Facile Self-Assembly of Neutral Dendritic Metallocycles via Oxygen-to-Platinum Coordination

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Neutral Rhomboidal Metallodendrimer   Neutral Hexagonal Metallodendrimer
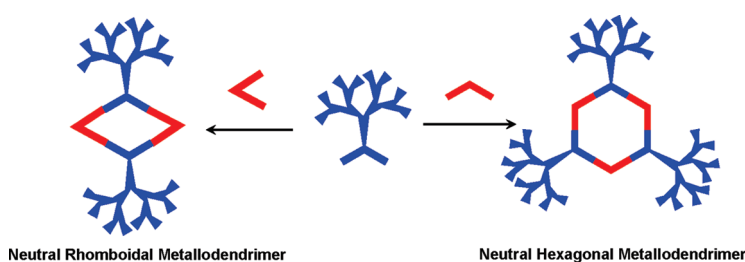
A new approach for the fabrication of neutral dendritic metallocycles is described. By combining rigid 120° dicarboxylate donor linkers funtionalized with [G0]−[G3] Fréchet-type dendrons and complementary rigid 60° and 120° di-Pt(II) acceptor subunits, neutral rhomboidal metallodendrimers and hexagonal metallodendrimers, respectively, were prepared under mild conditions in high yields. The assemblies have well-defined shapes and sizes and were characterized by multinuclear NMR (^{1}H and ^{31}P), mass spectrometry (ESI (+)-TOF-MS and APPI(+)-TOF-MS), and elemental analysis. Isotopically resolved mass spectrometry data support the formation of the neutral [2 + 2] rhomboidal, and [3 + 3] hexagonal metallodendrimers, and NMR data are consistent with the formation of all ensembles. The structures of the [G0] and [G1] neutral rhomboidal metallodendrimers (**3a** and **3b**) were unambiguously confirmed via single-crystal X-ray crystallography. The shape and size of [G3] neutral hexagonal metallodendrimer **5d** was established with MMFF force-field simulations.

Introduction

The directional-bonding approach of coordination-driven self-assembly[1] has proven to be a particularly powerful method for the construction of supramolecular two-dimensional (2D) and three-dimensional (3D) structures with well-defined shapes and sizes.[2] Dative metal−ligand bonds are highly directional and relatively strong compared to the weaker noncovalent interactions[3] such as hydrogen-bonding, van der Waals, and solvophobic interactions. The directional-bonding coordination-driven approach allows for the combination of rigid electron-poor metal centers and complementary, rigid, electron-rich organic donors to provide a wide variety of discrete polygonal and polyhedral coordination assemblies.[4]

In this area, square planar platinum and palladium metals have long been used in conjunction with neutral nitrogen-based organic building blocks such as substituted pyridines and nitriles. Upon formation, the resulting supramolecular structures are positivly charged, bearing as many positive charges as Pt−N or Pd−N coordination bonds. The coordination of

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anionic ligands to metals such as Mo,[5] Rh,[6] Re,[7] and Zn[8] to produce *neutral* supramolecules has also been explored. Neutral supramolecular assemblies have the advantage that they are more readily soluble in organic solvents and are likely to be more suitable for the encapsulation of neutral organic guests. Recently, oxygen-to-platinum coordination has been shown to be a suitable means of constructing neutral supramolecular self-assemblies.[9] For example, rigid or flexible dicarboxylate−based building blocks have been used to self-assemble neutral rectangles, rhomboids, and triangles with Pt(II)-based acceptors via Pt−O coordination-driven self-assembly methodology.[9a,b] In addition, various neutral functionalized polygons have also been prepared from dicarboxylate building blocks functionalized with ferrocene,[9c] carborane,[9d] and crown ether[9f] moieties. However, research involving the self-assembly of neutral dendritic metallocycles formed via oxygen-to-platinum coordination is still a challenge. Noncovalent routes to the facile preparation of neutral dendritic supramolecules are especially attractive given the wide-ranging applications of dendrimers, the ease of noncovalent self-assembly, and the greater range of organic media that neutral supramolecules are miscible in.

Since the pioneering work of Newkome et al.[10] and Balzani et al.[11] in the early 1990s, metallodendrimers[12] have received considerable attention because of their potential applications in catalysis,[13] in biological mimetics,[14] and in photo- and electrochemistry.[15] Newkome and co-workers have previously reported the synthesis of isomeric neutral metallodendrimers based on bis(2,2′:6′,2″-terpyridine)-ruthenium(II) connectivity[16a,b] as well as neutral metallodendrimers possessing adamantane termini.[16c] Very recently, we have developed a new strategy[17] to prepare metallodendrimers[18] with well-defined shapes and sizes through exofunctionalization, for example, the covalent attachment of Fréchet-type dendrons to the periphery of supramolecules. For example, by combining predesigned 120° angular dendritic organic donors with 180° di-Pt(II) acceptors, "snowflake-shaped" [6+6] metallodendrimers have been prepared via coordination-driven self-assembly.[18b]

With the aim of developing the new self-assembly paradigm that utilizes Pt−O coordination interactions, our attention has turned to the construction of *neutral* dendritic metallocycles with well-defined shapes and sizes. Herein we report the design, self-assembly, and characterization of a new family of platinum(II)-based neutral dendritic metallocycles with predetermined shapes (rhomboid and hexagon) from

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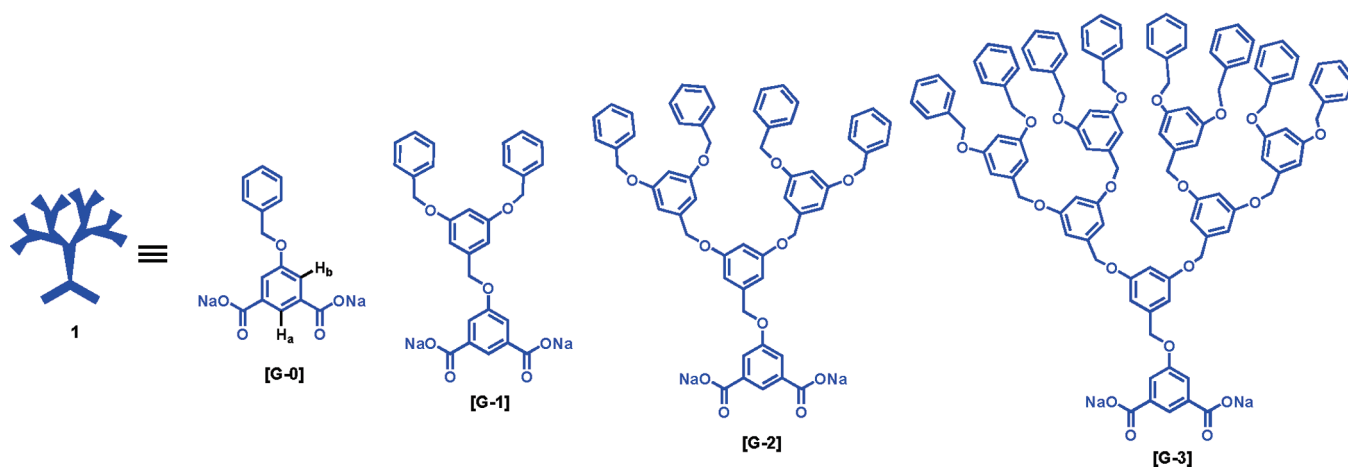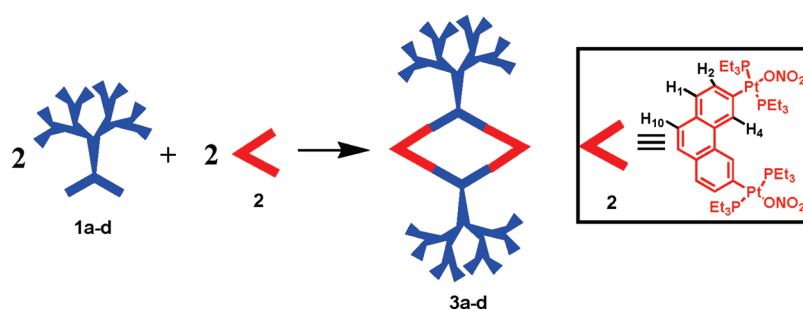
FIGURE 1. Schematic and chemical structures of 120° dendritic dicarboxylate donor subunits **1**.

SCHEME 1. Self-Assembly of [G0]−[G3] 120° Angular Dendritic Linkers 1a−d with 60° Di-Platinum Acceptor 2 To Afford Neutral Rhomboidal Metallodendrimers 3a−d

120° dendritic dicarboxylate donor tectons substituted with Fréchet-type dendrons[19] (Figure 1). Characterization of these new neutral metallodendrimers by X-ray crystallography, multinuclear NMR, mass spectroscopy, and elemental analysis is discussed.

Results and Discussion

Self-Assembly of Neutral Rhomboidal Metallodendrimers 3a−d. In general, the shape of an individual two-dimensional polygon is determined by the value of the turning angle within its angular components. According to the "directional bonding" and "symmetry interaction" models,[2a,e] discrete rhomboidal entities can be self-assembled via the combination of 60° units with 120° linking components. Upon the addition of an aqueous solution of 120° dendritic disodium carboxylate **1a−d** to an acetone solution of 60° angular acceptor 2,9-(*trans*-Pt(PEt₃)₂NO₃)₂-phenanthrene (**2**)[20] in a 1:1 molar ratio, a white precipitate of rhomboidal neutral metallodendrimers **3a−d** was formed (Scheme 1). In each case, the product was centrifuged and washed several times with water. The white solid was then dissolved in CD_2Cl_2 for ¹H and ³¹P{¹H} NMR studies.

Multinuclear NMR (¹H and ³¹P) analysis of [G0]−[G3] assemblies **3a−d** exhibited very similar characteristics, each

of which suggested the formation of discrete, highly symmetric rhomboidal dendritic metallocycles. The ¹H and ³¹P{¹H} NMR spectra of **3d** are shown in Figure 2 as representative examples. The ³¹P{¹H} NMR spectra of the [G0]−[G3] assemblies **3a−d** displayed a sharp singlet (ca. 19.0 ppm) shifted upfield from the starting platinum acceptor **2** by approximately 2.0 ppm. Compared to the charged rhomboidal metallodendrimers,[18b] where the corresponding shift is 6.4 ppm, this shift is noticeably smaller. This smaller shift can be attributed to the greater similarity between the newly formed platinum−oxygen bond and the Pt−ONO₂ bond in the starting material. Examination of the ¹H NMR spectrum of each neutral rhomboidal metallodendrimer **3a−d** is indicative of the formation of highly symmetrical structure. For example, two sharp singlets at 8.27 ppm and 7.80 ppm, respectively, were assigned to the protons (Hₐ and H_b) on the benzene ring of the dendritic dicarboxylate in **3d**. Moreover, the singlet and doublet at 8.70 and 7.74 ppm, respectively, were also observed in the ¹H NMR spectrum of **3d**, which can be attributed to the protons H₄ and H₂ on the phenanthrene ring (Figure 2). The sharp NMR signals in both the ³¹P and the ¹H NMR (see Supporting Information), along with the solubility of these species, ruled out the formation of oligomers in solution.

The structures of the neutral rhomboidal metallodendrimers **3a** and **3b** have also been confirmed by ESI-MS spectrometry. In the ESI mass spectra of the [G0] and [G1] assemblies, peaks attributable to [M + H]⁺ at $m/z = 2618.8$ for **3a** and $m/z = 3043.0$ for **3b**, where M represents the intact

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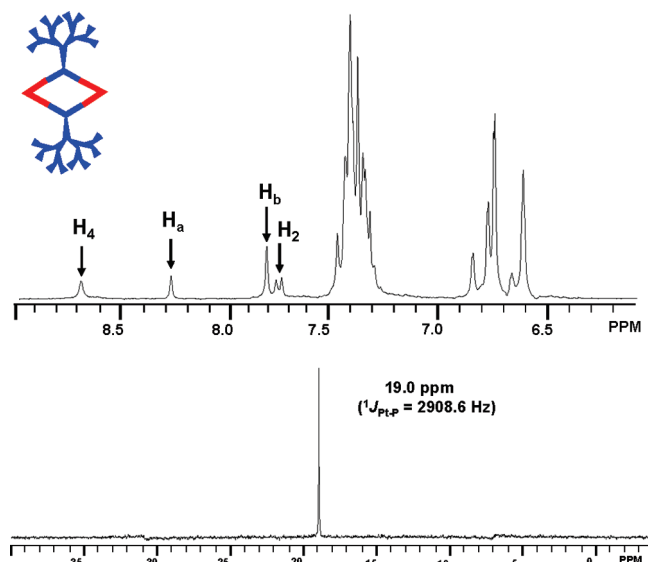(20) Kryschenko, Y. K.; Seidel, S. R.; Arif, A. M.; Stang, P. J. *J. Am. Chem. Soc.* **2003**, *125*, 5193.

FIGURE 2. Partial ¹H NMR (top) and ³¹P{¹H} NMR (bottom) spectra of [G3] neutral rhomboidal metallodendrimer **3d** (see Figure 1 and Scheme 1 for the structures of building blocks **1a−d** and **2**).
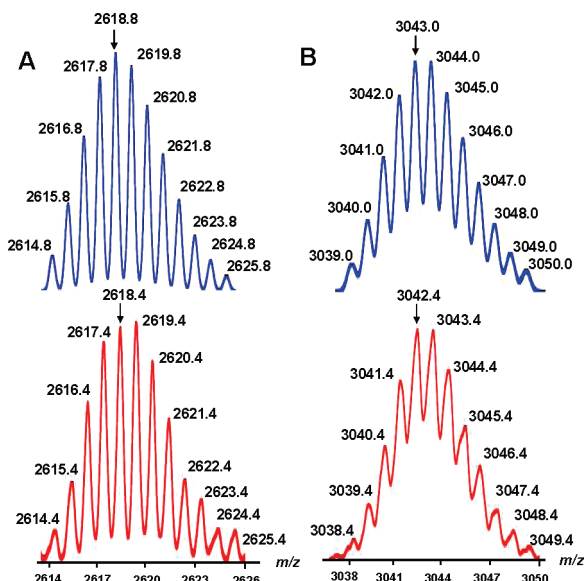

FIGURE 3. Calculated (top) and experimental (bottom) ESI-MS spectra of [G0] rhomboidal metallodendrimer (A) and [G1] rhomboidal metallodendrimer (B).

assemblies, were observed. These peaks were isotopically resolved and they agree very well with their respective theoretical distributions (Figure 3). The analysis of the signals observed in the full mass spectra confirmed that no other assembled species were formed during self-assembly.

X-ray crystallographic analysis unambiguously established the structures of **3a** and **3b** as discrete [G0] and [G1] neutral rhomboidal metallodendritic assembles (Figures 4 and 5). Crystals suitable for single-crystal X-ray analysis were grown by vapor diffusion of acetone into separate dichloromethane solutions of **3a** and **3b** at ambient temperatures for 2 days. Table 1 summarizes the data, structure solution, and refinement for **3a** and **3b**. At the molecular level, both structures feature a well-defined rhombus with an
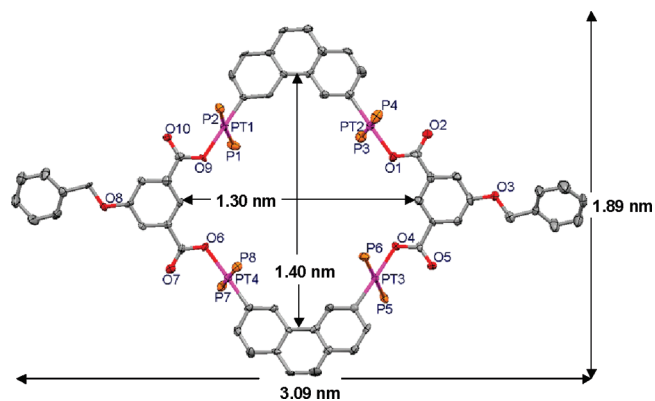
FIGURE 4. Crystal structure of [G0] neutral rhomboidal metallodendrimer **3a**. Hydrogen atoms have been removed for clarity.

approximately 2.4 × 1.3 nm cavity, similar to that of the cationic rhomboidal metallodendrimers reported previously (2.3×1.3 nm).[18b] The rhomboidal structure of **3a** has external dimensions of about 3.09 nm long and 1.89 nm wide, while **3b** spreads out over an area of about 4.11 × 1.91 nm². The geometry around each Pt metal center in both **3a** and **3b** is approximately square planar. For example, in **3a** an O(9)−Pt(1)−P(1) angle of 87.1, O(9)−Pt(1)−P(2) angle of 94.6, and a P(1)−Pt(1)−P(2) angle of 173.06 are observed, which is consistent with a square planar geometry. Selected bond lengths and angles are presented in Table 2.

Self-Assembly of Neutral Hexagonal Metallodendrimers 5a−d. Discrete hexagonal entities can be self-assembled via the combination of two complementary ditopic building blocks A^2 and X^2, each incorporating 120° angles between their coordination sites, allowing for the formation of hexagonal structures of type $A^2_3X^2_3$.[1d,2a] Recently, three-component and six-component multicationic hexagonal metallodendrimers have been prepared by using this strategy.[18] To extend the scope of this approach to the construction of neutral hexagonal metallodendrimers, we have investigated the self-assembly of 120° dendritic disodium carboxylates **1a−d** with 120° diplatinum acceptor **4**[21] (Scheme 2).

Neutral hexagonal metallodendrimers **5a−d** were prepared according to the same procedure used for in the self-assembly of neutral rhomboidal metallodendrimers **3a−d**. ³¹P{¹H} NMR analysis of each product is consistent with the formation of a single, highly symmetric species as indicated by the appearance of a sharp singlet (ca. 18.8 ppm) with concomitant ¹⁹⁵Pt satellites, shifted upfield by about 1.9 ppm as compared to **4**. As expected, this upfield shift is also smaller than that in the case of the previously reported charged hexagonal ones (ca. 5.5 ppm),[18a] which occurs for the similar reason discussed in the formation of neutral rhomboidal metallodendrimers. Likewise, the ¹H NMR spectra of metallodendrimers **5a−c** displayed very simple and sharp resonances, indicative of the generation of the desired symmetric hexagonal products. For instance, the ¹H NMR spectrum of **5d** presented two sharp singlets at 8.18 and 7.70 ppm, respectively, which can be assigned to the protons (H_a and H_b) on the benzene ring of the dendritic dicarboxylate (Figure 6). A doublet attributable to the

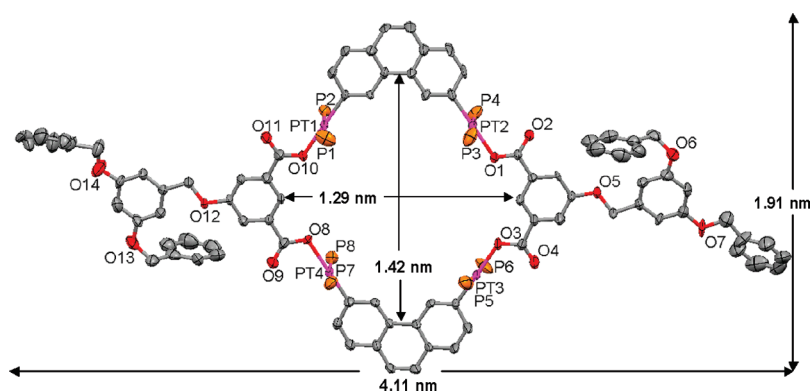(21) Leininger, S.; Schmitz, M.; Stang, P. J. *Org. Lett.* **1999**, *1*, 1921.

FIGURE 5. Crystal structure of [G1] neutral rhomboidal metallodendrimer **3b**. Hydrogen atoms have been removed for clarity.

TABLE 1. Crystal Data and Structure Refinement for 3a and 3b

	3a	3b
empirical formula	$C_{109}H_{162}O_{11}P_8Pt_4$	$C_{143}H_{198}O_{17}P_8Pt_4$
formula weight	2676.51	3217.13
temp (K)	150(1)	150(1)
cryst. system	monoclinic	triclinic
space group	$P2_1$	$P\bar{1}$
unit cell dimensions	$a = 15.5715(3)$Å	$a = 15.6185(2)$Å
	$b = 14.5131(4)$Å	$b = 16.1923(2)$Å
	$c = 25.4337(4)$Å	$c = 29.9377(4)$Å
	$\alpha = 90°$	$\alpha = 81.5975(8)°$
	$\beta = 99.9300(12)°$	$\beta = 81.9972(7)°$
	$\gamma = 90°$	$\gamma = 72.5629(8)°$
	$V = 5661.7(2)$ Å^3	$V = 7109.15(16)$ Å^3
	$Z = 2$	$Z = 2$
density (calcd, g/cm^3)	1.570	1.503
abs. coeff. (mm^{-1})	5.094	4.074
$F(000)$	2672	2672
cryst. size	$0.28 \times 0.28 \times 0.20$ mm^3	$0.28 \times 0.23 \times 0.13$ mm^3
θ range for data collection	1.33−27.54°	1.43−25.35°
reflns collected/unique	22371/22371 [R(int) = 0.0000]	40885/25919 [R(int) = 0.0546]
refinement method	full-matrix least-squares on F2	full-matrix least-squares on F2
data/restraints/params	22371/4/1135	25919/25/1380
GOF on F^2	1.035	1.040
final R indices [$F_0^2 > \sigma2(F_0^2)$]	$R1 = 0.0531$, $wR2 = 0.1051$	$R1 = 0.0788$, $wR2 = 0.1488$
largest peak and hole (e/Å^3)	2.618 and −1.586	1.967 and −1.398

TABLE 2. Selected Bond Lengths (Å) and Angles (deg) for 3a and 3b

3a					
Pt(1)−O(9)	2.133(8)	Pt(1)−P(1)	2.289(4)	Pt(1)−P(2)	2.299(4)
Pt(2)−O(1)	2.111(9)	Pt(2)−P(3)	2.302(3)	Pt(2)−P(4)	2.288(4)
O(9)−Pt(1)−P(1)	87.1(3)	O(9)−Pt(1)−P(2)	94.6(2)		
P(1)−Pt(1)−P(2)	173.06(14)	O(1)−Pt(2)−P(3)	87.8(3)		
O(1)−Pt(2)−P(4)	92.2(3)	P(3)−Pt(2)−P(4)	174.91(17)		

3b					
Pt(1)−O(10)	2.110(7)	Pt(1)−P(1)	2.292(4)	Pt(1)−P(2)	2.270(4)
Pt(2)−O(1)	2.129(7)	Pt(2)−P(3)	2.251(5)	Pt(2)−P(4)	2.328(4)
O(10)−Pt(1)−P(1)	92.8(3)	O(10)−Pt(1)−P(2)	90.0(3)		
P(1)−Pt(1)−P(2)	176.86(16)	O(1)−Pt(2)−P(3)	89.1(3)		
O(1)−Pt(2)−P(4)	90.8(2)	P(3)−Pt(2)−P(4)	179.84(16)		

proton (H$_c$) on the benzene ring attached to the platinum atom was found at 7.59 ppm in the ^{1}H NMR spectrum of **5d** as well. Upon stirring at 298 K for 72 h, the ^{31}P{^{1}H} and ^{1}H NMR of assemblies **5a-c** do not show any significant changes, demonstrating the stability of these novel supramolecular assemblies in solution. The formation of

oligomers was ruled out by the sharp NMR signals in both the ^{31}P{^{1}H} and ^{1}H NMR spectra (see Supporting Information) along with the solubility of these species.

Mass-spectrometric studies of metallodendrimers **5a−d** were performed by ESI(+)-TOF-MS and APPI(+)-TOF-MS spectrometry, which allows the assemblies to remain
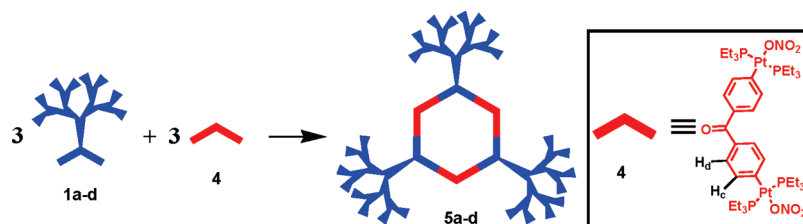
intact during the analysis process to obtain the high resolution required for the unambiguous determination of their absolute molecular weight and molecularity. However, due
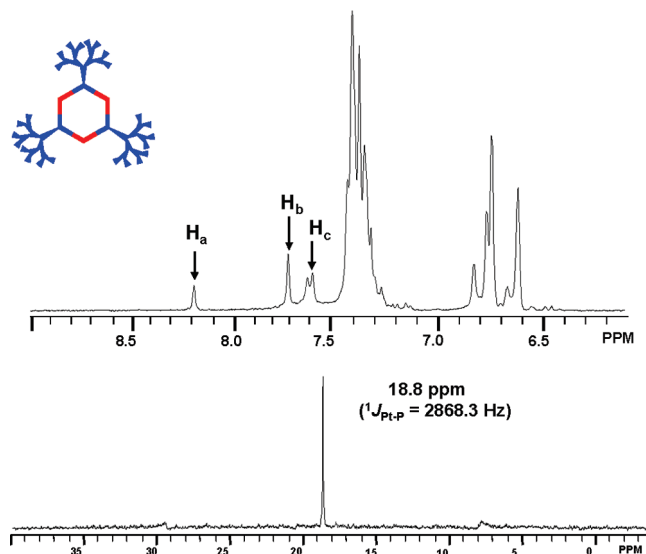

FIGURE 6. Partial ¹H NMR (top) and ³¹P{¹H} NMR (bottom) spectra of [G3] neutral hexagonal metallodendrimer **5d** (see Figure 1 and Scheme 2 for the structures of building blocks **1a–d** and **4**).

to the high molecular weight and relatively weak Pt(II)–O bonds formed between a soft metal and a hard ligand, it is more difficult to get strong mass signals even under the ESI(+)-TOF-MS or APPI(+)-TOF-MS conditions. With considerable effort, however, two peaks corresponding to the charge states [M+Na]⁺ and [M+2Na]²⁺ of [G0] assembly **5a** were observed in both ESI(+)-TOF-MS and APPI(+)-TOF-MS spectra: m/z = 3963.2 and 1993.6, respectively. These peaks were isotopically resolved (Figure 7) and agree well with their theoretically predicted distribution. The results of these mass studies provide strong support for the formation of neutral hexagonal metallodendrimers.

Close examination of the mass spectra of **5a** revealed no peaks indicating the formation or existence of [2 + 2] rhomboidal or [4 + 4] octagonal structures. It should be noted that it is not possible to form polygons with an odd number of sides (i.e., pentagon, heptagon, etc.) by combining 120° donors with 120° acceptors as they would require the direct connection of either two acceptor or two donor moieties. The similar characteristics observed in each ¹H and ³¹P NMR spectrum of [G0]–[G3] neutral assemblies **5a-d**, for example, the singularity of each ³¹P{¹H} NMR signal, along with the lack of mass spectral peaks corresponding to other polygon architectures in **5a** are supportive of the conclusion that [3 + 3] neutral hexagonal metallodendrimers are the products in each self-assembly. The elemental
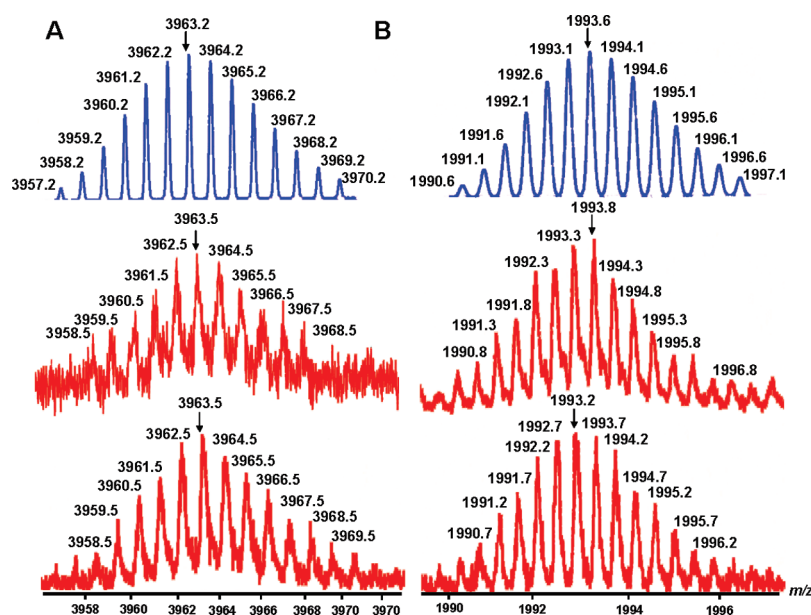

FIGURE 7. Calculated (top), experimental ESI(+)-TOF-MS (middle), and experimental APPI(+)-TOF-MS (bottom) spectra of [G0] neutral hexagonal metallodendrimer **5a** (column A shows the [M+Na]⁺ peak and column B shows the [M+2Na]²⁺ peak).
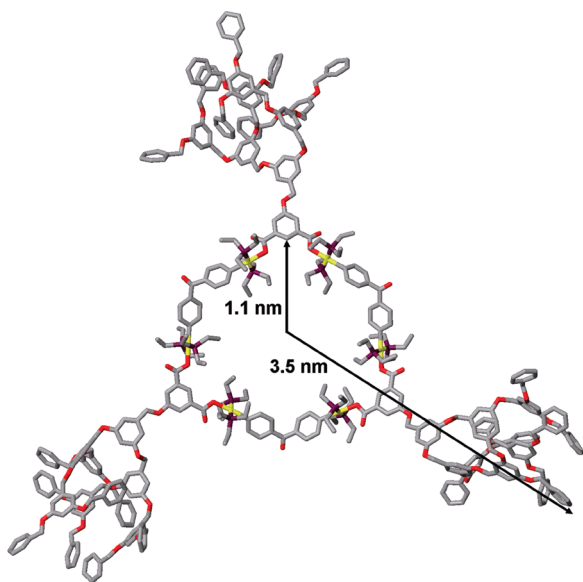
FIGURE 8. Simulated molecular model of [G3] neutral hexagonal metallodendrimer **5d** (C = gray, O = red, P = purple, Pt = yellow; hydrogen atoms have been removed for clarity).

analysis obtained for neutral hexagonal metallodendrimer assemblies **5a**−**d** all match their theoretical values.

Large supramolecular hexagonal structures and flexible, high generation dendrimers often prove difficult to crystallize. Hence, all attempts to grow X-ray quality single crystals of hexagonal metallodendrimers **5a**−**c** have proven unsuccessful to date. MMFF force-field simulations were employed to optimize the geometry of the [G3] neutral hexagonal metallodendrimer **5d**. The space-filling model of the simulated structure (Figure 8) indicates that **5d** has a roughly planar hexagonal ring at its core surrounded by flexible dendrons. The hexagonal ring-shaped metallodendrimer has an internal radius of approximately 1.1 nm and an average outer dendron radius of 3.5 nm.

Conclusion

The work presented here provides a simple yet effective approach to the construction of well-defined neutral metallodendrimers possessing predetermined sizes and shapes via oxygen-to-platinum coordination. [G0]−[G3] neutral rhomboidal metallodendrimers and hexagonal metallodendrimers were prepared by the combination of predesigned 120° dendritic dicarboxylate donor subunits and di-Pt(II) acceptors with appropriate complementary angles (60 and 120°, respectively) under mild conditions in high yields. Multinuclear NMR (^{1}H and ^{31}P) analysis of all assemblies displayed very similar characteristics that are indicative of the generation of discrete, highly symmetric species. All neutral metallodendrimers exhibit remarkable solubility in common organic solvents, such as dichloromethane and chloroform. The sharp NMR signals in both ^{31}P{^{1}H} and ^{1}H NMR spectra along with the solubility of these species ruled out the formation of oligomers. The structures of metallodendrimers **3a**, **3b**, and **5a** were further confirmed by mass spectrometry. The structures of [G0] and [G1] neutral rhomboidal dendrimers **3a** and **3b** were unambiguously established via X-ray crystallography.

We have provided a novel strategy for the design and synthesis of neutral dendritic metallocycles, in which the formation of Pt(II)−O bonds plays an essential role during the construction of the desired assemblies. This approach can be used to prepare a variety of neutral metallodendrimers with well-defined shapes and sizes through the proper choice of subunits with predefined angles and symmetry. For instance, the shape of the neutral dendritic metallocycles can be rationally designed to be either a rhomboid or a hexagon as described herein. This study offers a complementary approach to the synthesis of metallocycles that avoids the polycationic nature of analogous Pt−N based dendritic metallocycles. Extending this idea further to additional two-dimensional structures, such as squares, rectangles, and triangles, and even three-dimensional architectures like trigonal prisms and trigonal bipyramids is currently under investigation.

Experimental Section

General Procedure for the Preparation of Neutral Rhomboidal Metallodendrimers 3a−c and Neutral Hexagonal Metallodendrimers 5a−c. To a 2 mL acetone solution containing 0.005 mmol of 60° di-Pt(II) acceptor **2** or 120° di-Pt(II) acceptor **4** was added an aqueous solution (for [G3] the solution was acetone/water 1:1) of the appropriate [G0]−[G3] dendritic disodium carboxylate (0.005 mmol) drop by drop with continuous stirring (10 min), whereupon the white product precipitated. The reaction mixture was centrifuged, washed several times with acetone and water, and dried in an oven at 80 °C. The product was collected and redissolved in CD$_2$Cl$_2$ for NMR analysis.

[G0] Neutral Rhomboidal Metallodendrimer 3a. Yield: 6.41 mg (white solid), 98%. ^{1}H NMR (CD$_2$Cl$_2$, 300 MHz): δ 8.71 (s, 4H), 8.25 (s, 2H), 7.74−7.77 (m, 8H), 7.35−7.53 (m, 18H), 5.20 (s, 4H), 1.54−1.57 (m, 48H), 1.13−1.24 (m, 72H). ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$, 121.4 MHz): δ 18.9 (s, $^1J_{Pt-P}$ = 2908.8 Hz). Anal. Calcd for C$_{106}$H$_{156}$O$_{10}$P$_8$Pt$_4$·2H$_2$O: C, 47.96; H, 6.08. Found: C, 47.67; H, 5.98.

[G1] Neutral Rhomboidal Metallodendrimer 3b. Yield: 7.22 mg (white solid), 95%. ^{1}H NMR (CD$_2$Cl$_2$, 300 MHz): δ 8.72 (s, 4H), 8.27, (s, 2H), 7.79 (s, 4H), 7.76 (d, J = 8.1 Hz, 4H), 7.35−7.47 (m, 28H), 6.80 (d, J = 2.1 Hz, 4H), 6.59 (t, J = 2.1 Hz, 2H), 5.16 (s, 4H), 5.10 (s, 8H), 1.54−1.57 (m, 48H), 1.14−1.27 (m, 72H). ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$, 121.4 MHz): δ 19.0 (s, $^1J_{Pt-P}$ = 2903.8 Hz). Anal. Calcd for C$_{134}$H$_{180}$O$_{14}$P$_8$Pt$_4$·2H$_2$O: C, 52.27; H, 6.02. Found: C, 51.99; H, 5.88.

[G2] Neutral Rhomboidal Metallodendrimer 3c. Yield: 9.33 mg (white solid), 96%. ^{1}H NMR (CD$_2$Cl$_2$, 300 MHz): δ 8.71 (s, 4H), 8.27, (s, 2H), 7.80 (s, 4H), 7.75 (d, J = 7.8 Hz, 4H), 7.30−7.46 (m, 48H), 6.78 (s, 4H), 6.73 (d, J = 1.8 Hz, 8H), 6.57 (s, 6H), 5.15 (s, 4H), 5.07 (s, 16H), 5.03 (s, 8H), 1.52−1.55 (m, 48H), 1.13−1.26 (m, 72H). ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$, 121.4 MHz): δ 18.9 (s, $^1J_{Pt-P}$ = 2897.1 Hz). Anal. Calcd for C$_{190}$H$_{228}$O$_{22}$P$_8$Pt$_4$: C, 58.63; H, 5.90. Found: C, 58.22; H, 6.10.

[G3] Neutral Rhomboidal Metallodendrimer 3d. Yield: 13.41 mg (white glassy solid), 96%. ^{1}H NMR (CD$_2$Cl$_2$, 300 MHz): δ 8.70 (s, 4H), 8.27, (s, 2H), 7.80 (s, 4H), 7.74 (d, J = 7.8 Hz, 4H), 7.25−7.45 (m, 88H), 6.80 (d, J = 1.8 Hz, 4H), 6.72 (d, J = 1.8 Hz, 8H), 6.69 (d, J = 2.1 Hz, 16H), 6.61 (s, 2H), 6.55 (s, 12H), 5.14 (s, 4H), 5.00−5.07 (m, 56H), 1.52−1.55 (m, 48H), 1.11−1.21 (m, 72H). ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$, 121.4 MHz): δ 19.0 (s, $^1J_{Pt-P}$ = 2908.6 Hz). Anal. Calcd for C$_{302}$H$_{324}$O$_{38}$P$_8$Pt$_4$: C, 64.89; H, 5.84. Found: C, 65.13; H, 5.86.

[G0] Neutral Hexagonal Metallodendrimer 5a. Yield: 6.23 mg (white solid), 95%. ^{1}H NMR (CD$_2$Cl$_2$, 300 MHz): δ 8.16 (s, 3H), 7.68 (s, 6H), 7.61 (d, J = 7.2 Hz, 12H), 7.34−7.51 (m, 27H), 5.16

(s, 6H), 1.55–1.59 (m, 72H), 1.12–1.20 (m, 108H). $^{31}P\{^1H\}$ NMR (CD$_2$Cl$_2$, 121.4 MHz): δ 18.8 (s, $^1J_{Pt-P}$ = 2859.1 Hz). Anal. Calcd for C$_{156}$H$_{234}$O$_{18}$P$_{12}$Pt$_6$: C, 47.56; H, 5.99. Found: C, 47.58; H, 6.24.

[G1] Neutral Hexagonal Metallodendrimer 5b. Yield: 7.32 mg (white solid), 96%. ^{1}H NMR (CD$_2$Cl$_2$, 300 MHz): δ 8.19 (s, 3H), 7.70 (s, 6H), 7.62 (d, *J* = 7.8 Hz, 12H), 7.36–7.45 (m, 42H), 6.76 (s, 6H), 6.58 (s, 3H), 5.13 (s, 6H), 5.08 (s, 12H), 1.56–1.62 (m, 72H), 1.11–1.21 (m, 108H). $^{31}P\{^1H\}$ NMR (CD$_2$Cl$_2$, 121.4 MHz): δ 18.8 (s, $^1J_{Pt-P}$ = 2856.8 Hz). Anal. Calcd for C$_{198}$H$_{270}$O$_{24}$P$_{12}$Pt$_6$: C, 51.96; H, 5.95. Found: C, 51.92; H, 5.99.

[G2] Neutral Hexagonal Metallodendrimer 5c. Yield: 9.45 mg (white solid), 97%. ^{1}H NMR (CD$_2$Cl$_2$, 300 MHz): δ 8.18 (s, 3H), 7.70 (s, 6H), 7.60 (d, *J* = 7.5 Hz, 12H), 7.29–7.44 (m, 72H), 6.75 (s, 6H), 6.71 (d, *J* = 2.1 Hz, 12H), 6.56 (s, 9H), 5.11 (s, 6H), 5.05 (s, 24H), 5.01 (s, 12H), 1.54–1.56 (m, 72H), 1.09–1.19 (m, 108H). $^{31}P\{^1H\}$ NMR (CD$_2$Cl$_2$, 121.4 MHz): δ 18.8 (s, $^1J_{Pt-P}$ = 2873.3 Hz). Anal. Calcd for C$_{282}$H$_{342}$O$_{36}$P$_{12}$Pt$_6$·2H$_2$O: C, 57.54; H, 5.93. Found: C, 57.71; H, 6.35.

[G3] Neutral Hexagonal Metallodendrimer 5d. Yield: 13.29 mg (white glassy solid), 95%. ^{1}H NMR (CD$_2$Cl$_2$, 300 MHz): δ 8.18 (s, 3H), 7.70 (s, 6H), 7.59 (d, *J* = 7.8 Hz, 12H), 7.28–7.40 (m, 132H), 6.76, (s, 6H), 6.70 (s, 12H), 6.67 (d, *J* = 1.8 Hz, 24H), 6.59 (s, 3H), 6.54 (s, 18H), 5.09 (s, 6H), 4.98–5.01 (m, 84H), 1.53–1.55 (m, 72H), 1.07–1.17 (m, 108H). $^{31}P\{^1H\}$ NMR (CD$_2$Cl$_2$, 121.4 MHz): δ 18.8 (s, $^1J_{Pt-P}$ = 2868.3 Hz). Anal. Calcd for C$_{450}$H$_{486}$O$_{60}$P$_{12}$Pt$_6$: C, 64.37; H, 5.83. Found: C, 64.76; H, 5.75.

Supporting Information Available: Copies of NMR spectra for compounds (**3a–d** and **5a–d**) and crystallographic file (in CIF format) of **3a** and **3b**. This material is available free of charge via the Internet at http://pubs.acs.org.