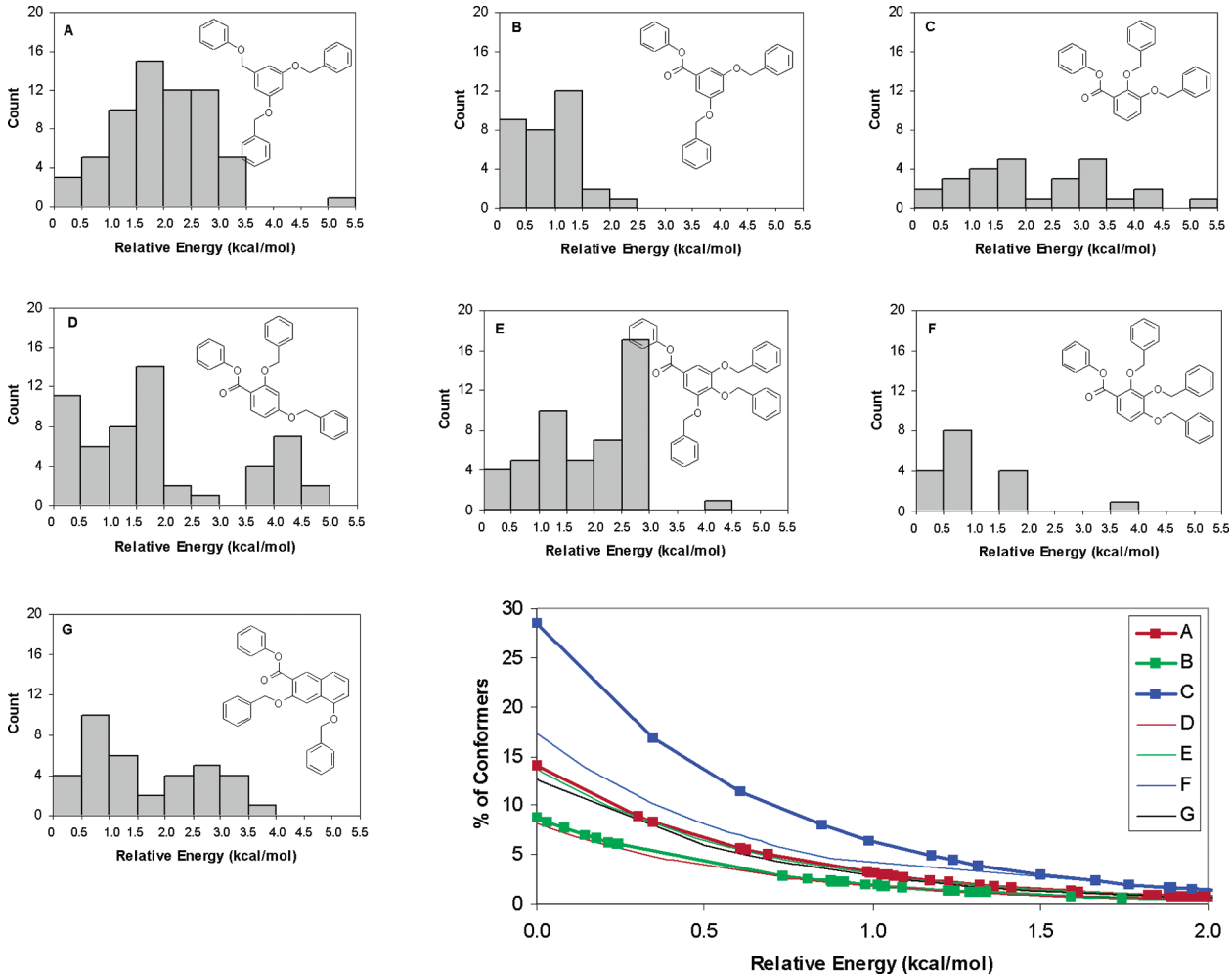


Figure 2. Histograms for dendritic structures showing the number of local minima (AM1) normalized to the global minimum (**A**−**G**), and the corresponding Boltzmann distribution at 60 °C for each histogram.

contrast, the ether has a lower barrier to rotation (∼7 kcal/mol) and a significantly wider range of accessible conformers within 2 kcal/mol of the energy minimum (60−300°). Additionally, the lowest energy conformer of the ester is further rigidified because it contains a phenyl ring locked into planarity with the ester group to preserve conjugation and an −OPh substituent that has a slight (∼2 kcal/mol) preference to be orthogonal to the plane of the ester. This analysis therefore suggested that templates with ester linkages should be significantly more rigid than templates with ether linkages. The rigidity of the ester linkage in the dendritic structure should serve to limit the conformational degrees of freedom of the dendritic phosphine ligand and thus improve the conformational homogeneity of the imprint.

To experimentally address the effect of increased rigidity in a metallomonomer imprint, we chose to replace the benzyl ether linkage in **2**, **3**, and **4** that was closest to the metal core. This was for two reasons: (1) ease of synthesis (vide infra) and (2) previous experiments showing the aryl(4-vinylbenzoate) ester linkage to be prone to hydrolysis.

To provide a semiquantitative measure of how such an ester for ether substitution would affect the conformational diversity, we performed a conformational analysis at the single dendron level, realizing that this approach would provide a simplistic but, perhaps, informative view. We hypothesized that a dendron with fewer low-energy conformers would provide a more effective imprint than a dendron with many such conformers.

The histograms in Figure 2 show the range of conformers for several dendritic fragments obtained from a semiempirical (AM1) Monte Carlo conformer search.[15] As expected, the substitution of an ester linkage for an ether linkage (**A** and **B**) reduced the total number of conformational minima, while simultaneously shifting the distribution of energies closer to the global minimum. Changing the dendron substitution pattern from the symmetric 3,5-disubstituted structure in **B** to the 2,3-disubstituted in **C** results in a much wider distribution of energies, though the total number of local minima is smaller. This wider distribution in energy could indicate that this set of structures is more diverse and thus would provide a less effective imprint. The 2,4-disubstituted dendron (**D**) is more similar to **B** than **C**; however, there are a number of higher energy conformations that become available. In the case of the trisubstituted dendrons **E** and **F**, the increase in steric

(15) The data were generated by first doing a Monte Carlo conformer distribution analysis with molecular mechanics (MMFF), keeping all minima within 10 kcal/mol of the global minimum. A semiempirical (AM1) geometry optimization of each local minimum was then carried out. The duplicate structures were removed from the data set, and each was normalized to the global minimum and plotted in histogram fashion (Macspartan 2002).

bulk caused by 2,3,4-trisubstitution results in a very narrow distribution of conformers, which must significantly affect the resulting imprint. The incorporation of a naphthalene repeat unit in **G** for the benzene repeat unit present in **B** broadens the distribution of conformers.

Although the pictorial representation of the energetic profiles is simplified by the use of the histograms shown in Figure 2, it must be stressed that the actual metallomonomers have four dendrons linked to a phosphine core, which not only multiplies the total number of conformations, but necessarily affects the relative energies of the conformers as they are forced to interact with each other and adopt compact, dense structures. This is especially true for the *ortho*-substituted cases (**C**, **D**, **F**, and **G**).

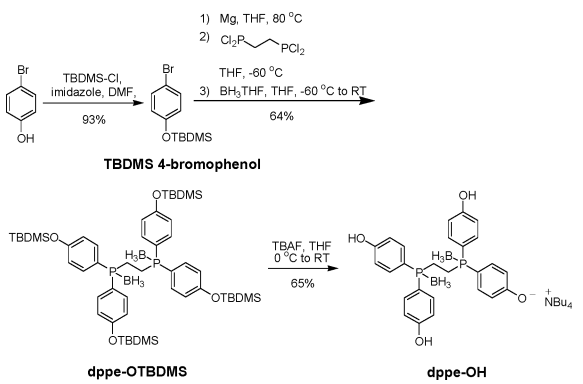
A histogram plot of energy and count is also not an accurate representation of the conformer populations since lower energy structures will naturally be more populated than those of higher energy. To continue the semiquantitative analysis of conformation, we calculated, based on a Boltzmann distribution at 60 °C, the polymerization temperature, the contribution of each of the conformers to the ensemble (Figure 2).[16] For the ether, even though there are many conformers within 5.5 kcal/mol of the global minimum (**A**), the three conformers within 0.5 kcal/mol comprise 31% of the Boltzmann distribution, and the eight conformers within 1.0 kcal/mol comprise 54% (red line, Figure 2). The ester linkage (**B**) results in a Boltzmann distribution (green line, Figure 2) wherein 62% of the conformers (9) lie within 0.5 kcal/mol of the global minimum and 81% (17) lie within 1.0 kcal/mol. When the substitution pattern of the ester dendron is changed from 3,5-disubstituted to 2,3-disubstituted (blue line, Figure 2), 45% of the conformers (2) lie within 0.5 kcal/mol and 71% (5) lie within 1.0 kcal/mol of the global minimum. These data clearly indicate a more complex structural picture than the histograms alone; steeper lines mean fewer contributing conformers.

The contrast between **A** and **B** was illuminating. Even though the ester dendron **B** contained fewer local minima than the ether dendron **A**, they tended to be closer in energy to the global minimum and, therefore, contributed more to the Boltzmann distribution (lower slope, more data points in the 0−0.5 kcal/mol range). The benzyl ether, by contrast, had many more available conformations, but they were further from the global minimum in energy, which minimized their population. Thus, the benzyl ether dendron may, in fact, be populated by fewer accessible conformers (higher slope), at least at this crude level of analysis.

The 2,3-disubstituted case (**C**), which has the fewest local minima in the low-energy region, has the highest slope of the cases shown in Figure 2. Of the three lowest energy structures (comprising 57% of the conformers), a superposition of the structures indicates that the polymerizable benzyl arms project in roughly the same region of space, a property that, a priori, might be expected to increase active site homogeneity.

Synthesis. The experimental approach to testing the key hypothesis was to synthesize a variety of closely related templates wherein a key ether linkage was replaced with an ester linkage and the substitution pattern of the dendron was varied. The necessary dendritic phosphine ligands were synthesized via a convergent approach[17] in which the phosphine core and dendritic arms were synthesized separately and then coupled through the ester linkage. This approach was particularly convenient in that a large variety of dendrons could be quickly and easily attached to the phosphine core. In contrast, the original synthesis of the benzyl ether metallomonomers (**2**, **3**, and **4**) coupled the dendron to the phosphine ligand though a sensitive P−C bond formation.[12]

Scheme 2



The synthesis of the hydroxy-functionalized phosphine core is shown in Scheme 2. Addition of the Grignard of 4-bromophenol *tert*-butyldimethylsilyl (TBDMS) ether to 1,2-bis(dichlorophosphino)ethane provided the desired diphosphine after borane protection (**dppe-OTBDMS**). The silyl ether protecting groups were then cleaved with tetrabutylammonium fluoride to give hydroxy-functionalized diphosphine ligand **dppe-OH** in moderate overall yield. Curiously, the functionalized phosphine was isolated with 1 equiv of tetrabutylammonium cation, which could not be removed by repeated precipitation. The absence of a ^{1}H NMR resonance for the phenol protons suggests that the product might be monoanionic wherein rapid proton exchange is occurring; it is depicted as such in Scheme 2.

The carboxylic acid-terminated dendrons were synthesized by reaction of vinyl benzyl chloride with the appropriate di- and trihydroxy benzoic acids or methyl benzoates using potassium carbonate, 18-crown-6 ether as a phase transfer agent, and a catalytic amount of tetrabutylammonium iodide in refluxing acetone.[17] The resultant dendritic esters were then hydrolyzed with potassium hydroxide in ethanol[18] or 2-propanol to reveal the desired carboxylic acid terminus after workup. Scheme 3 shows an example synthesis of dendron **G1-COOH** from 3,5-dihydroxy methyl benzoate, as well as the structures of the other dendrons synthesized in this manner (**G1(2,3)-COOH**, **G1(2,4)-COOH**, **G1t-COOH**, **G1t(2,3,4)-COOH**, and **G1n(3,5)-COOH**).

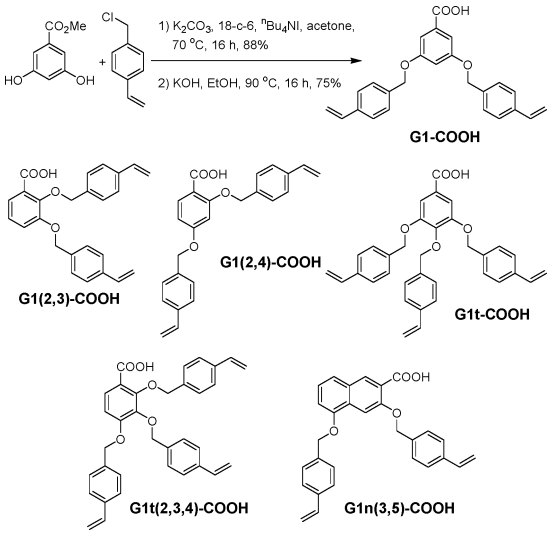
The diphosphine dendrons were then accessed by first utilizing a DCC (1,3-dicyclohexylcarbodiimide)-mediated

(16) Atkins, P. W. *Physical Chemistry*; W. H. Freeman and Company: New York, 1994; p 14. See Supporting Information for calculation details.

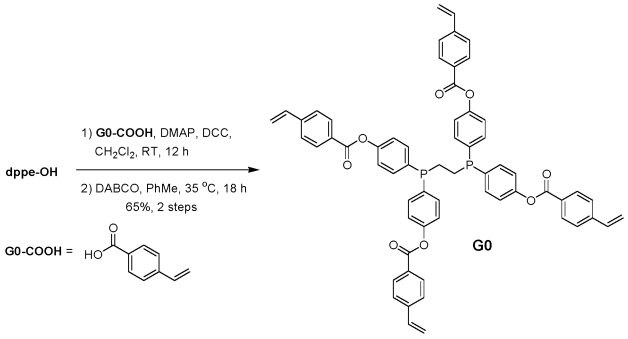
(17) (a) Grayson, S. M.; Fréchet, J. M. J. *Chem. Rev.* **2001**, *101*, 3819−3867. (b) Hawker, C. J.; Fréchet, J. M. J. *J. Am. Chem. Soc.* **1990**, *112*, 7638−7647.

(18) van Nunen, J. L. M.; Folmer, B. B. B.; Nolte, R. J. M. *J. Am. Chem. Soc.* **1997**, *119*, 283−291.

Scheme 3



Scheme 4



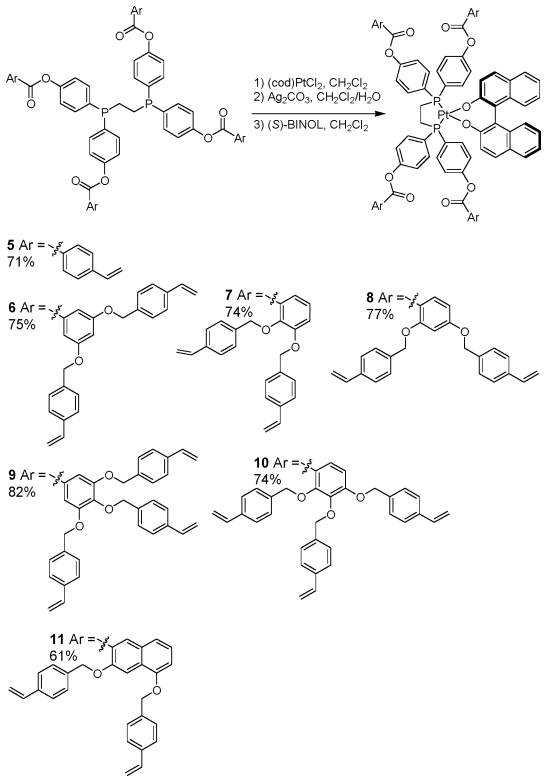
coupling of the acid and **dppe-OH** (the NBu_4^+ does not appear to interfere), followed by borane deprotection by treatment with 1,4-diazabicyclo[2.2.2]octane (DABCO). Other standard deprotection conditions (e.g., Et_2NH, morpholine, HBF_4) were incompatible with the ester linkage and/or the vinyl functionality. The resultant diphosphine ligands are not oxidized upon benchtop exposure to air. The dendrons shown in Scheme 3 as well as 4-vinylbenzoic acid (**G0-COOH**) were coupled to **dppe-OH** to form diphosphine ligands for use in MIPs (Scheme 4).

From the deprotected diphosphines, metallomonomers **5**−**11** (Scheme 5) were synthesized in three efficient steps from (1,4-cyclooctadiene)$PtCl_2$. First, the diphosphine ligands were coordinated to platinum to form the corresponding platinum dichloride in excellent yield. The platinum dichloride was then converted to the platinum carbonate by silver carbonate in wet dichloromethane,[19] followed by addition of (*S*)-BINOL to form the metallomonomer. Excess BINOL was removed by washing with diethyl ether, and the metallomonomers were isolated as yellow and brown powders in good overall yields.

The desired MIPs were synthesized from metallomonomers **5**−**11** by heating (60 °C) under nitrogen a solution of metallomonomer (1.5 mol %) and AIBN (1 mol %) in an equal volume of ethylene glycol dimethacrylate (97.5 mol %) and chlorobenzene. This composition

(19) Andrews, M. A.; Gould, G. L.; Klooster, W. T.; Koenig, K. S.; Voss, E. J. *Inorg. Chem.* **1996**, *35*, 5478−5483.

Scheme 5



was used in previous organometallic MIP experiments and is known to yield high surface area (460 m^2/g) materials.[20] The solutions gelled within 5 min, and after 24 h the polymerizations were complete, yielding yellow monolithic polymers. After polymerization, the polymers were washed with dichloromethane in a Soxhlet extractor for 6 h to remove chlorobenzene and then dried overnight under vacuum. The theoretical platinum content of these polymers was calculated to be 60−65 μmol Pt/g dry polymer.

Site Accessibility. The polymerization procedure caused a small amount of (*S*)-BINOL to be cleaved from the metallomonomers. This BINOL was recovered from the Soxhlet extraction filtrate and quantified by HPLC analysis. The results are collected in Figure 3 (white bars) and show that more BINOL loss occurs with the present metallomonomers than with the nondendritic

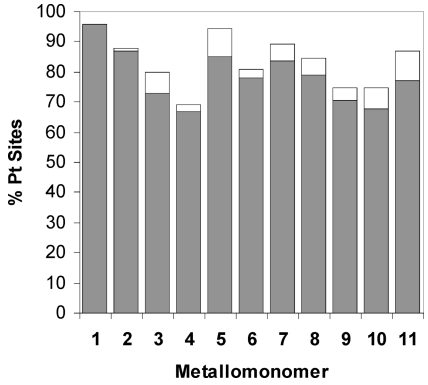
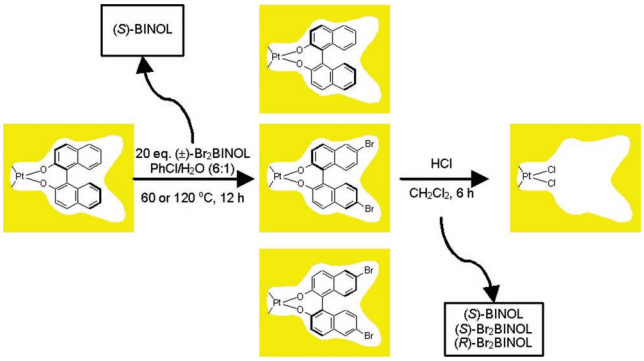


Figure 3. BINOL loss during polymerization (white bars) and site accessibility (gray bars) in MIPs expressed as a percentage of theoretical platinum sites. Each data point represents an average of three separate polymer preparations.

Scheme 6



metallomonomer **1**. Previous experiments had shown that the amount of BINOL loss at this stage could be correlated to the basicity of the diphosphine; more electron deficient ligands had less loss.[12] An ester moiety, in contrast to the original benzyl ether, possesses enough electron-withdrawing character to stabilize the metallodendrimer so that BINOL loss is limited to less than 10% of the platinum sites.

The total number of accessible sites in these polymers was quantified by adding concentrated hydrochloric acid to a suspension of the polymer in dichloromethane. This procedure cleaves the BINOL from the platinum and thus (after quantification) evaluates the degree of site availability or, perhaps more precisely, the number of sites with an available pathway for BINOL egress from the polymer interior (Figure 3, gray bars). The dendritic systems **2**−**11** all have fewer accessible sites than the nondendritic system presumably due to increased congestion around the metal center. As expected, there is a generation-dependent decrease in the number of accessible sites as shown by P-**5**, P-**6**, and P-**9** similar to the trend previously shown by P-**2**, P-**3**, and P-**4**.[12] Polymers synthesized from the trisubstituted dendrons (P-**4**, P-**9**, and P-**10**) show the lowest site accessibility, presumably due to their greater steric protection of the metal center, while polymers P-**2** and P-**5** have the largest percentage of accessible sites.

From the data we conclude that the replacement of an ether linkage with an ester linkage has little effect on the overall site accessibility of the MIPs. Substitution patterns of the dendrons also do not greatly affect the amount of BINOL cleaved, as evidenced by comparing P-**6**, P-**7**, and P-**8** as well as P-**9** and P-**10**.

Site Enantioselectivity. The selectivity of the platinum sites in the MIPs was studied by a BINOL/Br_2-BINOL exchange reaction (Scheme 6).[8,12] The polymer was treated with an excess (20 equiv relative to the theoretical platinum content of the polymer) of racemic Br_2BINOL ((±)-6,6′-dibromo-1,1′-bi-2-naphthol) in a 6:1 mixture of chlorobenzene and water at either 60 or 120 °C for 12 h. Those sites that are able to accommodate the associative exchange mechanism displaced the (*S*)-BINOL ligand with either (*S*)- or (*R*)-Br_2BINOL based on the selectivity imparted by the polymer surrounding the platinum site. Some sites were too hindered for BINOL exchange to occur and thus retained (*S*)-BINOL. The polymer was then washed for 16 h in a Soxhlet extractor to remove unreacted Br_2BINOL as well as the cleaved (*S*)-BINOL before treatment with hydrochloric acid to excise all BINOL species for quantification. The enantiomeric excess of the rebound Br_2BINOL proved to be a key metric for site characterization.

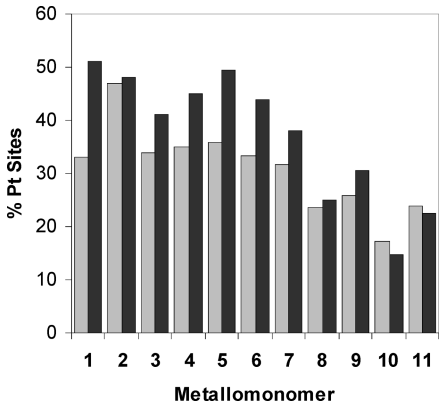


Figure 4. Percentage of total platinum sites that exchanged Br_2BINOL for (*S*)-BINOL at 60 °C (gray) and 120 °C (black). Each data point represents an average of three separate polymer preparations.

An ideal MIP, one that most closely resembles a homogeneous enzyme active site, should contain identical platinum sites that each react to exchange Br_2-BINOL at the same rate and with the same enantioselectivity. Because our MIPs have a heterogeneous distribution of sites, the reactivity and enantioselectivity of the sites vary with temperature, with the more open, less selective, sites reacting at lower temperatures.[8,12] We studied the BINOL/Br_2BINOL exchange reaction at two temperatures (60 and 120 °C) and assumed that the difference in the number of platinum sites to react and the enantiomeric excess of the rebound Br_2BINOL could be used to estimate the heterogeneity of the platinum sites. A large difference would indicate a wide site distribution, while conversely, a small variation would be most consistent with a narrow site distribution.

As shown in Figure 4, P-**1** synthesized from the nondendritic metallomonomer showed the expectedly large increase in the number of sites to react with Br_2-BINOL at 60 and 120 °C.[8] In contrast, the polymers prepared from dendritic metallomonomers tended to show much smaller reactivity changes with temperature. As the data show, the ester linkage substitution has no systematic effect on the differential reactivity at 60 and 120 °C (compare P-**2** with P-**5**, P-**3** with P-**6**, and P-**4** with P-**9**). Most notable were the metallomonomers with *ortho*-styryl substituents (**7**, **8**, **10**, and **11**), which tended to show diminished site accessibility and attenuated differences in reactivity between 60 and 120 °C, consistent with more hindered sites.

Unlike accessibility differences, the polymers prepared from ester dendritic metallomonomers **5**−**11** do, in general, show higher enantioselectivities for rebinding Br_2BINOL (Figure 5). These polymers however also show a larger increase in enantioselectivity with temperature than their ether counterparts, a phenomenon that previously we have ascribed to active site heterogeneity.

Site Deactivation. The observation that P-**10** and P-**11** had fewer sites rebind Br_2BINOL at 120 °C than at 60 °C, and yet had an increase in enantioselectivity,

(20) Santora, B. P.; Gagné, M. R. *Macromolecules* **2001**, *34*, 658–661.

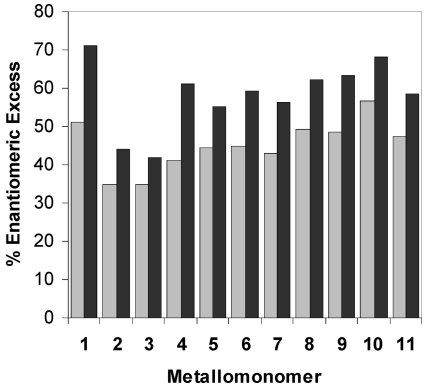


Figure 5. Enantiomeric excess of rebound Br_2BINOL at 60 °C (gray) and 120 °C (black). Each data point represents an average of three separate polymer preparations.

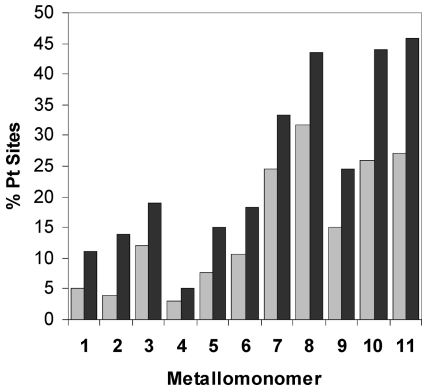


Figure 6. Percentage of platinum sites inactivated during rebinding at 60 °C (gray) and 120 °C (black). Each data point represents an average of three separate polymer preparations.

was most unusual and opposite of the normally observed trend. Equally confusing, but informative, was the fact that the amount of residual (*S*)-BINOL after the final cleavage dropped by 20% on going from 60 to 120 °C, this despite the lack of compensating bound Br_2BINOL at the higher temperature. Thus, it appears that some of the active sites became deactivated, i.e., lose (*S*)-BINOL but do not rebind Br_2BINOL. Since the enantiomeric excess of the rebound Br_2BINOL actually increased, the deactivated sites must therefore be those that are otherwise less selective for the imprinted BINOL enantiomer. In other words, *the less selective sites deactivate under the reaction conditions*.

The loss of active sites during the rebinding can be quantified by subtracting from the total number of accessible sites before thermolysis (Figure 3) the sum of Br_2BINOL and residual (*S*)-BINOL cleaved after the thermal exchange. As shown in Figure 6, each of the polymers had some loss of sites, but it was always larger at higher temperatures, especially for those metallomonomers with *ortho* substituents (**7**, **8**, **10**, and **11**).

In principle, this scenario should be testable by quantifying the amount of (*S*)-BINOL that is released during the Br_2BINOL exchange; however the excess Br_2-BINOL overwhelms the residual (*S*)-BINOL and the analysis is problematic. Instead, samples of P-**5** and P-**6** were exposed to the rebinding reaction conditions in the absence of Br_2BINOL (12 h at 120 °C in 6:1 chlorobenzene/water). The polymers were then washed in a Soxhlet extractor with dichloromethane, and the extract

Table 1. Site Deactivation in MIPs Expressed as a Percentage of Platinum Sites that Excised BINOL at 120 °C

	polymer[a]	
	P-**5**	P-**6**
accessible Pt Sites (%)[b]	87	81
BINOL lost (%)[c]	14	19
BINOL cleaved (%)[d]	74	62
total sites (%)[e]	88	80

[a] The data come from single experiments. [b] Before thermolysis. [c] Quantified by HPLC after thermolysis at 120 °C for 12 h. [e] BINOL lost + BINOL cleaved.

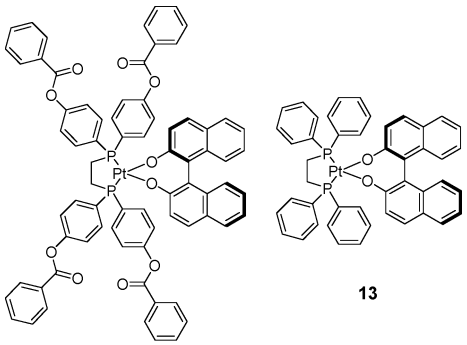
was quantitatively analyzed for (*S*)-BINOL by HPLC. A typical HCl cleavage experiment was conducted on the washed polymers, and the excised BINOL was quantified by HPLC. The results are summarized in Table 1. It was found that in P-**5** 14% of the platinum sites became inactive at 120 °C, while the number of "accessible" sites decreased from 87% to 74%. P-**6** experienced BINOL loss from 19% of platinum sites, and the site accessibility decreased from 81% to 62%. These figures are in agreement with the amount of BINOL lost from P-**5** and P-**6** under the standard Br_2BINOL exchange conditions (Figure 6) and are internally consistent with the number of sites that were accessible prior to thermolysis.

Thus, *thermolytic deactivation of the less selective sites* is sufficient to explain the trend of decreasing site accessibility coupled with increased enantioselectivity in the more hindered metallomonomers. We have no evidence that this reactivity pattern holds for the varied metallomonomers studied to date. Nevertheless, this possibility adds, unfortunately, contributes a significant uncertainty to our attempts to establish structure/activity/selectivity relationships for achieving further improvements. Equally uncertain is the intriguing possibility that such an effect could be used as a general strategy for increasing active site selectivity and homogeneity.

To further investigate the mechanism of BINOL loss at the rebinding conditions, we studied the thermolysis of **12**, a nonpolymerizable analogue of **5**. The reaction of this compound in a 6:1 mixture of chlorobenzene to water was monitored by phosphorus NMR. After 14 h at 120 °C, complete decomposition of the P_2Pt(BINOL) was observed. A mixture of unidentified products with ^{31}P chemical shifts ranging from 30 to 50 ppm was obtained along with platinum black.

Similar thermolysis of (dppe)Pt(*S*-BINOL), **13**, indicated a significantly reduced thermal sensitivity, as only a trace of **13** had decomposed (apparently to (dppe)-$PtCl_2$) after 14 h at 120 °C.[21] These results indicated that the compounds are indeed sensitive to solution thermolysis, but that this is significantly mitigated in the constrained environment of a rigid cross-linked polymer. Perhaps the more open sites, those most prone to deactivation, are those that are also flexible enough for decomposition (like solution).

(21) The possibility that platinum sites in the polymer were abstracting chlorine atoms from the chlorinated solvent during the rebinding process was considered; however, BINOL loss was still observed when P-**5** was heated at 110 °C for 12 h in a 6:1 mixture of toluene and water.



12 13

Summary

A number of MIPs were prepared from metallomonomers comprised of dendritic phosphine ligands with comparatively rigid ester linkages containing variable arrangements of polymerizable arms. The reactivity and enantioselectivity of these MIPs in a BINOL exchange reaction were investigated to determine which structural variables were key to achieving optimum selectivity and homogeneity. The data clearly showed that the rigidity of the ester linkage indeed increased the enantioselectivity over more flexible benzyl ether MIPs. Unfortunately, a mechanism for BINOL cleavage competes with the exchange process and results in inactive sites, making it impossible to rigorously characterize the homogeneity of sites contained within these MIPs based solely on reactivity and selectivity variations with temperature. Nevertheless, these systems once again show that it is possible to achieve enantiomer-selective reactivities in platinum MIPs where none is possible in solution (the dppe ligand is achiral). Significant challenges remain to realizing the potential of this approach.

Experimental Section

General Methods. Racemic Br_2BINOL,[22] (COD)$PtCl_2$,[23] G1-CO_2Me, and G1t-CO_2Me[12] were synthesized according to literature procedures. The platinum complexes P_2PtCl_2, P_2PtCO_3, and P_2Pt(BINOL) were synthesized by procedures similar to those published for dppe analogues.[8,24] All chemicals were purchased from Aldrich except 1,2-bis(dichlorophosphino)ethane (Strem) and *S*-BINOL (Kankyo Kagaku Center Co., Ltd., Japan) and used as received. Before use, acetone was distilled from $CaSO_4$. Tetrahydrofuran, dichloromethane, and toluene were passed through a column of activated alumina. Chlorobenzene was distilled from P_2O_5 and freeze−pump−thaw degassed before use in polymerizations, but was used as received for rebinding experiments. AIBN (2,2′-azobis(isobutyro)nitrile) was recrystallized from methanol, dried in vacuo, and stored under nitrogen at −35 °C. EDMA (ethylene glycol dimethacrylate) 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 nitrogen at −35 °C. Polymerizations were performed in an MBraun LabMaster 100 glovebox. Reactions performed under nitrogen 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 are referenced to the residual solvent peaks (^{1}H and ^{13}C NMR) or to an external standard (85% H_3PO_4, ^{31}P NMR). The dendritic P_2PtCl_2 compounds were not soluble enough in chloroform to allow carbon spectra to be recorded even overnight. Many of the carbon signals in **G1t-(2,3,4)** and the Pt(BINOL)s overlap, and therefore signals were not detected for all carbons in the compounds. Carbon spectra for phosphorus-containing compounds were recorded while decoupling both hydrogen and phosphorus nuclei. Carbon spectra for **dppe-OTBDMS** and **dppe-OH** are shown in the Supporting Information as evidence of purity because these compounds did not combust completely for elemental analysis (δ%C was repeatedly >10%). Microanalysis of the P_2Pt(BINOL) compounds was difficult because these compounds tend to retain traces of solvent.

HPLC analysis was performed on a Hewlett-Packard Series 1100 instrument, using a Daicel Chiralcel OD-H column (95% hexanes/5% ethanol, 0.8 mL/min flow rate). Chromatograms were recorded at wavelengths of 220, 232, 254, 289, and 333 nm and compared to a calibration curves to determine analyte concentration.

TBDMS 4-Bromophenol. A solution of 4-bromophenol (10.0 g, 57.8 mmol) and imidazole (5.9 g, 86.7 mmol) in 200 mL of dimethylformamide was cooled to 0 °C, and *tert*-butyldimethylsilyl chloride (TBDMS-Cl, 9.6 g, 63.6 mmol) was added. The solution was stirred for 12 h and allowed to warm to room temperature. A saturated aqueous solution of ammonium chloride (100 mL) was added, and the mixture was extracted with 200 mL of ethyl acetate. The ethyl acetate was washed with 100 mL of 0.5 M NaOH and with 100 mL of brine, dried over magnesium sulfate, and filtered. The solvent was removed in vacuo to give TBDMS 4-bromophenol (15.5 g, 93% yield). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.34 (d, J = 8.4 Hz, 2H), 6.74 (d, J = 8.4 Hz, 2H), 1.02 (s, 9H), 0.22 (s, 6H). ^{13}C NMR (100.6 MHz, $CDCl_3$, δ): 155.1, 132.6, 122.2, 113.9, 26.0, 18.5, −4.2. Anal. Calcd for $C_{12}H_{19}$BrOSi: C, 50.17; H, 6.67. Found: C, 50.02; H, 6.68.

dppe-OTBDMS. Magnesium turnings (2.0 g, 83.5 mmol) were flame dried inside a 100 mL Schlenk flask. The flask was cooled and 2.0 mL of THF was added, followed by 0.25 mL (4.3 mmol) of methyl iodide. The mixture was stirred for several minutes until cloudy. The liquid was removed by cannula, and the magnesium was rinsed three times with 2 mL of THF. A solution of 12.0 g (41.8 mmol) of TBDMS 4-bromophenol in 40 mL of THF was added to the magnesium, and the mixture was refluxed for 3 h. After cooling, the solution was filtered via cannula from the magnesium into a flame-dried 250 mL Schlenk flask. The solution was cooled to −50 °C, and a solution of 1.26 mL (8.35 mmol) of 1,2-bis(dichlorophosphino)ethane was added dropwise. The solution was stirred at −50 °C for 4 h before quenching with 2.0 mL of deoxygenated methanol. Borane−tetrahydrofuran complex (60 mL of a 1.0 M solution in tetrahydrofuran) was added, and the solution was allowed to warm to room temperature overnight. The volume of the solution was reduced in vacuo until a white solid appeared. Ethanol (25 mL) was added, and the mixture was stored at −26 °C overnight. The white solid was collected by vacuum filtration (5.1 g, 64% yield). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.45 (m, 8H), 6.84 (d, J = 8.4 Hz, 8H), 2.22 (br, 4H), 0.95 (s, 36H), 0.19 (s, 24H). ^{13}C NMR (75.5 MHz, $CDCl_3$, δ): 158.8, 133.9, 120.8, 120.1, 25.7, 20.3, −4.2. ^{31}P NMR (161.3 MHz, $CDCl_3$, δ): 15.5.

dppe-OH. dppe-OTBDMS (3.0 g, 3.17 mmol) was dissolved in 75 mL of THF and cooled to 0 °C. A solution of tetrabutylammonium fluoride (1.0 M in THF, 16 mL) was added dropwise. The solution was allowed to stir 16 h and warm to room temperature. A white precipitate formed. The volume of the solution was reduced in vacuo to 10 mL, and 25 mL of ethanol was added to further precipitate the product. The

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white solid was collected by vacuum filtration and dried in vacuo. The product contained 1 equiv of tetrabutylammonium ion that could not be removed by repeated precipitation (1.46 g, 64% yield). ^{1}H NMR (400 MHz, DMSO-d_6, δ): 7.25 (m, 8H), 6.70 (d, J = 8.4 Hz, 8 H), 3.17 (m, 8H), 2.00 (br, 4H), 1.55 (m, 8H), 1.31 (q, J = 7.2 Hz, 8H), 0.94 (t, J = 7.2 Hz, 12H). ^{13}C NMR (75.5 MHz, DMSO-d_6, δ): 164.9, 134.2, 117.8, 117.7, 114.5, 58.5, 24.0, 21.3, 20.1, 14.4. ^{31}P NMR (162.1 MHz, DMSO-d_6, δ): 13.1.

G0 (Method A). dppe-OH (0.25 g, 0.342 mmol), 4-vinylbenzoic acid (0.25 g, 1.71 mmol), and 4-(dimethylamino)-pyridine (0.13 g, 1.03 mmol) were dissolved in 40 mL of dichloromethane. 1,3-Dicyclohexylcarbodiimide (0.35 g, 1.71 mmol) was added, and the mixture was stirred for 16 h at room temperature under nitrogen. The reaction was then eluted through a pad of silica with 75 mL of ethyl acetate. After removal of the solvent in vacuo, methanol was added to the resultant oil to precipitate a solid. The solid was collected by vacuum filtration and rinsed with methanol and hexanes. The solid was dissolved along with 1,4-diazabicyclo[2.2.2]octane (0.15 g, 1.37 mmol) in 30 mL of toluene, and the solution was stirred at 35 °C under nitrogen for 16 h. The solution was reduced in volume to 5 mL, and 25 mL of methanol was added to precipitate the product. A white solid was collected by vacuum filtration, rinsed with methanol, and dried in vacuo to give G0 (0.22 g, 65% yield). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.12 (d, J = 8.4 Hz, 8H), 7.49 (d, J = 8.0 Hz, 8H), 7.42 (m, 8H), 7.19 (d, J = 8.4 Hz, 8H), 6.76 (dd, J = 17.6, 10.8 Hz, 4H), 5.89 (d, J = 17.6 Hz, 4H), 5.41 (d, J = 10.8 Hz, 4H), 2.12 (br, 4H). ^{13}C NMR (75.5 MHz, $CDCl_3$, δ): 165.0, 151.9, 143.0, 136.3, 135.5, 134.3, 130.9, 128.8, 126.6, 122.3, 117.3, 24.4. ^{31}P NMR (162.1 MHz, $CDCl_3$, δ): −12.6. Anal. Calcd for $C_{62}H_{48}O_8P_2$: C, 75.76; H, 4.92. Found: C, 75.71; H, 4.95.

(G0)PtCl$_2$ (Method B). A solution of G0 (0.20 g, 0.200 mmol) in 10 mL of dichloromethane was added to a solution of (COD)$PtCl_2$ (0.075 g, 0.200 mmol) in 10 mL of dichloromethane. The solution was stirred for 1 h before the solvent was removed in vacuo. Methanol (20 mL) was added, and the white solid was collected by vacuum filtration, rinsed with methanol, and dried in vacuo to give (G0)$PtCl_2$ (0.21 g, 85% yield). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.14 (d, J = 8.0 Hz, 8H), 7.97 (dd, J = 11.8, 8.4 Hz, 8H), 7.53 (d, J = 8.0 Hz, 8H), 7.38 (dd, J = 8.4, 2.0 Hz, 8H), 6.78 (dd, J = 17.6, 10.8 Hz, 4 H), 5.91 (d, J = 17.6 Hz, 4H), 5.43 (d, J = 10.8 Hz, 4H), 2.42 (m, 4H). ^{31}P NMR (162.1 MHz, $CDCl_3$, δ): 40.7 (J_{Pt-P} = 3592 Hz).

5 (Method C). To a solution of (G0)$PtCl_2$ (0.119 g, 0.095 mmol) in 25 mL of dichloromethane was added silver carbonate (39.4 mg, 0.143 mmol) and 5 drops of distilled water. The mixture was stirred at room temperature, protected from light until all the $PtCl_2$ was converted to $PtCO_3$, as monitored by ^{31}P NMR. The mixture was filtered through a pad of Celite to remove the silver salts. *S*-BINOL (30.0 mg, 0.105 mmol) was added to a solution of the $PtCO_3$ in 25 mL of dichloromethane, and the solution was stirred at room temperature until ^{31}P NMR showed complete conversion to the Pt(BINOL). The dichloromethane was removed in vacuo, and 25 mL of diethyl ether was added. The yellow solid was collected by vacuum filtration and rinsed with an additional 25 mL of diethyl ether to remove excess BINOL. After drying overnight in vacuo **5**, (G0)Pt(*S*-BINOL) (0.117 g, 84% yield), was obtained. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.19 (d, J = 8.4 Hz, 4H), 8.08 (m, 8H), 7.81 (m, 4H), 7.68 (d, J = 8.0 Hz, 2H), 7.54 (m, 6H), 7.47 (d, J = 8.4 Hz, 4H), 7.35 (d, J = 7.2 Hz, 4H), 7.26 (d, J = 7.6 Hz, 4H), 7.06 (m, 2H), 6.96 (m, 4H), 6.79 (dd, J = 17.6, 10.8 Hz, 2H), 6.74 (dd, J = 17.6, 10.8 Hz, 2H), 6.54 (d, J = 8.8 Hz, 2H), 5.93 (d, J = 17.6 Hz, 2H), 5.87 (d, J = 17.6 Hz, 2H), 5.45 (d, J = 10.8 Hz, 2H), 5.40 (d, J = 10.8 Hz, 2H), 2.23 (m, 4H). ^{13}C NMR (75.5 MHz, $CDCl_3$, δ): 164.8, 164.6, 161.6, 154.2, 154.1, 143.3, 143.2, 136.2, 136.0, 135.5, 135.1, 134.2, 131.1, 131.0, 129.1, 128.31, 128.27, 127.7, 126.73, 126.68, 126.2, 125.6, 124.9, 124.6, 123.7, 123.1, 122.9, 121.4, 117.6, 27.6. ^{31}P NMR (162.1 MHz, $CDCl_3$, δ): 27.1 (J_{Pt-P} = 3621 Hz). Anal. Calcd for $C_{82}H_{60}O_{10}P_2Pt$: C, 67.35; H, 4.14. Found: C, 66.32; H, 4.43.

G1-COOH. G1-CO_2Me[12] (3.0 g, 7.49 mmol) was suspended in 125 mL of absolute ethanol. Crushed potassium hydroxide pellets (1.1 g, 18.7 mmol) were added to the suspension, and the mixture was refluxed for 16 h. The ethanol was removed in vacuo, and the residue was taken up in 100 mL of ethyl acetate and acidified with an equal volume of 1 M hydrochloric acid. The aqueous layer was removed, and the ethyl acetate was washed again with 100 mL of 1 M hydrochloric acid, then with 100 mL of distilled water, and finally with 100 mL of brine. After drying over magnesium sulfate, the ethyl acetate was removed in vacuo. The resulting yellow solid was partially dissolved in dichloromethane, and hexanes was added to induce precipitation. Upon collection by filtration, 2.3 g of a white solid was obtained (75% yield). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.42 (d, J = 8.0 Hz, 4H), 7.37 (d, J = 8.4 Hz, 4H), 7.34 (d, J = 2.4 Hz, 2H), 6.82 (t, J = 2.4 Hz, 1H), 6.71 (dd, J = 17.6 Hz, 10.8 Hz, 2H), 5.76 (dd, J = 17.6 Hz, 0.8 Hz, 2H), 5.25 (dd, J = 10.8 Hz, 0.8 Hz, 2H), 5.06 (s, 4H). ^{13}C NMR (100.6 MHz, $CDCl_3$, δ): 172.0, 160.1, 137.9, 136.7, 136.2, 131.4, 128.1, 126.8, 114.6, 109.3, 108.6, 70.4. Anal. Calcd for $C_{25}H_{22}O_4$: C, 77.70; H, 5.74. Found: C, 77.73; H, 5.77.

G1 (Method A). G1-COOH (0.26 g, 1.71 mmol). Yield: 0.37 g, 56%. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.39 (m, 48H), 7.18 (d, J = 8.4 Hz, 8H), 6.82 (t, J = 2.0 Hz, 4H), 6.70 (dd, J = 17.6, 10.8 Hz, 8H), 5.74 (d, J = 17.6 Hz, 8H), 5.24 (d, J = 10.8 Hz, 8 H), 5.05 (s, 16H), 2.12 (br, 4H). ^{13}C NMR (75.5 MHz, $CDCl_3$, δ): 164.9, 160.1, 151.9, 137.8, 136.7, 136.1, 135.6, 134.3, 131.5, 128.1, 126.8, 122.4, 122.3, 114.6, 109.2, 70.4, 24.6. ^{31}P NMR (162.1 MHz, $CDCl_3$, δ): −13.7. Anal. Calcd for $C_{126}H_{104}O_{16}P_2$: C, 78.16; H, 5.41. Found: C, 77.99; H, 5.29.

(G1)PtCl$_2$ (Method B). G1 (0.39 g, 0.200 mmol). Yield: 0.41 g, 92%. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.98 (m, 8H), 7.40 (m, 48H), 6.85 (s, 4H), 6.71 (dd, J = 17.6, 10.8 Hz, 8H), 5.75 (d, J = 17.6 Hz, 8H), 5.25 (d, J = 10.8 Hz, 8H), 5.06 (s, 16H), 2.45 (m, 4H). ^{31}P NMR (162.1 MHz, $CDCl_3$, δ): 40.6 ppm (J_{Pt-P} = 3600 Hz).

6 (Method C). (G1)$PtCl_2$ (0.210 g, 0.095 mmol). Yield: 0.186 g, 81%. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.11 (m, 2H), 7.85 (m, 2H), 7.70 (d, J = 8.0 Hz, 2H), 7.55 (d, J = 8.8 Hz, 2H), 7.38 (m, 48H), 7.08 (m, 2H), 6.88 (m, 2H), 6.83 (m, 2H), 6.72 (m, 8H), 6.56 (d, J = 8.8 Hz, 2H), 5.77 (d, J = 17.6 Hz, 4H), 5.74 (d, J = 17.6 Hz, 4H), 5.26 (d, J = 10.8 Hz, 4H), 5.24 (d, J = 10.8 Hz, 4H), 4.99 (s, 8H), 4.93 (s, 8H), 2.25 (m, 4H). ^{13}C NMR (75.5 MHz, $CDCl_3$, δ): 164.7, 164.5, 161.6, 160.3, 160.2, 154.2, 154.1, 137.9, 137.8, 136.7, 136.1, 136.0, 135.5, 135.2, 131.12, 131.08, 129.1, 128.2, 128.1, 127.7, 126.8, 126.3, 125.6, 125.0, 124.6, 123.9, 123.1, 122.9, 121.4, 117.6, 109.4, 109.4, 108.5, 70.5, 70.4, 27.6. ^{31}P NMR (162.1 MHz, $CDCl_3$, δ): 27.0 (J_{Pt-P} = 3580 Hz).

G1(2,3)-COOH. Vinyl benzyl chloride (9.0 mL, 64.9 mmol) was added to a suspension of 2,3-dihydroxybenzoic acid (1.0 g, 6.49 mmol), potassium carbonate (3.6 g, 26.0 mmol), 18-crown-6 (0.34 g, 1.30 mmol), and tetrabutylammonium iodide (0.12 g, 0.324 mmol) in 40 mL of acetone. The mixture was heated to reflux for 16 h under nitrogen until TLC showed complete consumption of the benzoic acid. Insoluble salts were removed by vacuum filtration, and the solvent was removed from the filtrate in vacuo. The residue was then redissolved in 50 mL of dichloromethane and washed 3 times with 50 mL of distilled water, then dried over magnesium sulfate. The dichloromethane was removed in vacuo to yield a yellow oil. 2-Propanol (50 mL) and potassium hydroxide (1.8 g, 32.4 mmol) were added to the oil, and this mixture was heated to reflux for 16 h. Then an additional 1.8 g (32.4 mmol) of potassium hydroxide was added, and reflux was continued for 24 h until TLC showed complete consumption of starting material. After the 2-propanol was removed in vacuo, 50 mL of ethyl acetate and 50 mL of 1 M hydrochloric acid were added, and the mixture was stirred for 30 min. The aqueous

layer was removed and the ethyl acetate was washed again with 50 mL of 1 M hydrochloric acid, then twice with 50 mL of distilled water, and finally with 50 mL of brine. The ethyl acetate was dried over magnesium sulfate and filtered. After removing the ethyl acetate in vacuo, 10 mL of dichloromethane was added to dissolve the product followed by 20 mL of hexanes, and the mixture was stored at −26 °C overnight to induce precipitation. Upon collection by filtration, 1.5 g of a yellow solid was obtained (58% yield). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.72 (dd, J = 8.0, 1.6 Hz, 1H), 7.45 (d, J = 8.0 Hz, 2H), 7.41 (d, J = 8.0 Hz, 2H), 7.34 (d, J = 8.0 Hz, 2H), 7.27 (d, J = 8.0 Hz, 2H), 7.22 (d, J = 1.6 Hz, 1H), 7.17 (t, J = 8.0 Hz, 1H), 6.74 (dd, J = 17.6, 10.8 Hz, 1H), 6.67 (dd, J = 17.6, 10.8 Hz, 1H), 5.78 (d, J = 17.6 Hz, 1H), 5.74 (d, J = 17.6 Hz, 1H), 5.29 (d, J = 10.8 Hz, 1H), 5.27 (d, J = 10.8 Hz, 1H), 5.23 (s, 2H), 5.15 (s, 2H). ^{13}C NMR (100.6 MHz, $CDCl_3$, δ): 165.5; 151.6; 147.4; 138.9; 138.3; 136.6; 136.5; 135.6; 134.4; 129.9; 128.4; 127.0; 125.4; 124.9; 123.4; 119.4; 115.3; 115.0; 71.7. Anal. Calcd for $C_{25}H_{22}O_4$: C, 77.70; H, 5.74. Found: C, 77.72; H, 5.82.

G1(2,3) (Method A). G1(2,3)-COOH (0.26 g, 1.71 mmol). Yield: 0.32 g, 47%. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.52 (dd, J = 7.8, 1.4 Hz, 4H), 7.37 (m, 24H), 7.28 (m, 16H), 7.13 (m, 16H), 6.72 (dd, J = 17.6, 10.8 Hz, 4H), 6.63 (dd, J = 17.6, 10.8 Hz, 4H), 5.76 (d, J = 17.6 Hz, 4H), 5.66 (d, J = 17.6 Hz, 4H), 5.26 (d, J = 10.8 Hz, 4H), 5.17 (d, J = 10.8 Hz, 4H), 5.11 (s, 16H), 2.12 (br, 4H). ^{13}C NMR (75.5 MHz, $CDCl_3$, δ): 164.5, 153.2, 151.8, 149.3, 137.8, 137.6, 137.1, 136.9, 136.7, 136.3, 135.5, 134.3, 129.2, 128.2, 126.8, 126.5, 126.2, 124.4, 123.7, 122.3, 119.0, 114.6, 114.2, 75.9, 71.5, 24.7. ^{31}P NMR (162.1 MHz, $CDCl_3$, δ): −13.3. Anal.Calcd for $C_{126}H_{104}O_{16}P_2$: C, 78.16; H, 5.41. Found: C, 77.95; H, 5.36.

[G1(2,3)]$PtCl_2$ (Method B). G1(2,3) (0.39 g, 0.200 mmol). Yield: 0.41 g, 93%. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.91 (dd, J = 11.8, 8,4 Hz, 8H), 7.54 (dd, J = 8.0, 1.6 Hz, 4H), 7.39 (m, 16H), 7.29 (m, 24H), 7.15 (m, 8H), 6.72 (dd, J = 17.6, 10.8 Hz, 4H), 6.65 (dd, J = 17.6, 10.8 Hz, 4H), 5.76 (d, J = 17.6 Hz, 4H), 5.68 (d, J = 17.6 Hz, 4H), 5.26 (d, J = 10.8 Hz, 4H), 5.17 (d, J = 10.8 Hz, 4H), 5.13 (s, 8H), 5.09 (s, 8H), 2.37 (m, 4H). ^{31}P NMR (162.1 MHz, $CDCl_3$, δ): 40.7 ppm (J_{Pt-P} = 3596 Hz).

7 (Method C). [G1(2,3)]$PtCl_2$ (0.210 g, 0.095 mmol). Yield: 0.184 g, 80%. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.07 (m, 4H), 7.81 (m, 4H), 7.66 (d, J = 8.0 Hz, 2H), 7.61 (dd, J = 7.6, 1.6 Hz, 2H), 7.52 (m, 4H), 7.35 (m, 34H), 7.10 (m, 20H), 6.74 (dd, J = 17.6, 10.8 Hz, 2H), 6.71 (dd, J = 17.6, 10.8 Hz, 2H), 6.62 (dd, J = 17.6, 10.8 Hz, 2H), 6.60 (dd, J = 17.6, 10.8 Hz, 2H), 6.53 (d, J = 8.8 Hz, 2H), 5.78 (d, J = 17.6 Hz, 2H), 5.76 (d, J = 17.6 Hz, 2H), 5.64 (d, J = 17.6 Hz, 2H), 5.63 (d, J = 17.6 Hz, 2H), 5.28 (d, J = 10.8 Hz, 2H), 5.26 (d, J = 10.8 Hz, 2H), 5.14 (m, 20H), 2.25 (m, 4H). ^{13}C NMR (75.5 MHz, $CDCl_3$, δ): 154.1, 153.3, 153.2, 149.5, 149.4, 137.9, 137.8, 137.7, 137.6, 137.0, 136.7, 136.2, 136.0, 135.4, 135.1, 129.3, 129.2, 129.1, 128.2, 128.1, 127.8, 126.80, 126.77, 126.6, 126.5, 126.3, 126.2, 125.7, 125.6, 125.0, 124.53, 124.46, 123.7, 123.2, 123.0, 121.3, 119.3, 119.2, 114.6, 114.4, 114.3, 75.9, 75.8, 71.5, 27.6. ^{31}P NMR (162.1 MHz, $CDCl_3$, δ): 27.2 (J_{Pt-P} = 3620 Hz). Anal. Calcd for $C_{146}H_{116}O_{18}P_2Pt$: C, 72.60; H, 4.84. Found: C, 72.09; H, 4.43.

G1(2,4)-CO_2Me. Methyl 2,4-dihydroxy benzoate (1.0 g, 5.95 mmol), potassium carbonate (2.1 g, 14.9 mmol), 18-crown-6 (0.31 g, 1.19 mmol), and tetrabutylammonium iodide (0.11 g, 0.297 mmol) were suspended in 30 mL of acetone. Vinyl benzyl chloride (1.8 mL, 12.5 mmol) was then added, and the mixture was refluxed under nitrogen for 16 h. Insoluble salts were removed by vacuum filtration, and the solvent was removed from the filtrate in vacuo. The residue was redissolved in 50 mL of ether and washed three times with 50 mL of distilled water. The ether layer was dried over magnesium sulfate and evaporated to dryness in vacuo to give a pale yellow oil. Hexanes (1 mL) was added, and the mixture was stored at −26 °C for several days to give a white solid. The solid was dried in vacuo to give 2.0 g (85% yield). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.87 (d, J = 8.4 Hz, 1H), 7.38 (m, 8H), 6.71 (dd, J = 17.6, 10.8 Hz, 2H), 6.56 (m, 2H), 5.76 (d, J = 17.6 Hz, 1H), 5.75 (d, J = 17.6 Hz, 1H), 5.26 (d, J = 10.8 Hz, 1H), 5.24 (d, J = 10.8 Hz, 1H), 5.12 (s, 2H), 5.02 (s, 2H), 3.86 (s, 3H). ^{13}C NMR (100.6 MHz, $CDCl_3$, δ): 166.4, 163.4, 160.4, 137.8, 137.3, 136.7, 136.6, 136.4, 135.9, 134.2, 128.0, 127.2, 126.7, 126.6, 114.6, 113.4, 106.3, 101.7, 70.6, 70.2, 51.9.

G1(2,4)-COOH. G1(2,4)-CO_2Me (1.5 g, 3.75 mmol) was suspended in 75 mL of absolute ethanol. Crushed potassium hydroxide pellets (0.53 g, 9.36 mmol) were added to the suspension, and the mixture was refluxed for 16 h. The ethanol was removed in vacuo, and the residue was taken up in 50 mL of ethyl acetate and acidified with an equal volume of 1 M hydrochloric acid. The aqueous layer was removed, and the ethyl acetate was washed again with 50 mL of 1 M hydrochloric acid, then with 50 mL of distilled water, and finally with 50 mL of brine. After drying over magnesium sulfate, the ethyl acetate was removed in vacuo. The resulting yellow solid was partially dissolved in dichloromethane, and hexanes was added to induce precipitation. Upon collection by filtration, 1.0 g of a white solid was obtained (72% yield). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.13 (d, J = 8.8 Hz, 1H), 7.38 (m, 8H), 6.70 (m, 3H), 6.65 (d, J = 2 Hz, 1H), 5.78 (dd, J = 17.6, 10.8 Hz, 1H), 5.76 (dd, J = 17.6, 10.8 Hz, 1H), 5.30 (dd, J = 10.8 Hz, 0.4 Hz, 1H), 5.27 (dd, J = 10.8 Hz, 0.4 Hz, 1H), 5.20 (s, 2H), 5.08 (s, 2H). ^{13}C NMR (100.6 MHz, $CDCl_3$, δ): 165.4; 164.3; 159.0; 138.9; 138.2; 136.6; 136.4; 136.0; 135.5; 133.8; 128.5; 128.1; 127.3; 126.9; 115.4; 114.9; 111.4; 108.2; 101.1; 72.3; 70.6. Anal. Calcd for $C_{25}H_{22}O_4$: C, 77.70; H, 5.74. Found: C, 77.71; H, 5.69.

G1(2,4) (Method A). G1(2,4)-COOH (0.26 g, 1.71 mmol). Yield: 0.34 g, 49%. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.03 (d, J = 8.8 Hz, 4H), 7.38 (m, 42H), 7.15 (d, J = 8.4 Hz, 8H), 6.67 (m, 16H), 5.76 (d, J = 17.6 Hz, 4H), 5.68 (d, J = 17.6 Hz, 4H), 5.26 (d, J = 10.8 Hz, 4H), 5.18 (d, J = 10.8 Hz, 4H), 5.07 (s, 8H), 5.05 (s, 8H), 2.10 (br, 4H). ^{13}C NMR (75.5 MHz, $CDCl_3$, δ): 164.1, 163.7, 161.3, 152.0, 138.0, 137.4, 136.8, 136.6, 136.2, 135.8, 135.1, 134.9, 134.2, 128.1, 127.4, 126.8, 126.7, 122.5, 114.7, 114.3, 112.4, 106.5, 101.6, 70.6, 70.3, 24.7. ^{31}P NMR (162.1 MHz, $CDCl_3$, δ): −13.6. Anal. Calcd for $C_{126}H_{104}O_{16}P_2$: C, 78.16; H, 5.41. Found: C, 77.89; H, 5.35.

[G1(2,4)]$PtCl_2$ (Method B). G1(2,4) (0.39 g, 0.200 mmol). Yield: 0.40 g, 90%. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.05 (d, J = 9.2 Hz, 4H), 7.91 (m, 8H), 7.39 (m, 42H), 6.67 (m, 16H), 5.76 (d, J = 17.6 Hz, 4H), 5.70 (d, J = 17.6 Hz, 4H), 5.26 (d, J = 10.8 Hz, 4H), 5.19 (d, J = 10.8 Hz, 4H), 5.13 (s, 8H), 5.08 (s, 8H). ^{31}P NMR (162.1 MHz, $CDCl_3$, δ): 40.8 ppm (J_{Pt-P} = 3608 Hz).

8 (Method C). [G1(2,4)]$PtCl_2$ (0.210 g, 0.095 mmol). Yield: 0.195 g, 85%. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.13 (d, J = 9.2 Hz, 2H), 8.03 (m, 6H), 7.82 (m, 4H), 7.66 (d, J = 8.0 Hz, 2H), 7.52 (d, J = 8.8 Hz, 2H), 7.39 (m, 36H), 7.27 (d, J = 7.6 Hz, 4H), 7.00 (m, 6H), 6.67 (m, 16H), 6.54 (d, J = 8.4 Hz, 2H), 5.75 (m, 8H), 5.28 (m, 4H), 5.11 (m, 20H), 2.25 (m, 4H). ^{13}C NMR (75.5 MHz, $CDCl_3$, δ): 163.3, 163.25, 163.16, 161.8, 161.5, 161.4, 154.4, 154.3, 138.0, 137.9, 137.6, 137.4, 136.6, 136.1, 136.0, 135.7, 135.0, 129.1, 128.1, 128.1, 127.6, 127.4, 126.82, 126.79, 126.7, 126.3, 125.7, 124.9, 124.5, 123.3, 123.1, 121.2, 114.7, 114.4, 114.3, 111.7, 106.6, 101.7, 101.6, 70.6, 70.4, 27.6. ^{31}P NMR (162.1 MHz, $CDCl_3$, δ): 27.3 (J_{Pt-P} = 3621 Hz). Anal. Calcd for $C_{146}H_{116}O_{18}P_2Pt$: C, 72.60; H, 4.84. Found: C, 71.20; H, 4.19.

G1t-COOH. G1t-CO_2Me[12] (1.5 g, 2.82 mmol) was suspended in 50 mL of absolute ethanol. Crushed potassium hydroxide pellets (0.40 g, 7.04 mmol) were added to the suspension, and the mixture was refluxed for 16 h. The ethanol was removed in vacuo, and the residue was taken up in 50 mL of ethyl acetate and acidified with an equal volume of 1 M hydrochloric acid. The aqueous layer was removed, and the ethyl acetate was washed again with 50 mL of 1 M hydrochloric acid, then

with 50 mL of distilled water, and finally with 50 mL of brine. After drying over magnesium sulfate, the ethyl acetate was removed in vacuo. The resulting yellow solid was partially dissolved in dichloromethane, and hexanes was added to induce precipitation. Upon collection by filtration, 0.91 g of a white solid was obtained (63% yield). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.38 (m, 10H), 7.32 (d, J = 8.0 Hz, 2H), 7.27 (d, J = 8.4 Hz, 2H), 6.72 (dd, J = 17.6 Hz, 10.8 Hz, 2H), 6.86 (dd, J = 16.4 Hz, 10.8 Hz, 1H), 5.76 (d, J = 17.6 Hz, 2H), 5.72 (d, J = 16.4 Hz, 1H), 5.26 (d, J = 10.8 Hz, 2H), 5.23 (d, J = 10.8 Hz, 1H), 5.11 (s, 6H). ^{13}C NMR (100.6 MHz, $CDCl_3$, δ): 171.5, 152.9, 143.4, 137.7, 137.6, 137.3, 136.9, 136.8, 136.4, 129.1, 128.1, 126.8, 126.4, 124.4, 114.5, 114.3, 110.0, 75.2, 71.3. Anal. Calcd for $C_{34}H_{30}O_5$: C, 78.74; H, 5.83. Found: C, 78.60; H, 5.84.

G1t (Method A). G1t-COOH (0.89 g, 1.71 mmol). Yield: 0.41 g, 47%. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.47 (s, 8H), 7.37 (m, 40H), (7.28 m, 16H), 7.16 (d, J = 8.4 Hz, 8 H), 6.69 (m, 12H), 5.74 (d, J = 17.6 Hz, 8H), 5.72 (d, J = 17.6 Hz, 4H), 5.24 (d, J = 10.8 Hz, 8H), 5.23 (d, J = 10.8 Hz, 4H), 5.10 (s, 24H), 2.12 (br, 4H). ^{13}C NMR (75.5 MHz, $CDCl_3$, δ): 164.8, 152.9, 151.9, 143.3, 137.7, 137.6, 137.2, 136.9, 136.8, 136.3, 135.6, 134.4, 129.1, 128.1, 126.7, 126.4, 124.5, 122.3, 114.5, 114.2, 109.9, 75.2, 71.3, 24.7. ^{31}P NMR (162.1 MHz, $CDCl_3$, δ): −13.5. Anal. Calcd for $C_{162}H_{136}O_{20}P_2$: C, 78.94; H, 5.56. Found: C, 78.69; H, 5.43.

(G1t)PtCl$_2$ (Method B). G1t (0.49 g, 0.200 mmol). Yield: 0.51 g, 94%. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.95 (m, 8H), 7.48 (s, 8H), 7.39 (m, 56H), 6.70 (m, 12H), 5.75 (d, J = 17.6 Hz, 8H), 5.73 (d, J = 17.6 Hz, 4H), 5.25 (d, J = 10.8 Hz, 8H), 5.24 (d, J = 10.8 Hz, 4H), 5.14 (s, 24H), 2.42 (m, 4H). ^{31}P NMR (162.1 MHz, $CDCl_3$, δ): 40.9 (J_{Pt-P} = 3597 Hz).

9 (Method C). (G1t)$PtCl_2$ (0.260 g, 0.095 mmol). Yield: 0.243 g, 87%. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.10 (m, 4H), 7.87 (m, 4H), 7.70 (d, J = 8.4 Hz, 2H), 7.55 (m, 6H), 7.35 (m, 60H), 7.10 (m, 2H), 7.01 (m, 4H), 6.70 (m, 12H), 6.58 (d, J = 8.4 Hz, 2H), 5.74 (m, 12H), 5.25 (m, 12H), 5.18 (s, 8H), 5.17 (s, 4H), 5.12 (s, 4H), 5.11 (s, 8H), 2.27 (m, 4H). ^{13}C NMR (75.5 MHz, $CDCl_3$, δ): 164.6, 164.4, 161.6, 154.2, 154.2, 153.0, 152.9, 143.5, 143.4, 137.8, 137.7, 137.6, 137.6, 137.1, 136.9, 136.7, 136.6, 136.2, 136.2, 136.0, 135.3, 129.11, 129.09, 128.14, 128.09, 126.7, 126.4, 125.0, 124.7, 124.0, 123.1, 122.9, 121.4, 114.5, 114.3, 110.0, 75.24, 75.21, 71.4, 71.3, 27.5. ^{31}P NMR (162.1 MHz, $CDCl_3$, δ): 27.0 (J_{Pt-P} = 3577 Hz). Anal. Calcd for $C_{182}H_{148}O_{22}P_2Pt$: C, 74.25; H, 5.07. Found: C, 73.29; H, 4.80.

G1t(2,3,4)-COOH. Vinyl benzyl chloride (8.4 mL, 58.8 mmol) was added to a suspension of 2,3,4-trihydroxybenzoic acid (1.0 g, 5.88 mmol), potassium carbonate (3.3 g, 23.5 mmol), 18-crown-6 (0.31 g, 1.18 mmol), and tetrabutylammonium iodide (0.11 g, 0.294 mmol) in 60 mL of acetone. The mixture was heated to reflux for 16 h under nitrogen until TLC showed complete consumption of the benzoic acid. Insoluble salts were removed by vacuum filtration, and the solvent was removed from the filtrate in vacuo. The residue was then redissolved in 50 mL of dichloromethane and washed three times with 50 mL of distilled water, then dried over magnesium sulfate. The dichloromethane was removed in vacuo to yield a yellow oil. 2-Propanol (100 mL) and potassium hydroxide (1.7 g, 29.4 mmol) were added to the oil, and this mixture was heated to reflux for 16 h. Then an additional 1.7 g (29.4 mmol) of potassium hydroxide was added, and reflux was continued for 24 h until TLC showed complete consumption of starting material. After the 2-propanol was removed in vacuo, 100 mL of ethyl acetate and 100 mL of 1 M hydrochloric acid were added, and the mixture was stirred for 30 min. The aqueous layer was removed, and the ethyl acetate was washed again with 100 mL of 1 M hydrochloric acid, then twice with 100 mL of distilled water, and finally with 100 mL of brine. The ethyl acetate was dried over magnesium sulfate and filtered. After removing the ethyl acetate in vacuo, 10 mL of dichloromethane was added to dissolve the product, followed by 20 mL of hexanes, and the mixture was stored at −26 °C overnight to induce precipitation. Upon collection by filtration, 1.4 g of a yellow solid was obtained (46% yield). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.87 (d, J = 8.8 Hz, 1H); 7.35 (m, 12H); 6.87 (d, J = 8.8 Hz, 1H); 6.72 (m, 3H); 5.76 (m, 3H); 5.27 (m, 3H); 5.25 (s, 2H); 5.15 (s, 2H); 5.05 (s, 2H). ^{13}C NMR (100.6 MHz, $CDCl_3$, δ): 165.4; 157.7; 152.2; 141.1; 138.9; 138.14; 138.10; 136.7; 136.6; 136.50; 136.47; 135.5; 134.3; 129.9; 129.3; 128.9; 128.2; 127.0; 126.9; 126.6; 115.7; 115.3; 114.9; 126.6; 115.7; 115.3; 114.9; 114.7; 110.0; 77.8, 76.0, 71.2. Anal. Calcd for $C_{34}H_{30}O_5$: C, 78.74; H, 5.83. Found: C, 78.94; H, 5.84.

G1t(2,3,4) (Method A). G1t(2,3,4)-COOH (0.89 g, 1.71 mmol). Yield: 0.43 g, 49%. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.77 (d, J = 8.4 Hz, 4H), 7.32 (m, 56H), 7.13 (d, J = 8.4 Hz, 8H), 6.70 (m, 16H), 5.77 (d, J = 17.6 Hz, 4H), 5.73 (d, J = 17.6 Hz, 4H), 5.68 (d, J = 17.6 Hz, 4H), 5.27 (d, J = 10.8 Hz, 4H), 5.24 (d, J = 10.8 Hz, 4H), 5.18 (d, J = 10.8 Hz, 4H), 5.091 (s, 8H), 5.089 (s, 8H), 5.00 (s, 8H), 2.13 (br, 4H). ^{13}C NMR (75.5 MHz, $CDCl_3$, δ): 163.7, 157.5, 154.8, 151.9, 143.0, 137.9, 137.69, 137.67, 137.0, 136.9, 136.7, 135.8, 135.3, 134.3, 129.4, 129.3, 128.0, 126.8, 126.5, 126.5, 122.4, 118.0, 114.7, 114.3, 109.0, 76.4, 75.7, 71.0, 24.7. ^{31}P NMR (162.1 MHz, $CDCl_3$, δ): −13.0. Anal. Calcd for $C_{162}H_{136}O_{20}P_2$: C, 78.94; H, 5.56. Found: C, 78.76; H, 5.49.

[G1t(2,3,4)]PtCl$_2$ (Method B). G1t(2,3,4) (0.49 g, 0.200 mmol). Yield: 0.48 g, 88%. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.93 (m, 8H), 7.80 (d, J = 8.8 Hz, 4H), 7.33 (m, 56H), 6.83 (d, J = 8.8 Hz, 4H), 6.71 (m, 12H), 5.78 (d, J = 17.6 Hz, 4H), 5.73 (d, J = 17.6 Hz, 4H), 5.71 (d, J = 17.6 Hz, 4H), 5.28 (d, J = 10.8 Hz, 4H), 5.24 (d, J = 10.8 Hz, 4H), 5.19 (d, J = 10.8 Hz, 4H), 5.15 (s, 8H), 5.14 (s, 8H), 5.02 (s, 8H), 2.40 (m, 4H). ^{31}P NMR (162.1 MHz, $CDCl_3$, δ): 40.9 (J_{Pt-P} = 3596 Hz).

10. To a solution of [G1t(2,3,4)]$PtCl_2$ (0.260 g, 0.095 mmol) in 25 mL of dichloromethane were added silver carbonate (39.4 mg, 0.143 mmol) and 5 drops of distilled water. The mixture was stirred at room temperature, protected from light until all the $PtCl_2$ was converted to $PtCO_3$ as monitored by ^{31}P NMR. The mixture was filtered through a pad of Celite to remove the silver salts. *S*-BINOL (30.0 mg, 0.105 mmol) was added to a solution of the $PtCO_3$ in 25 mL of dichloromethane, and the solution was stirred at room temperature until ^{31}P NMR showed complete conversion to the Pt(BINOL). The dichloromethane was removed in vacuo, and 25 mL of diethyl ether was added. The ether was decanted from the yellow oil, and this process was repeated three times. After drying overnight in vacuo **10** [G1t(2,3,4)]Pt(*S*-BINOL) (0.233 g, 84% yield) was obtained as a foamy solid from which complete solvent removal was impossible. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.08 (m, 4H), 7.87 (d, J = 8.8 Hz, 2H), 7.81 (m, 4H), 7.76 (d, J = 8.8 Hz, 2H), 7.54 (d, J = 8.8 Hz, 2H), 7.31 (m, 58H), 7.03 (m, 6H), 6.87 (d, J = 8.8 Hz, 2H), 6.70 (m, 12H), 6.54 (d, J = 8.8 Hz, 2H), 5.73 (m, 12H), 5.28 (m, 8H), 5.13 (m, 28H), 2.23 (m, 4H). ^{13}C NMR (75.5 MHz, $CDCl_3$, δ): 155.0, 154.9, 154.3, 154.2, 153.2, 143.1, 143.0, 138.0, 137.9, 137.8, 137.71, 137.66, 137.0, 136.92, 136.85, 136.7, 136.0, 135.8, 135.5, 135.0, 134.0, 129.4, 129.3, 129.1, 128.08, 128.05, 126.8, 126.6, 126.51, 126.47, 125.0, 124.6, 123.2, 123.1, 121.3, 117.5, 117.4, 114.7, 114.3, 109.2, 76.4, 75.71, 75.66, 71.0. ^{31}P NMR (162.1 MHz, $CDCl_3$, δ): 27.5 (J_{Pt-P} = 3630 Hz).

G1n(3,5)-COOH. Vinyl benzyl chloride (7.0 mL, 49.0 mmol) was added to a suspension of 3,5-dihydroxy-2-naphthoic acid (1.0 g, 4.90 mmol), potassium carbonate (2.7 g, 19.6 mmol), 18-crown-6 (0.26 g, 0.979 mmol), and tetrabutylammonium iodide (91 mg, 0.249 mmol) in 30 mL of acetone. The mixture was heated to reflux for 16 h under nitrogen until TLC showed complete consumption of the naphthoic acid. Insoluble salts were removed by vacuum filtration, and the solvent was removed from the filtrate in vacuo. The residue was then redissolved in 50 mL of dichloromethane and washed three times with 50 mL of distilled water, then dried over magne-

sium sulfate. The dichloromethane was removed in vacuo to yield a yellow oil. 2-Propanol (50 mL) and potassium hydroxide (1.4 g, 24.5 mmol) were added to the oil, and this mixture was heated to reflux for 16 h. Then an additional 1.4 g (24.5 mmol) of potassium hydroxide was added, and reflux was continued for 24 h until TLC showed complete consumption of starting material. After the 2-propanol was removed in vacuo, 50 mL of ethyl acetate and 50 mL of 1 M hydrochloric acid were added, and the mixture was stirred for 30 min. The aqueous layer was removed, and the ethyl acetate was washed again with 50 mL of 1 M hydrochloric acid, then twice with 50 mL of distilled water, and finally with 50 mL of brine. The ethyl acetate was dried over magnesium sulfate and filtered. After removing the ethyl acetate in vacuo, 10 mL of dichloromethane was added to dissolve the product, followed by 20 mL of hexanes, and the mixture was stored at −26 °C overnight to induce precipitation. Upon collection by filtration, 0.87 g of a yellow solid was obtained (41% yield). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.74 (s, 1H), 7.81 (s, 1H); 7.45 (m, 9H), 7.32 (t, J = 8.0 Hz, 1H), 6.96 (d, J = 8.0 Hz, 1H), 6.72 (m, 2H), 5.79 (d, J = 17.6 Hz, 1H), 5.77 (d, J = 17.6 Hz, 1H), 5.34 (s, 2H), 5.30 (d, J = 10.8 Hz, 1H), 5.29 (d, J = 10.8 Hz, 1H), 5.22 (s, 2H). ^{13}C NMR (100.6 MHz, $CDCl_3$, δ): 165.8; 153.6; 153.5; 138.7; 137.9; 136.6; 136.5; 136.4; 136.1; 134.2; 129.8; 129.1; 128.7; 128.1; 127.2; 126.8; 125.7; 122.1; 118.9; 115.3; 114.8; 108.8; 104.0; 72.4; 70.6. Anal. Calcd for $C_{29}H_{24}O_4$: C, 79.80; H, 5.54. Found: C, 79.51; H, 5.54.

G1n(3,5) (Method A). G1n(3,5)-COOH (0.75 g, 1.71 mmol). Yield: 0.41 g, 53%. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.46 (s, 4H), 7.72 (s, 4H), 7.32 (m, 56H), 6.91 (d, J = 7.6 Hz, 4H), 6.75 (dd, J = 17.6, 10.8 Hz, 4H), 6.66 (dd, J = 17.6, 10.8 Hz, 4H), 5.79 (d, J = 17.6 Hz, 4 H), 5.69 (d, J = 17.6 Hz, 4H), 5.22 (m, 24H), 2.17 (br, 4H). ^{13}C NMR (75.5 MHz, $CDCl_3$, δ): 164.6, 155.0, 153.4, 152.0, 137.7, 137.4, 136.8, 136.7, 136.5, 135.5, 134.3, 133.6, 133.5, 128.9, 127.9, 127.7, 126.8, 126.7, 124.7, 122.4, 121.7, 121.6, 114.6, 114.2, 108.2, 103.8, 103.7, 70.6, 70.4, 25.3. ^{31}P NMR (162.1 MHz, $CDCl_3$, δ): −12.9. Anal. Calcd for $C_{142}H_{112}O_{16}P_2$: C, 79.68; H, 5.25. Found: C, 79.72; H, 5.26.

[G1n(3,5)]$PtCl_2$ (Method B). G1n(3,5) (0.49 g, 0.200 mmol). Yield: 0.42 g, 88%. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.49 (s, 4H), 7.98 (m, 8H), 7.45 (s, 4H), 7.39 (m, 48H), 6.92 (d, J = 7.6 Hz, 4H), 6.72 (m, 8H), 5.79 (d, J = 17.6 Hz, 4H), 5.71 (d, J = 17.6 Hz, 4H), 5.25 (m, 24H), 2.43 (m, 4H). ^{31}P NMR (162.1 MHz, $CDCl_3$, δ): 40.9 (J_{Pt-P} = 3601 Hz).

11 (Method C). [G1n(3,5)]$PtCl_2$ (0.229 g, 0.095 mmol). Yield: 0.171 g, 69%. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.58 (s, 2H), 8.46 (s, 2H), 8.12 (m, 4H), 7.87 (m, 4H), 7.80 (s, 2H), 7.73 (s, 2H), 7.68 (d, J = 8.0 Hz, 2H), 7.56 (d, J = 8.8 Hz, 2H), 7.42 (m, 48H), 7.02 (m, 8H), 6.92 (d, J = 7.6 Hz, 2H), 6.76 (dd, J = 17.6, 10.8 Hz, 2H), 6.74 (dd, J = 17.6, 10.8 Hz, 2H), 6.64 (dd, J = 17.6, 10.8 Hz, 2H), 6.62 (dd, J = 17.6, 10.8 Hz, 2H), 6.58 (d, J = 8.4 Hz, 2H), 5.80 (d, J = 17.6 Hz, 2H), 5.78 (d, J = 17.6 Hz, 2H), 5.66 (d, J = 17.6 Hz, 2H), 5.65 (d, J = 17.6 Hz, 2H), 5.25 (m, 24H), 2.29 (m, 4H). ^{13}C NMR (75.5 MHz, $CDCl_3$, δ): 154.4, 154.3, 153.5, 153.4, 153.3, 137.7, 137.5, 137.4, 136.7, 136.5, 136.0, 135.5, 135.1, 134.0, 133.9, 130.9, 129.4, 129.2, 129.1, 128.93, 128.86, 128.0, 127.8, 126.8, 126.7, 126.3, 125.5, 125.0, 124.9, 124.6, 123.6, 123.3, 123.1, 121.7, 121.4, 121.1, 118.4, 112.6, 114.3, 112.4, 108.4, 104.0, 103.9, 70.7, 70.4, 27.7. ^{31}P NMR (162.1 MHz, $CDCl_3$, δ): 28.2 (J_{Pt-P} = 3645 Hz). Anal. Calcd for $C_{162}H_{124}O_{18}P_2Pt$: C, 74.39; H, 4.78. Found: C, 71.75; H, 4.03.

Polymerization. AIBN (6.8 mg, 41 μmol), metallomonomer (62 μmol), EDMA (0.80 g, 4.0 mmol), and chlorobenzene (0.76 mL) were weighed quantitatively into a scintillation vial. The vial was sealed, and the mixture was shaken to completely dissolve the template. The vial was then placed in a 60 °C heating block for 24 h. The polymers were removed from the glovebox and manually broken into 3−4 pieces, then Soxhlet extracted with 40 mL of dichloromethane for 6 h. After extraction, the polymer was dried in vacuo for 16 h before being broken into ∼2 mm pieces with a mortar and pestle. The polymers contained 60−65 μmol Pt/g polymer.

BINOL Loss Experiment. The solvent from the Soxhlet extraction filtrate was removed in vacuo, and the residue was quantitatively transferred into a 5 mL volumetric flask and diluted to the mark with HPLC grade 2-propanol. The concentration of BINOL in the solution was determined by HPLC analysis.

HCl Cleavage Experiment. Polymer (0.25 g) was weighed quantitatively and suspended in 20 mL of dichloromethane. Concentrated hydrochloric acid (10 drops) was added, and the mixture was stirred for 6 h. The polymer was filtered through a Soxhlet frit and rinsed with an additional 20 mL of CH_2Cl_2. The polymer was Soxhlet extracted for 16 h with the filtrate. The solvent was removed from the filtrate in vacuo, and the residue was quantitatively transferred to a 10 mL volumetric flask and diluted to the mark with HPLC grade 2-propanol. The concentration of BINOL in the solution was determined by HPLC analysis.

Rebinding Experiment. Polymer (0.30 g) and *rac*-Br_2-BINOL (0.15 g) were weighed quantitatively and added to a Schlenk tube and were dried under vacuum for 1 h. Under nitrogen, 3.0 mL of chlorobenzene and 0.50 mL of distilled water were added. The tube was sealed and placed in a 60 or 120 °C oil bath for 12 h. The polymer was filtered through a Soxhlet frit and rinsed with 40 mL of dichloromethane, then Soxhlet extracted for 14 h. After drying for 1 h in vacuo, the polymer was subjected to a standard HCl cleavage experiment. The residue from the Soxhlet extraction was dissolved in 2.00 mL of 2-propanol and analyzed by HPLC.

dppe-OCO-Ph. To a suspension of dppe-OH (0.25 g, 0.342 mmol) in 20 mL of dichloromethane was added benzoyl chloride (0.20 mL, 1.71 mmol), followed by triethylamine (0.25 mL, 1.71 mmol). The suspension was stirred for 1 h under nitrogen until TLC showed the consumption of dppe-OH and the formation of a product. The mixture was eluted through a pad of silica with 50 mL of ethyl acetate. The solvent was removed in vacuo to give a white solid. The solid was collected by vacuum filtration and rinsed with methanol and hexanes. The solid was dissolved along with DABCO (0.15 g, 1.37 mmol) in 30 mL of toluene, and the solution was stirred at 35 °C under nitrogen for 16 h. The solution was reduced in volume to 10 mL, and 25 mL of methanol was added to precipitate the product. A white solid was collected by vacuum filtration, rinsed with methanol, and dried in vacuo to give dppe-OCO-Ph (0.18 g, 60% yield) with a small amount of toluene remaining. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.17 (d, J = 7.2 Hz, 8H), 7.62 (t, J = 7.6 Hz, 4H), 7.48 (t, J = 7.6 Hz, 8H), 7.42 (m, 8H), 7.21 (d, J = 8.4 Hz, 8H), 2.13 (br, 4H). ^{13}C NMR (75.5 MHz, $CDCl_3$, δ):165.3, 151.9, 135.6, 134.4, 130.6, 130.5, 129.7, 128.9, 122.3, 24.7. ^{31}P NMR (162.1 MHz, $CDCl_3$, δ): −13.6. Anal. Calcd for $C_{54}H_{40}O_8P_2$: C, 73.80; H, 4.59. Found: C, 72.90; H, 4.64.

(dppe-OCO-Ph)$PtCl_2$. A solution of dppe-OCO-Ph (0.15 g, 0.17 mmol) in 10 mL of dichloromethane was added to a solution of (cod)$PtCl_2$ (0.067 g, 0.17 mmol) in 10 mL of dichloromethane. The solution was stirred for 1 h before the solvent was removed in vacuo. Methanol (25 mL) was added, and the white solid was collected by vacuum filtration, rinsed with methanol, and dried in vacuo to give (dppe-OCO-Ph)$PtCl_2$ (0.16 g, 82% yield). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.18 (d, J = 8.4 Hz, 8H), 7.97 (dd, J = 11.8, 8.4 Hz, 8H), 7.65 (t, J = 7.2 Hz, 4H), 7.51 (t, J = 8.0 Hz, 8H), 7.38 (dd, J = 8.4, 2.0 Hz, 8H), 2.43 (m, 4H). ^{31}P NMR (162.1 MHz, $CDCl_3$, δ): 40.8 ppm (J_{Pt-P} = 3598 Hz).

12. To a solution of (dppe-OCO-Ph)$PtCl_2$ (0.100 g, 0.0873 mmol) in 25 mL of dichloromethane was added silver carbonate (36.1 mg, 0.131 mmol) and 5 drops of distilled water. The mixture was stirred at room temperature, protected from light until all the $PtCl_2$ was converted to $PtCO_3$ as monitored by ^{31}P NMR. The mixture was filtered through a pad of Celite to

remove the silver salts. *S*-BINOL (27.5 mg, 0.0961 mmol) was added to a solution of the $PtCO_3$ in 25 mL of dichloromethane, and the solution was stirred until ^{31}P NMR showed complete conversion to the Pt(BINOL). The dichloromethane was removed in vacuo, and 25 mL of diethyl ether was added. The yellow solid was collected by vacuum filtration and rinsed with an additional 25 mL of diethyl ether to remove excess BINOL. After drying overnight in vacuo (dppe-OCO-Ph)Pt(*S*-BINOL) (0.0886 g, 73% yield) was obtained. ^1H NMR (400 MHz, $CDCl_3$, δ): 8.25 (d, $J = 7.2$ Hz, 4H), 8.15 (d, $J = 7.2$ Hz, 4H), 8.10 (dd, $J = 11.2$, 8.4 Hz, 4H), 7.81 (dd, $J = 11.2$, 8.4 Hz, 4H), 7.68 (t, $J = 7.6$ Hz, 4H), 7.61 (t, $J = 7.6$ Hz, 2H), 7.55 (m, 10H), 7.48 (t, $J = 7.6$ Hz, 4H), 7.34 (d, $J = 7.6$ Hz, 4H), 7.29 (d, $J = 7.6$ Hz, 4H), 2.26 (m, 4H). ^{13}C NMR (75.5 MHz, $CDCl_3$, δ): 165.0, 164.9, 161.5, 154.3, 154.2, 136.0, 135.6, 135.5, 135.2, 134.3, 130.8, 130.6, 129.32, 129.26, 129.2, 129.0, 127.7, 127.1, 126.3, 125.5, 125.0, 124.6, 123.6, 123.2, 122.9, 121.4, 118.4, 27.749. ^{31}P NMR (162.1 MHz, $CDCl_3$, δ): 27.7 ($J_{Pt-P} = 3619$ Hz). Anal. Calcd for $C_{74}H_{52}O_{10}P_2Pt$: C, 65.44; H, 3.86. Found: C, 65.56; H, 3.84.

Thermolysis of Model Metallomonomer. To a Schlenk tube was added 47.3 mg of **12** (36.8 mmol), and the compound was dried under vacuum for 1 h. Under nitrogen, 6.0 mL of chlorobenzene and 1.0 mL of distilled water were added to form a yellow solution. The tube was sealed and placed in a 120 °C oil bath for 14 h. The brown solution was transferred to a flask, and the solvent was removed in vacuo. Dichloromethane (2 mL) was added, and the thermolysis products were analyzed by ^{31}P NMR.

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Supporting Information Available: Sample Boltzmann distribution analysis for dendron models. ^{13}C NMR spectra for **dppe-OTBDMS** and **dppe-OH**. This material is available free of charge via the Internet at http://pubs.acs.org.

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