Flexible Bidentate Pyridine and Chiral Ligands in the Self-Assembly of Supramolecular 3-D Cages

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Abstract: Discrete, nanoscopic 3-D cages are prepared in high yield via coordination-driven self-assembly from a variety of building blocks, including bidentate 3-substituted pyridines, chiral, and silicon-based tripods. All are characterized by NMR (31P, 1H) and electrospray ionization mass spectrometry.

An abundance of discrete 3-D supramolecular species assembled from simple building blocks has been reported in recent years.1−10 Of all the noncovalent interactions, the coordination bonding motif has proven itself to be a highly useful tool for their preparation. By employing a rational transition-metal-mediated approach,11 complex nanoscopic supramolecules are formed via self-assembly of appropriately designed precursors.

Recently, supramolecular prisms of D3h symmetry were reported by our group.12 X-ray crystallography of one cage showed a single nitrate anion incarcerated within its cavity. Likewise, new tetrahedral phosphorus and silicon-based assemblies of similar geometry and size were prepared.13 These achiral examples contain only rigid moieties also shift slightly upfield (ca. 0.3 ppm) in the 1H NMR. The pyridine hydrogens adjacent to the nitrogen nucleus experience small shifts (ca. 0.3 ppm) downfield due to the loss of electron density that occurs upon coordination. The central anthracene proton (H-9) of 3e,f moves 0.5 ppm to higher field.

Satisfactory elemental analyses of 3a,c as the nitrate salts were obtained. For the other assemblies 3b,d,f it was necessary to precipitate them as hexafluorophosphate salts first by addition of KPF6. This also revealed further evidence of the structure of 3e,f. The elemental analysis revealed only five nitrate counterions had been exchanged with hexafluorophosphates. This was confirmed by using electrospray ionization mass spectrometry. Peaks attributable to the consecutive loss of hexafluorophosphate counterions, [M − 2PF6]2− (m/z 2216.9), [M − 3PF6]3− (m/z 1429.5), and [M − 4PF6]4− (m/z 1035.0), where M represents the intact 3-D cage with a single encapsulated NO3−, were observed in the spectrum of 3e,f. The former was isotonically resolved and matches the theoretical distribution very well. On the basis of X-ray analysis of analogous structures,14 it is likely the main products.
lone nitrate counterion is trapped within the molecular cavity. The molar rotation \([\phi_D]\) of 3e (201) was similar in magnitude but opposite in sign to its enantiomer 3f (+205).

Mass spectra of the other cages 3a–d were obtained as the nitrate salts. A small peak for the \([M - 2\text{NO}_3]^{2+}\) species (m/z range 1944–1995) was isotopically resolved for each product. These were complemented by much larger peaks for the \([M - 3\text{NO}_3]^{3+}\) (m/z 1275–1310) and \([M - 4\text{NO}_3]^{4+}\) (m/z 941–967) species.

In conclusion we have prepared and characterized several nanoscopic 3-D assemblies from a variety of building blocks. Cages 3a–d are the first examples of discrete 3-D supramolecules formed from flexible 3-substituted pyridines 2a, b and organoplatinum reagents. Clearly 2a, b prefer to self-assemble into closed systems despite their ability to vary their bonding directionality. Cages 3e, f represent an additional example of the few chiral 3-D systems where both self-assembled enantiomers are prepared. Moreover, tripod 1c, d is readily available making it a valuable building block for construction of a variety of chiral 3-D structures.

**Experimental Section**

**Methods and Materials.** 1,2-Bis(3-pyridyl)ethyne 2a, 1,4-bis(3-pyridyl)-1,3-butadiyne 2b and organoplatinum compounds 1a, b and 2c were all prepared as reported.

**General Procedure for the Preparation of Assemblies 3.** The pyridine linker (10 μmol 1c, d, 6 μmol 2a, b) and platinum acceptor (4 μmol 1a, b, 15 μmol 2c) were placed in a 1-dram vial. Acetone-d₆ (0.5 mL) and D₂O (0.5 mL) were added. The vial was sealed with Teflon tape and the reaction stirred and heated in an oil bath at 60 °C for 24 h. The solution was then transferred to an NMR tube for analysis. In the case of 3a and 3c, the reaction was filtered and the solvent removed under a stream of N₂. The solid residue obtained was washed twice with diethyl ether then dried overnight in vacuo. In the case of 3b–f, excess KPF₆ was added to precipitate the product, which was collected and washed with water then dried in vacuo.

**3a:** Yield 98%. Mp 156–158 °C dec. 1H NMR (acetone-d₆/D₂O 1:1, 300 MHz) \(\delta\) 9.11 (d, \(J = 1.84\) Hz, 6H, Ha), 8.83 (d, \(J = 5.57\) Hz, 6H, Hb), 8.26 (d, \(J = 8.30\) Hz, 6H, Hc), 7.82 (d, \(J = 7.82\) Hz, 6H, Hf), 6.95 (d, \(J = 7.74\) Hz, 6H, He), 6.36 (d, \(J = 8.04\) Hz, 6H, He'), 5.35 (t, \(J = 7.39\) Hz, 6H, He''), 1.30 (m, 72H, PCH₂), 1.03 (m, 108H, PCH₂CH₃), 0.90 (s, 6H, Si-CH₃); 31P{¹H} NMR (acetone-d₆/D₂O 1:1, 121 MHz) \(\delta\) 16.1 (s, 195Pt satellites, \(J_{Pt-P} = 2682\) Hz). Anal. Calcd for C₁₄₆H₂₃₄N₁₂O₁₈P₁₂Pt₆Si₂: C, 43.36; H, 5.83; N, 4.16. Found: C, 43.46; H, 6.09; N, 3.78.

**3b:** Yield 96%. Mp > 300 °C dec. 1H NMR (acetone-d₆/D₂O 1:1, 300 MHz) \(\delta\) 8.97 (d, \(J = 1.58\) Hz, 6H, Ha), 8.84 (d, \(J = 5.29\) Hz, 6H, Hb), 8.21 (d, \(J = 8.08\) Hz, 6H, Hc), 7.79 (dd, \(J = 8.16\) Hz, 6H, Hf), 7.38 (m, 12H, Hf'), 7.26 (d, \(J = 7.82\) Hz, 6H, Hf), 7.18 (m, 12H, Hf), 6.95 (d, \(J = 7.74\) Hz, 6H, He), 6.36 (d, \(J = 8.04\) Hz, 6H, He'), 5.35 (t, \(J = 7.39\) Hz, 6H, He''), 1.30 (m, 72H, PCH₂), 1.03 (m, 108H, PCH₂CH₃), 0.90 (s, 6H, Si-CH₃); 31P{¹H} NMR (acetone-d₆/D₂O 1:1, 121 MHz) \(\delta\) 16.1 (s, 195Pt satellites, \(J_{Pt-P} = 2682\) Hz). Anal. Calcd for C₁₄₆H₂₃₄N₁₂O₁₈P₁₂Pt₆Si₂: C, 43.36; H, 5.83; N, 4.16. Found: C, 43.46; H, 6.09; N, 3.78.

**3c:** Yield 98%. Mp 156–158 °C dec. 1H NMR (acetone-d₆/D₂O 1:1, 300 MHz) \(\delta\) 9.11 (d, \(J = 1.84\) Hz, 6H, Ha), 8.83 (d, \(J = 5.57\) Hz, 6H, Hb), 8.26 (d, \(J = 8.30\) Hz, 6H, Hc), 7.82 (d, \(J = 7.82\) Hz, 6H, Hf), 6.95 (d, \(J = 7.74\) Hz, 6H, He), 6.36 (d, \(J = 8.04\) Hz, 6H, He'), 5.35 (t, \(J = 7.39\) Hz, 6H, He''), 1.30 (m, 72H, PCH₂), 1.03 (m, 108H, PCH₂CH₃), 0.90 (s, 6H, Si-CH₃); 31P{¹H} NMR (acetone-d₆/D₂O 1:1, 121 MHz) \(\delta\) 16.1 (s, 195Pt satellites, \(J_{Pt-P} = 2682\) Hz). Anal. Calcd for C₁₄₆H₂₃₄N₁₂O₁₈P₁₂Pt₆Si₂: C, 43.36; H, 5.83; N, 4.16. Found: C, 43.46; H, 6.09; N, 3.78.
Hz, δ = 5.77 Hz, 6H, H₃), 7.35 (d, δ = 7.61 Hz, 6H, H or H₇),
7.31 (d, δ = 7.61 Hz, 6H, H or H₇), 7.24 (d, δ = 7.49 Hz, 6H,
H or H₇), 6.81 (d, δ = 7.63 Hz, 6H, H₂ or H₆), 1.27 (m, 72H,
PCH₂), 1.00 (m, 108H, PCH₂C₃), 0.87 (s, 6H, Si-CH₃); 3¹P-
{¹H} NMR (acetone-d₂/D₂O 1:1, 121 MHz) δ 16.8 (s, 195Pt
satellites, 1JPt-P = 2672 Hz). Anal. Calcd for C₁₅₂H₂₃₄F₃₆N₆P₁₈-
Pt₆Si₂: C, 39.57; H, 5.11; N, 1.82. Found: C, 39.73; H, 5.23; N,
1.80.

3c: Yield 99%. Mp > 200 °C dec. ¹H NMR (acetone-d₂/D₂O
1:1, 300 MHz) δ 9.04 (d, δ = 1.57 Hz, 6H, H₃), 8.81 (d, δ =
5.62 Hz, 6H, H₃), 8.23 (d, δ = 8.16 Hz, 6H, H₃), 7.81 (dd, δ =
8.16 Hz, δ = 5.61 Hz, 6H, H₃), 7.27 (d, δ = 7.99 Hz, 6H, H₇ or
H₇), 7.13 (m, 12H, 6H or 6H and 6H or 6H₆), 6.31 (d, δ =
7.99 Hz, 6H, H or H₆), 2.20 (s, 6H, C-CH₃), 1.32 (m, 12H,
PCH₂), 1.03 (m, 108H, PCH₂C₃); 3¹P-{¹H} NMR (acetone-d₂/
D₂O 1:1, 121 MHz) δ 16.3 (s, 195Pt satellites, 1JPt-P = 2696 Hz).
Anal. Calcd for C₁₄₈H₂₃₆N₁₂O₁₉P₁₂Pt₆H₂O: C, 44.11; H, 5.90; N,
4.17. Found: C, 44.31; H, 5.88; N, 4.19.

3d: Yield 96% Mp > 300 °C dec. ¹H NMR (acetone-d₂/D₂O
1:1, 300 MHz) δ 9.05 (d, δ = 1.64 Hz, 6H, H₃), 8.86 (d, δ =
5.46 Hz, 6H, H₃), 8.23 (d, δ = 8.26 Hz, 6H, H₃), 7.81 (dd, δ =
8.19 Hz, δ = 5.69 Hz, 6H, H₃), 7.28 (d, δ = 8.27 Hz, 6H, H or H₇),
7.15 (m, 12H, 6H or 6H and 6H or 6H₆), 6.27 (d, δ = 8.01
Hz, 6H, H or H₆), 2.24 (s, 6H, C-CH₃), 1.32 (m, 12H,
PCH₂), 1.03 (m, 108H, PCH₂C₃); 3¹P-{¹H} NMR (acetone-d₂/D₂O
1:1, 121 MHz) δ 16.3 (s, 195Pt satellites, 1JPt-P = 2696 Hz). Anal.
Calcd for C₁₅₄H₂₃₄F₃₆N₆P₁₈Pt₆: C, 40.37; H, 5.15; N, 1.88. Found:
C, 40.45; H, 5.19; N, 1.88.

3e–f: Yield 91% of 3e; 89% of 3f. Mp 256–258 °C dec. [α]D
= -4.25 (3e), +4.34 (3f). ¹H NMR (acetone-d₂/D₂O 1:1, 300 MHz) δ 8.96 (m, 12H, H₃-₇), 8.91 (s, 3H, H₉), 8.35 (s, 3H, H₁₀), 7.82 (br d, δ = 4.22 Hz, 6H, H₆-₇),
7.70 (m, 18H, H₆-₇ and H₂₃₄₅), 7.41 (s, 10H, Hphenyl), 7.12 (t,
6H, δ = 7.44 Hz, H₆), 4.22 (t, 2H, δ = 7.74 Hz, C(O)-CH₃),
2.20 (m, 2H, C(O)-CH₂-CH), 1.90 (m, 2H, C(O)-CH₂-CH),
1.34 (m, 72H, PCH₂-CH₂), 0.82 (m, 114H, P-CH₂-CH₃ and
C(O)-CH₂-CH₂-CH₃); 3¹P-{¹H} NMR (acetone-d₂/D₂O 1:1,
121 MHz) δ 9.81 (s, 195Pt satellites, 1JPt-P = 2639 Hz). Anal.
Calcd for C₁₆₆H₂₅₀F₃ₐN₁₂O₁₉P₁₇Pt₆: C, 42.22; H, 5.34; N, 2.08.
Found: C, 42.17; H, 5.25; N, 2.15.

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Supporting Information Available: Experimental pro-
cedure for the synthesis of 3c, d and NMR and mass spectral
data for assemblies 3. This material is available free of charge
via the Internet at http://pubs.acs.org.

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