Synthesis and Structural Characterization of Carborane-Containing Neutral, Self-Assembled Pt-Metallacycles

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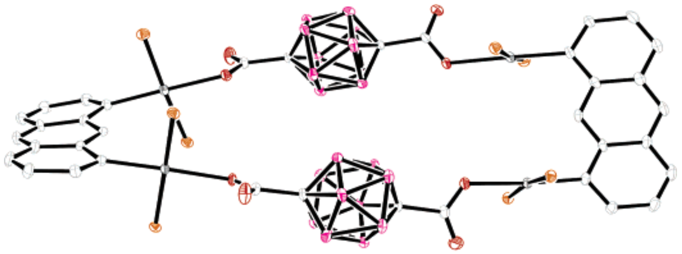

We have combined carborane chemistry with the newly developed directional bonding strategy to synthesize neutral macrocycles. The *m*- and *p*-carborane dicarboxylates were utilized as the donor linkers in conjunction with 1,8-bis[*trans*-Pt(PEt_3)$_2$$NO_3$]anthracene **3**, 2,9-bis[*trans*-Pt(PEt_3)$_2$$NO_3$]-phenanthrene **5**, and *cis*-Pt(PEt_3)$_2$(NO_3)$_2$ unit **6**. Three new platinum-based macrocycles, **4**, **7**, and **8**, were thus synthesized. $^{31}P\{^1H\}$ NMR as well as the X-ray characterization of Pt-metallacycles reveal the formation of single highly symmetrical neutral species.

Introduction

Self-assembly of simple building units into finite, nanoscopic two-dimensional (2D) and three-dimensional (3D) supramolecular structures with well-defined shapes is a prominent field of research in contemporary chemistry.[1,2] Formation of discrete supramolecular species by coordination-driven self-assembly is now a well-established phenomenon.[3−15] This approach offers a variety of opportunities for the preparation of nanoscopic supramolecular ensembles of predetermined shape, size, and symmetry, such as molecular rectangles,[4,5,8,16] triangles,[3,6,10−13,16] squares,[13,14,17−20] hexagons,[21−23] and higher order polygons.[9,22] Square planar platinum complexes in which two or three positions are occupied by strong Pt−P or Pt−C bonds and the remaining position(s) are coordinated by labile, weakly coordinating anion(s) (e.g., ONO_2, OTf)

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have long been the favorite acceptor units in this area. The design and synthesis of the desired species have mostly focused on the use of rigid, neutral nitrogen donor organic linkers.[10,24–26] Recently, we have reported that oxygen–platinum coordination is also an effective way of preparing neutral (2D) Pt-macrocycles.[8,16] The organometallic "clip" **3** and the Pt(II)-based 60° building block **5** were linked with linear and angular dicarboxylate anions (terephthalate, fumarate, isophthalate, muconate, etc.) to produce molecular rectangles, triangles, and rhomboids.[8,16] The efficacy of this newly developed methodology to synthesize neutral 2D nanoscale architectures prompted us to design more complex macrocycles containining carborane clusters. The coordination chemistry of functionalized carborane is one of the most exciting and dynamic areas of modern research. These polyhedral boron clusters have several interesting properties, such as three-dimensional aromaticity,[27] chemical inertness, thermal stability, and hydrophobic character.[28] The best known and most investigated carboranes are the three 12-vertex ortho, meta, and para isomers $C_2B_{10}H_{12}$, dicarbo-*closo*-dodecaboranes. The acidity of the terminal C–H bonds and the specific reactivity of the B–H groups in these boron clusters can be used to selectively functionalize both vertices, thereby generating a series of building blocks to be used in the synthesis of various kinds of supramolecular materials. There have been numerous examples where carborane units have been used for the synthesis of liquid crystalline materials,[29,30] catalysts,[31] highly stable polymers,[32–35] nonlinear optical materials,[36,37] pharmaceuticals (for boron capture neutron therapy),[38–44] and rigid molecular rods (for nanoarchitecture).[45–48] It has also been shown that carborane cages are capable of transmitting "electronic" information between two Co_2C_2 tetrahedral clusters.[49] Grimes and coworkers described the synthesis of a "planar octagonal cobaltacarborane" and studied its electrochemical properties.[50] Likewise Endo and co-workers exploited the hydrophobicity of the carborane core to design potent estrogen agonists and ER antagonists and studied their estrogen receptor activity.[51] Recently Stang and coworkers synthesized pyridine-containing donor and Pt-containing acceptor linkers with a carborane backbone.[52] These newly designed tectons were utilized for the synthesis of five two-dimensional supramolecular complexes using the metal-directed directional bonding approach. Since these carborane-containing macrocycles utilized Pt–N bonding, the resulting complexes were ionic in nature. Taking into consideration the hydrophobicity of the carborane cage and the newly developed strategy for the synthesis of carboxylate-based Pt-macrocycles, we were also interested to self-assemble neutral supramolecular species containing both platinum centers and carborane clusters. Herein we report the synthesis of three carborane-containing organometallic macrocycles in high yields and their characterization, including X-ray crystal data.

Results and Discussion

Synthesis of Carborane-dicarboxylates. The carborane-dicarboxylates were synthesized by the passage of dry CO_2 gas through a THF solution of the dilithiated *p*- and *m*-carborane, respectively, yielding the dicarboxylates **1** and **2** as lithium salts.

Synthesis of Carborane Assemblies. Addition of an aqueous solution of **1** to an acetone solution of the anthracene-based platinum acceptor **3**[26] resulted in gradual precipitation of the neutral rectangular macrocycle **4** in 93% isolated yield as indicated in Scheme 1. $^{31}P\{^1H\}$ NMR analysis of the precipitate indicated the formation of a single highly symmetrical species due to the appearance of a sharp singlet with concomitant ^{195}Pt satellites at 12.58 ppm compared to 14.60 ppm in **3**. The small change (2.02 ppm) in the position of the phosphorus resonance in comparison to the starting material **3** is expected as a result of the formation of a Pt–O coordinate bond replacing a similar Pt–O coordinate bond (Pt–OOC vs Pt–ONO_2) in the starting molecular "clip" **3**.

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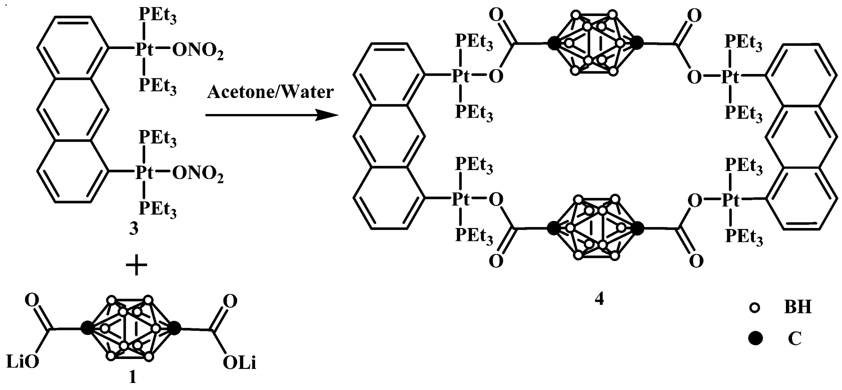
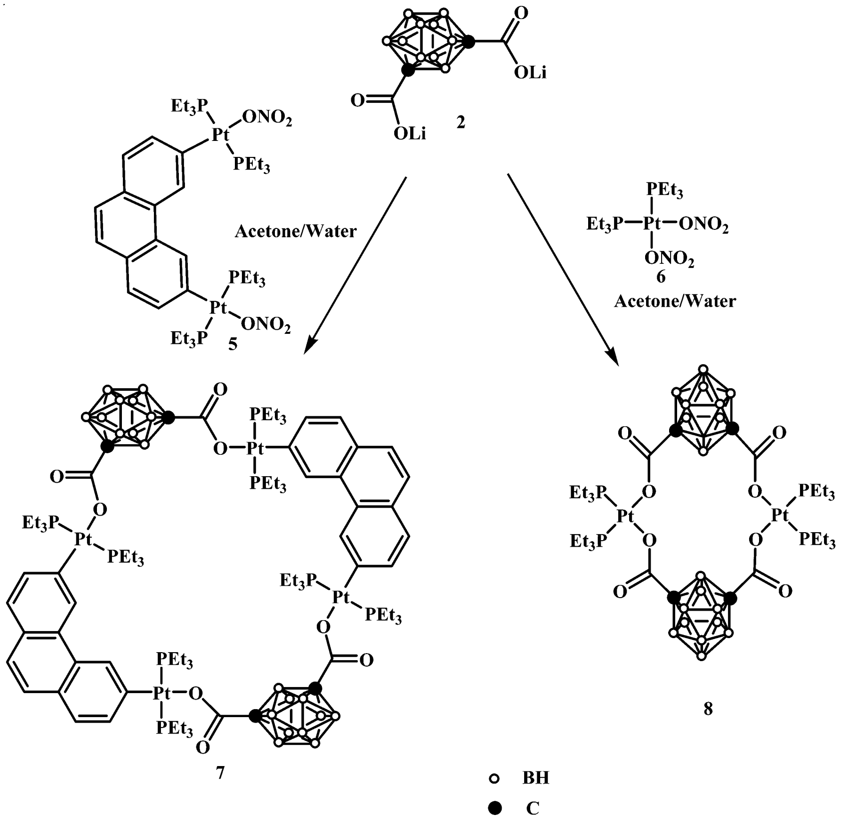
SCHEME 1. Self-Assembly of Rectangular Macrocycle 4



SCHEME 2. Self-Assembly of Macrocycles 7 and 8



Likewise, reaction of the 60° platinum acceptor **5**[10] with **2** yielded **7** in 91% isolated yield as shown in Scheme 2. The $^{31}P\{^{1}H\}$ NMR for **7** was similar to that of **4** with a single resonance near 17.08 ppm compared to 19.4 ppm for the 60° phenanthrene-based unit, **5**. Finally addition of an aqueous solution of **2** to an acetone solution of the 90° Pt linker **6**[53] in a 1:1 molar ratio resulted in the immediate precipitation of the neutral assembly **8** in 94% isolated yield (Scheme 2). In this case also, the formation of a single and highly symmetrical species was indicated by the appearance of a sharp singlet at 1.87 ppm with concomitant ^{195}Pt satellites in the $^{31}P\{^{1}H\}$ NMR spectrum. The upfield shift in the ^{31}P resonance with respect to the 90° Pt linker **6** was 2.68 ppm.

Examination of the ^{1}H NMR spectra of each self-assembled product **4**, **7**, and **8** showed that the dicarba-*closo*-dodecaborane dicarboxylates had indeed been successfully incorporated as evident from the characteristic carborane B–H broad resonances between 1.6 and 3.8 ppm.

Crystal Structure of Rectangular Assembly 4. X-ray quality crystals of **4** were obtained by vapor diffusion of acetone into a concentrated solution of the corresponding compound in CHCl$_3$. The ORTEP of neutral rectangle **4** is shown in Figures 1A and 1B. The molecular structure of **4** consists of two molecular clips connected by two *p*-carborane dicarboxylate anions through one oxygen atom of each carboxylate group in a *syn-syn* fashion (through O2 and O3) to form a highly twisted molecular rectangle as shown in Figure 1B.

The platinum oxygen bond distances are Pt(1)–O(3) = 2.149(4) Å, Pt(2)–O(5) = 2.139(4) Å, Pt(3)–O(7) = 2.149(4) Å, Pt(4)–O(2) = 2.147(4) Å. The C–O (coordinated) bond distances are longer than the C–O (uncordinated) one, as expected. The carboxylate groups in the

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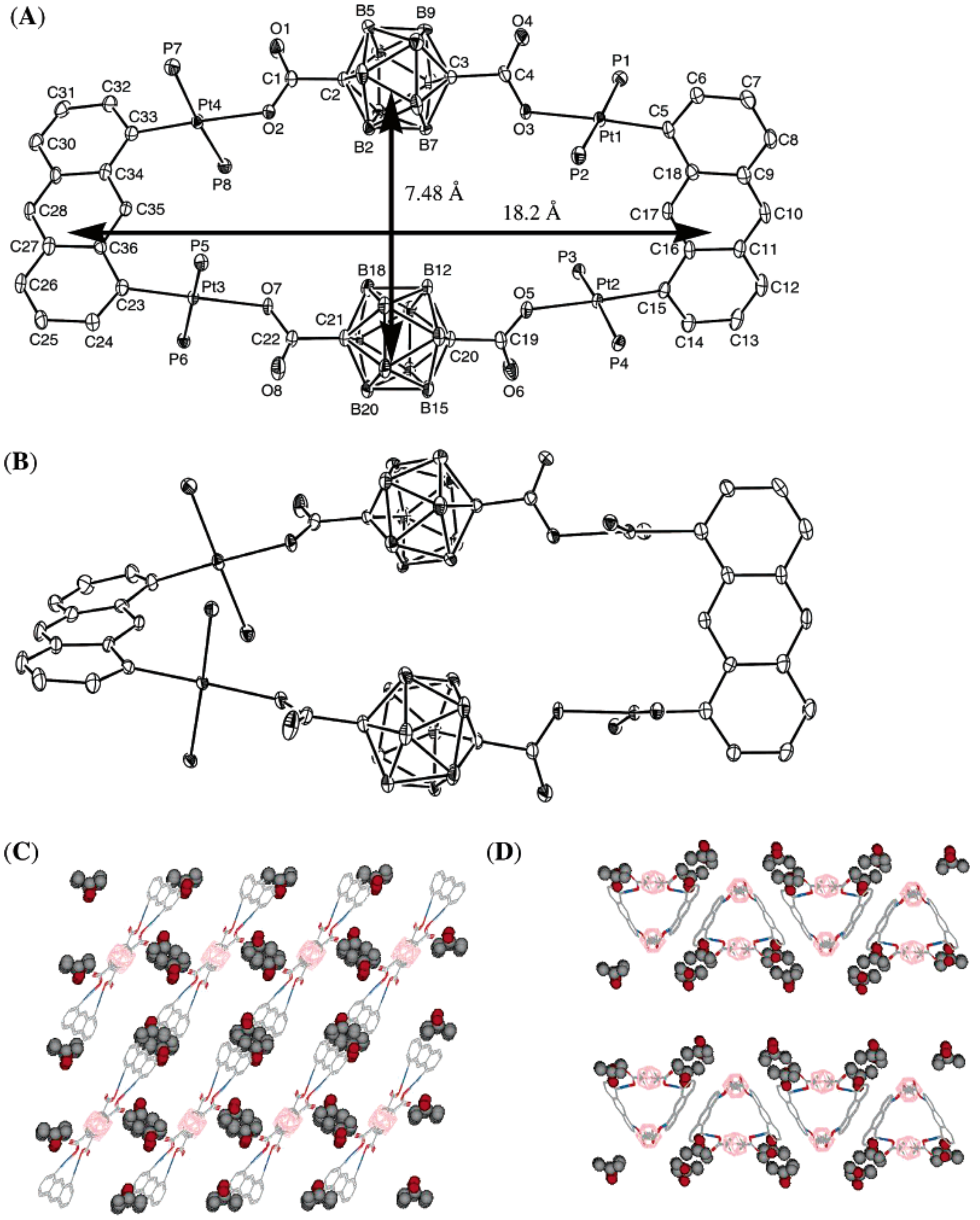

FIGURE 1. (A) ORTEP diagram of **4**. (B) Ortep diagram illustrating the inherent twist present in the molecular rectangle **4**. Hydrogen atoms and the ethyl groups attached to the phosphorus atoms and solvent molecules have been omitted for clarity. Thermal ellipsoids are drawn to 30% probability. Packing diagram of **4** with acetone molecules (CPK) (C) along the *b*-axis and (D) along the *a*-axis showing twist in the molecular rectangle **4**.

individual carborane-dicarboxylate dianion are not in the same plane. The distance between Pt(1)−Pt(2) is 5.33 Å and that between Pt(3)−Pt(4) is 5.30 Å. The length of **4** is 18.2 Å as defined by the distance between the central benzene rings of the anthracene moieties (Figure 1A). The width, as defined by the distance between the centroids of the carborane cages is 7.48 Å. The torsion angle between O(3)−C(4)−C(1)−O(2) is 53° and that between O(5)−C(19)−C(22)−O(7) is 79°. As a result the molecular rectangle (**4**) is twisted severely (Figure 1B) from planarity; the twist angle between the two anthracene moieties is 51°. The Pt−C bonds in a particular anthracene moiety are also not in the same plane. The Pt(1)−C(5)-C(15)−Pt(2) and Pt(3)−C(23)-C(33)−Pt(4) torsion angles in **4** are −29° and −26°, respectively. Ideally it should be 0° in an undistorted species. Among the several molecular rectangles previously reported containing **3**, this is the second instance where the rectangle is severely twisted, the first example being the rectangle formed by the coordination of two oxalate ions with two molecular “clips”.[54] There are two highly disordered acetone solvent molecules per rectangle (Figure 1C). The crystal lattice packing diagram reveals that the shortest distance between two adjacent rectangles is 20.1 Å along the *a*-axis. However, since the rectangle is highly twisted,

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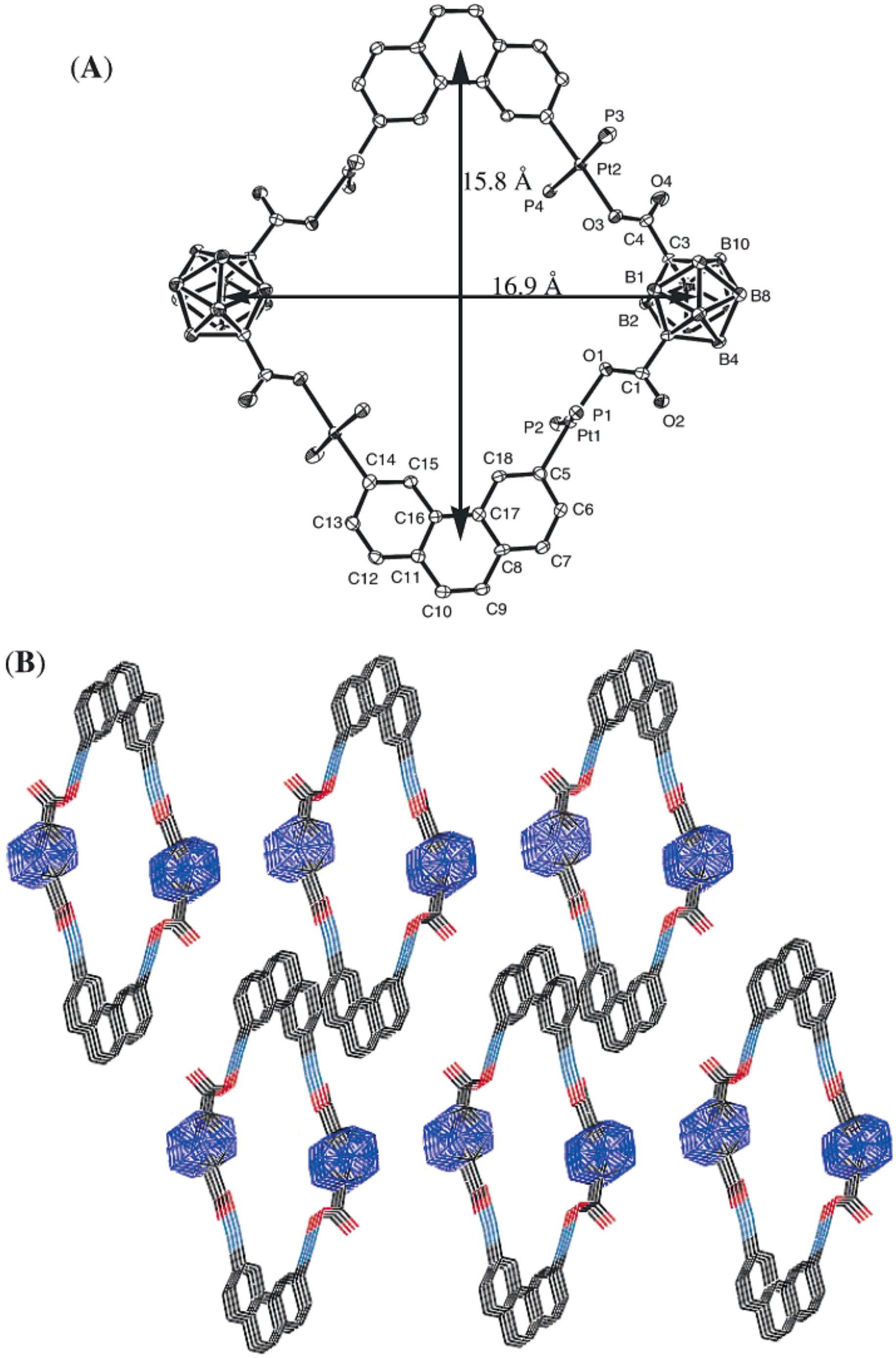

FIGURE 2. (A) ORTEP diagram of **7**. Hydrogen atoms and the ethyl groups attached to the phosphorus atoms have been omitted for clarity. Thermal ellipsoids are drawn to 30% probability. (B) Packing diagram of **7** along the *b*-axis.

it assumes a triangular shape when viewed along *a*-axis as shown in Figure 1D.

Crystal Structure of Rhomboidal Assembly 7. X-ray quality crystals of **7** were obtained by vapor diffusion of acetone into a concentrated solution of the corresponding compound in a $CHCl_3/CH_2Cl_2$ (1:1, v/v) mixture. The bridging dicarboxylate **2** is linked in a *syn-syn* fashion (through O1 and O3) in this case. Crystal structure analyses reveal that the main molecule of **7** is sitting on an inversion center. The average C−B distance is 1.713 Å, while the average B−B distance is 1.773 Å.

The platinum oxygen bond distances are Pt(1)−O(1) = 2.152(7) Å and Pt(2)−O(3) = 2.127(7) Å. The dimensions of the rhomboid are 16.9 and 15.8 Å as measured by the distances between the centroid of the phenanthrene rings and the centroid of the two carborane cages, respectively, as shown in Figure 2A. The crystal lattice packing diagram of **7** reveals that the distance between any two rhomboid molecules along the *b*-axis is 15.8 Å. There are no solvent molecules in the crystal lattice of **7.** A view of the packing of complex **7** along the *b* axis is shown in Figure 2B.

Crystal Structure of Macrocycle 8. X-ray quality crystals of self-assembled macrocycle **8** were obtained by vapor diffusion of acetone into a concentrated solution of the corresponding compound in dichloromethane. The

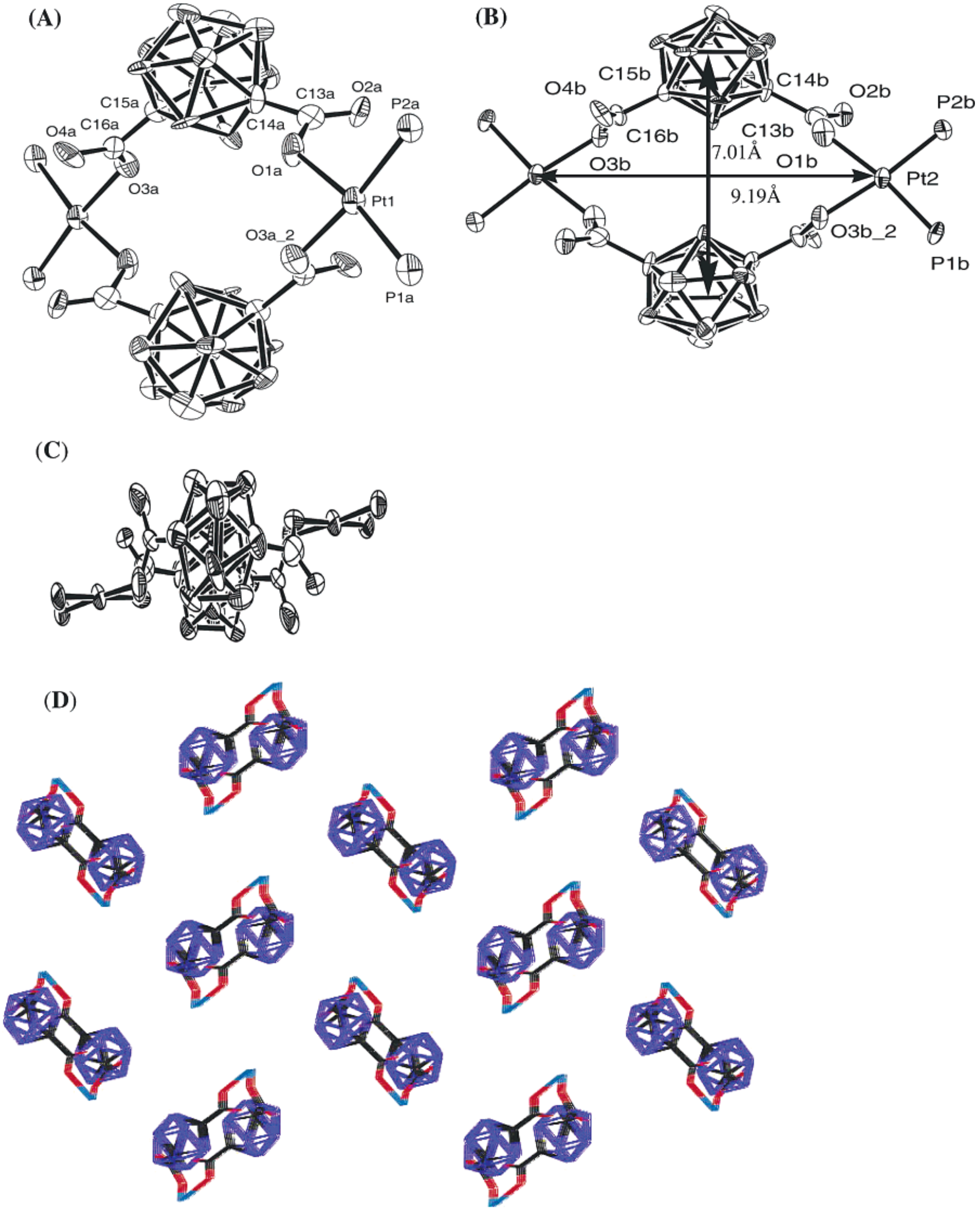

FIGURE 3. ORTEP view of (A) molecule A and (B) molecule B of **8** showing the numbering scheme used. (C) ORTEP view of the molecule **8** depicting its nonplanarity. Hydrogen atoms and the ethyl groups attached to the phosphorus atoms have been omitted for clarity. Thermal ellipsoids are drawn to 30% probability. (D) Packing diagram of **8** along the *b*-axis.

molecular structure of **8** consists of two Pt(PEt_3)$_2$ units connected by two *m*-carborane dicarboxylate dianoins through one oxygen atom of each carboxylate group as evident from the crystal structure. The bridging dicarboxylate **2** is linked in a *syn-anti* fashion (through O1 and O3) in this case, unlike that in complexes **4** and **7**, where it is *syn-syn*. There are no solvent molecules present in the crystal lattice. Structure analysis revealed that there were two centrosymmetric $[C_{32}H_{80}B_{20}O_8P_4Pt_2]_{1/2}$ moieties (**8**) in the unit cell, each sitting on an inversion center. The two moieties have been designated as "molecule A" and "molecule B". Each individual molecule has a pseudo-rhomboidal shape and they have the same dimensions; however, they have slightly different bond parameters with respect to each other. Selected bond distances and angles indicating these small differences in the bonding parameters between molecules A and B have been listed in Table 1.

The dimensions of this rhomboid macrocycle are 9.19 and 7.01 Å as measured by the distance between the two

TABLE 1. Selected Bond Lengths (Å) and Angles (deg) for Molecules A and B of $[C_{16}H_{40}B_{10}O_4P_2Pt]_2$

	Molecule A		
Pt1−O1A	2.08(2)	Pt1−P1A	2.235(11)
Pt1−P2A	2.281(11)	C13A−C14A	1.49(5)
Pt1−O3A[a]	2.12(3)	C15A−C16A	1.47(5)
O2A−C13A−O1A	123(4)	O2A−C13A−C14A	131(4)
O1A−C13A−O14A	106(3)	O4A−C16A−O3A	127(4)
O4A−C16A−C15A	121(4)	O3A−C16A−C15A	111(3)
	Molecule B		
Pt2−O1B	2.12(3)	Pt2−P1B	2.261(10)
Pt2−P2B	2.217(10)	C13B−C14B	1.58(5)
Pt2−O3B[b]	2.07(2)	C15B−C16B	1.50(5)
O1B−C13A−O2B	132(4)	O2B−C13B−C14B	116(4)
O1B−C13B−O14B	112(4)	O4B−C16B−O3B	128(4)
O4B−C16B−C15B	118(3)	O3B−C16B−C15B	114(3)

[a] Symmetry transformations used to generate equivalent atoms: $-x + 2, -y + 2, -z + 1$. [b] Symmetry transformations used to generate equivalent atoms: $-x + 1, -y + 1, -z + 2$.

Pt atoms and the centroid of the two carborane cages as shown in the Figure 3B. The average C−B bond distances are 1.749 Å (molecule A) and 1.725 Å (molecule B), while the average B−B distances are 1.777 Å (molecule A) and 1.785 Å (molecule B).

Since the coordination mode of the bridging carborane dicarboxylates is *syn-anti*, the two Pt atoms in a particular macrocycle are not present in the same plane (Figure 3C). The Pt1_2−C15A−C14A−Pt1 dihedral angle is −45.2°, while the Pt2_2−C15B−C14B−Pt2 dihedral angle is −49.2°. The packing diagram of molecule **8** is shown in Figure 3D. The shortest distance (14.2 Å) between any two neighboring rhomboidal molecules is along the *b*-axis. The distances between adjacent macrocycles along the *a*- and *c*-axes are 17.7 Å. The geometry around the platinum atom is nearly square planar in all three complexes irrespective of the distortions present in the molecule. The cis angles around the platinum are all 90° ± 9° and the trans angles are all 180° ± 10°.

Conclusion

Having established the efficacy of our coordination-driven, self-assembly paradigm for the synthesis of neutral Pt-macrocycles, we have extended the technique to the next level of complexity by combining it with carborane chemistry. Using the newly developed directional bonding approach (platinum−oxygen coordination), three carborane-containing Pt-metallacycles were synthesized in 91−94% yields. In the previous report describing the self-assembly of coordination-driven supramolecular complexes with a carborane backbone,[52] the preparation of various carborane-containing linkers required multiple steps involving rigorous organic synthesis. However, carborane-containing dicarboxylates **1** and **2** are easy to obtain in a single-step reaction from the respective carborane. Just like the ionic carborane-containing complexes, macrocycles **4**, **7**, and **8** have high solubility in common organic solvents (dichloromethane and chloroform), which aids in the characterization of these species by NMR. Our current research is in extending this protocol to synthesize 3-dimensional nanoscalar structures such as capsules and cubes incorporating carboranes.

Experimental Section

General Procedure for the Preparation of Compounds 4, 7, and 8. To a 2 mL acetone solution containing 0.010 mmol of the appropriate Pt-acceptor linker **3**, **5**, or **6** was added an aqueous solution (2 mL) of the dilithium salt of the appropriate acid (**1** or **2**) (0.010 mmol) drop by drop with continuous stirring (15 min). The products, which precipitated, were filtered and washed with acetone and water. Single crystals for structure analysis were obtained by vapor diffusion of acetone into the chloroform/dichloromethane solution of the products.

Cyclobis[(1,8-bis[*trans*-Pt(PEt_3)$_2$]anthracene)(μ-1,2-*p*-$C_4B_{10}O_4$)] (4). Yield 93%. Anal. Calcd for $C_{84}H_{156}B_{20}O_8P_8$-$Pt_4$.$CH_3COCH_3$: C, 40.24; H, 6.29. Found: C, 40.30; H, 6.15. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 121.4 MHz): δ 12.58 (s, $^1J_{PPt} = 2860$ Hz). ^1H NMR ($CDCl_3$, 300 MHz): δ 0.98 (m, 72H, PCH_2CH_3), 1.57 (m, 48H, PCH_2CH_3), 3.6−1.2 (m, 20H, BH), 6.94 (t, 4H, $H_{3,6}$), 7.52 (dd, 8H, $H_{4,5}$ and $H_{2,7}$), 8.13 (s, 2H, H_{10}), 9.51 (s, 2H, H_9).

Cyclobis[(2,9-bis[*trans*-Pt(PEt_3)$_2$]phenanthrene)(μ-1,2-*m*-$C_4B_{10}O_4$)] (7). Yield 91%. Anal. Calcd for $C_{84}H_{156}B_{20}O_8P_8$-$Pt_4$: C, 39.74; H, 6.19. Found: 39.98; H, 6.27. $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 121.4 MHz): δ 17.08 (s, $^1J_{PPt} = 2898$ Hz). ^1H NMR (CD_2Cl_2, 300 MHz): δ 1.15 (m, 72H, PCH_2CH_3), 1.50 (m, 48H, PCH_2CH_3), 3.6−1.8 (m, 20H, BH), 7.37 (d, 6H, $^3J_{H4-H3} = 8.05$ Hz, H_4), 7.44 (s, 6H, H_5), 7.59 (d, 6H, H_3), 8.59 (s, 6H, H_1).

Cyclobis[{Pt(PEt_3)$_2$}{μ-1,2-*m*-$C_4B_{10}O_4$}] (8). Yield 94%. Anal. Calcd for $C_{32}H_{80}$ $B_{20}O_8P_4Pt_2 \cdot 2CH_3COCH_3$: C, 31.71; H, 6.44. Found: C, 31.58; H, 6.10 $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 121.4 MHz): δ 1.87 (s, $^1J_{PPt} = 3690$ Hz). ^1H NMR (CD_2Cl_2, 300 MHz): δ 1.15 (m, 36H, PCH_2CH_3), 1.50 (m, 24H, PCH_2CH_3), 3.6−1.8 (m, 20H, BH).

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Supporting Information Available: General methods, X-ray data collection, structure and refinement for compounds **4**, **7**, and **8**; crystallographic data and refinement parameters for compounds **4**, **7**, and **8** (Table 1); ^{31}P and ^1H NMR spectra and X-ray crystallographic data of assemblies **4**, **7**, and **8** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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