Communications to the Editor

A Nano-Scale Barrel and Cube: Transition Metal-Mediated Self-Assembly of CpCoCb-Derived Ligand Scaffolds

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Received November 20, 2000

The synthetic strategies, challenges, and opportunities in transition metal-mediated supramolecular self-assembly (SSA) have been reviewed recently by Stang, Fujita, and Jones.[1] Alternative topological motifs will continue to emerge as the SSA field evolves, providing more options for preparation of novel nanoscale architectures. In this regard, we wish to report the seminal results of our recent efforts to demonstrate the immediate utility of the CpCo-cyclobutadienyl (CpCoCb) metallocene in SSA, thereby identifying a readily accessible scaffold for which numerous synthetic modifications are conceivable. In particular, our work applies the CpCo-tetrakis(3- and 4-pyridyl)cyclobutadiene scaffolds in SSA to illustrate a set of novel complements for selecting the directionality of nitrogen chelating vectors and easily controlling size and topology of our target assemblies. We detail below construction of a nanoscale barrel **1** and a nanoscale cube **2**.[2]

Synthesis of self-assembled barrel **1** requires only two steps from readily available starting materials (eq 1). Cobalt-mediated [2+2][3] dimerization of **3**[4] provided ligand-scaffold_meta **4**, which was treated subsequently with enPd(NO₃)₂ in CH₃OH−H₂O to

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(1) (a) Leininger, S.; Olenyuk, B.; Stang, P. J. *Chem. Rev.* **2000**, *100*, 853. (b) Fujita, M. *Chem. Soc. Rev.* **1998**, *27*, 417. (c) Jones, C. J. *Chem. Soc. Rev.* **1998**, *27*, 289.
(2) Alternatively, self-assembly **2** can be construed as a truncated cube if one defines the solid shape derived by *formally* drawing lines between the Pd atoms.
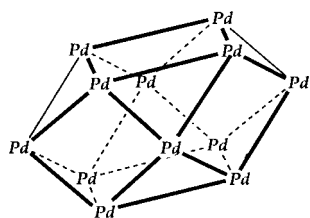
(3) For recent applications of Co-mediated [2+2] annulation, see the following. (a) In mixed cyclophane synthesis: Brisbois, R. G.; Fogel, L. E.; Nicaise, O. J.-C.; DeWeerd, P. J. *J. Org. Chem.* **1997**, *62*, 6708. (b) In organometallic dehydroannulene construction: Bunz, U. H. F.; Roidl, G.; Altmann, M.; Enkleman, V.; Shimizu, K. D. *J. Am. Chem. Soc.* **1999**, *121*, 10719. (c) In efforts toward a planar-chiral catalyst: Stevens, A. M.; Richards, C. J. *Organometallics* **1999**, *18*, 1346.
(4) Negishi, E.; Xu, C.; Tan, Z.; Korta, M. *Heterocycles* **1997**, *46*, 209.

1 · (NO₃)₈

2 · (NO₃)₂₄
[*M* = enPd]
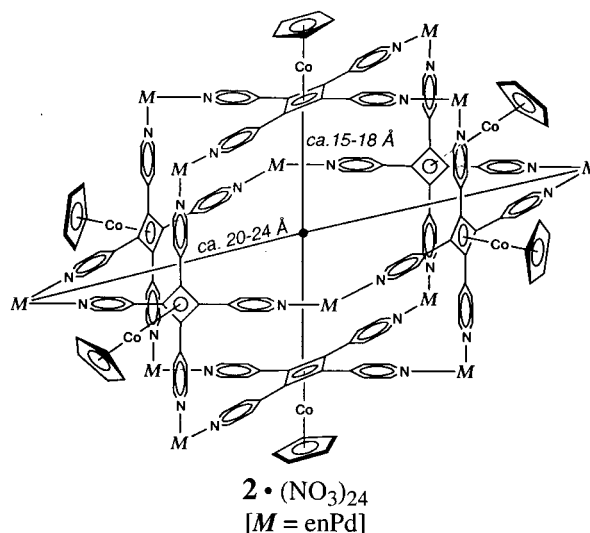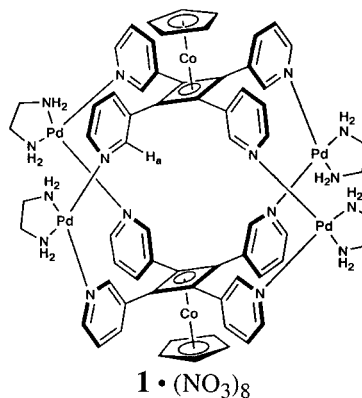
give a quantitative yield of **1**. The exceedingly simple proton and carbon NMR spectra, each of which exhibits only a single set of resonances, are entirely consistent with a single entity possessing the indicated structure **1**.[5a] Of particular note is the chemical shift observed for the H_a in **1**. In the precursor ligand-scaffold **4**, H_a appears at δ 8.65, whereas in the self-assembled "barrel" H_a shifts upfield to δ 7.76. We attribute this upfield shift to anisotropic

(5) (a) Preparation and physical properties of **1**·(NO₃)₃: To a solution of **4** (0.11 mmol) in methanol (20 mL) was added ethylenediamine palladium-(II) nitrate (0.22 mmol) dissolved in 50% aqueous methanol (20 mL). After 15 min at ambient temperature, the solvent was removed in vacuo and a yellow powder precipitated, which was collected and dried under reduced pressure giving rise to **1**·(NO₃)₈ in 100% yield: mp (DSC) 161.2 °C; ¹H NMR [300 MHz, CD₃OD:D₂O (1:2), TMS as an extenal standard] δ 8.71 (d, 8H, *J* = 6.0 Hz), 7.97 (d, 8H, *J* = 8.0 Hz), 7.76 (s, 8H), 7.40(dd, 8H, *J* = 6.0, 8.0 Hz), 4.75 (s, 10H), 2.61 (m, 16H); ¹³C NMR [75 MHz, CD₃OD:D₂O (1:1)] δ 150.2, 144.5, 140.4, 131.1, 126.2, 83.4, 68.7; IR (KBr, cm⁻¹) 3419, 3210, 3081, 1574, 1490, 1355, 1196, 1133, 998, 825, 699; ESI-MS (2% ammonium hydroxide) calcd for C₆₆H₇₄N₂₄O₂₄Co₂Pd₄ 2128.0111, found *m/z* 1003 [M + 2H − 2NO₃]²⁺, 648 [M + 3H − 3NO₃]³⁺, 626 [M + 3H − 3NO₃ − Cp]³⁺, 471 [M + 4H − 4NO₃]⁴⁺. (b) Preparation and physical properties of **2**·(NO₃)₂₄: To a solution of **6** (0.10 mmol) in methanol (20 mL) was added a solution of ethylenediamine palladium(II) nitrate (0.20 mmol) in 50% aqueous methanol. After 15 min at ambient temperature, the solvent was removed under reduced pressure and a brown powder precipitated, which was filtered and dried in vacuo giving rise to **2**·(NO₃)₂₄ in 100% yield: mp (DSC) 173.2 °C; ¹H NMR [300 MHz, CD₃OD:D₂O (1:1)] δ 8.17 (bs, 48H), 7.40 (bs, 48H), 4.65(s, 30H), 2.81 (bs, 48H); ¹³C NMR [75 MHz, CD₃OD:D₂O (1:1)] δ 151.9, 148.7, 125.8, 85.8, 72.4, 47.6; IR (KBr, cm⁻¹) 3429, 3206, 3087, 1609, 1507, 1359, 1059, 833; ESI-MS (MeOH:H₂O (1:1), 5% HOAc) calcd for C₁₉₈H₂₂₂N₇₂O₇₂Co₆Pd₁₂ 6385.035, found *m/z* 6385.266.

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J. Am. Chem. Soc., Vol. 123, No. 16, 2001 **3819**

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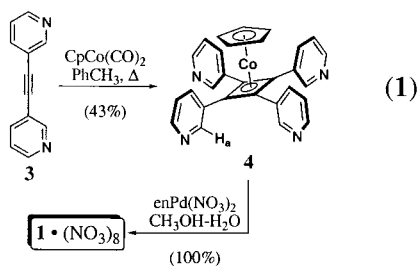
shielding exerted on H_a by the CpCoCb moiety. Differential scanning calorimetry (DSC) shows no change in melting point upon heating a previously melted sample, suggesting the "barrel" is in its most stable amorphous state.

Simple permutation of the nitrogen chelation directionality effects a dramatic control over SSA stoichiometry and product topology. Again, straightforward Co-mediated [2+2] dimerization of **5**[6] provides ligand-scaffold$_{para}$ **6** (eq 2); however, treatment

$$(2)$$
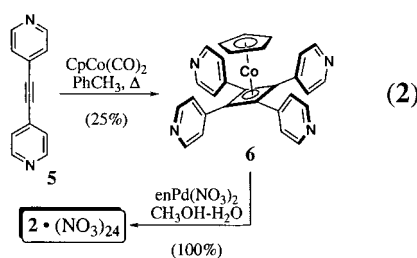
with enPd(NO_3)$_2$ in CH_3OH-H_2O in this case produces cube **2**, resulting from the quantitative self-assembly of 12 equiv of enPd-(NO_3)$_2$ and 6 equivs of **6**. Cube **2** features a very large internal volume, which we estimate to be approximately 4000 Å^3. The high symmetry of cube **2** results in simple proton and carbon NMR spectra which are highly indicative of a single entity.[5b] The significantly greater complexity of **2** (i.e. versus **1**) required application of nested ion mobility/time-of-flight mass spectrometric measurements, and these were obtained with a prototype instrument. Thorough characterization of cube **2** with this analytical technique clearly illustrates that future developments in SSA will continue to rely on it.

The prototype ion mobility/time-of-flight instrument used for mass spectrometric analyses of **2** has been described previously.[7] Briefly, a solution of **2** (0.5 mg/mL in CH_3OH-H_2O, 1:1, 5% HOAc) was electrosprayed[8] into the ion mobility instrument containing ~150 Torr of He[9] buffer gas. As ions drift across this instrument, they separate due to differences in their mobilities through the gas, which depend on the *shape and charge state* of

the ion. Upon exiting the drift tube the mobility-separated ions are pulsed into a reflectron geometry time-of-flight mass spectrometer to determine mass-to-charge (m/z) ratios.

Evidence for the structure of **2** (MF = $C_{198}H_{222}N_{72}O_{72}Co_6Pd_{12}$) was obtained from (1) comparison of experimental m/z values with theoretical m/z values for the expected product, (2) consideration of experimental peak shapes with calculated isotopic distributions for species having multiple Pd atoms, and (3) comparison of experimental mobilities with values that are calculated for rigid trial geometries[10] of the expected product. Ions exhibiting features with maxima at m/z values of 850.8, 1003.0, and 1215.7 have experimental mobilities of 8.40×10^{-5}, 7.26×10^{-5}, and 6.27×10^{-5} m$^2\cdot$V$^{-1}\cdot$s^{-1}, respectively. These m/z values are consistent with theoretical values of 850.148, 1002.173, and 1215.007 that were calculated for maxima of each isotopic distribution for the [**2**-5NO$_3$]$^{5+}$, [**2**-6NO$_3$]$^{6+}$, and [**2**-7NO$_3$]$^{7+}$ ions, respectively. Theoretical mobilities for these ions are 8.40×10^{-5}, 7.20×10^{-5}, and 6.02×10^{-5} m$^2\cdot$V$^{-1}\cdot$s^{-1}, respectively, which are in agreement with the observed experimental values. A further confirmation of this assignment comes from high-resolution Fourier transform mass spectrometry measurements. Values of m/z 929.839, 940.018, 951.013, 961.193, 970.857, 981.692, and 992.022 were measured for the maximum of the isotopic distribution for [**2**-nNO$_3$]$^{6+}$ (where $n = 7$ to 13). From these data, it was determined that the average mass for the maximum of the isotopic distribution for **2**·(NO_3)$_{24}$ is 6385.266, a value that is within 36 parts per million of 6385.035, the theoretical value.

We believe that our initial exploration of the CpCoCb scaffold in SSA complements and augments this rapidly developing field. The relative synthetic ease with which barrel **1** and cube **2** are obtained also serves as an excellent harbinger for future progress involving the CpCoCb scaffold. We are actively investigating the general topological scope and limitations of the CpCoCb core, particularly as a function of ligand attachment about the periphery of the Cb-deck. In addition, we will exploit the synthetic and structural possibilities offered by the Cp-deck.[11] Our results will be reported in due course.

Supporting Information Available: Two-dimensional ion mobility/time-of-flight dataset for **2**·(NO_3)$_{24}$, the mass spectrum obtained by integrating intensities over all drift time windows of the two-dimensional data, and isotopically resolved FTMS data for the m/z 912 to 1016 region (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(6) Harrison, R. M.; Brotin, T.; Noll, B. C.; Michl, J. *Organometallics* **1997**, *16*, 3401.

(7) (a) Hoaglund, C. S.; Valentine, S. J.; Sporleder, C. R.; Reilly, J. P.; Clemmer, D. E. *Anal. Chem.* **1998**, *70*, 2236. (b) Henderson, S. C.; Valentine, S. J.; Counterman, A. E.; Clemmer, D. E. *Anal. Chem.* **1999**, *71*, 291.

(8) Fenn, J. B.; Mann, M.; Keng, C. K.; Wong, S. F.; Whitehouse, C. M. *Science* **1989**, *246*, 64.

(9) Air Products, UHP Zero Grade.

(10) For a recent discussion of methods for calculating mobilities for trial structures, see: Hoaglund-Hyzer, C. S.; Counterman, A. E.; Clemmer, D. E. *Chem. Rev.* **1999**, *99*, 3037 and references therein.

(11) A wide variety of derivatized Co-reagents (R-CpCoL$_2$), which have been reported, participate in Co-mediated [2+2+2] and [2+2] annulation reactions.