

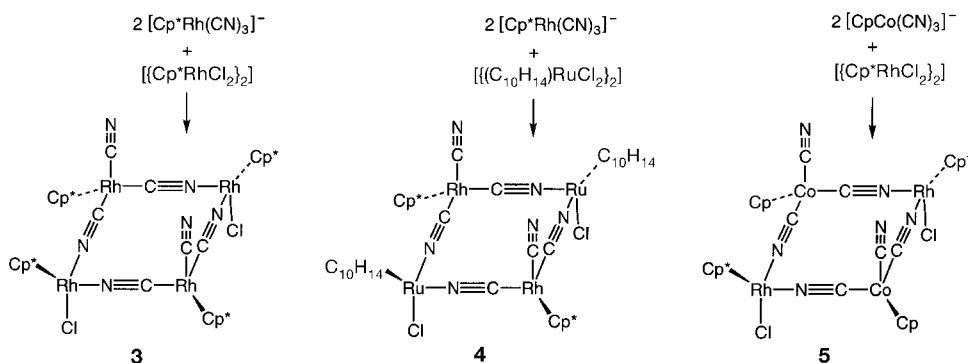
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Stepwise Assembly of $[(C_5H_5)_4(C_5Me_5)_4Co_4Rh_4(CN)_{12}]^{4+}$, an “Organometallic Box”**

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Solid-state coordination polymers^[1] and molecular coordination ensembles^[2–4] 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 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^[5] metal octahedra, a subunit of the polymeric hexacyanometalates. Prussian Blue complexes^[6] such as $Fe_4[Fe(CN)_6]_3$ are polymeric by virtue of the sixfold bridging of the octahedral $[M(CN)_6]^{n-}$ 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.



Scheme 1. Assembly of $M_2M'_2(CN)_4$ squares.

The tricyanometalates $Et_4N[Cp^*Rh(CN)_3]$ (**1**)^[7] and $K[CpCo(CN)_3]$ (**2**)^[8] were employed to prepare a series of molecular squares ($Cp^* = C_5Me_5$, $Cp = C_5H_5$). Thus, **1** reacts with $[Cp^*RhCl_2]_2$ (CH_2Cl_2 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 ¹H NMR spectrum of **3** indicates that the Rh–C bonds are retained in the assembly process. Although other $M_4(CN)_4$ squares are known,^[9] the $2M(CN)_2 + 2M'$ route is novel.^[10] The complex $[(cymene)RuCl_2]_2$ (cymene = 4-isopropyltoluene) reacts with **1** to give **4**. The ¹H NMR signal of C_5Me_5 group in **4** matches one of the signals of **3** and is assigned to the $Cp^*Rh(\mu-CN)_2(CN)$ moiety. A Co_2Rh_2 square **5** was prepared analogously with $[CpCo(CN)_3]^-$; 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]

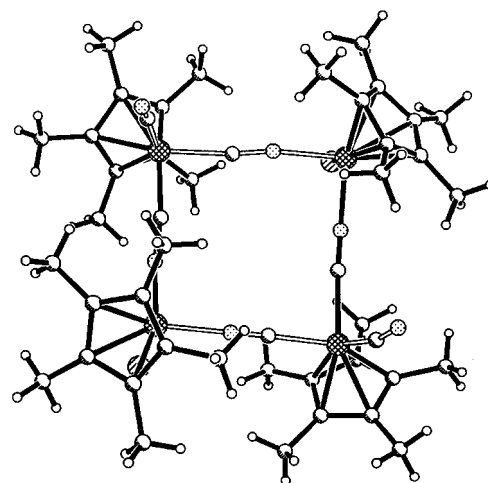


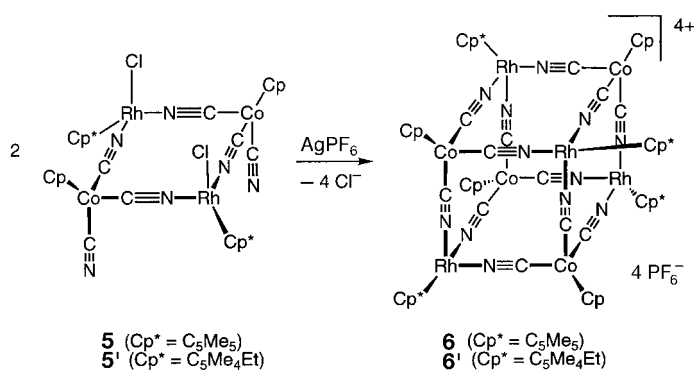
Figure 1. ORTEP plot of the structure of **3** with thermal ellipsoids drawn at the 50% probability level.

It is probable that many kinds of molecular objects could be prepared by using $[(C_5R_5)M(CN)_3]^-$ as metalloligands. Of particular interest are “molecular boxes” of the type $[(C_5R_5)_8M_8(\mu-CN)_{12}]$ in which metal centers occupy all eight corners. Molecular models show that $Cp^* - Cp^*$ steric interactions would inhibit the assembly of the cubic cage $[Cp^*_8M_8(CN)_{12}]$; however, such boxlike architectures could be realized if half of the Cp^* ligands were replaced by the smaller Cp groups.

The synthesis of the box was effected by removal of the chloride ligands from **5** with $AgPF_6$ (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 $[Co_2Rh_2(CN)_6]$ precursors without the need to break any M–C bonds. The 500 MHz ¹H NMR spectrum of the product is simple: it consists of one signal

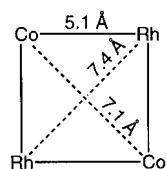
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Scheme 2. Synthesis of **6**-4PF₆ and **6'**-4PF₆.

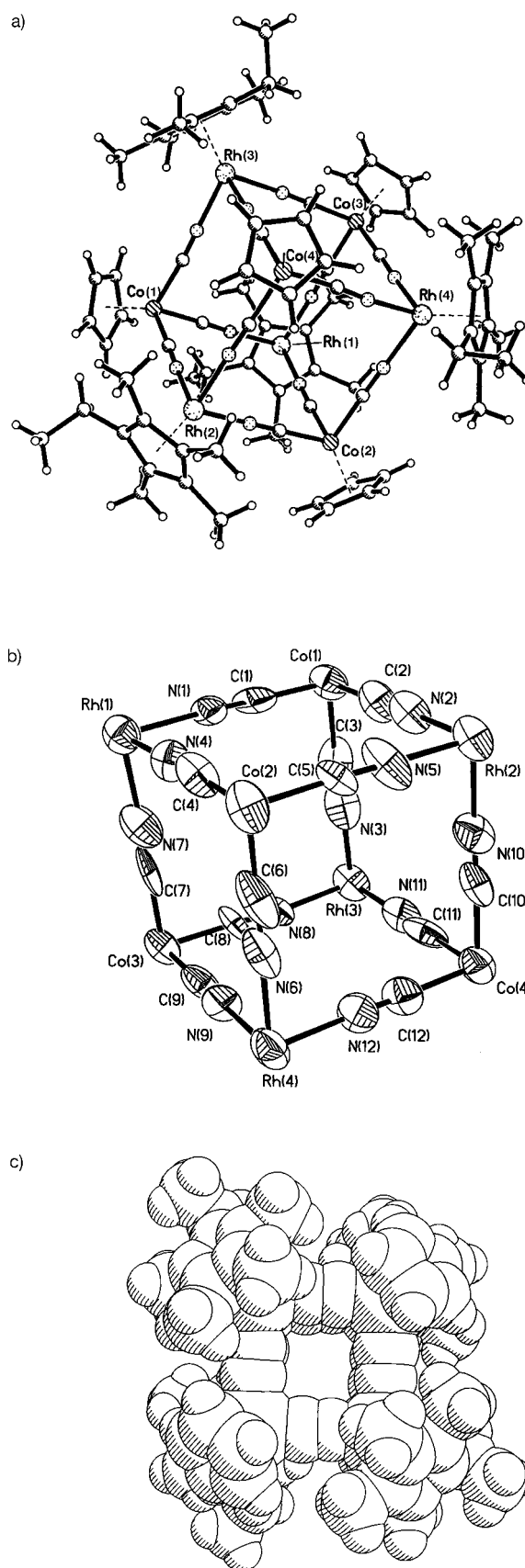
each for Cp and Cp* in a ratio of 1:3. The simplicity of the ¹H NMR spectrum also indicates that the Co–C bonds are retained, and the cage has idealized T_d symmetry. Compound **6** was also characterized by its electrospray mass spectrum which shows a peak for the molecular ion of [[Cp*Rh]₄][[CpCo(μ-CN)₃]]⁴⁺ (P) at *m/z* = 440.5 [P⁴⁺], as well as signals for the expected ion pairs at 1025 ([P · 2 PF₆]²⁺) and 2195 ([P · 3 PF₆]⁺). We also characterized the closely related and more easily crystallized derivative **6'**, which was obtained from the corresponding square **5'**. We conducted ¹³C NMR measurements on samples of **5'** and **6'** that had been isotopically enriched by using 30% ¹³CN⁻ in the synthesis to investigate the symmetry of the metal centers. In the case of **5'**, we observed CN signals at δ = 130.2 and 120 in an intensity ratio of 2:1, as expected for μ-CN and terminal CN ligands, respectively; for **6'**, we observed one intense CN signal at δ = 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

Scheme 3. Dimensions of the Rh₂Co₂(CN)₄ faces of **6'**.

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 Å³.

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.

Figure 2. a) ORTEP plot of the Rh₄Co₄(CN)₁₂ framework in **6'** with thermal ellipsoids drawn at the 50% probability level. b) The inner Co₄Rh₄(CN)₁₂ framework; thermal ellipsoids set at the 50% probability level. c) Space-filling model of the cationic cage viewed perpendicular to a square face.

Experimental Section

6': A solution of **5'** (0.105 g, 0.107 mmol) in CH₃CN (20 mL) was added to a solution of AgPF₆ (0.054 g, 0.214 mmol) in CH₃CN (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 CH₃CN. The addition of 50 mL of Et₂O gave 0.078 g of product (60% based on **5'**). ¹H NMR (500 MHz, [D₃]CH₃CN, 22 °C, TMS): δ = 5.71 (s, 20H, C₅H₅), 2.34 (q, 8H, CH₃CH₂), 1.77 (d, 48H, (CH₃)₄C₅), 1.17 (t, 12H, CH₃CH₂); ¹³C NMR (125 MHz, [D₃]CH₃CN, 22 °C, TMS, sample enriched to 30% ¹³C): δ = 132.4 ppm (s, CN); IR (KBr pellet): $\tilde{\nu}$ = 2180 cm⁻¹ (C≡N); elemental analysis calcd for C₇₆H₈₈N₁₂Co₄F₂₄P₄Rh₄: C 38.09, H 3.70, N 7.01; found (two independently synthesized batches): batch A: C 37.61, H 3.74, N 6.51; batch B: C 37.75, H 3.75, N 6.40.

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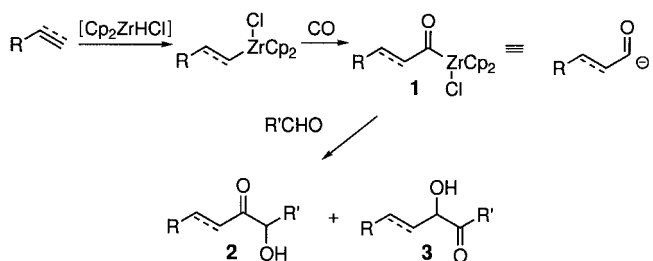
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- [10] The boxes **6** and **6'** can also be prepared by eight-component condensations of the monometallic precursors (s. Contakes, unpublished results).
- [11] Crystal data for **3** (C₄₆H₆₀N₆Cl₂Rh₄): crystal dimensions 0.18 × 0.07 × 0.05 mm, *T* = 175 K; λ = 0.71073 Å; tetragonal, space group *P4*₂*c*; *a* = *b* = 16.8743(8), *c* = 8.7257 Å; *Z* = 2; *V* = 2484.6(2) Å³; ρ_{calcd} = 1.577 g cm⁻³; μ = 1.449 mm⁻¹; 3036 reflections; GOF on *F*² = 1.146; *R*₁ = 0.0570, *wR*₂ = 0.0968.
- [12] X-ray structure analysis of **6'-4PF₆ · 6MeCN** (C₈₈H₁₀₆N₁₈Co₄F₂₄P₄Rh₄): crystal dimensions 0.28 × 0.20 × 0.06 mm; *T* = 175 K; λ = 0.71073 Å; monoclinic, space group *P2*₁/*c*: *a* = 15.177700(10), *b* = 49.7980(6), *c* = 16.1562(2) Å, β = 116.1830(10)°; *Z* = 4; *V* = 10957.7(2) Å³; ρ_{calcd} = 1.602 g cm⁻³; 32454 reflections (*R*_{int} = 0.1116), 5656 observed reflec-

tions (*I* > 2σ(*I*)); GOF on *F*² = 1.048; *R*₁(observed data) = 0.122, *wR*₂ = 0.2835. 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-101 173. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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 carboxylic acids and their derivatives.^[1] Extensive structural studies and work on the reactivity of acylzirconocene compounds have been carried out by many research groups^[2] to elucidate the characteristic features of the acylzirconocene derivatives. While the generation of very reactive acylmetals in which the metal species is a main group metal is a very attractive field,^[3] 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.^[4] To the best of our knowledge, there is no report regarding the carbon–carbon bond forming reactions of **1** with carbonyls in which an acyl group of **1** reacts as an acyl anion to give α-ketol derivatives **2**. We describe here the first reactions of acylzirconocene chloride complexes **1** with aldehydes to give α-ketol derivatives **2** in fair to good yields under mild Lewis acid mediated conditions (Scheme 1).



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

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