

Self-Assembly of Metallamacrocycles via a Rigid Phosphorus Donor Linker[#]

Sushobhan Ghosh and Partha Sarathi Mukherjee*

Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore-560012, India

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The coordination-driven self-assembly of a series of discrete 2D metallamacrocycles from a rigid diphosphine donor linker and Pd/Pt-containing 90° acceptors is described. All these assemblies are characterized by multinuclear NMR and, in four cases, X-ray crystallography. The selective formation of a diphosphine bridged macrocycle, [(en)Pd(μ -*trans*-PPh₂CH=CHPPh₂)₂Pd(en)]⁴⁺, from a 1:1:1 mixture of *cis*-Pd(en)(NO₃)₂, *trans*-Ph₂PCH=CHPPh₂, and 1,2-bis(4-pyridyl)ethane is also established.

Introduction

The self-assembly of finite structures via a directional bonding approach has become a very topical field of research.¹ The most important aspect of this process is the rational design of structures of various shapes, sizes, and symmetries. Several discrete assemblies including extended polymeric frameworks have been reported in the last few years.^{1,2} Much of the finite assemblies have been prepared using Pt(II)/Pd(II) ions as acceptor units with nitrogen donor bridging linkers except a very few recent examples where Stang and his co-workers have introduced oxygen donor linkers into neutral Pt nanostructures.³ Both nitrogen and phosphorus are members of the same group in the periodic table. Phosphorus is softer base compared to nitrogen and thus expected to be a better donor for soft acceptors such as Pd(II) or Pt(II). Most surprisingly, phosphorus donor linkers are not preferred in directed self-assembly except in the case of a few recent reports on metallamacrocycles and a few polymers.^{2j,4a} This may be due to the fact that most alkyl-substituted polyphosphines are pyrophoric and aryl-substituted analogues are not expected to be suitable linkers because of

the presence of bulky aryl groups on donor phosphorus. Hence, it was of interest whether Pd/Pt–P bonding could be used as driving forces to afford finite supramolecules. Herein, we report five stable Pd/Pt–P bond directed metallamacrocycles (**2a–e**) prepared via the self-assembly of a rigid diphosphine ligand (**L**) and *cis*-blocked 90° metal acceptors [Scheme 1, **L** = *trans*-1,2-bis(diphenylphosphino)ethylene]. Four of the assemblies were fully characterized by X-ray single-crystal structure determination and showed the formation of chair-shaped metallamacrocycles. NMR and ESI mass spectrometry established the formation of 2:2 macrocycles for the remaining one. A preliminary investigation established that phosphorus donor linkers could also be used as potential bridging ligands in directed self-assembly, and this could be even better than widely used nitrogen donor pyridyl linkers despite the presence of bulky aryl groups on phosphorus. Despite the possibility of forming a bpe [bpe = 1,2-bis(4-pyridyl)ethane]-bridged macrocycle, [(en)Pd(μ -bpe)₂Pd(en)](NO₃)₄, the self-selection of **2a**, [(en)-Pd(μ -*trans*-Ph₂PCH=CHPPh₂)₂Pd(en)](NO₃)₄, was exclusively achieved by treating a 1:1 mixture of **L** and 1,2-bis(4-pyridyl)ethane (bpe) with 1 equiv of *cis*-(en)Pd(NO₃)₂.

[#] Dedicated to Prof. Peter J. Stang for his wide contributions in the field of directed self-assembly.

* Corresponding author. E-mail: psm@ipc.iisc.ernet.in.

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Results and Discussions

Synthesis and Spectroscopic Characterizations. When the dichloromethane solution of the rigid diphosphine linker **L** [**L** = *trans*-1,2-bis(diphenylphosphino)ethylene] was treated with an equivalent amount of the linker **1a** in methanol, the [2+2] self-assembly of the metallamacrocycle **2a** occurred (Scheme 1). The peak in the ³¹P NMR spectrum of the free ligand **L** appeared at –7.53 ppm (CDCl₃). A downfield shift of the phosphorus peak of 29 ppm in **2a** from the starting **L** was a clear indication of the strong phosphorus to metal coordination (Figure 1). The formation of a single product was indicated by the appearance of a sharp singlet in the ³¹P spectrum. ¹H NMR of the product also indicated the formation of a symmetric macrocycle with the expected shifts for proton signals. Similar treatment of **L** with **1b–e** yielded analogous macrocycles **2b–e**, which were also identified by NMR and were consistent with the formation of a single product. In case of Pt assemblies the downfield shift of the phosphorus peak in the ³¹P NMR was in

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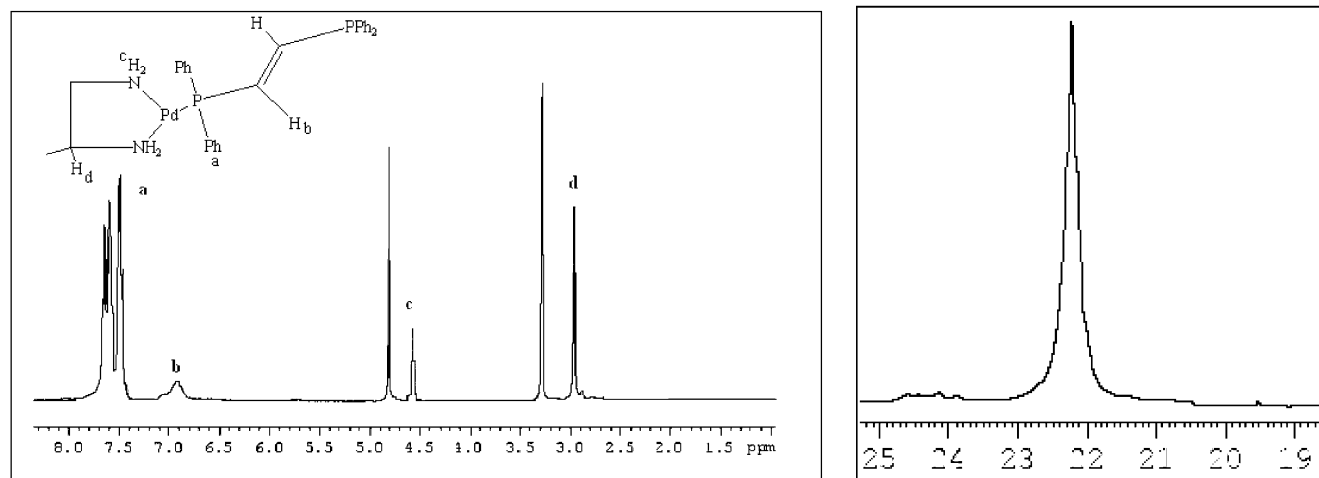
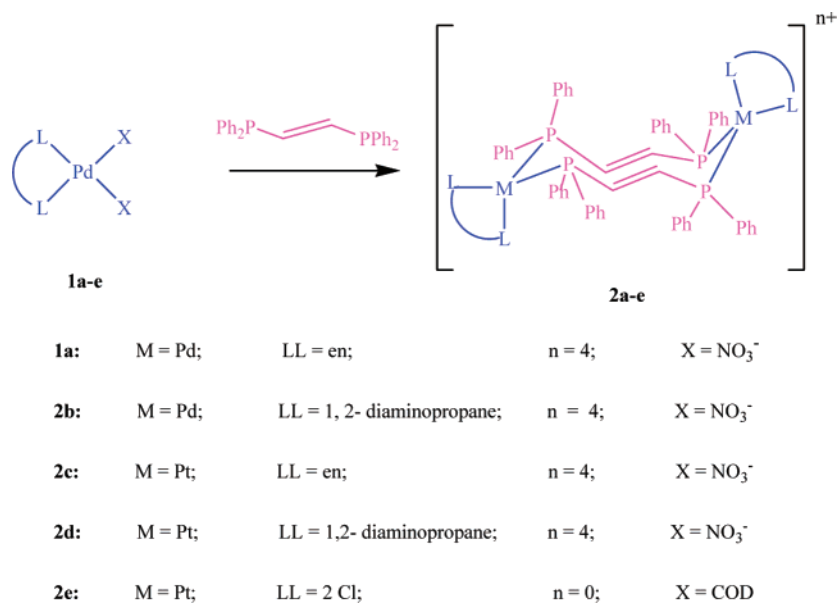


Figure 1. ^1H (left) and ^{31}P NMR (right) spectra of **2a** in CD_3OD .

Scheme 1. Self-Assembly of the Macrocycles **2a–e**



the range 8–15 ppm. Expected Pt satellites were observed in the ^{31}P NMR spectra of all the Pt macrocycles. Despite the possibility of forming a mixture of isomeric products due to the presence of nonsymmetric chelating amine in **1b** and **1d**, a single isomeric product (**2b** and **2d**) was formed exclusively in both cases. The phosphorus signals for both these complexes looked like broad doublets due to the nonsymmetric nature of the amine ligand, which makes the coordinated phosphorus atoms nonequivalent. Complex **2e** was prepared from Pt(COD) Cl_2 , where COD = 1,5-cyclooctadiene. The facile reaction was identified by the release of an intense smell of COD upon treatment of Pt(COD) Cl_2 with the diphosphine linker. Adding ether to the reaction mixture precipitated the product. The precipitate was washed and dried under reduced pressure to remove the evolved COD completely. A similar reaction using *cis*-Pt(PhCN) $_2\text{Cl}_2$ instead of Pt(COD) Cl_2 also yielded **2e**. To the best of our knowledge COD has never been used as a leaving group for direct self-assembly of metallamacrocycles using nitrogen donor bridging ligands. This is probably due to the chelating nature of COD and softness of the ethylenic moieties, which make it a relatively stronger ligand. However, in our present case the softness of the phosphorus donor bridging ligand

makes it possible to replace the coordinated COD in a facile way to form the macrocycle **2e**.

Moreover, when a methanolic slurry of the stable known macrocycle **3**^{4b} [**3** = (en) $_2\text{Pd}_2(\mu\text{-bpe})_2(\text{NO}_3)_4$, where bpe = 1,2-bis(4-pyridyl)ethane] was treated with **L** in 1:2 molar ratio, immediately the macrocycle **2a** was formed exclusively along with the release of free ligand bpe (Scheme 2). The formation of **2a** and the free bpe was verified by NMR.⁵ The complete conversion was verified by the absence of any peak corresponding to the free ligand **L** in the ^{31}P spectrum of the mixture. The macrocycle **2a** was isolated by precipitating as perchlorate salt by adding NET_4ClO_4 in excess to the mixture. The precipitate was washed several times with methanol, and NMR spectroscopy identified this precipitate as pure **2a**.

When **1a**, **L**, and bpe were mixed in a mixture of methanol and dichloromethane in 1:1:1 molar ratio, a mixture of macro-

(5) See Supporting Information file.

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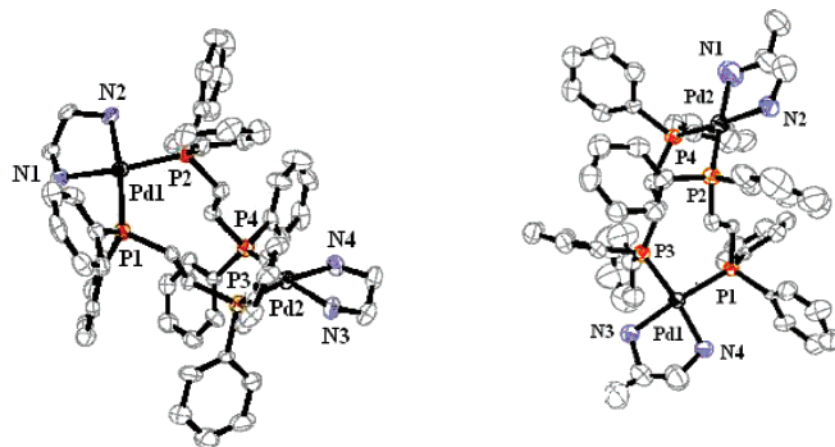
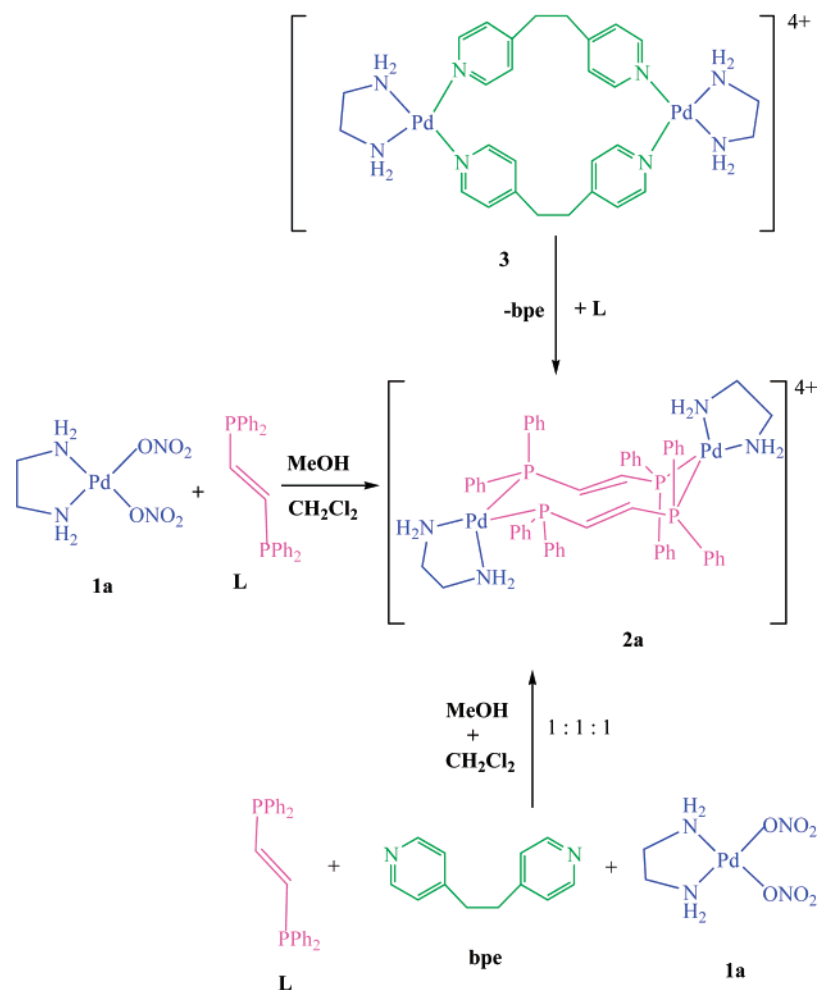


Figure 2. ORTEP (50% probability) view of the macrocycles **2a** and **2b** with atom-numbering scheme of the coordinated atoms to palladium centers.

Scheme 2. Facile Formation of 2a from 3 and Self-Selection of 2a in the Presence of bpe



cycle **2a** and the free ligand **bpe** was formed as the sole product. This self-selection of **2a** was confirmed by NMR spectroscopy. Finally, the formation of a mixture of **2a** and **3** was ruled out since no peak corresponding to the residual **L** was found in the NMR spectra (^{31}P and ^1H) of the mixture. Perchlorate addition precipitated out only **2a**.

Structure Descriptions. Diffraction-quality single crystals of **2a** were grown by ether diffusion into the nitromethane solution of the perchlorate salt of **2a**, whereas **2b** and **2c** were crystallized directly by diffusing ether into the methanol solution of the products. Single crystals of **2e** were obtained by diffusing

ether into a nitromethane solution of the product. Crystals in all cases were solvent dependent. Figure 2 shows the view of the molecular structures of **2a** and **2b**. Crystallographic parameters are assembled in Table 1.

The structure of **2a** is a chair-shaped macrocycle with a Pd–Pd distance of 6.7 Å. This macrocycle is slightly squeezed in the middle due to the weak π – π interaction of the opposite ethylenic moieties. The distance between the centroids of the ethylenic parts in **2a** is 3.0 Å. H-bonding between the counteranions and the macrocycles helps to form a porous network in the solid state. Similarly, the crystal structure of **2b** shows

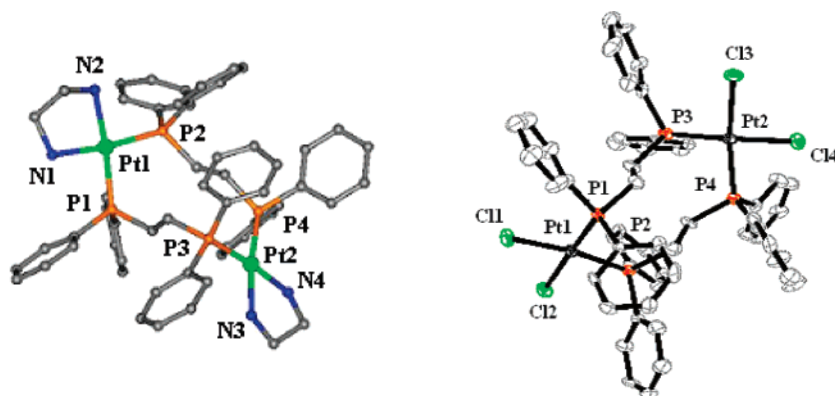


Figure 3. View of molecular structure of **2c** (left) and ORTEP of **2e** (right) with atom numbering of the coordinated atoms to Pt centers.

Table 1. Crystal Data and Structure Refinement Parameters of 2a, 2b, 2c, and 2e

| | 2a | 2b | 2c | 2e |
|---|---|---|---|---|
| empirical formula | C _{59.5} H ₆₉ C ₁₄ N ₅ O _{17.5} P ₄ Pd ₂ | C ₅₈ H ₆₄ N ₈ O _{12.5} P ₄ Pd ₂ | C ₅₆ H ₆₀ N ₈ O ₁₂ P ₄ Pt ₂ | C _{52.5} H ₄₇ Cl ₅ OP ₄ Pt ₂ |
| fw | 1612.68 | 1406.83 | 1548.14 | 1385.21 |
| T/K | 150(2) K | 150(2) K | 150(2) K | 150(2) K |
| space group | <i>P2₁/c</i> | <i>P2₁/n</i> | <i>P4₂bc</i> | <i>P2₁/c</i> |
| <i>a</i> /Å | 12.0427(5) | 11.9286 (7) | 32.2910(3) | 10.8981(8) |
| <i>b</i> /Å | 24.4381(11) | 24.5101 (18) | 32.2910(3) | 13.8392(10) |
| <i>c</i> /Å | 23.0694(10) | 22.6167(16) | 12.6462(15) | 18.6187(14) |
| α /deg | 90.00 | 90.00 | 90.00 | 93.896(6) |
| β /deg | 96.068(4) | 92.483(7) | 90.00 | 106.842(6) |
| γ /deg | 90.00 | 90.00 | 90.00 | 108.217(6) |
| <i>V</i> /Å ³ | 6751.3(5) | 6606.3(8) | 13187(2) | 2513.8(3) |
| <i>Z</i> | 4 | 4 | 6 | 2 |
| μ (Mo K α)/mm ⁻¹ | 0.857 | 0.704 | 0.997 | 0.991 |
| λ /Å | 0.71073 | 0.71073 | 0.71073 | 0.71073 |
| <i>R_w</i> ^a | 0.1893 | 0.2650 | 0.2011 | 0.1564 |
| <i>R</i> ^a | 0.0687 | 0.1183 | 0.1008 | 0.0564 |
| <i>D</i> /Mg m ⁻³ | 1.455 | 1.547 | 1.284 | 1.830 |

$$^a R = \sum ||F_o| - |F_c|| / \sum |F_o|; R_w = [\sum \{w(F_o^2 - F_c^2)^2\} / \sum \{w(F_o^2)^2\}]^{1/2}.$$

an identical type of chairlike macrocycle. The geometry around each Pd was distorted square planar. The distance between the centers of the ethylenic moiety of the two bridging **L**'s is 3.1 Å, while the length of this macrocycle measured by the Pd–Pd distance is also 6.7 Å.

X-ray structural analyses of **2c** and **2e** showed (Figure 3) also pseudo-chair-shaped macrocyclic structures with intramolecular Pt–Pt distances of 6.65 and 6.76 Å, respectively. Although the connectivity of the ligand to the metal and the final shape of the macrocycle were clearly established, the structure of **2c** was highly disordered. This may be due to the highly solvent dependent nature of the crystals. The distance between the centroids of the ethylenic moieties in **2c** is 3.03 Å, while for **2e** it was measured to be 3.06 Å. Complex **2e** is neutral in nature, and thus the 3D packing diagram showed the formation of porous structure without any counterions in the pores (Figure 4).

While NMR spectroscopy provides preliminary insight about the metal–ligand coordination and formation of a single product, it does not provide any information about the shape of this kind of product. ESI mass spectrometry has proven to be a useful tool in the corroboration of structural assignments for this kind of self-assemblies.⁹ Electrospray mass spectrometry clearly confirmed the **1c₂L₂** and **1d₂L₂** compositions with the molecular weight of 1548 and 1576 for **2c** and **2d**, respectively. The ESI mass spectrum of **2c** showed the signals corresponding to the

consecutive loss of nitrate counterions [M – 2NO₃]²⁺ and [M – 4NO₃]⁴⁺, while **2d** showed signals corresponding to the consecutive loss of counterions [M – NO₃]⁺, [M – 2NO₃]²⁺, and [M – 4NO₃]⁴⁺. For **2c**: [M – 2NO₃]²⁺ [*m/z* = 712.4 (calcd 712.10)] and [M – 4NO₃]⁴⁺ [*m/z* = 325.50 (calcd 325.00)]. For **2d**: [M – NO₃]⁺ [*m/z* = 1514.6 (calcd 1514.00)]; [M – 2NO₃]²⁺ [*m/z* = 726.4 (calcd 726.00)] and [M – 4NO₃]⁴⁺ [*m/z* = 332.40 (calcd 332.00)]. These molecular compositions are fully consistent with the other dimeric assemblies.

Several attempts to obtain single crystals of **2d** failed, and thus a force field MM2 energy-minimized model was applied to visualize the probable shape of this macrocycle (Figure 5). The calculated Pt–Pt distance was 6.9 Å.

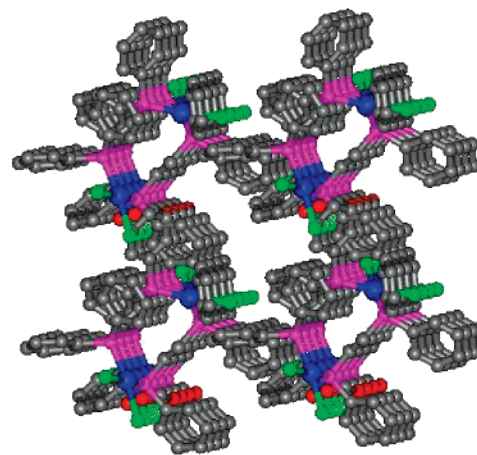


Figure 4. Packing diagram of **2e** in the solid state.

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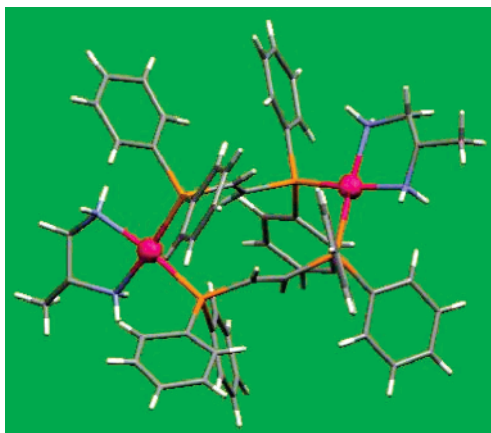


Figure 5. Predicted shape of the macrocycle **2d**. Pink = Pt, blue = N, gray = C, yellow = P, white = H.

UV–Visible Spectroscopic Studies and Binding Constant Determination for **2a.** NMR studies showed the facile formation of **2a** upon treatment of **L** with the known stable macrocycle **3**. Moreover, **2a** was formed selectively even in the presence of bpe. To corroborate these observations, we measured the binding constants for the formation of **2a** and **3** separately by UV–visible spectroscopy.⁵ In both cases the ligand solution was added in small portions to a 3.0×10^{-3} M concentrated solution of Pd(en)(NO₃)₂. The plots of optical density versus wavelength of the corresponding reactions are shown in the Supporting Information file. The isosbestic points at 350 and 320 nm are due to the 1:1 binding for **2a** and **3**, respectively. Binding constants were determined (2.3×10^3 and 0.6×10^3 M⁻¹ for **2a** and **3**, respectively) by applying the binding isotherm equation,⁵ and it was found that the binding constant for the

formation of **2a** is 4 times that of **3**. The accumulation of hard moieties around a soft center can significantly reduce the softness of the center due to a symbiotic effect.⁶ However, in the case of **2a** the reverse symbiosis was found despite the presence of two hard donor-coordinated nitrogens in **1a**. This implies that the soft–soft interaction between Pd and P dominates over the symbiotic effect.

In conclusion, the above results indicate that the Pd/Pt–P bonding interaction can be used as a driving force to construct finite assemblies instead of the much more widely used Pd/Pt–nitrogen interaction. The facile formations of **2a** from the stable dipyridyl analogue **3** as well as the self-selection for the formation of **2a** even in the presence of the nitrogen donor ligand bpe are established. Multinuclear NMR and X-ray single-crystal structure analysis unambiguously established the formation of chair-shaped metallamacrocycles in case of four assemblies (**2a**, **2b**, **2c**, and **2e**). NMR and ESI mass spectrometry were consistent with the formation of a dimeric assembly in the case of **2d**, and the shape was predicted from MM2 simulations. The use of phosphorus donor rigid linkers in conjunction with Pd/Pt acceptors and formation of finite assemblies has the potential to considerably expand the range of the directional bonding paradigm in self-assembly.

Experimental Section

Methods and Materials. Deuterated solvents, 1,2-bis(4-pyridyl)ethane (**L'**), and *trans*-1,2-bis(diphenylphosphino)ethylene (**L**) were purchased from Aldrich Chemical Co. Metal-based linkers **1a–d** were prepared from their chloride analogues by treating with AgNO₃. ¹H and ³¹P NMR spectra were recorded using a Bruker 400 MHz machine. ¹H NMR chemical shifts (**2a–d**) are reported relative to the residual protons of deuterated methanol (δ 3.3 ppm)

Table 2. Selected Bond Lengths (Å) and Angles (deg) of **2a**, **2b**, **2c**, and **2e**

| 2a | | | | | |
|-------------------|------------|------------------|------------|-------------|-----------|
| Pd(1)–P(1) | 2.270(2) | Pd(1)–P(2) | 2.279(2) | Pd(1)–N(1) | 2.072(5) |
| Pd(1)–N(2) | 2.121(6) | Pd(2)–P(3) | 2.282(2) | Pd(2)–P(4) | 2.288(19) |
| Pd(2)–N(3) | 2.087(6) | Pd(2)–N(4) | 2.089(6) | | |
| N(1)–Pd(1)–N(2) | 81.0(2) | P(1)–Pd(1)–P(2) | 95.14(7) | | |
| N(1)–Pd(1)–P(1) | 92.08(17) | N(2)–Pd(1)–P(1) | 172.86(17) | | |
| N(1)–Pd(1)–P(2) | 172.55(17) | P(4)–Pd(2)–P(3) | 96.31(7) | | |
| N(3)–Pd(2)–N(4) | 81.8(2) | N(3)–Pd(2)–P(4) | 171.07(18) | | |
| 2b | | | | | |
| Pd(1)–P(1) | 2.298(2) | Pd(1)–P(2) | 2.303(3) | Pd(1)–N(1) | 2.093(7) |
| Pd(1)–N(2) | 2.113(7) | Pd(2)–P(3) | 2.265(2) | Pd(2)–P(4) | 2.286(2) |
| Pd(2)–N(3) | 2.069(7) | Pd(2)–N(4) | 2.103(10) | | |
| N(1)–Pd(1)–N(2) | 80.9(3) | P(1)–Pd(1)–P(2) | 95.01(8) | | |
| N(1)–Pd(1)–P(1) | 92.40(2) | N(2)–Pd(1)–P(1) | 171.8(2) | | |
| N(1)–Pd(1)–P(2) | 172.0(2) | P(4)–Pd(2)–P(3) | 95.80(8) | | |
| N(3)–Pd(2)–N(4) | 81.5(4) | N(3)–Pd(2)–P(4) | 170.2(2) | | |
| 2c | | | | | |
| Pt(1)–P(1) | 2.251(10) | Pt(1)–P(2) | 2.266(11) | Pt(1)–N(1) | 2.100(3) |
| Pt(1)–N(2) | 2.090(3) | Pt(2)–P(3) | 2.256(11) | Pt(2)–P(4) | 2.271(10) |
| Pt(2)–N(3) | 2.069(7) | Pt(2)–N(4) | 2.103(10) | | |
| N(1)–Pt(1)–N(2) | 80.9(3) | P(1)–Pt(1)–P(2) | 94.10(4) | | |
| N(1)–Pt(1)–P(1) | 92.60(9) | N(2)–Pt(1)–P(1) | 173.5(11) | | |
| N(1)–Pt(1)–P(2) | 173.1(9) | P(4)–Pt(2)–P(3) | 94.00(4) | | |
| N(3)–Pt(2)–N(4) | 79.4(14) | N(3)–Pt(2)–P(4) | 172.2(10) | | |
| 2e | | | | | |
| Pt(1)–P(1) | 2.252(2) | Pt(1)–P(2) | 2.237(19) | Pt(1)–Cl(1) | 2.362(19) |
| Pt(1)–Cl(2) | 2.341(2) | Pt(2)–P(3) | 2.243(19) | Pt(2)–P(4) | 2.252(2) |
| Pt(2)–N(3) | 2.160(4) | Pt(2)–N(4) | 2.130(3) | | |
| N(1)–Pt(1)–N(2) | 81.20(13) | P(1)–Pt(1)–P(2) | 95.50(7) | | |
| N(2)–Pt(1)–P(1) | 84.45(7) | Cl(2)–Pt(1)–P(1) | 172.5(7) | | |
| Cl(1)–Pt(1)–P(2) | 176.0(7) | P(4)–Pt(2)–P(3) | 96.31(7) | | |
| Cl(3)–Pt(2)–Cl(4) | 81.8(2) | Cl(3)–Pt(2)–P(4) | 171.07(18) | | |

and deuterated dichloromethane (δ 5.3 ppm) for **2e**. $^{31}\text{P}\{\text{H}\}$ NMR chemical shifts are reported relative to an external, unlocked sample of H_3PO_4 ($\delta = 0.0$ ppm). UV-vis spectra were recorded on a Perkin-Elmer spectrophotometer.

Crystallographic Data Collection and Refinement. X-ray single-crystal data for **2a,b** were collected with Mo $K\alpha$ radiation using an Oxford Diffraction X-Calibur CCD system. A Bruker SMART APEX CCD diffractometer, equipped with a fine-focus sealed-tube Mo $K\alpha$ X-ray source, was used for the other two complexes. SMART was used for data acquisition, and SAINT was used for data extraction. The crystals were positioned at 50 mm from the CCD; 321 frames were measured with a counting time of 10 s. Data analysis was carried out with the CrysAlis program.⁷ The structures were solved using direct methods with the Shelx97 program.⁸ The non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms bonded to carbons were included in geometric positions and given thermal parameters equivalent to 1.2 times those of the atom to which they were attached.

General Procedure for the Preparation of the Assemblies 2a–d. To a 2 mL dichloromethane solution containing 3.98 mg (0.01 mmol) of *trans*-1,2-bis(diphenylphosphino)ethylene (**L**) was added drop-by-drop a methanolic solution (1 mL) of the appropriate corner metal liner (**1a–d**) (0.01 mmol) with stirring (10 min). Precipitating out by ether addition isolated the products. **2a**: $^{31}\text{P}\{\text{H}\}$ NMR (CD_3OD , 121.4 MHz): δ 22.7 (s). ^1H NMR ($\text{DMSO}-d_6$): δ 2.84 (dd, 8H, CH_2); 4.83 (bs, 8H, NH_2); 6.75 (bs, 4H, *ethylenic-H*); 7.5–7.67 (m, 40H, *Ph-H*). Yield: 94%. Anal. Calcd for $\text{C}_{28}\text{H}_{30}\text{P}_2\text{N}_4\text{O}_6$ -Pd: C, 48.91; H, 4.36; N, 8.15. Found: C, 49.16; H, 4.62; N, 8.35. **2b**: $^{31}\text{P}\{\text{H}\}$ NMR (CD_3OD , 121.4 MHz): δ 22.2 (t). ^1H NMR ($\text{CH}_3\text{OH}-d_4$): δ 1.14 (d, 6H, CH_3); 2.9 (dd, 4H, CH_2); 3.5 (m, 2H, CH); 6.85 (bs, 4H, *ethylenic H*); 7.45–7.85 (m, 40H, *phenyl H*). Yield: 96%. Anal. Calcd for $\text{C}_{29}\text{H}_{32}\text{P}_2\text{N}_4\text{O}_6$ -Pd: C, 49.64; H, 4.56; N, 7.98. Found: C, 50.00; H, 4.72; N, 8.21. **2c**: $^{31}\text{P}\{\text{H}\}$ NMR (CD_3OD , 121.4 MHz): δ 1.1 (s). ^1H NMR ($\text{CH}_3\text{OH}-d_4$): δ 2.9

(dd, 8H, CH_2); 7.0 (bs, 4H, *ethylenic H*); 7.4–7.8 (m, 40H, *phenyl H*). Yield: 91%. Anal. Calcd for $\text{C}_{28}\text{H}_{30}\text{P}_2\text{N}_4\text{O}_6$ -Pt: C, 43.34; H, 3.86; N, 7.22. Found: C, 43.60; H, 3.72; N, 7.59. ESI-MS: $[\text{M} - 2\text{NO}_3]^{2+}$ [$m/z = 712.4$ (calcd 712.10)] and $[\text{M} - 4\text{NO}_3]^{4+}$ [$m/z = 325.50$ (calcd 325.00)]. **2d**: $^{31}\text{P}\{\text{H}\}$ NMR (CD_3OD , 121.4 MHz): δ 1.5 (t). ^1H NMR ($\text{CH}_3\text{OH}-d_4$): δ 1.2 (d, 6H, CH_3); 2.9 (dd, 4H, CH_2); 3.5 (m, 2H, CH); 6.8 (bs, 4H, *ethylenic H*); 7.4–7.9 (m, 40H, *phenyl H*). Yield: 89%. Anal. Calcd for $\text{C}_{29}\text{H}_{32}\text{P}_2\text{N}_4\text{O}_6$ -Pt: C, 44.21; H, 4.06; N, 7.11. Found: C, 44.50; H, 4.32; N, 7.41. ESI-MS: $[\text{M} - \text{NO}_3]^+$ [$m/z = 1514.6$ (calcd 1514.00)]; $[\text{M} - 2\text{NO}_3]^{2+}$ [$m/z = 726.4$ (calcd 726.00)] and $[\text{M} - 4\text{NO}_3]^{4+}$ [$m/z = 332.40$ (calcd 332.00)].

Preparation of 2e. To a 2 mL dichloromethane solution containing 3.98 mg (0.01 mmol) of **L** was added drop-by-drop a dichloromethane solution (1 mL) of $\text{Pt}(\text{COD})\text{Cl}_2$ (0.01 mmol) with stirring (30 min). An intense smell of COD started to evolve. Ether was added to the resulting solution to obtain the product as white precipitate. The COD was removed completely by washing with ether and kept under vacuum for 2 h. $^{31}\text{P}\{\text{H}\}$ NMR (CD_2Cl_2 , 121.4 MHz): δ 9.2 (s). ^1H NMR (CD_2Cl_2): δ 6.7 (bs, 4H, *ethylenic H*); 7.3–7.9 (m, 40H, *Ph-H*). Yield: 96%. Anal. Calcd for $\text{C}_{26}\text{H}_{22}\text{P}_2\text{Cl}_2$ -Pt: C, 47.14; H, 3.36. Found: C, 46.86; H, 3.22.

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Supporting Information Available: X-ray crystallographic files for **2a**, **2b**, **2c**, and **2e** in CIF format. ^{31}P and ^1H spectra of **2a–e** and binding constant calculations for **2a** and **3** in PDF format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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