Stepwise Assembly of 
\[(\text{C}_5\text{H}_5)_4(\text{C}_5\text{Me}_5)_4\text{Co}_4\text{Rh}_4(\text{CN})_{12}\]‡, an “Organometallic Box” **

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Solid-state coordination polymers and molecular coordination ensembles are typically constructed with bifunctional organic ligands such as 4,4'-bipyridine, and the vertices of the compounds are often square-planar or tetrahedral metal centers. An important advance in this area would involve the use of the most common geometry for transition metals, the octahedron. Octahedral building blocks would allow the assembly of cube-shaped structures. Here we report the realization of this goal by the synthesis of a cubic array of cyano-linked metal octahedra, a subunit of the polymeric hexacyanometalates. Prussian Blue complexes such as Fe₄[Fe(CN)₆]₃ are polymeric by virtue of the sixfold bridging of the octahedral \([\text{M(CN)}_6]^n\) subunits. In our approach, we have replaced three of these CN groups with a cyclopentadienyl ligand, which blocks one face of the octahedron. Polymerization is thus inhibited, and a family of cages with boxlike architectures results.

The tricyanometalates \(\text{Et}_4\text{N}[(\text{C}_5\text{R}_5)\text{Rh(CN)}_3]\) (1) and \(\text{K}[\text{Co(CN)}_3]\) (2) were employed to prepare a series of molecular squares \((\text{C}_5^* = \text{C}_5\text{Me}_5, \text{Cp} = \text{C}_5\text{H}_5)\). Thus, 1 reacts with \([\text{Cp}^*\text{RhCl}_2]\)₂ (CH₂Cl₂ solution, 25°C, 2 h) to give 3, which was isolated as orange crystals after purification on Sephadex LH-20 (Scheme 1). The two-line \(^1\text{H} \)NMR spectrum of 3 indicates that the Rh – C bonds are retained in the assembly process. Although other \(\text{M}_4(\text{CN})_4\) squares are known, the \(2\text{M(CN)}_2\) route is novel. The complex \([\text{(cymene)}\text{RuCl}_2]\)₂ (cymene = 4-isopropyltoluene) reacts with 1 to give 4. The \(^1\text{H} \)NMR signal of \(\text{C}_5\text{Me}_5\) group in 4 matches one of the signals of 3 and is assigned to the \(\text{Cp}^*\text{Rh(μ-CN)}\) moiety. A Co₂Rh₂ square 5 was prepared analogously with \([\text{Cp}^*\text{Co(CN)}_3]\). In 5, the Rh center is bound to the N atom of the cyanide ion. A single-crystal X-ray diffraction study confirmed the structure of 3 (Figure 1).[11]

It is probable that many kinds of molecular objects could be prepared by using \([\text{C}_5\text{R}_5]\text{M(CN)}_3\) as metalloligands. Of particular interest are “molecular boxes” of the type \([\text{C}_5\text{R}_5]\text{M}_8(\mu-\text{CN})_{12}\) in which metal centers occupy all eight corners. Molecular models show that \(\text{Cp}^* - \text{Cp}^*\) steric interactions would inhibit the assembly of the cubic cage \([\text{Cp}^*\text{M}_4(\text{CN})_{12}]\); however, such boxlike architectures could be realized if half of the \(\text{Cp}^*\) ligands were replaced by the smaller \(\text{Cp}\) groups.

The synthesis of the box was effected by removal of the chloride ligands from 5 with AgPF₆ (Scheme 2; MeCN solution, 25°C, 12 h). According to NMR measurements, the yield is nearly quantitative. Note that all twelve \(\mu\)-CN units are provided by the two \([\text{Co}_2\text{Rh}_2(\text{CN})_6]\) precursors without the need to break any \(\text{M} - \text{C}\) bonds. The 500 MHz \(^1\text{H} \)NMR spectrum of the product is simple: it consists of one signal.

Figure 1. ORTEP plot of the structure of 3 with thermal ellipsoids drawn at the 50% probability level.
each for Cp and Cp* in a ratio of 1:3. The simplicity of the 1H NMR spectrum also indicates that the Co–C bonds are retained, and the cage has idealized Td symmetry. Compound 6 was also characterized by its electrospray mass spectrum which shows a peak for the molecular ion of \( [\text{Cp}^\text{8-Rh}]_4[\text{CpCo(\mu-CN)}]_4 \)\(^+\) (P) at \( m/z = 440.5 \) [P\(^+\)], as well as signals for the expected ion pairs at 1025 (P\(^-\) 2PF\(_6^+\)) and 2195 (P\(^-\) 3PF\(_6^+\)). We also characterized the closely related and more easily crystallized derivative 6', which was obtained from the corresponding square 5'. We conducted \(^{13}\)C NMR measurements on samples of 5' and 6' that had been isotopically enriched by using 30% \(^{13}\text{CN}\) in the synthesis to investigate the symmetry of the metal centers. In the case of 5', we observed CN signals at \( \delta = 130.2 \) and 120 in an intensity ratio of 2:1, as expected for \( \mu\)-CN and terminal CN ligands, respectively; for 6', we observed one intense CN signal at \( \delta = 132.4 \).

Crystallographic studies show that the cation in 6' (Figure 2) is highly symmetrical;\(^{[12]}\) it contains eight octahedral metal centers (alternating Co and Rh positions), which are bridged by twelve CN ligands. The metal–ligand distances and angles indicate an unstrained species, consistent with the facile assembly process. The regularity of the boxlike cage is indicated by the fact that all C-Co-C angles lie in the range 90–95°, and the N-Rh-N angles in the range 85–89°. The differences in these ranges reflect the relative sizes of the two types of cyclopentadienyl ligands. Six molecules of MeCN solvent are located near the six faces of the box but are neither bonded to nor inserted into the cage. The size of the cluster can be estimated from the dimensions of the nearly square faces (Scheme 3). If one assumes an ideal cube whose angles are all 90° and whose edges are 5.1 Å long, then the volume of the box is approximately 132 Å\(^3\).

We have prepared a family of cubic molecular cages, the boxlike cores of which resemble subunits of an Prussian Blue lattice. The large volume of the box invites a study of the host–guest behavior of these species. It also appears that the synthetic methodology could be adapted to the preparation of related organometallic cyanometallates.
Experimental Section

A solution of 5 (0.105 g, 0.107 mmol) in CH₂CN (20 mL) was added to a solution of Ag₂PF₆ (0.054 g, 0.214 mmol) in CH₂CN (2 mL). After 12 h the slurry was centrifuged for 15 min at 5000 rpm. The supernatant was allowed to stand for a further 24 h, and the solvent was evaporated to give a yellow oil (further AgCl was removed by filtration through Celite). The oil was extracted into 3 mL of CH₂CN. The addition of 50 mL of Et₂O gave 0.078 g of product (60% based on 5). ¹H NMR (500 MHz, [D₆]CH₂CN, 22°C) TMS, sample enriched to 30% ¹³C; δ = 132.4 ppm (s, CN); IR (KBr pellet): v = 2180 cm⁻¹ (C=O); elemental analysis calcd for C₆H₇N₂Cl₂F₂P⁺R₂⁻Rh: C 38.09, H 3.70, N 7.01; found (two independently synthesized batches): C 37.61, H 3.74, N 6.51; batch A: C 37.61, H 3.74, N 6.51; batch B: C 37.75, H 3.75, N 6.40.

Keywords: cage compounds · cobalt · coordination chemistry · cyanide · rhodium

[7] Full details of the synthesis of [Cr³⁺(M(CN)₄)]⁻ (M = Ir, Rh) will be presented elsewhere: S. E. Contakes, K. K. Klausmeyer, T. B. Rauchfuss, unpublished results.
[10] The boxes 6 and 6' can also be prepared by eight-component condensations of the monometallic precursors (s. Contakes, unpublished results).

Crystal data for 3 (C₆H₇N₂Cl₂Rh): crystal dimensions 0.18 × 0.07 × 0.05 mm, T = 175 K; κ = 1.70173 Å; τ = 0.2835 Å. Data were collected on a Siemens CCD diffractometer. The structure was solved by direct methods (SHELX suite). The PF₆ counterions are disordered. 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-101173. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

Scheme 1. Preparation of acylzirconocenes and their reactions with aldehydes.

Acylzirconocene Chloride as an “Unmasked” Acyl Anion**

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Easy access to stable acylzirconocene chloride derivatives 1 through a sequential treatment of alkenes or alkynes with zirconocene hydrochloride ([Cp²ZrHCl], Schwartz reagent) and carbon monoxide has brought about the synthetic utility of 1 for the preparation of carbonyl acids and their derivatives. Extensive structural studies and work on the reactivity of acylzirconocene compounds have been carried out by many research groups to elucidate the characteristic features of the acylzirconocene derivative. While the generation of very reactive acylmetals in which the metal species is a main group metal is a very attractive field, their use as an “unmasked” acyl anion for organic synthesis is limited due to their instability. The transition metal acyl complexes have also long attracted much attention because of their intrinsic usefulness as an acyl anion equivalent in organic synthesis. To the best of our knowledge, there is no report regarding the carbon–carbon bond forming reactions of 1 with carboxyls in which an acyl group of 1 reacts as an acyl anion to give α,α-ketol derivatives 2. We describe here the first reactions of acylzirconocene chloride complexes 1 with aldehydes to give α,α-ketol derivatives 2 in fair to good yields under mild Lewis acid mediated conditions (Scheme 1).

Scheme 1. Preparation of acylzirconocenes and their reactions with aldehydes.

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