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Self-Assembly of Neutral Platinum-Based Supramolecular Ensembles Incorporating Oxocarbon Dianions and Oxalate

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Five neutral platinum-based macrocycles incorporating cyclic oxocarbondianions, squarate and croconate and their acyclic analogue, oxalate, have been synthesized in 90–95% yield via self-assembly. The combination of the diplatinum molecular clip with all three dianions afforded molecular rectangles, whereas a platinum-based 60° acceptor unit produced a supramolecular rhomboid with croconate ion but a triangle with squarate ion. In all cases, multinuclear NMR spectra were consistent with the formation of single highly symmetrical species. The three rectanglular and the rhomboid assemblies were characterized by single-crystal X-ray crystallography. The triangular species was characterized by FAB mass spectrometry.

Introduction

Formation of discrete supramolecular species by coordination-driven self-assembly is now a well-established phenomenon.[1] This approach offers a variety of opportunities for the preparation of nanoscopic supramolecular ensembles of predetermined shape, size, and symmetry.[2,3] 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) 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 except in a few cases where flexible linkers were used to generate discrete ionic macrocyclic structures.[4,5] Anionic oxygen donor ligands have not been used for the construction of finite supramolecular self-assemblies of Pt(II), presumably due to the weakness of the platinum−oxygen bond, until recently when we reported a series of neutral structures using dicarboxylate linkers.[6] To further exploit this newly developed strategy for the formation of neutral assemblies using anionic oxygen donor ligands, we decided to explore oxocarbondianions as potential donor tectons. The oxocarbon dianions ($C_nO_n^{2-}$) are an interesting class of cyclic compounds having aromaticity and various bridging properties.[7] Their complexes with transition metals are well known for their interesting magnetic and optoelectronic properties.[8−10] A new interest

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(1) (a) Lehn, J.-M. *Supramolecular Chemistry: concepts and perspectives*; VCH: New York, 1995. (b) Chambron, J.-C.; Dietrich-Buchecker, C.; Sauvage, J.-P. In *Comprehensive Supramolecular Chemistry*; Lehn, J.-M., Chair, E., Atwood, J. L., Davis, J. E. D., MacNicol, D. D., Vogtle, F., Eds.; Pergamon Press: Oxford, 1996; Vol. 9, Chapter 2, p 43. (c) Uller, E.; Demleitner, I.; Bernt, I.; Saalfrank, R. W. Synergistic Effect of Serendipity and Rational Design in Supramolecular Chemistry. In *Structure and Bonding*; Fujita, M., Ed.; Springer: Berlin, 2000; Vol. 96, p 149. (d) Leininger, S.; Olenyuk, B.; Stang, P. J. *Chem. Rev.* **2000**, *100*, 853. (e) Seidel, S. R.; Stang, P. J. *Acc. Chem. Res.* **2002**, *35*, 972. (f) Cotton, F. A.; Lin, C.; Murillo, C. A. *Acc. Chem Res.* **2001**, *34*, 759. (g) Caulder, D. L.; Raymond, K. N. *Acc. Chem. Res.* **1999**, *32*, 975. (h) Fujita, M. *Chem. Soc. Rev.* **1998**, *27*, 417. (g) Swiegers, G. F.; Malefetse, T. J. *Coord. Chem. Rev.* **2002**, *225*, 91.

(2) (a) Pak, J. J.; Greaves, J.; McCord, D. J.; Shea, K. J. *Organometallics* **2002**, *21*, 3552. (b) Lee, S. J.; Lin, W. *J. Am. Chem. Soc.* **2002**, *124*, 4554. (c) Liu, X.; Stern, C. L.; Mirkin, C. A. *Organometallics* **2002**, *21*, 1017. (d) Han, G.; Dong, G.; Duan, C.-Y.; Mo, H.; Meng, Q.-J. *New J. Chem.* **2002**, *26*, 1371. (e) Sun, S.-S.; Anspach, J. A.; Lees, A. J. *Inorg. Chem.* **2002**, *41*, 1862. (f) Manimaran, B.; Thanasekaran, P.; Rajendran, T.; Lin, R.-J.; Chang, I.-J.; Lee, G.-H.; Peng, S.-M.; Rajagopal, S.; Lu, K.-L. *Inorg. Chem.* **2002**, *41*, 5323. (g) Abourahma, H.; Moulton, B.; Kravtsov, V.; Zaworotko, M. J. *J. Am. Chem. Soc.* **2002**, *124*, 9990. (h) Cui, Y.; Ngo, H. L.; Lin, W. *Inorg. Chem.* **2002**, *41*, 1033. (i) Cotton, F. A.; Lin, C.; Murillo, C. A. *J. Am. Chem. Soc.* **2001**, *123*, 2670. (j) Cotton, F. A.; Daniels, L. M.; Lin, C.; Murillo, C. A.; Yu, S.-Y. *J. Chem. Soc., Dalton Trans.* **2001**, 502. (k) Kuehl, C. J.; Huang, S. D.; Stang, P. J *J. Am. Chem. Soc.* **2001**, *123*, 9634. (l) Campos-Fernandez, C. S.; Clerac, R.; Koomen, J. M.; Russell, D. H.; Dunbar, K. R. *J. Am. Chem. Soc.* **2001**, *123*, 773. (m) Kuehl, C. J.; Mayne, C. L.; Arif, A. M.; Stang, P. J. *Org. Lett.* **2000**, *2*, 3727. (n) Schmitz, M.; Leininger, S.; Fan, J.; Arif, A. M.; Stang, P. J. *Organometallics* **1999**, *18*, 4817. (o) Habicher, T.; Nierengarten, J.-F.; Gramlich, V.; Diederich, F. *Angew. Chem., Int. Ed.* **1998**, *37*, 1916. (p) Stang, P. J.; Persky, N. E.; Manna, J. *J. Am. Chem. Soc.* **1997**, *119*, 4777. (q) Hartshorn, C. M.; Steel, P. J. *Inorg. Chem.* **1996**, *35*, 6902.

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in these compounds arose with the development of crystal engineering of organometallic compounds.[11] The structural topology of the coordination polymers resulting from these dianions can be designed by selection of such parameters as the stereoelectronic preferences of the metal ions, spatial disposition of the donor oxygen atoms and the reaction conditions. In addition to the oxo groups that coordinate to the metal, these ligands contain additional oxygen atoms that can act as acceptors in hydrogen bonding.

Among the four monocyclic oxocarbon dianions, deltate ($C_3O_3^{2-}$) and rhodizonate ($C_6O_6^{2-}$) are rather unstable.[12] Other than deltic acid itself, none of their compounds has been structurally characterized.[13] The coordination behavior of the other two members of this family, i.e., squarate ($C_4O_4^{2-}$) and croconate ($C_5O_5^{2-}$), has been thoroughly investigated and compared with that of oxalate ($C_2O_4^{2-}$) for their planar stereochemistry, oxygen donor atoms, and identical overall charge. Single-crystal X-ray analyses, as well as solution studies, reveal a closer similarity between croconate and oxalate than between the two cyclic oxocarbon dianions.[8] The squarate is known to coordinate the metal centers as a μ-1,2-bismonodentate, μ-1,3-bismonodentate, or tetramonodentate bridging ligand.[9] The croconate complexes show that the dianion can coordinate to the metal ions as terminal bidentate, bridging bidentate/monodentate, or as a bridging bis-bidentate ligand.[10] In platinum systems, oxalate invariably acts as a chelating bidentate ligand[14] except in one compound where it is unidentate;[15] only two compounds of squarate are structurally characterized, and in both of them, it acts as a μ-1,2-bismonodentate ligand.[16]

Herein, we report self-assembled platinum(II)-based neutral and finite supramolecular macrocycles incorporating these interesting functional oxocarbon dianions, as well as their acyclic analogue, the oxalate moiety. The main difference between the dicarboxylates and oxocarbondianions is that the two carboxylate groups of the former are oriented in a definite direction and they act as rigid linkers to form assemblies of predetermined shape and size. The latter, on the other hand, contain more than two oxygen atoms in different directions, all of which are capable of coordination to the metal centers. Thus, their incorporation provides yet another test for the preference of formation of the highly symmetrical cyclic species over the oligomeric complexes. The derived macrocycles containing these flexidentate dianions also give an insight into the importance of entropy in controlling the size of the self-assembled species.

Results and Discussion

Syntheses and Spectral Studies. The neutral supramolecular assemblies were synthesized as shown in Schemes 1 and 2. Addition of an aqueous solution of linkers **3**−**5** to an acetone solution of diplatinum clip **1** in a 1:1 molar ratio resulted in immediate precipitation of the neutral assemblies **6**−**8**, respectively, in 90−98% isolated yields (Scheme 1). Similar treatment of the 60° platinum acceptor unit **2** with linker **5** and **4**, respectively, produced the supramolecular rhomboid **9** and triangle **10** in 85−90% yields (Scheme 2). The oxalate ion (**3**) does not react with **2** to form any cyclic assembly.

The ^{31}P NMR spectra of the macrocycles **6**−**10** are consistent with the formation of a single, highly symmetrical species, as indicated by the appearance of sharp singlets with concomitant ^{195}Pt satellites. For rectangles **6**−**8**, these singlets

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(3) (a) Qin, Z.; Jennings, M. C.; Puddephatt, R. J. *Inorg. Chem.* **2002**, *41*, 3967 (b) Qin, Z.; Jennings, M. C.; Puddephatt, R. J. *Chem. Commun.* **2001**, 2676. (c) Schweiger, M.; Seidel, S. R.; Arif, A. M.; Stang, P. J. *Angew. Chem., Int. Ed*. **2001**, *40*, 3467. (d) Sun, S.-S.; Lees, A. J. *Inorg. Chem.* **1999**, *38*, 4181. (e) Cotton, F. A.; Lin, C.; Murillo, C. A. *Inorg. Chem*. **2001**, *40*, 575. (f) Kryschenko, Y. K.; Seidel, S. R.; Arif, A. M.; Stang, P. J. *J. Am. Chem. Soc*. **2003**, *125*, 5193. (g) Chi, K.-W.; Addicott, C.; Arif, A. M.; Stang, P. J. *J. Am. Chem. Soc*. **2004**, *126*, 16569.

(4) (a) Tabellion, F. M.; Seidel, S. R.; Arif, A. M.; Stang, P. J. *J. Am. Chem. Soc.* **2001**, *123*, 7740. (b) Tabellion, F. M.; Seidel, S. R.; Arif, A. M.; Stang, P. J. *J. Am. Chem. Soc.* **2001**, *123*, 11982. (c) Chatterjee, B.; Noveron, J. C.; Resendiz, M. J. E.; Liu J.; Yamamoto, T.; Parker, D.; Cinke, M.; Nguyen, C. V.; Arif, A. M.; Stang, P. J. *J. Am. Chem. Soc.* **2004**, *126*, 10645.

(5) (a) Fujita, M.; Ibukuro, F.; Seki, H.; Kamo, O.; Imanari, M.; Ogura, K. *J. Am. Chem. Soc.* **1996**, *118*, 899−900. (b) Fujita, M.; Aoyagi, M.; Ibukuro, F.; Ogura, K.; Yamaguchi, K. *J. Am. Chem. Soc.* **1998**, *120*, 611−612. (c) Fujita, M.; Ibukuro, F.; Yamaguchi, K.; Ogura, K. *J. Am. Chem. Soc.* **1995**, *117*, 4175−4176.

(6) (a) Das, N.; Mukherjee, P. S.; Arif, A. M.; Stang, P. J. *J. Am. Chem. Soc.* **2003**, *125*, 13950. (b) Mukherjee, P. S.; Das, N.; Kryschenko, Y. K.; Arif, A. M.; Stang, P. J. *J. Am. Chem. Soc.* **2004**, *126*, 2464.

(7) (a) West, R.; Niu, H. Y. *J. Am. Chem. Soc.* **1963**, *85*, 2586. (b) Baenziger, N. C.; Hegenbarth, J. J. *J. Am. Chem. Soc.* **1964**, *86*, 3250. (c) Glick, M. D.; Downs, G. L.; Dahl, L. F. *Inorg. Chem.* **1964**, *3*, 1712. (d) Schleyer, P. R.; Najafian, K.; Kiran, B.; Jiao, H. *J. Org. Chem.* **2000**, *65*, 426.

(8) (a) Castro, I.; Sletten, J.; Faus, J.; Julve, M. *J. Chem. Soc., Dalton Trans.* **1992**, 2271. (b) Castro, I.; Faus, J.; Julve, M.; Mollar, M. A.; Monge, A.; Gutiérrez-Puebla, E. *Inorg. Chim. Acta* **1989**, *161*, 97. (c) Castro, I.; Faus, J.; Julve, M.; Muñoz, M. C.; Díaz, W.; Solans, X. *Inorg. Chim. Acta* **1991**, *179*, 59. (d) Castro, I.; Faus, J.; Julve, M.; Gleizes, A. *J. Chem. Soc., Dalton Trans.* **1991**, 1937. (e) Castro, I.; Faus, J.; Julve, M.; Journaux, Y.; Sletten, J. *J. Chem. Soc., Dalton Trans.* **1991**, 2533.

(9) (a) Xanthopoulos, C. E.; Sigalas, M. P.; Katsoulos, G. A.; Tsipis, C. A.; Hadjikostas, C. C.; Terzis, A.; Mentzafos, M. *Inorg. Chem*. **1993**, *32*, 3743 and references therein. (b) Castro, I.; Sletten, J.; Calatayud, M. L.; Julve, M.; Cano, J.; Lloret, F.; Caneschi, A. *Inorg. Chem*. **1995**, *34*, 4903 and references therein. (c) Akhriff, Y.; Server-Carrio, J.; Sancho, A.; Garcia-Lozano, J.; Escriva, E.; Soto, L. *Inorg. Chem*. **2001**, *40*, 6832. (d) Konar, S.; Corbella, M.; Zangrando, E.; Ribas, J.; Chaudhuri, N. R. *Chem. Commun.* **2003**, 1424.

(10) (a) Castro, I.; Sletten, J.; Glærum, L. K.; Lloret, F.; Faus, J.; Julve, M. *J. Chem. Soc., Dalton Trans.* **1994**, 2777. (b) Deguenon, D.; Bernardinelli, G.; Tuchagues, J. P.; Castan, P. *Inorg. Chem.* **1990**, *29*, 3031. (c) Wang, C.-C.; Yang, C.-H.; Lee, G.-H. *Inorg. Chem.* **2002**, *41*, 1015. (d) Castro, I.; Sletten, J.; Faus, J.; Julve, M.; Journaux, Y.; Lloret, F.; Alvarez, S. *Inorg. Chem.* **1992**, *31*, 1889. (e) Castro, I.; Calatayud, M. L.; Lloret, F.; Sletten J.; Julve, M. *J. Chem. Soc., Dalton Trans.* **2002**, 2397. (f) Maji, T. K.; Konar, S.; Mostafa, G.; Zangrando, E.; Lu. T.-H.; Chaudhuri, N. R. *Dalton Trans.* **2003**, 171. (g) Wang, C.-C.; Yang, C.-H.; Tseng, S.-M.; Lee, G.-H.; Chiang, Y.-P.; Sheu, H.-S. *Inorg. Chem.* **2003**, *42*, 8294.

(11) Braga, D.; Grepioni, F. *Chem. Commun.* **1998**, 911.

(12) Serratosa, F. *Acc. Chem Res*. **1983**, *16*, 170.

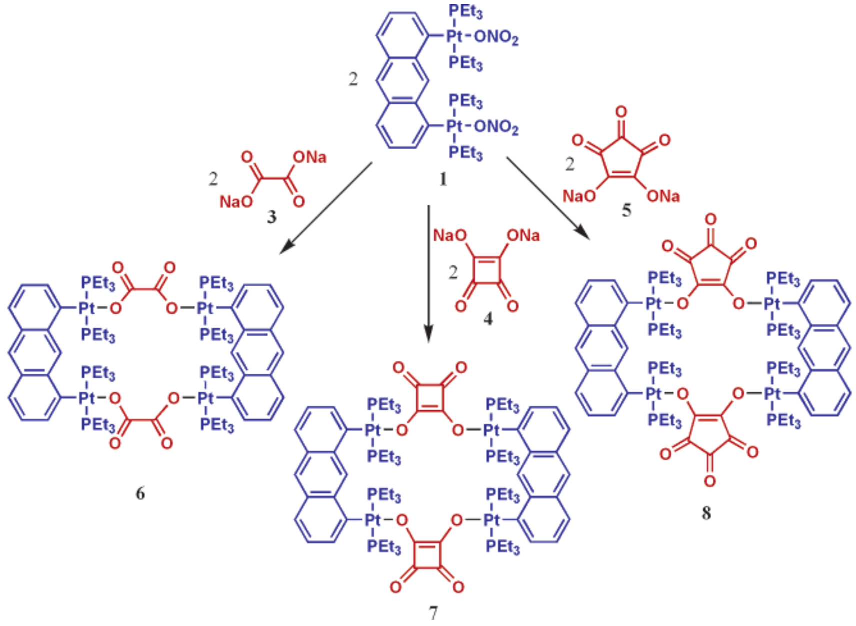
(13) Semmingsen, D.; Groth, P. *J. Am. Chem. Soc.* **1987**, *109*, 7238.

(14) (a) Mizuno, M.; Underhill, A. E.; Carneiro, K. *J. Chem. Soc., Dalton Trans.* **1983**, 1771. (b) Bowler, B. E.; Ahmed, K. J.; Sundquist, W. I.; Hollis, L. S.; Whang, E. E.; Lippard, S. J. *J. Am. Chem. Soc*. **1989**, *111*, 1299. (c) Xu, Q.; Khokhar, A. R.; Bear, J. L. *Inorg. Chim. Acta*. **1990**, *178*, 107. (d) Utrecht, J.-G.; Preetz *Z. Anorg. Allg. Chem*. **2001**, *627*, 1459. (e) Al-Allaf, T. A. K.; Schmidt, H.; Merzweiler, K.; Wagner, C.; Steinborn, D. *J. Organomet. Chem.* **2003**, *678*, 48. (f) Abu-Surrah, A. S.; Al-Allaf, T. A. K.; Klinga, M.; Ahlgren, M. *Polyhedron* **2003**, *22*, 1529.

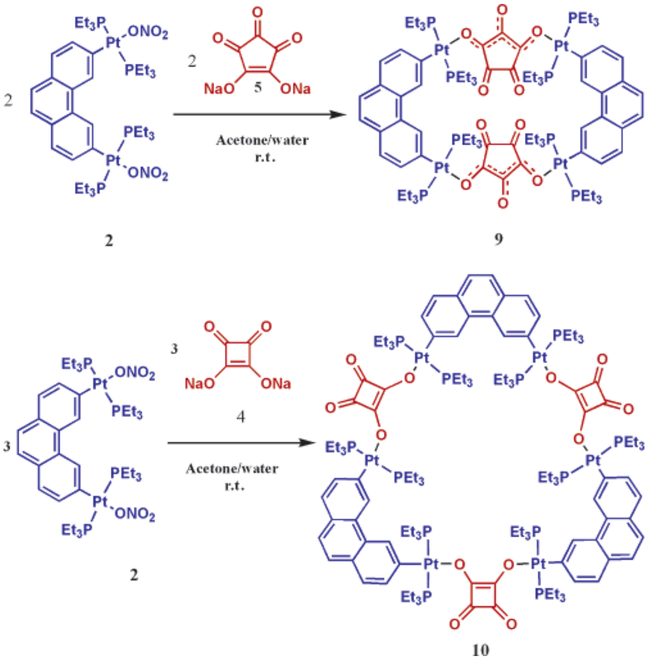
(15) Villa, A. C.; Manfredotti A. G.;Giacomelli, A.; Guastini, C.; Indelli, A. *Inorg. Chem*. **1975**, *14*, 1654.

(16) (a) Simonsen, O.; Toftlund, H. *Inorg. Chem*. **1981**, *20*, 4044. (b) Bernardinelli, G.; Castan, P.; Soules, R. *Inorg. Chim. Acta* **1986**, *120*, 205.

Scheme 1. Self-Assembly of Oxocarbon Dianions and Oxalate with Platinum-Based Acceptor Linker **1**



Scheme 2. Self-Assembly of Oxocarbon Dianions (**4**, **5**) with Platinum-Based Acceptor Linker **2**



appear at 13.2, 12.6, and 11.0 ppm, respectively, compared to 14.6 ppm in **1**. The rhomboid, **9**, and the triangle, **10**, show the singlet ^{31}P resonance at 18.0 and 18.1 ppm, respectively, compared to 19.4 ppm for the 60° unit, **2**. The smaller upfield shift of the phosphorus signal in comparison to that of bipyridyl-type nitrogen donor ligands[2k,3f] can be attributed to the poorer π-acceptor property of the oxygen donor ligands. A similar shift of the phosphorus signal upon complexation was also observed in the ensembles with the dicarboxylate bridging ligands.[6] The structures of macrocycles **6**−**9** were unambiguously determined by X-ray crystallography. Attempts to obtain X-ray-quality single crystals of **10** failed. Therefore, support for its structure was provided by fast atom bombardment mass spectrometry (FABMS) with a molecular ion peak at 3453.1 (Figures S13 and S14, Supporting Information).

The IR spectrum of **6** displays characteristic strong bands of the oxalate ligand at 1634 (ν_{as}COO) and 1276 cm^{-1} (ν_s-COO). The large difference of 358 cm^{-1} between the two bands indicates that the carboxylate group of the oxalate ligand is coordinated to the metal in a monodentate fashion.[17] The IR spectra of **7** and **10** present a strong absorption at 1480 and 1470 cm^{-1}, respectively, which corresponds to the strong broad band at ca. 1530 cm^{-1} found in the spectrum of $Na_2C_4O_4$ and which has been tentatively assigned to a combination of C−C and C−O stretching vibrations.[18] The two weak bands at 1794 and 1700 cm^{-1} for **7** and 1778 and 1684 cm^{-1} for **10** have been assigned to the localized C═O and are consistent with the 1,2-bismonodentate coordination of the squarate ion in both of them.[9,19]

For the assemblies **8** and **9**, the characteristic, strong C−O and C−C stretching vibrations of $C_nO_n^{2-}$ appear at 1483 and 1477 cm^{-1}, respectively. Additional weak bands are observed above 1700 cm^{-1} (1706 and 1743 cm^{-1} for **8**; 1705 and 1739 cm^{-1} for **9**), which may be taken as evidence for the presence of uncoordinated carbonyl groups of the croconate ligand.[10] The presence of medium-strength absorptions at 1606 and 1660 cm^{-1} for **8** and 1604 and 1655 cm^{-1} for **9** may be assigned to the coordinated carbonyl groups.[10]

Crystal Structures of the Assemblies 6−9. X-ray quality crystals of **6**−**9** 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 ORTEP of neutral rectangles **6**−**8** and rhomboid **9** are shown in Figures 1−4, respectively. The molecular structure of **6** consists of two

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(17) (a) Kim, J. C.; Cho, J.; Lough, A. J. *Inorg. Chim. Acta* **2001**, *317*, 252. (b) Li, M.-X.; Xie, G.-Y.; Jin, S.-L.; Gu, Y.-D.; Chen, M.-Q.; Liu, J.; Xu, Z.; You, X.-Z. *Polyhedron* **1996**, *15*, 535.

(18) Ito, M.; West, R. *J. Am. Chem. Soc.* **1963**, *85*, 2580.

(19) (a) Reinprecht, J. T.; Miller, J. G.; Vogel, G. C.; Haddad, M. S.; Hendrickson, D. N. *Inorg. Chem.* **1980**, *19*, 927. (b) Pierpont, C. G.; Francesconi, L. C.; Hendrickson, D. N. *Inorg. Chem.* **1978**, *17*, 3470.

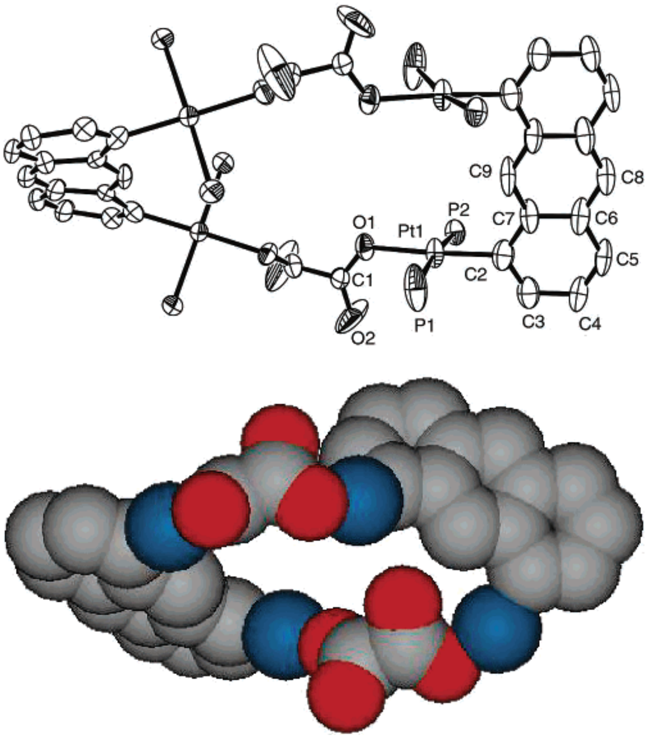

Figure 1. (a) ORTEP presentation of **6** (30% thermal ellipsoids). Hydrogen atoms, the ethyl groups of PEt_3, and solvent molecules have been omitted for clarity. (b) Theoretical model of cyclobis[(1,8-bis[*trans*-Pt(PEt_3)$_2$]-anthracene)(μ-1,2-C_2O_4)] (**6**) optimized with MM2 force field stimulation.[21] Key: blue = Pt, gray = C, red = O. Hydrogen atoms and triethyl phosphine groups are omitted for clarity.

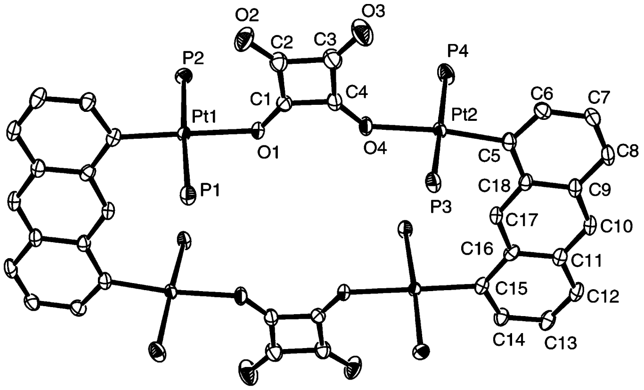

Figure 2. ORTEP presentation of **7** (30% thermal ellipsoids). Hydrogen atoms, the ethyl groups of PEt_3, and solvent molecules have been omitted for clarity.

molecular clips connected by two oxalate anions through one oxygen atom of each carboxylate group, i.e., in a cis-bismonodentate mode (Figure 1a). This coordination mode is very rare for oxalate, and to our knowledge, among the plethora of oxalato-bridged complexes, only three such complexes are reported in the literature.[17a,20] The main molecule is sitting on 2.22 site symmetry.

The Pt−O bond distance is 2.124(7). The C−O (coordinated) bond distance [1.266(12) Å] is longer than the C−O (uncoordinated) [1.189(14) Å] distance as expected. The oxalate group, with a 2-fold axis passing through the middle

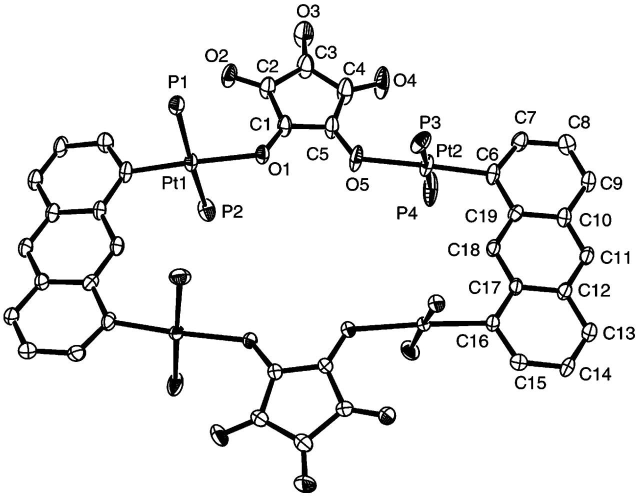

Figure 3. ORTEP presentation of **8** (30% thermal ellipsoids). Hydrogen atoms, the ethyl groups of PEt_3, and solvent molecules have been omitted for clarity.

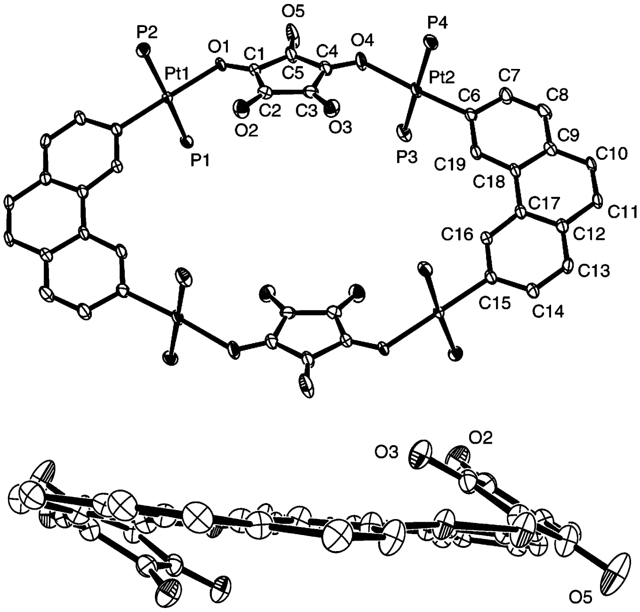

Figure 4. (a) ORTEP presentation of **9** (30% thermal ellipsoids). Hydrogen atoms, the ethyl groups of PEt_3, and solvent molecules have been omitted for clarity. (b) Nonplanarity of croconate and phenanthrene in **9**. Hydrogen atoms and triethyl phosphine groups have been omitted for clarity. Thermal ellipsoids are drawn to 30% probability.

of the C−C bond, is not planar and the two $-CO_2$ entities are twisted 67° with respect to each other. The molecular rectangle (**6**) itself is also severely twisted from planarity; the twist angle between the two anthracene moieties is 39°. The torsion angle between the two Pt−C bonds in an anthracene moiety is 31.5°; ideally, it should be 0° in an undistorted species. Of the several molecular rectangles previously reported,[2k] this is the first example where the rectangle is severely twisted. The previous rectangles employed rodlike rigid linkers, but here we used the oxalate ion in which the two carboxylate groups are free to rotate along the C−C single bond. This free rotation allows the molecule to be twisted in order to attain minimum nonbonded interactions. We optimized the structure of **6** by MM2 force field simulation[21] to check if the twisting of the molecule was

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(20) (a) Castillo, O.; Luque, A.; Sertucha, J.; Roman, P.; Lloret, F. *Inorg. Chem.* **2000**, *39*, 6142. (b) He, W.; Liu, F.; Duan, C.; Guo, Z.; Zhou, S.; Liu, Y.; Zhu, L. *Inorg. Chem.* **2001**, *40*, 7065.

due to the requirement of the crystal lattice for close packing or if it is inherent in the molecule. The calculations indicate that the twist is inherent in the molecule (Figure 1b).

The length of **6** is 13.5 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 metals, is 5.6 Å. There are four disordered chloroform solvent molecules per rectangle. They are situated between the rectangles, as can be seen by the top view along the *b* axis (Figure S1, Supporting Information). The shortest distance between two parallel rectangles along the *b* axis is 10.9 Å.

Crystal structure analyses reveal that the main molecule of **7** is sitting on an inversion center and that of **8** is sitting on a 2-fold axis. The squarate and croconate dianions join the platinum metals in a μ-1,2-bismonodentate mode to form the molecular rectangles (Figures 2 and 3). The coordination mode in **7** is rather common in squarato-bridged complexes,[9] but that in **8** is unknown for complexes of croconate. The platinum oxygen bond distances are slightly different in these two molecules [Pt(1)−O(1) = 2.125(3), Pt(2)−O(4) = 2.119(3) for **7** and Pt(1)−O(1) = 2.155(3), Pt(2)−O(5) = 2.134(4) for **8**]. In both cases, the C−O bond distances satisfy the trend: $\mathrm{C{-}O_{coord}}$ [O(1)−C(1) 1.277(7), O(4)−C(4) 1.268(6) for **7** and O(1)−C(1) 1.275(6), O(5)−C(5) 1.295(6) for **8**] > $\mathrm{C{-}O_{uncoord}}$ [O(2)−C(2) 1.228(7), O(3)−C(3) 1.222(7) for **7** and O(2)−C(2) 1.230(6), O(3)−C(3) 1.220(7), O(4)−C(4) 1.224(7) for **8**], as expected from the polarization of charge density toward to metal-bonded oxygen atoms. The shorter C−C bond distances between the carbon atoms attached to the coordinated oxygen [C(1)−C(4) = 1.431(7), C(2)−C(3) = 1.506(8) for **7** and C(1)−C(5) = 1.440(7), C(2)−C(3) = 1.499(7) for **8**] also corroborate the partial localization of the π electrons upon coordination.

Both the squarate and croconate groups are essentially planar; the O(1)−C(1)−C(4)−O(4) and O(1)−C(1)−O(5)−C(5) torsion angles in **7** and **8**, respectively, are 0° and 1.5°. The twist angles between the anthracene moieties are 0° and 1°, and the torsion angles between the two Pt−C bonds in an anthracene moiety are 7° and 8.9° in **7** and **8**, respectively. Thus, unlike **6**, both rectangles **7** and **8** are nearly planar, as the presence of the planar cyclic rings between the two donor oxygen atoms restricts the torsion angle between them close to zero. The length and width of rectangles **7** and **8** are 14.2, 13.8 and 5.4, 5.6 Å, respectively. There are two disordered dichloromethane solvent molecules per rectangle of **7**, and they are situated between the rectangles in two different directions, as can be seen in the top view (along the *b* axis) of the packing (Figure S2, Supporting Information). There are two disordered chloroform molecules per rectangle of **8**, and they are also situated between the molecules (Figure S3, Supporting Information). The shortest distances between the repeating rectangles along the *b* axis are 14.8 and 15.1 Å for **7** and **8**, respectively.

In complex **9**, two croconate dianoins join two 60° platinum acceptor units in a μ-1,3-bismonodentate mode to form the centrosymmetric rhomboid molecule (Figure 4a).

This coordination mode of croconate ion is also unprecedented. The platinum−oxygen bond distances are Pt(1)−O(1) = 2.128(3) and Pt(2)−O(4) = 2.139(3). The uncoordinated oxygen atoms show a ketonic form with shorter bond distances [O(2)−C(2) = 1.226(5) Å, O(3)−C(3) = 1.230 Å, and O(5)−C(5) = 1.237(5) Å] compared to the C−O distances [O(1)−C(1) = 1.264(5) Å, O(4)−C(4) = 1.254(5) Å] of the metal-coordinated oxygen atoms. The C−C bond distances of the croconate moiety are, however, not very different—the shortest one being C(1)−C(5) = 1.462(6) and the longest one, C(2)−C(3) = 1.488(6). The dimensions of the rhomboid are 16.59 and 10.07 Å as measured by the distance between the centroid of the phenanthrene rings and the two coordinated oxygen atoms O1 and O4#1 ($-x,-y,-z$), respectively. The shortest distance between any two rhomboid molecules along the *b* axis is 14.2 Å. There are four chloroform molecules per molecule of **9**. Two of them are ordered, while the other two are disordered. A view of the packing of complex **9** along the *c* axis is shown in Figure S4 (Supporting Information).

The croconate and phenanthrene rings are not in the same plane (Figure 4b). The torsion angle between C(15)−C(6)−C(5) and C(6)−C(5)−O(5) is 146.9°. The geometry around the platinum atom is nearly square planar in all four complexes irrespective of the distortions present in the molecule. The cis angles around the platinum are all within 5.2° of 90°, and the trans angles are within 10° of 180°.

Crystal structures of **6**−**9** reveal that, although all of them have been crystallized in a similar way (from $CHCl_3$/CH_2Cl_2 mixture by diffusion of acetone), three of them (**6**, **8**, **9**) have chloroform and **7** has dichloromethane as solvent of crystallization. Thus, the inclusion of solvent molecules into the lattice occurs selectively as per the requirement of the crystal lattice.

Coordination Modes of Oxocarbondianions and the Size of Assemblies. It is noteworthy that the croconate dianions join the molecular "clip" **1** in a μ-1,2-bismonodentate mode but the 60° tecton **2** via a μ-1,3-bismonodentate mode, i.e., in the former, it acts as linear, but in the later, as a 120° linker. As in both modes, the croconate ions act as a bismonodentate ligand, the enthalpy of formation should be more or less the same. However, as a linear linker (μ-1,2-bismonodentate) the croconate ion should undergo 3:3 addition with the 60° platinum acceptor unit to form a molecular triangle (Scheme 3) instead of a 2:2 addition needed for the formation of rhomboid **9**. Entropically, the formation of a triangle is disfavored, as a smaller number of triangular assemblies would result compared to the number of rhomboidal macrocycles that can be generated using the same number of building blocks. Therefore, the flexidentate croconate ion changes its coordination mode in order to form the entropically favorable supramolecular assembly **9**. On the other hand, the squarate ion yields rectangle **7** with the "clip" and triangle **10** with the 60° Pt linker. To form a triangular assembly (3:3 addition), it is required that the squarate ion acts as a linear linker with a μ-1,2-bismonodentate coordination mode similar to that observed in macrocycle **7**. Unlike croconate, the other alternative bridging

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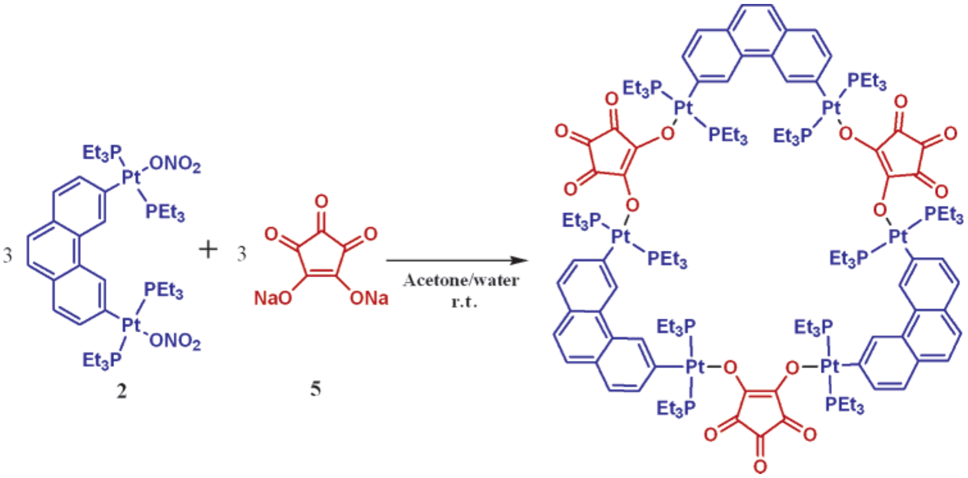
(21) *CS ChemBats3D Ultra 7.0.0*; CambridgeSoft Corporation: Cambridge, MA, 2001.

Scheme 3. Self-Assembly of Hypothetical Triangular Macrocycle from **2** and **5**



mode of squarate (1,3-bismonodentate) cannot provide an angle around 120°, and consequently, formation of a rhomboid by 2:2 addition with **2** could not take place.

Photophysical Properties. Among the three dianions, croconate is yellow in color and shows an absorption maximum at 366 nm. Oxalate and squarate show absorption bands below 280 nm. In this region, the platinum compounds **1** and **2** also show strong absorption bands. Upon formation of the assemblies (**8** and **9**), the band due to croconate broadens and the intensity decreases significantly. The spectra of **1**, **5**, and **8** are shown in Figure 5 to illustrate the change of absorption properties upon assembly formation.

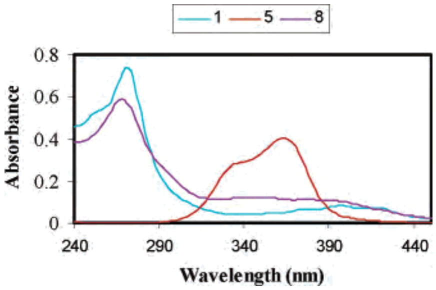


Figure 5. Absorption spectra of supramolecular rectangle **8** (5 μM) and building blocks **5** (10 μM) and **1** (10 μM).

This observation is in contrast with that of the molecular rectangles formed by dicarboxylic acids with **1**, where a remarkable increase in intensity was observed.[6] In all the assemblies, the intensities of the anthracene- and phenanthrene-based absorptions decrease slightly on complex formation and the position of the absorption maxima does not experience much shift in wavelength.

Conclusion

The formation of discrete platinum-based metallacycles incorporating flexidentate oxocarbon dianions and oxalate by self-assembly are described. The assembly formed by the oxalate and clip is the first example of a severely twisted rectangle. The bismonodentate bridging mode which has been used by all the linkers to form the assemblies is very rare for the oxalate and was unknown for croconate, as they possess a very favorable bite angle for chelation. The molecular “clip” (**1**) and the 60° tecton (**2**), however, were designed in such a way that only the weakly coordinated nitrate anion can be replaced by the oxygen or nitrogen donor linkers. Therefore the oxalate and croconate ions were dictated by the requirement of Pt-based acceptor units to act in a bismonodentate fashion. As all of the linkers contain more than two oxygen atoms that can be coordinated to the metal centers, there are possibilities for formation of ensembles with different shape, size, and dimension, as well as acyclic oligomers with their different coordination modes. However, the NMR spectra and X-ray crystal structures clearly established that the cyclic assembly, i.e., rectangle or rhomboid, which requires the association of smallest number (2:2) of building blocks is the only product in four cases (**6**−**9**). The squarate ion and the 60° tecton undergo 3:3 addition to yield molecular triangle **10** as the squarate ion, which, with its various coordination modes, is unable to provide the geometrical requirement for a rhomboid formation. Thus, such flexible linkers preferably change their coordination modes to yield entropically driven smaller assemblies whenever possible.

Experimental Section

General Methods. Oxalic acid, squaric acids, and disodium croconate were purchased from Aldrich and used as received. The disodium salts of the acids were prepared by neutralizing the corresponding acids with $NaHCO_3$ in aqueous medium. The 1,8-bis[*trans*-Pt(PEt_3)$_2$$NO_3$]anthracene[2k], **1**, and 2,9-bis[*trans*-Pt(PEt_3)$_2$-NO_3]-phenanthrene[3f], **2**, were prepared according to known procedures. Deuterated solvents were purchased from Cambridge Isotope Laboratories. All NMR spectra were recorded on Varian Unity 300 or Varian XL-300 spectrometers. ^{1}H chemical shifts are reported relative to the residual protons of deuterated dichloromethane (δ = 5.32 ppm) or relative to the residual protons of deuterated chloroform (δ = 7.27 ppm). $^{31}P\{^1H\}$ chemical shifts are reported relative to an external, unlocked sample of H_3PO_4 (δ = 0.0 ppm). Elemental analyses were performed by Atlantic Microlab, Norcross, GA. IR spectra were recorded on a Nicolet 520 FTIR spectrometer in KBr pellets. UV−vis spectra were recorded on a Hewlett-Packard 8452A spectrophotometer. The mass spectrum of **6** was obtained with a Finnigan MAT 95 mass spectrometer with a Finnigan MAT ICIS II operating system under positive fast atom bombardment (FAB) conditions. 3-Nitrobenzyl alcohol was used as a matrix in $CHCl_3$ as a solvent.

Table 1. Crystallographic Data and Refinement Parameters for Compounds **6**−**9**

	6	**7**	**8**	**9**
formula	$C_{84}H_{140}Cl_{12}O_8P_8Pt_4$	$C_{86}H_{140}Cl_4O_8P_8Pt_4$	$C_{88}H_{138}Cl_6O_{10}P_8Pt_4$	$C_{90}H_{140}Cl_{12}O_{10}P_8Pt_4$
fw	2731.48	2471.90	2596.80	2835.54
temp (K)	150(1)	150(1)	150(1)	150(1)
λ (Å)	0.710 73	0.710 73	0.710 73	0.710 73
cryst syst	tetragonal	monoclinic	monoclinic	monoclinic
space group	$P4_22_12$	$P2_1/n$	$C2/c$	$P2_1/n$
a (Å)	14.8806(4)	17.5260(3)	27.4052(5)	19.762293)
b (Å)	14,8806(4)	14.8251(3)	15.0715(3)	14.1900(2)
c (Å)	23.7853(7)	18.8229(3)	23.8497(3)	19.9798(2)
α (deg)	90	90	90	90
β (deg)	90	104.6539(10)	99.2702(10)	97.2834(8)
γ (deg)	90	90	90	90
V (Å^3)	5266.8(3)	4731.6(1)	9722.2(3)	5557.6(1)
Z	2	2	4	2
D_{calc}(g/cm^3)	1.722	1.735	1.774	1.694
μ (mm^{-1})	5.769	6.194	6.088	5.472
F(000)	2688	2440	5210	2792
reflns collected	8136	18 458	18 482	22 867
unique reflns	4791	10 795	11 117	12 593
max and min trans	0.4782,0.3504	0.4568, 0.3066	0.5050, 0.2245	0.3416, 0.2504
GOF on F^2	1.070	1.034	1.020	1.031
R1 [$I > 2\sigma(I)$]	0.0485	0.0393	0.0360	0.0320
wR2	0.0971	0.0794	0.0845	0.0738

X-Ray Data Collection, Structure Solution, and Refinement. A single crystal of the corresponding complex (**6**−**9**) was selected from the reaction product and was mounted on a glass fiber with traces of viscous oil and then transferred to a Nonius KappaCCD diffractometer equipped with Mo Kα radiation ($\lambda = 0.71073$ Å). Ten frames of data were collected at 150(1) K with an oscillation range of 1°/frame and an exposure time of 20 s/frame.[22] Indexing and unit cell refinement were based on all of the observed reflections from those 10 frames. Structures were solved by a combination of direct methods and heavy atom using SIR 97.[23] All of the non-hydrogen atoms were refined with anisotropic displacement coefficients. Hydrogen atoms were assigned isotropic displacement coefficients U(H) = 1.2U(C) or 1.5U(C-methyl), and their coordinates were allowed to ride on their respective carbons using SHELXL97.[24] Scattering factors were taken from the International Table of Crystallography, Vol. C.[25,26] The weighting scheme employed was $w = 1/[\sigma^2(F_o^2) + (0.0253P)^2 + 18.4225P]$, where $P = (F_o^2 + 2F_c^2)/3$. Details of the data collection, structure solution, and refinement are given in Table 1.

General Procedure for the Preparation of Compounds 6−8. To a 2 mL acetone solution containing 11.62 mg (0.010 mmol) of **1**, an aqueous solution (2 mL) of the disodium salt of appropriate acid (**3**, **4**, or **5**) (0.010 mmol) was added drop by drop with continuous stirring (15 min). The yellow 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-C$_2$O$_4$)] (6). Yield (90.4%). Anal. Calcd for $C_{80}H_{136}O_8P_8Pt_4$: C, 42.63; H, 6.08. Found: C, 42.60; H, 6.06. ^{31}P{^{1}H} NMR (CDCl$_3$, 121.4 MHz): δ 13.20 (s, $^1J_{\text{PPt}} = 2889$ Hz). ^{1}H NMR (CDCl$_3$, 300 MHz): δ 9.58 (s, 2H, H$_9$), 8.19 (s, 2H, H$_{10}$), 7.69 (d, 4H, $^3J_{\text{HH}} = 6.84$ Hz, H$_{4,5}$), 7.55 (d, 4H, $^3J_{\text{HH}} = 8.05$ Hz, H$_{2,7}$), 6.97 (t, 4H, H$_{3,6}$), 1.57 (m, 48H, PCH$_2$CH$_3$), 1.05 (m, 72H, PCH$_2$CH$_3$).

Cyclobis[(1,8-bis[*trans*-Pt(PEt$_3$)$_2$]anthracene)(μ-1,2-C$_4$O$_4$)] (7). Yield (98.1%). Anal. Calcd for $C_{84}H_{136}O_8P_8Pt_4 \cdot H_2O$: C, 43.49; H, 6.00. Found: C, 43.43; H, 6.11. ^{31}P{^{1}H} NMR (CDCl$_3$, 121.4 MHz): δ 12.59 (s, $^1J_{\text{PPt}} = 2870$ Hz). ^{1}H NMR (CDCl$_3$, 300 MHz): δ 9.72 (s, 2H, H$_9$), 8.19 (s, 2H, H$_{10}$), 7.67 (d, 4H, $^3J_{\text{HH}} = 6.73$ Hz, H$_{4,5}$), 7.54 (d, 4H, $^3J_{\text{HH}} = 8.38$ Hz, H$_{2,7}$), 6.96 (t, 4H, H$_{3,6}$), 1.60 (m, 48H, PCH$_2$CH$_3$), 1.00 (m, 72H, PCH$_2$CH$_3$).

Cyclobis[(1,8-bis[*trans*-Pt(PEt$_3$)$_2$]anthracene)(μ-1,2-C$_5$O$_5$)] (8). Yield (97.8%). Anal. Calcd $C_{86}H_{136}O_{10}P_8Pt_4 \cdot 2H_2O$: C, 43.14; H, 5.89. Found: C, 42.97; H, 5.74 ^{31}P{^{1}H} NMR (CDCl$_3$, 121.4 MHz): δ 10.95 (s, $^1J_{\text{PPt}} = 2922$ Hz). ^{1}H NMR (CDCl$_3$, 300 MHz): δ 9.52 (s, 2H, H$_9$), 8.21 (s, 2H, H$_{10}$), 7.93 (d, 4H, $^3J_{\text{HH}} = 6.84$ Hz, H$_{4,5}$), 7.58 (d, 4H, $^3J_{\text{HH}} = 8.05$ Hz, H$_{2,7}$), 7.00 (t, 4H, H$_{3,6}$), 1.57 (m, 48H, PCH$_2$CH$_3$), 1.00 (m, 72H, PCH$_2$CH$_3$).

General Procedure for the Preparation of Compounds 9 and 10. Compounds **9** and **10** were obtained as yellow and white precipitates, respectively, by adding an aqueous solution of disodium salt of the appropriate acid (**4** and **5**) (0.01 mmol) to 11.62 mg of **2** (0.01 mmol) in acetone in a 1:1 stoichiometric ratio. Pale yellow prismatic single crystals of **9** for X-ray structure analysis were grown by diffusion of acetone into the chloroform/dichloromethane mixture solution of the compound.

Cyclobis[(2,9-bis[*trans*-Pt(PEt$_3$)$_2$]phenanthrene)(μ-1,3-C$_5$O$_5$)] (9). Yield (90.1%). Anal. Calcd for $C_{86}H_{136}O_{10}P_8Pt_4.4CH_3COCH_3$: C, 45.44; H, 6.23. Found: C, 45.36; H, 6.13 ^{31}P{^{1}H} NMR (CDCl$_3$, 121.4 MHz): δ 18.00 (s, $^1J_{\text{PPt}} = 2916$ Hz). ^{1}H NMR (CDCl$_3$, 300 MHz): 8.75 (s, 4H, H$_1$), 7.59 (d, 4H, $^3J_{\text{H4-H3}} = 8.05$ Hz, H$_3$), 7.50 (s, 4H, H$_5$), 7.42 (d, 4H, $^3J_{\text{H4-H3}} = 8.05$ Hz, H$_4$), 1.50 (m, 48H, PCH$_2$CH$_3$), 1.15 (m, 72H, PCH$_2$C*H*$_3$).

Cyclotris[(2,9-bis[*trans*-Pt(PEt$_3$)$_2$]phenanthrene)(μ-1,2-C$_4$O$_4$)] (10). Yield (85.8%). Anal. Calcd for $C_{126}H_{204}O_{12}P_{12}Pt_6$: C, 43.83; H, 5.95. Found: C, 43.76; H, 6.03 ^{31}P{^{1}H} NMR (CDCl$_3$, 121.4 MHz): δ 18.06 (s, $^1J_{\text{PPt}} = 2896$ Hz). ^{1}H NMR (CDCl$_3$, 300

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(22) *COLLECT Data Collection Software*; Nonius B. V., 1998.

(23) Altomare, A.; Burla, M. C.; Camalli, M.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A.; Moliteni, A. G. G.; Polidori, G.; Spagna, R. SIR97 (Release 1.02): A program for automatic solution and refinement of crystal structure.

(24) Sheldrick, G. M. *SHELX97 [Includes SHELXS97, SHELXL97, CIFTAB]*−*Programs for Crystal Structure Analysis (Release 97-2)*; University of Göttingen: Göttingen, Germany, 1997.

(25) Maslen, E. N.; Fox, A. G.; O'Keefe, M. A. In *International Tables for Crystallography: Mathematical, Physical and Chemical Tables*; Wilson, A. J. C., Ed.; Kluwer: Dordrecht, The Netherlands, 1992; Vol. C, Chapter 6, pp 476−516.

(26) Creagh, D. C.; McdAuley, W. J. In *International Tables for Crystallography: Mathematical, Physical and Chemical Tables*; Wilson, A. J. C., Ed.; Kluwer: Dordrecht, The Netherlands, 1992; Vol. C, Chapter 4, pp 206−222.

MHz): 8.67 (bs, 6H, H_1), 7.70 (bd, 6H, $^3J_{H4-H3} = 8.05$ Hz, H_3), 7.47 (s, 6H, H_5), 7.39 (d, 6H, $^3J_{H4-H3} = 8.05$ Hz, H_4), 1.48 (m, 72H, PCH_2CH_3), 1.15 (m, 108H, PCH_2CH_3). M_w calcd for $C_{126}H_{204}O_{12}P_{12}Pt_6$: 3453.11. Found (FAB): 3453.1.

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Supporting Information Available: ^{31}P and ^1H NMR spectra of compounds **6**−**10**, X-ray crystallographic data of assemblies **6**−**9** (CIF), UV−vis spectra of compounds **3**, **4**, and **6**−**10**, and FABMS of **10**. This material is available free of charge via the Internet at http://pubs.acs.org.

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