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Bidentate Ligands Capable of Variable Bond Angles in the Self-Assembly of Discrete Supramolecules

Ki-Whan Chi,*,† Chris Addicott,* Atta M. Arif, Neeladri Das, and Peter J. Stang*

Department of Chemistry, University of Utah, 315 South 1400 East, Salt Lake City, Utah 84112

stang@chem.utah.edu

Received September 19, 2003

Flexible donor ligands like 1,2-bis(3-pyridyl)ethyne or 1,4-bis(3-pyridyl)-1,3-butadiyne self-assemble into discrete supramolecules instead of infinite networks upon combination with organoplatinum 90, 120, and 180 degree acceptor units. These systems are unique examples of versatile pyridine donors adjusting their bonding directionality to accommodate rigid platinum acceptors in the formation of closed macrocycles.

Introduction

A plethora of discrete two- and three-dimensional (2- and 3-D) supramolecules have been prepared via coordination-driven self-assembly.[1−9] This methodology involves the rational design of higher architectures by the combination of simpler starting materials.[10,11] Often, one of the building blocks contains two or more rigid 4-substituted pyridine rings. This type of ligand maintains the same bonding directionality regardless of any rotation of these rings. In contrast, conformationally flexible 3-substituted pyridines **1a**,**b** (where **1a** is 1,2-bis(3-pyridyl)ethyne and **1b** is 1,4-bis(3-pyridyl)-1,3-butadiyne) are capable of orientating their nitrogen atoms to any dihedral angle between 0° and 180°, thus producing marked structural differences in reaction products. For example, Loye and co-workers[12] have shown that the pyridine nitrogen donors in coordination polymers of **1a** with cadmium(II) nitrate and cobalt(II) nitrate are oriented in a trans-type fashion. However, in polymers with copper(II) nitrate, the nitrogen atoms of **1a** bond in a cis arrangement,[12] while **1b** adopts a trans orientation.[13] Conversely, reactions between 4-substituted pyridyl-based ligands and less labile platinum compounds tend to form discrete supramolecular systems.[14−16]

We were interested to see if flexible, bidentate ligands **1** and organoplatinum molecules **5**−**7** (shown in Scheme 1) would self-assemble into closed supramolecular structures or acyclic, infinite oligomers. Herein, we report the results of our investigations.

Results and Discussion

Heating **1a** with 90° platinum acceptor **5** in CD_3NO_2 for 3.5 h gave the [2 + 2] assembly **2a** in quantitative yield. The $^{31}P\ \{^{1}H\}$ NMR spectrum showed a single sharp peak at −27.9 ppm. This peak is shifted approximately 8 ppm upfield relative to that of **5** as a result of back-donation from the platinum atoms. In the ^{1}H NMR, both α-hydrogen nuclei of the pyridine rings experienced downfield shifts (H_a 1 ppm, H_d 0.3 ppm) relative to those of **1a**. These shifts are consistent with the loss of electron density upon coordination of the pyridine-N. Further evidence was obtained with ESI-MS (Figure 1). The isotopically resolved peak at *m*/*z* 1501 was assigned as the $[M - OTf]^+$ species where M represents the intact macrocycle. The base peak at *m*/*z* 675 was assigned to the $[M - 2OTf]^{2+}$ species.

Combination of **1b** and **5** under similar conditions gave **2b**. The mass spectrum was similar to that of **2a**. The isotopically resolved base peak (*m*/*z* 1549) was assigned to the $[M - OTf]^+$ ion. Unexpectedly, two chair−boat-type conformers of **2b** (Figure 2) were detected in the product NMR spectra. Two peaks of nearly equal intensity separated by 0.02 ppm were observed in the $^{31}P\ \{^{1}H\}$ NMR spectrum at room temperature. When the sample was warmed to 80 °C, coalescence of these peaks was

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[†] Visiting Professor from the Department of Chemistry, University of Ulsan, Ulsan 680-749, Republic of Korea.

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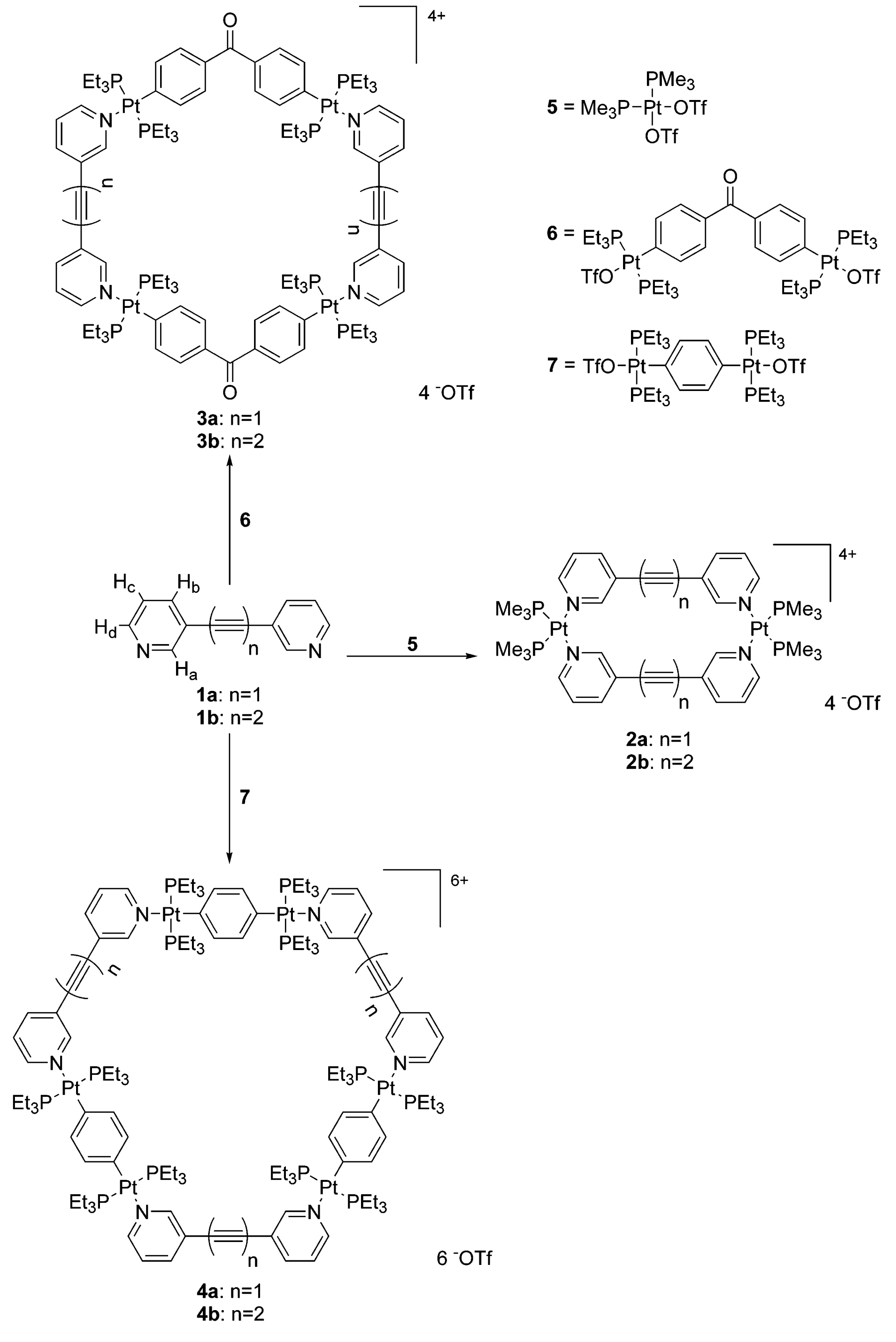
10.1021/jo0353785 CCC: $25.00

SCHEME 1. Self-Assembly of 1 with Platinum Acceptors 5−7



observed. The ^{1}H NMR spectrum also showed two sets of similar signals at room temperature.

At 80 °C, the two phosphine methyl group doublets merge into one signal. Only partial coalescence of the signal from H_a was observed. A possible explanation for this is the close proximity of the neighboring H_a proton nuclei during conformer interconversion. When the sample was cooled back to room temperature, the NMR spectra return to their original appearance. X-ray quality crystals were grown by vapor diffusion of ether into a nitromethane solution of **2b**. The ORTEP picture shown in Figure 3 is of the chair conformer which crystallizes preferentially over the boat form. The dihedral angle between the pyridine rings is approximately 107°. Further inspection of the bond angles associated with the acetylene moieties shows that they deviate slightly from linearity resulting in a curved "bridge" connecting the pyridine rings.

An analogous conformer mixture of **2a** was not observed. The closer proximity of the phosphine groups in a boat conformation of **2a** may make this structure much less energetically favorable than its chair counterpart. Use of the longer ligand **1b** results in more spatial separation between the phosphine groups in the assembly **2b**. Our observation that each conformer is formed in approximately equal amounts suggests that they are much closer in energy.

When **1a** was reacted with 120° platinum linker **6**, self-assembly **3a** was formed. The ^{31}P {^{1}H} NMR spectrum showed only one signal (14.8 ppm) with the consistent upfield shift from that of **6**. The mass spectrum adds support to the structure. Peaks attributable

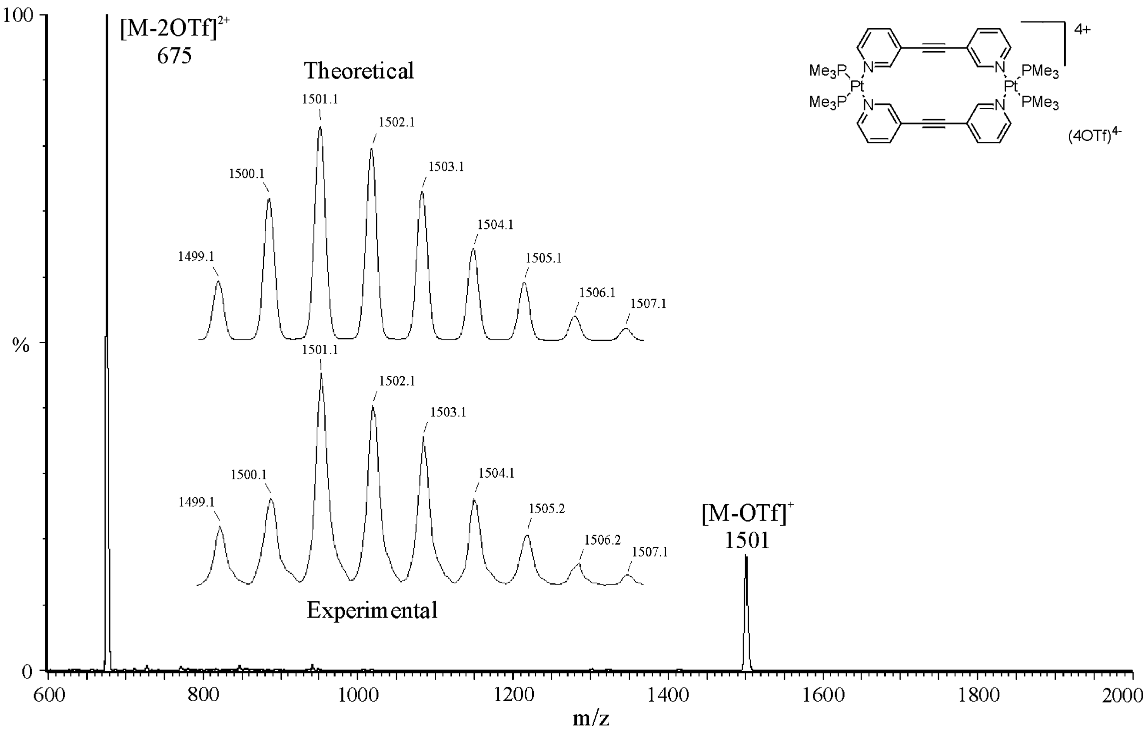


FIGURE 1. ESI-MS of assembly **2a**.

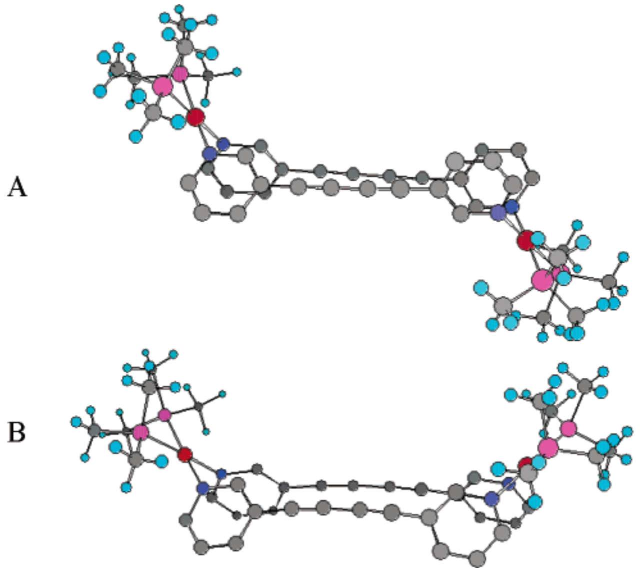


FIGURE 2. Chair (A) and boat (B) conformers of **2b**. Atom key: gray = C, blue = N, red = Pt, pink = P, green = H.

to the consecutive loss of triflate anions were observed: [M − OTf]$^+$ (m/z 2893), [M − 2OTf]$^{2+}$ (m/z 1372), and [M − 3OTf]$^{3+}$ (m/z 865). The former and latter were isotopically resolved and agree very well with the theoretical distribution. In contrast to that of **2a**, the H$_a$ signal of **3a** (9.06 ppm) experiences a smaller shift to lower field (0.26 ppm). The aromatic region of the ^{1}H spectrum showed small amounts (<5%) of byproducts. The broadened appearance of these signals suggests that they may be of an oligomeric nature. Likewise, larger cycle **3b** was made from **1b** and **6**. Its NMR and mass spectra were similar to those of **3a**: peaks for [M − OTf]$^+$ (m/z 2940), [M − 2OTf]$^{2+}$ (m/z 1396), and [M − 3OTf]$^{3+}$ (m/z 881) were observed. The isotopically resolved patterns of the former and latter peaks are in excellent agreement with theory.

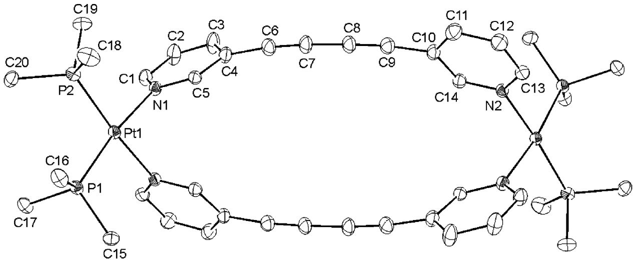


FIGURE 3. ORTEP diagram of **2b**.

The [3 + 3] assemblies **4** were made from **1** and linear platinum linker **7**. Both display strong ^{31}P signals (14.6 ppm **4a**, 14.9 ppm **4b**). Small amounts of byproducts give weak shoulder bands on either side of these resonances. These impurities are less evident in the proton NMR spectra, which are fairly similar as expected. One difference is the signals for the aromatic proton nuclei of the linker **7**. Assembly **4a** shows two singlets for these nuclei; **4b** shows only one singlet. The benzene rings of **4a** must be hindered in their rotation leading to distinct inner and outer nuclei. These signals did not coalesce when the sample was heated to 80 °C. In the mass spectra of **4**, the most intense peaks were assigned to the consecutive loss of triflate ions: [M − 2OTf]$^{2+}$ (m/z 1976 **4a**, 2012 **4b**), [M − 3OTf]$^{3+}$ (m/z 1267 **4a**, 1292 **4b**), [M − 4OTf]$^{4+}$ (m/z 913 **4a**, 932 **4b**), and [M − 5OTf]$^{5+}$ (m/z 701 **4a**, 715 **4b**).

In conclusion, we have described the first discrete supramolecules prepared from organoplatinum reagents and bidentate pyridine donors **1**. Despite their ability to vary their bonding directionality, ligands **1** prefer to self-assemble into closed macrocycles regardless of the geometrical features of the platinum acceptor. This provides further evidence of thermodynamic control favoring formation of discrete entities over oligomeric networks, which is presumably due to the added gain in enthalpy from the additional dative Pt−N bond in the closed system.

Experimental Section

Methods and Materials. 1,2-Bis(3-pyridyl)ethyne **1a** was prepared using previously described conditions.[17] 1,4-Bis(3-pyridyl)-1,3-butadiyne **1b** was prepared as reported.[18] The starting organoplatinum compounds **5**,[19] **6**,[20] and **7**[21] were obtained as reported.

General Procedure for Preparation of Assemblies 2−4. The pyridine linker **1** (5 μmol) and platinum acceptor **5**−**7** (1 equiv) were placed in a 1 dram vial. CD_3NO_2 (0.9 mL) was added. The vial was sealed with Teflon tape, and the reaction mixture was stirred and heated in an oil bath at 60 °C for 3−4 h. The solution was then transferred to an NMR tube for analysis. The solvent was evaporated, and the solid residue was washed twice with diethyl ether and then dried overnight in vacuo.

2a. Yield = 96%. ^{1}H NMR (CD_3NO_2, 300 MHz) δ 9.84 (br s, 4H, H_a), 8.83 (m, 4H, H_d), 8.09 (ddd, $^3J = 8.1$ Hz, $^4J = 2.0$ Hz, $^4J = 1.4$ Hz, 4H, H_b), 7.69 (dd, $^3J = 8.1$ Hz, $^3J = 5.7$ Hz, 4H, H_c), 1.76 (d, $^2J_{H-P} = 11.3$ Hz, 36H, CH_3). $^{31}P\{^1H\}$ NMR (CD_3NO_2, 121 MHz) δ −27.9 (s, ^{195}Pt satellites, $^1J_{Pt-P} = 3181$ Hz). Anal. Calcd for $C_{40}H_{52}F_{12}N_4O_{12}P_4Pt_2S_4$: C, 29.10; H, 3.17; N, 3.39. Found: C, 28.74; H, 3.34; N, 3.56.

2b. Yield = 98%. Mixture of conformers. ^{1}H NMR (CD_3NO_2, 300 MHz) δ 9.36 (br s, 4H, H_a), 9.30 (br s, 4H, $H_{a'}$), 8.88 (m, 8H, H_d and $H_{d'}$), 8.14 (m, 8H, H_b and $H_{b'}$), 7.71 (m, 8H, H_c and $H_{c'}$), 1.74 (d, $^2J_{H-P} = 11.3$ Hz, 36H, CH_3), 1.73 (d, $^2J_{H-P} = 11.3$ Hz, 36H, $CH_3{}'$). $^{31}P\{^1H\}$ NMR (CD_3NO_2, 121 MHz) δ −27.64 (s, ^{195}Pt satellites, $^1J_{Pt-P} = 3176$ Hz), −27.66 (s, ^{195}Pt satellites, $^1J_{Pt-P} = 3176$ Hz). Anal. Calcd for $C_{44}H_{52}F_{12}N_4O_{12}P_4Pt_2S_4$: C, 31.10; H, 3.08; N, 3.30. Found: C, 30.89; H, 3.09; N, 3.29.

3a. Yield = 97%. ^{1}H NMR (CD_3NO_2, 300 MHz) δ 9.06 (d, $^4J = 1.7$ Hz, 4H, H_a), 8.90 (dd, $^3J = 5.6$ Hz, $^4J = 1.4$ Hz, 4H, H_d), 8.27 (dt, $^3J = 8.1$ Hz, $^4J = 1.4$ Hz, 4H, H_b), 7.85 (dd, $^3J = 8.1$ Hz, $^3J = 5.6$ Hz, 4H, H_c), 7.80−7.50 (m, 16H, H_{phenyl}), 1.49 (m, 48H, CH_2), 1.21 (m, 72H, CH_3). $^{31}P\{^1H\}$ NMR (CD_3NO_2, 121 MHz) δ 14.8 (s, ^{195}Pt satellites, $^1J_{Pt-P} = 2644$ Hz). Anal. Calcd for $C_{102}H_{152}F_{12}N_4O_{14}P_8Pt_4S_4$: C, 40.26; H, 5.04; N, 1.84. Found: C, 40.17; H, 5.14; N, 2.14.

3b. Yield = 99%. ^{1}H NMR (CD_3NO_2, 300 MHz) δ 9.10 (d, $^4J = 1.6$ Hz, 4H, H_a), 8.91 (dd, $^3J = 5.6$ Hz, $^4J = 1.1$ Hz, 4H, H_d), 8.24 (dt, $^3J = 8.0$ Hz, $^4J = 1.6$ Hz, 4H, H_b), 7.82 (dd, $^3J = 8.0$ Hz, $^3J = 5.6$ Hz, 4H, H_c), 7.75−7.51 (m, 16H, H_{phenyl}), 1.47 (m, 48H, CH_2), 1.20 (m, 72H, CH_3). $^{31}P\{^1H\}$ NMR (CD_3NO_2, 121 MHz) δ 14.7 (s, ^{195}Pt satellites, $^1J_{Pt-P} = 2633$ Hz). Anal. Calcd for $C_{106}H_{152}F_{12}N_4O_{14}P_8Pt_4S_4$: C, 41.19; H, 4.96; N, 1.81. Found: C, 41.04; H, 5.08; N, 2.07.

4a. Yield = 99%. ^{1}H NMR (CD_3NO_2, 300 MHz) δ 9.06 (br d, $^4J = 1.8$ Hz, 6H, H_a), 8.90 (dd, $^3J = 5.4$ Hz, $^4J = 1.4$ Hz, 6H, H_d), 8.30 (dt, $^3J = 8.1$ Hz, 2 × $^4J = 1.4$ Hz, 6H, H_b), 7.81 (dd, $^3J = 8.1$ Hz, $^3J = 5.4$ Hz, 6H, H_c), 7.26 (br s, 6H, H_{phenyl}), 7.20 (br s, 6H, H_{phenyl}), 1.50 (m, 72H, CH_2), (m, 108H, CH_3). $^{31}P\{^1H\}$ NMR (CD_3NO_2, 121 MHz) δ 14.6 (s, ^{195}Pt satellites, $^1J_{Pt-P} = 2722$ Hz). Anal. Calcd for $C_{132}H_{216}F_{18}N_6O_{18}P_{12}Pt_6S_6$: C, 37.29; H, 5.12; N, 1.98. Found: C, 37.59; H, 5.19; N, 2.16.

4b. Yield = 97%. ^{1}H NMR (CD_3NO_2, 300 MHz) δ 9.00 (d, $^4J = 1.7$ Hz, 6H, H_a), 8.92 (dd, $^3J = 5.5$ Hz, $^4J = 1.2$ Hz, 6H, H_d), 8.24 (ddd, $^3J = 8.1$ Hz, $^4J = 1.7$ Hz, $^4J = 1.2$ Hz, 6H, H_b), 7.79 (dd, $^3J = 8.1$ Hz, $^3J = 5.5$ Hz, 6H, H_c), 7.20 (br s, 12H, H_{phenyl}), 1.48 (m, 72H, CH_2), 1.18 (m, 108H, CH_3). $^{31}P\{^1H\}$ NMR (CD_3NO_2, 121 MHz) δ 14.9 (s, ^{195}Pt satellites, $^1J_{Pt-P} = 2711$ Hz). Anal. Calcd for $C_{138}H_{216}F_{18}N_6O_{18}P_{12}Pt_6S_6$: C, 38.33; H, 5.04; N, 1.94. Found: C, 38.34; H, 5.14; N, 1.99.

Acknowledgment. Financial support from the National Science Foundation (Grant CHE-0306720) and the National Institutes of Health (Grant 5R01GM57052) is gratefully acknowledged.

Supporting Information Available: NMR and mass spectral data for products **2**−**4**; crystallographic data for **2b** in cif format. This material is available free of charge via the Internet at http://pubs.acs.org.

JO0353785

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