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

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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, we apply 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] dimerization of 3 provides ligand-scaffold en 4, which was treated subsequently with enPd(NO3)2 in CH3OH to 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 1.2 Of particular note is the chemical shift for H6 in 1. Of the precursor ligand-scaffold 4, H6 appears at δ 8.65, whereas in the self-assembled “barrel” H6 shifts upfield to δ 7.76. We attribute this upfield shift to anisotropic...
shielding exerted on H₄ 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 provides ligand-scaffold 6 (eq 2); however, treatment

with enPd(NO₃)₂ in CH₃OH−H₂O in this case produces cube 2, resulting from the quantitative self-assembly of 12 equiv of enPd(NO₃)₂ and 6 equivs of 6. Cube 2 features a very large internal volume, which we estimate to be approximately 4000 Å³. The high symmetry of cube 2 results in simple proton and carbon NMR spectra which are highly indicative of a single entity. The significantly greater complexity of 2 (i.e. versus 1) required application of nested ion mobility/time-of-flight mass spectrometric analyses of 1, 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. Briefly, a solution of 2 (0.5 mg/mL in CH₃OH−H₂O, 1:1, 5% HOAc) was electrosprayed into the ion mobility instrument containing ~150 Torr of He⁹ 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 = C₉₀H₂₂₂N₇P₂O₇CoPd₃) 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 species mobilities with values that are calculated for rigid trial geometries 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 m²·V⁻¹·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 [2-5NO₃]³⁺, [2-6NO₃]²⁺, and [2-7NO₃]⁺ ions, respectively. Theoretical mobilities for these ions are 8.40 × 10⁻⁵, 7.20 × 10⁻⁵, and 6.02 × 10⁻⁵ m²·V⁻¹·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-nNO₃]ⁿ⁺ (where n = 7 to 13). From these data, it was determined that the average mass for the maximum of the isotopic distribution for 2-(NO₃)₂ 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.

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Supporting Information Available: Two-dimensional ion mobility/time-of-flight dataset for 2-(NO₃)₂, 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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(11) A wide variety of derivatized Co-reagents (R-CpCoL₂) which have been reported, participate in Co-mediated [2+2+2] and [2+2] annulation reactions.