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Metal-Driven and Covalent Synthesis of Supramolecular Grids from Racks: A Convergent Approach to Heterometallic and Heteroleptic Nanostructures

Michael Schmittel,*,† Venkateshwarlu Kalsani,† and Jan W. Bats‡

Center of Micro and Nanochemistry and Engineering, Organische Chemie I, Universität Siegen, Adolf-Reichwein-Strasse, D-57068 Siegen, Germany, and Institut für Organische Chemie und Chemische Biologie, Johann Wolfgang Goethe-Universität, Marie-Curie-Strasse 11, D-60439 Frankfurt am Main, Germany

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Supramolecular nanogrids were prepared from dynamic supramolecular racks through the coupling of terminal alkynes using either a covalent (with CuCl/O$_2$) or a coordinative (with [*trans*-(PEt$_3$)$_2$PtCl$_2$]) approach. Because of the rapid equilibration of the racks (as tested by exchange reactions), oligomeric adducts potentially formed in the coupling process will selectively furnish the nanogrids through an entropically driven self-repair mechanism. To ascertain the structural assignment, the nanogrids were also synthesized by an independent strategy.

The masterful use of metal coordination chemistry is a *conditio sine qua non* for the preparation of discrete metallosupramolecular aggregates, such as cylinders,[1] racks,[2] nanoscaffolds,[1] and grids.[3] To date, most of these structures have been assembled using bis- or polyhomoleptic coordination motifs, but there is growing interest in preparing heteroleptic aggregates,[4] for which several strategies have been designed.[1] In this context, we have recently introduced the HETPHEN[5] approach, allowing heteroleptic bisphenanthroline metal complexes of tetrahedrally coordinated metal ions to be built.[6] Utilizing this methodology, several supramolecular nanoscale structures, such as nanobaskets,[7] ring-in-ring structures,[8] nanoscaffolds,[9] nanoracks, and nanogrids[10] were afforded that, by their heteroleptic nature, are ideally suited for functional applications.[11]

We recently reported on dynamic bisphenanthroline copper(I) racks[10b] that contrast to the large multitude of kinetically stable ruthenium-based complexes.[2,12] Herein, we describe the self-assembly of functionalized rack motifs that are equipped with bromo and alkyne termini. The latter feature suggested to us that we use the racks as versatile precursors[12] for supramolecular nanostructures, such as pseudorotaxanes/rotaxanes, cylinders, or grids (Figure 1). As a demonstration of the power of this approach, we present two strategies, a covalent route and a coordinative route, to fabricate heteroleptic grids directly from supramolecular racks.

Ligands **1** and **2** were prepared by known procedures[13] using sequential Sonogashira coupling reactions (Chart 1). The synthesis of phenanthrolines **3**−**5**, whose 2,9-disubstitution with bulky aryl groups (mesityl = Mes or duryl = Dur) is dictated by the HETPHEN[6] approach, was described elsewhere.[8,13]

The combination of ligand **1** or **2** with **3**[10b] or **4** in the presence of [Cu(CH$_3$CN)$_4$]$^+$ (1:2:2) produced the racks **R1**−**R4** in basically quantitative yields. For all racks **R1**−**R4**, the ESI-MS exhibited a single set of signals resulting from the successive loss of counterions (see Supporting Informa-

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* To whom correspondence should be addressed. E-mail: schmittel@chemie.uni-siegen.de. Fax: (+49) 271 740 3270.

† Universität Siegen.

‡ Johann Wolfgang Goethe-Universität.

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(5) The HETPHEN (heteroleptic bisphenanthroline) approach is based on steric and electronic effects originating from bulky aryl substituents at the bisimine coordination sites (as seen in **3**−**5**, **7**, and **8**) to control the coordination equilibrium both kinetically and thermodynamically.

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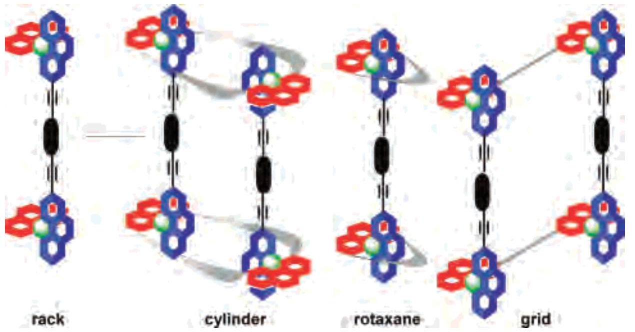
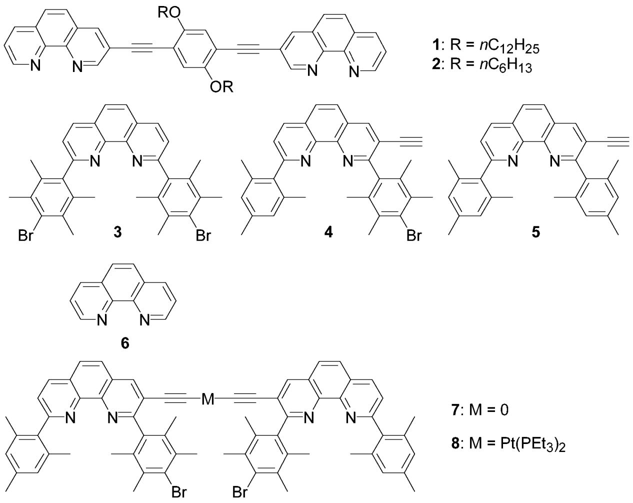


Figure 1. Cartoon representation of a rack as a potential precursor to cylinder, pseudorotaxane/rotaxane, and grid motifs.

Chart 1. Ligands Used for the Construction of Heteroleptic, Functionalized Racks

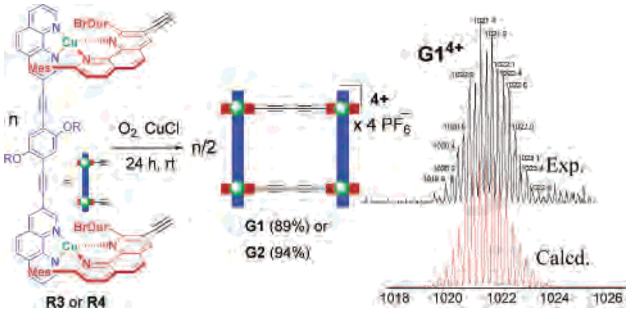


tion). Moreover, the characteristic high-field shifts in the ^{1}H NMR spectra for the MesH and DurMe protons of **3** and **4** in **R1**−**R4** were indicative of the formation of a heteroleptic bisphenanthroline complex.[6]

$$\begin{array}{c} \mathbf{1} \\ \text{or} \\ \mathbf{2} \end{array} + \begin{array}{c} \mathbf{3} \\ \text{or} \\ \mathbf{4} \end{array} \xrightarrow{\mathrm{Cu^I}} \begin{array}{l} \mathbf{R1} = [\mathrm{Cu_2}(\mathbf{1})(\mathbf{3})_2]^{2+} \\ \mathbf{R2} = [\mathrm{Cu_2}(\mathbf{2})(\mathbf{3})_2]^{2+} \\ \mathbf{R3} = [\mathrm{Cu_2}(\mathbf{1})(\mathbf{4})_2]^{2+} \\ \mathbf{R4} = [\mathrm{Cu_2}(\mathbf{2})(\mathbf{4})_2]^{2+} \end{array}$$

As mentioned above, racks with functional groups, such as terminal alkynes, can serve as precursors for higher supramolecular aggregates (Figure 1). In a first try, **R3** and **R4** were reacted under oxidative conditions typical for the homocoupling of terminal alkynes (O_2, CuCl, NEt_3, CH_2Cl_2)[14] to furnish **G1** (89%) and **G2** (94%) in high yield (see Supporting Information). ^{1}H NMR spectra confirmed the grid structure, showing a single set of signals characterized by the lack of the acetylene proton at δ ~3.5 ppm and the presence of a diagnostic signal for the heteroleptic complex at δ ~6 ppm (MesH). Moreover, the ESI-MS analysis showed the signals of the grids **G1** and **G2** (see Supporting Information and Scheme 1) with a correct isotopic distribution of the 3+ and 4+ charged species. All other data[15] were equally in accordance with those of previously reported nanogrid structures.[10a]

Scheme 1. Synthesis of Grids **G1** and **G2**[15] under Oxidative Conditions from Racks **R3** and **R4**, Respectively[a]



[a] ESI-MS signal of **G1**$^{4+}$ provided as inset.

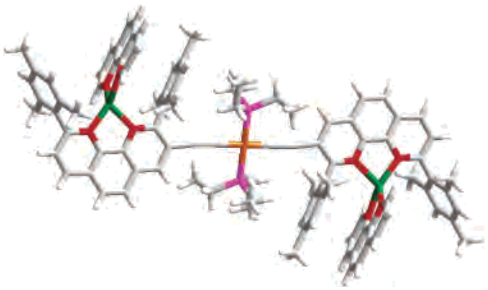


Figure 2. Single-crystal structure of **R5**; stick representation.

Recently, connecting terminal alkynes through Pt(II) or Pd(II) centers by a coordinative approach was utilized by Lin *et al.*[16] for the formation of polygons. As an extension, we decided to probe the self-recognition of Cu(I) ions and phenanthrolines and that of Pt(II) ions and alkynyl ligands in one pot. The mixing of **5**, **6**, and $[Cu(CH_3CN)_4]^+$ (1:1:1, respectively) in dichloromethane at room temperature,[7] followed by a posttreatment with [*trans*-$(PEt_3)_2PtCl_2$],[16] afforded the heterometallic rack **R5** exclusively, as verified by ^{1}H NMR, ESI-MS, and ^{31}P{H} NMR (δ 13.3 ppm) analysis. The structure of **R5** was confirmed by crystal structure analysis (Figure 2).[17] The molecule is centrosymmetric with the Pt atom at a crystallographic inversion center.[10] The Cu atom shows a heavily distorted tetrahedral coordination sphere. N−Cu−N angles range from 82.1(2)° to 141.5(2)°. The Cu−N distances range from 1.989(5) to 2.088(4) Å. The Pt atom exhibits a square-planar coordination, and the Pt−P distances of 2.296(2) Å and Pt−C distances of 1.976(6) Å agree with values found in related structures.[18] The crystal packing showed an intermolecular

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(14) Carina, R. F.; Dietrich-Buchecker, C.; Sauvage, J. P. *J. Am. Chem. Soc.* **1996**, *118*, 9110−9116.

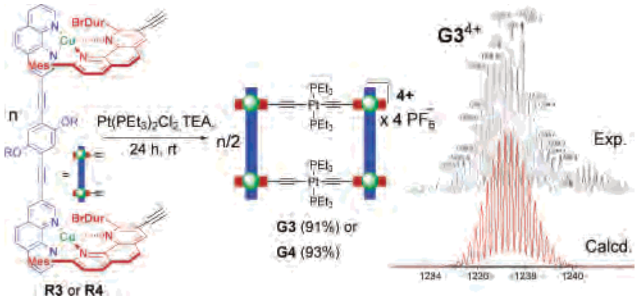
(15) Broadening of a few ^{1}H NMR signals tentatively points to the presence of several isomers, such as cisoid, transoid, and intertwined grid isomers.

(16) Jiang, H.; Lin, W. *J. Am. Chem. Soc.* **2004**, *126*, 7426−7427 and references therein.

(17) Crystal data for **R5**: Crystals were obtained by slow diffusion of toluene into a dichloromethane solution of the complex. $C_{100}H_{100}N_8P_2Cu_2Pt\cdot 2PF_6\cdot 2$toluene, triclinic, space group $P\bar{1}$, $a = 12.893(3)$ Å, $b = 13.701(3)$ Å, $c = 16.224(3)$ Å, $\alpha = 76.032(17)°$, $\beta = 80.039(17)°$, $\gamma = 73.553(17)°$, $V = 2650.4(9)$ Å^3, $Z = 1$, $D_{calcd} = 1.424$ Mg/m^3, $\mu = 1.847$ mm^{-1}, final R indices $[I > 2\sigma(I)]$ R1 = 0.0592, wR2 = 0.1195, R indices (all data) R1 = 0.1143, wR2 = 0.1361.

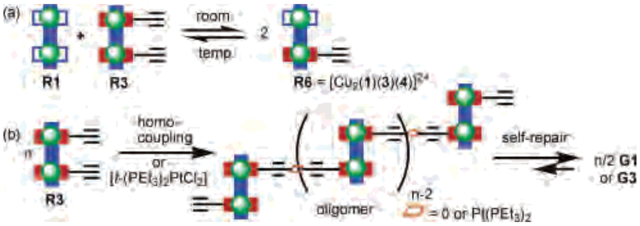
(18) Osakada, K.; Hamada, M.; Yamamoto, T. *Organometallics* **2000**, *19*, 458−468.

Scheme 2. Synthesis of Grids **G3** and **G4**[15] from **R3** and **R4**, Respectively, in the Presence of [*trans*-(PEt3)2PtCl2][a]



[a] ESI-MS signal of **G3**$^{4+}$ provided as inset.

Scheme 3. Cartoon Representation of (a) the Equilibration of Racks at Room Temperature and (b) the Entropically Driven Repair Mechanism that Will Suppress Formation of Oligomeric Aggregates Because of the Kinetic Lability of the Rack Assembly



$\pi-\pi$ interaction (3.4 Å) between the phenanthrolines (see Supporting Information).

When **R3** or **R4** were reacted with [*trans*-$(PEt_3)_2PtCl_2$],[16] the heterometallic[19] and heteroleptic grids **G3** and **G4** formed (Scheme 2), as demonstrated by ESI-MS (see Supporting Information).

The isotopic distributions of the 3+ and 4+ charged species were in good agreement with the calculated ones. ^{1}H[15] and $^{31}P\{^{1}H\}$ NMR spectroscopies, ESI-MS, and elemental analysis point to the formation of a single heterometallic grid species. For example, the $^{31}P\{^{1}H\}$ NMR spectra of **G3** and **G4** exhibited a single peak at $\delta \sim 11.6$ ppm with a set of Pt^{II} satellites (see Supporting Information).[16]

The above results demonstrate that the racks could be coupled to grids in high yield (~90%) under both covalent or coordinative conditions. In contrast to the systems of Siegel et al.,[12] equilibration of the racks at room temperature is rapid, as demonstrated by the ligand exchange reaction **R1** + **R3** $\rightleftharpoons$ 2**R6** (Scheme 3a).[20] Hence, such ligand exchange in potentially formed oligomeric adducts (Scheme 3b) will always lead to **G1** and **G3** because grid formation from oligomers is driven by entropy (self-repair!).

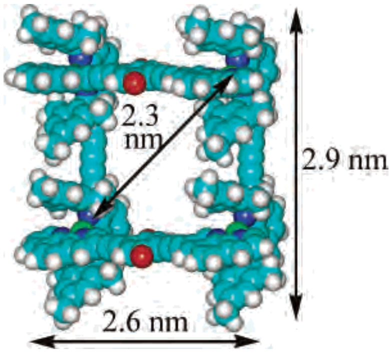


Figure 3. Space-filling model of **G1** and **G2** (the two differ only by the alkoxy chain) optimized with the MM+ force field.[22] Alkoxy chains are omitted for clarity.

To ascertain the above assignment beyond doubt, we prepared the ligands **7**[13] and **8** from **4** through oxidative coupling (O_2, CuCl, NEt_3) and coordination with [*trans*-$(PEt_3)_2PtCl_2$], respectively.[21] In analogy to our recent work on the synthesis of nanogrids,[10] **G1**−**G4** were prepared independently by combination of **1** and **2** with **7** and **8**, respectively, in the presence of $[Cu(CH_3CN)_4]^+$. Full agreement of their spectral data with those of the grids prepared by routes shown in Schemes 1 and 2 was obtained. As in previous reports, the assignments were further confirmed by UV/vis and ESI-MS titrations (see Supporting Information).[10]

Because suitable crystals for X-ray structure determination could not be obtained, the dimensions of these nanogrids were assessed from calculated energy-minimized structures.[22] As depicted in Figure 3, the dimensions of **G1** and **G2** are 2.9 nm (extension along the bisphenanthroline) and 2.3 nm for the Cu−Cu diagonal.

The present results suggest that functionalized racks can be used as precursors to supramolecular grids and possibly for even more complex aggregates, such as rotaxanes and cylinders. As some of the grids are both heterometallic and heteroleptic, the present approach should be fruitful for the preparation of highly diversified assemblies. Hence, further studies are in progress to transform racks into higher aggregates and to study their properties.

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Supporting Information Available: Experimental details and characterization for all racks and grids, including crystal data for **R5** (cif file). This material is available free of charge via the Internet at http://pubs.acs.org.

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(19) Petitjean, A.; Kyritsakas, N.; Lehn, J.-M. *Chem. Commun.* **2004**, 1168−1169 and references therein.

(20) Full equilibration after 5 min was observed by ESI-MS. ^{1}H NMR experiments for the **R1**−**R3**−**R6** equilibration could not be performed because of signal overlap. However, in a similar Cu(I)-based rack system, the dynamic nature could readily be observed by ^{1}H NMR spectroscopy (see **R7** in the Supporting Information).

(21) The synthesis of a family of Pt-linked bisphenanthrolines and their complexes will be described in detail in a forthcoming paper. Schmittel, M.; Kalsani, V., manuscript in preparation. ^{1}H, ^{13}C, ^{31}P NMR, and ESI-MS data are in agreement with their structure.

(22) Hyperchem 6.02 Release for Windows by Hypercube, Inc., Gainesville, FL, 2000. MM+ force field.