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Supramolecular Arrays of 4,7-Phenanthroline Complexes: Self-Assembly of Molecular Pd_6 Hexagons**

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The formation of supramolecular arrays of metal ions and ligands is favored by a metal-directed, self-assembly mechanism, which allows for high-yield synthesis under thermodynamic control.[1] Rigid complexes can be synthesized in which the overall structure is dictated by a combination of the binding constraints of the ligand and the geometrical requirements of the metal ions.[2] For example, tetranuclear squares were first prepared by combining the approximately 90° angles of a square-planar palladium complex with the linearly oriented donor atoms of 4,4′-bipyridine.[3] In a similar fashion, polypyridine ligands and metal ions have produced a fascinating variety of squares,[4] boxes,[3b, 5] helicates,[6] catenanes,[7] rotaxanes,[8] racks,[9] grids,[10] and ladders.[11]

To increase the scope of such assemblies, we have begun to explore the use of predesigned organometallic fragments as building blocks.[12] A similar strategy was recently employed to prepare dendrimers[13] as well as nanoscale squares[14] and hexagons.[15] Here we report the self-assembly of a rigid, cyclic structure that contains 4,7-phenanthroline (**1**) and the linear organopalladium complex fragments **2a** or **2b** as building blocks. Self-assembly of these complimentary molecular building blocks with angular requirements of 60 and 180° results in a six-component [3+3] cyclic array.

Complexes **2a** and **2b** are readily prepared by palladation of the thioether ligands 1,2,4,5-tetrakis(*n*-butylthiomethyl)benzene and 1,2,4,5-tetrakis(phenylthiomethyl)benzene, respectively, with two equivalents of $[Pd(MeCN)_4][BF_4]_2$ in acetonitrile. Combining equimolar amounts of **1** and **2a**$[BF_4]_2$ or **2b**$[BF_4]_2$ in an appropriate solvent (**2a**, CH_2Cl_2; **2b**, $(CH_3)_2CO$) resulted in quantitative formation of the hexanuclear complexes **3a** and **3b** (Scheme 1). These complexes can be isolated as BF_4^- salts in the form of air- and moisture-stable, pale yellow, microcrystalline solids; their solubility depends on the R group attached to the sulfur center.

The ^{1}H NMR spectra of **3a** and **3b** are consistent with highly symmetrical structures and show large coordination shifts for the phenanthroline ring protons, in the range from $\Delta\delta = 0.65$ for H1 and H10 to $\Delta\delta = 1.63$ for H5 and H6. Integration of the signals indicates a 1:1 ratio of organometallic complex fragment to 4,7-phenanthroline, and this is supported by elemental analyses. In attempts to observe intermediates in the self-assembly process, experiments involving stepwise addition of metal to ligand and ligand to metal were monitored by ^{1}H NMR spectroscopy. In no case were species other than the cyclic product and the component in excess

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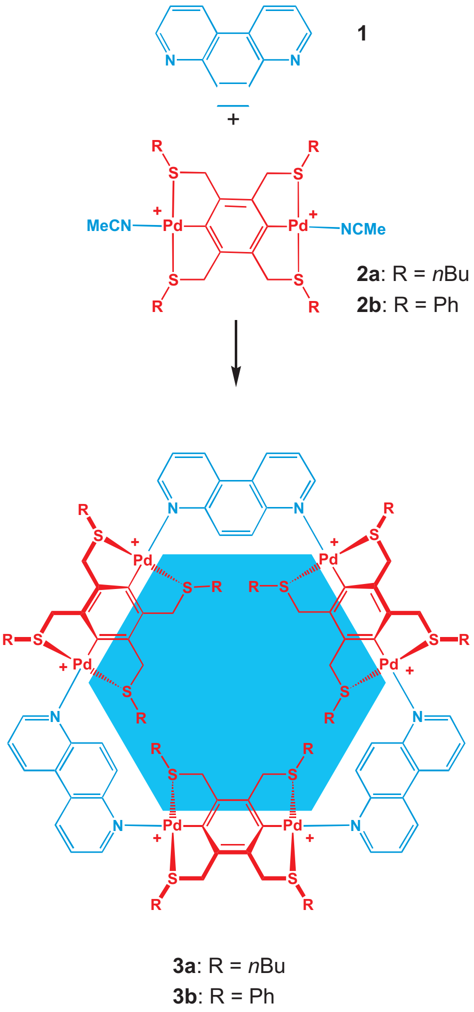

Scheme 1. Reaction of **1** with solvated **2a** and **2b** to give **3a** and **3b**, respectively (counterion BF_4^-).

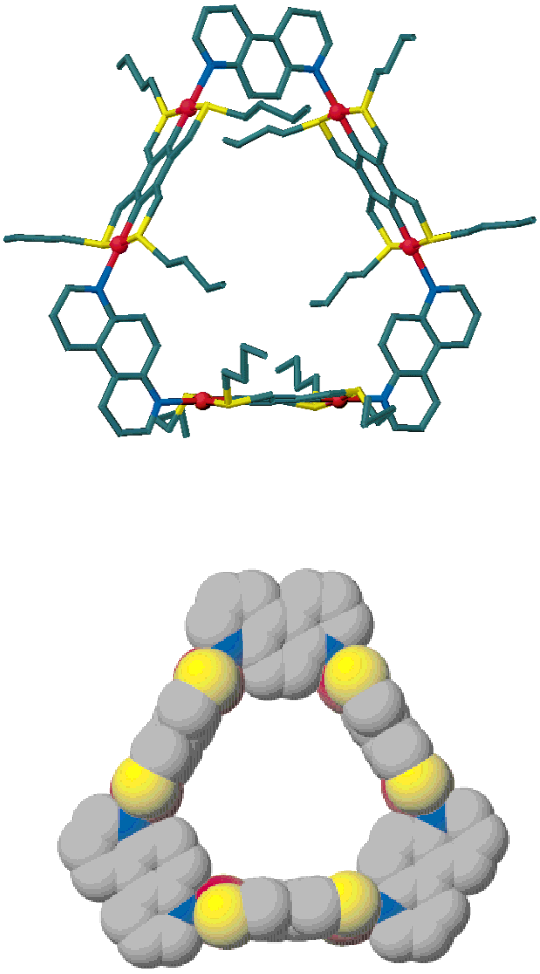

Figure 1. Crystal structure of **3a**. Top: Representation of the bonds in the framework (red = Pd, yellow = S, blue = N, gray = C). Bottom: space-filling representation (*n*Bu groups omitted for clarity).

observed. This is consistent with rapid formation of the thermodynamically favored cyclic product. An X-ray structural study of **3a** confirmed the postulated hexanuclear structure (Figure 1).[16]

As planned, the metalated aromatic units form three "walls" of the supramolecular array, and the 4,7-phenanthroline ligands form three corner pieces. The planes of the two different fragments are approximately perpendicular to each other. The Pd ⋯ Pd distances within the organopalladium unit average 6.83 Å, whereas the distance between two Pd atoms across the 4,7-phenanthroline ligand averages 7.80 Å. Since all six palladium atoms are constrained to lie in a single plane and the Pd-Pd-Pd angles are about 120° because of the geometrical requirements of the the phenanthroline bridges, the metal array approximates a Pd_6 hexagon. In overall dimensions, this rigid framework is about 2.0 nm in width, about 0.5 nm in depth (not including the *n*Bu groups), and contains a permanent cavity of approximately 1.2 nm in diameter.

In solution, two dynamic processes affect the line shape of the NMR signals of the benzylic protons: inversion at the sulfur center and rotation about the Pd–N bond. Variable-temperature ^1H NMR spectra of **3b** show that at elevated temperature (323 K, CD_2Cl_2) inversion at the sulfur center is rapid on the NMR time scale, but rotation about the Pd–N bond is restricted due to the steric requirements of the phenyl groups. This gives rise to an AB pattern at high temperature due to coupling of the benzylic protons which are constrained "inside" and "outside" of the cyclic structure. This is not observed for **3a**, which contains the smaller *n*Bu groups. The high-temperature spectrum of **3a** exhibits a single, sharp signal for the benzylic protons, which nonetheless provides evidence for the cyclic nature of this species in solution.

4,7-Phenanthroline is a simple, commercially available ligand that favors bridging over chelation and provides a rigid 60° corner for creating unique metal–ligand arrays. The self-assembly strategy allows the construction of large, rigid cavities, and this bodes well for the future development of metal-based receptors and nanoscale materials. An advantage of employing the organopalladium complex fragments described here is the readily variable substituent on the sulfur atom, which allows the physical properties to be modified. We are currently investigating the incorporation of R groups that make the product water-soluble so that solvophobic interactions inside the cavity become possible.

Experimental Section

3a: Equimolar solutions of 4,7-phenanthroline and **2a** were mixed in CH_2Cl_2 or acetone. The concentration range from $3.29\,\mu$M to 1.54 M was studied. The solvent was allowed to evaporate slowly. Pale yellow crystals were obtained from acetone, and microcrystalline powders from CH_2Cl_2. No further purification was required. In all cases, the yield of isolated product was greater than 90%. ^{1}H NMR (300 MHz, [D_6]acetone, 300 K): $\delta = 9.81$ (m, 12 H, phen), 9.68 (m, 6 H, phen), 8.28 (qt, 6 H, phen), 4.69 (br s, 24 H, Bz), 3.10 (br m, 24 H, SCH_2), 1.63 (br m, 24 H) 1.18 (br m, CH_2CH_3), 0.69 (br t, 36 H, CH_3); FAB-MS: m/z = 965 $[M - 3\,BF_4]^{3+}$; elemental analysis calcd for $C_{114}H_{156}B_6F_{24}N_6Pd_6S_{12}$: C 43.40, H 4.98, N 2.66; found: C 43.33, H 4.96, N 2.59.

3b: Equimolar solutions of 4,7-phenanthroline and **2b** were mixed in CH_2Cl_2, acetone, or MeOH. Neither the rate of addition nor the order of addition affected the product quality and yield. The concentration range from $3.17\,\mu$M to 1.54 M was studied. The solvent was allowed to evaporate slowly. Crystalline material was obtained from CH_2Cl_2, and microcrystalline powders from acetone and MeOH. No further purification was required. In all cases, the yield of isolated product was greater than 90%. ^{1}H NMR (300 MHz, CD_2Cl_2, 323 K): $\delta = 9.42$ (d, 6 H, phen), 9.00 (br s, 6 H, phen), 8.84 (br s, 6 H, phen), 7.82 (qt, 6 H, phen) 7.71 (m, 24 H, SPh), 7.44 (m, 24 H, SPh), 5.27 (dd, 24 H, Bz); FAB-MS: $m/z = 1610$ $[M - 2\,BF_4]^{2+}$. LSI-MS: $m/z = 1045$ $[M - 3\,BF_4]^{3+}$; elemental analysis calcd for $C_{138}H_{108}B_6F_{24}N_6Pd_6S_{12}$: C 48.83, H 3.21, N 2.48; found: C 48.67, H 3.13, N 2.33.

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[16] Crystal data[17] for **3b**$[BF_4]_6$: monoclinic, space group $C2/c$, $a = 26.8628(3)$, $b = 24.1205(2)$, $c = 28.4165(1)$ Å, $\beta = 113.504(1)^\circ$, $V = 16884.7(2)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.241$ g cm^{-3}, $2\theta_{max} = 42.0^\circ$, $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å), $T = 296$ K. A pale yellow, crystal ($0.2 \times 0.2 \times 0.3$ mm^3), grown by slow evaporation of a saturated solution in acetone, was sealed with the mother liquor in a thin-walled glass capillary. Of 8710 reflections measured, 7422 were observed ($I > 2\sigma(I)$) and integrated from frame data obtained from programmed hemisphere scan routine on a Siemens SMART CCD diffractometer. Decay (< 1%) was monitored by 50 standard data frames measured at the beginning and end of data collection. Systematic absences in the diffraction data and determined unit-cell parameters were consistent with Cc and $C2/c$. Solution in the centrosymmetric space group yielded chemically reasonable and computationally stable refinement results. Lorentzian and polarization corrections and a semi-empirical absorption correction, based on redundant data at varying effective azimuthal angles, were applied to the data ($\mu = 0.837$ cm^{-1}, min/max transmission = 0.3516/0.4663). The structure was solved by direct methods, completed by subsequent Fourier syntheses, and refined with full-matrix least-squares methods against F^2 to $R(F) = 0.1277$, $wR(F^2) = 0.3627$, $N_o/N_v = 8704/456$. The cation is located on a twofold axis. One of three symmetry-unique BF_4^- counterions was located and refined as a geometrically idealized rigid group. Attempts to model nine peaks with substantial electron density, remote from the cation and the located counterion, as disordered BF_4^- counterions or as chemically reasonable solvent molecules were unsuccessful. These peaks were assigned arbitrary carbon identities but replaced in calculations for intrinsic properties by the expected number of anions. Remaining peaks in the final difference map (max. 1.7 e Å^{-3}) were associated with the heavy atoms and considered to be artifacts arising from nonideal absorption corrections. The non-carbon and non-hydrogen atoms. as well as the phenyl ring carbon atoms of the cation were refined with anisotropic displacement coefficients. All other non-hydrogen atoms were refined isotropically. Hydrogen atoms were treated as idealized contributions. Scattering factors and anomalous dispersion coefficients are contained in the SHELXTL 5.03 program library (G. M. Sheldrick, Madison, WI).

[17] Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-100501. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: int. code + (44) 1223-336033; e-mail: deposit@ccdc.cam.ac.uk).