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The Seven-Component Assembly of the Bowl-Shaped Cages $Cp^*{}_7Rh_7(CN)_{12}{}^{2+}$ and $Cp^*{}_7Rh_3Ir_4(CN)_{12}{}^{2+}$

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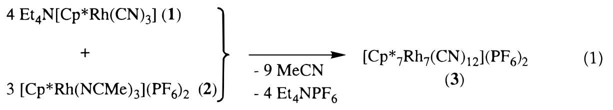
Summary: A novel bowl-shaped cyanometalate cage $[Cp^*{}_7Rh_7(CN)_{12}]^{2+}$ (**3**) *forms via the reaction between MeCN solutions of* $Et_4N[Cp^*Rh(CN)_3]$ *and* $[Cp^*Rh(NCMe)_3](PF_6)_2$*; this seven-component condensation proceeds in 89% yield.* ^1H *and* ^{13}C *NMR spectroscopic measurements as well as a single-crystal X-ray diffraction studies show that* **3** *features a* C_{3v} $Rh_7(CN)_9$ *cage, which can be described as a fragment of a* $Rh_8(CN)_{12}$ *box.*

The prevailing interest in supramolecular coordination complexes,[1,2] together with recent advances in cyanometalates,[3,4] makes the study of cyanometalate cages topical and opportune. Most work in this area has focused on nonmolecular solids. Our recent synthesis[5] of the "molecular box", $Cp_4Cp^*{}_4Co_4Rh_4(CN)_{12}{}^{4+}$, however, establishes the feasibility of constructing molecular cages based on M−C−N−M linkages.[6] We now report results on a simple homometallic condensation process leading efficiently to organometallic species with bowl-shaped architectures.[7,8]

The key experiment involves the condensation of $Et_4N[Cp^*Rh(CN)_3]$ (**1**) and $[Cp^*Rh(NCMe)_3](PF_6)_2$ (**2**)[9] according to the ratios shown in eq 1.[10]



$$\left.\begin{array}{l} 4\ Et_4N[Cp^*Rh(CN)_3]\ (\mathbf{1}) \\ \quad + \\ 3\ [Cp^*Rh(NCMe)_3](PF_6)_2\ (\mathbf{2}) \end{array}\right\} \xrightarrow[-\,4\ Et_4NPF_6]{-\,9\ MeCN} \underset{(\mathbf{3})}{[Cp^*{}_7Rh_7(CN)_{12}](PF_6)_2} \qquad (1)$$

This transformation is conveniently monitored by ^1H NMR spectroscopy, which, as independent studies show,[11] easily resolves Cp* signals for $Rh(CN)_3$ ($\sim\delta$ 2.0) versus

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[9] White, C.; Yates, A.; Maitlis, P. M. *Inorg. Synth.* **1992**, *29*, 228.

[10] A solution of 186 mg (0.414 mmol) $Et_4N[(Cp^*)Rh(CN)_3]$ in 10 mL of MeCN was added to a solution of 200 mg (0.307 mmol) of $[(Cp^*)Rh(MeCN)_3](PF_6)_2$ in 10 mL of MeCN. After 24 h, the reaction solution was concentrated to ca. 5 mL and diluted with 50 mL of Et_2O to give 240 mg of the product **3** (89%).

[11] Contakes, S. M.; Klausmeyer, K. K.; Rauchfuss, T. B. Unpublished results.

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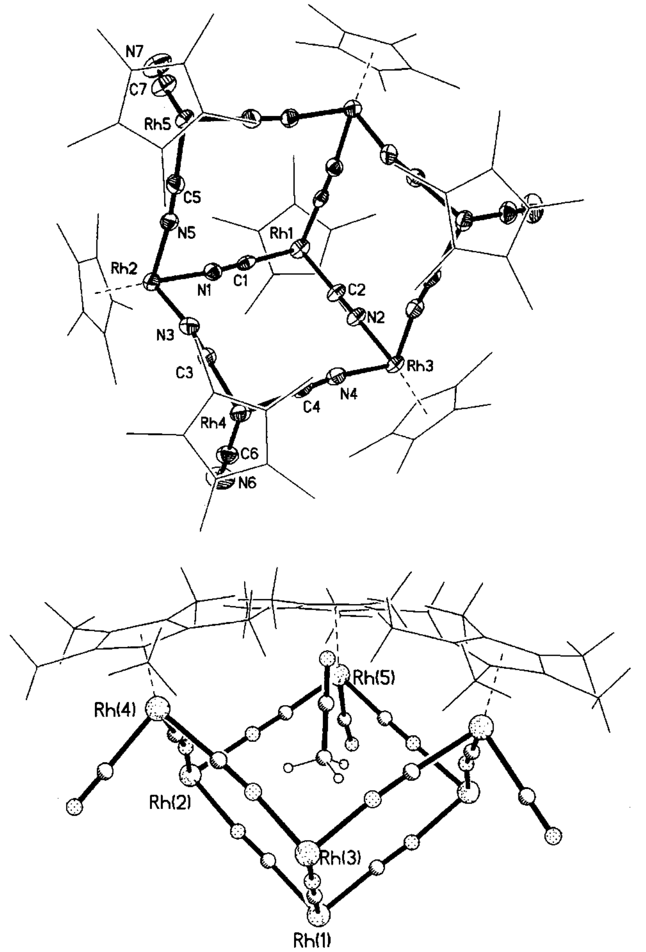

Figure 1. Structure of $Cp^*_7Rh_7(CN)_{12}{}^{2+}$ from two perspectives with thermal ellipsoids drawn at the 35% level. In the top perspective, the cation is viewed down the idealized 3-fold symmetry axis (molecules of solvation are not shown). In the bottom view, the $Rh_7(CN)_{12}$ core is shown together with the intracage solvent molecule (in this view, we included three Cp* groups to highlight the degree to which the unique MeCN unit is inserted into the cage). Selected angles: C(1)−Rh(1)−C(1)′, 94.0(4)°; C(1)−Rh(1)−C(2), 88.7(2)°; C(4)−Rh(4)−C(6), 88.9(3)°; C(3)−Rh(4)−C(4), 87.0(2)°; C(3)−Rh(4)−C(6), 87.8(3)°; N(1)−Rh(2)−N(3), 88.3(2)°; N(1)−Rh(2)−N(5), 87.1(2)°; N(3)−Rh(2)−N(5), 90.6(2)°; N(2)−Rh(3)−N(4), 88.9(2)°. Rh−N−C angles range from 169(2)° for C(3)−N(3)−Rh(2) to 178.7(7)° for C(2)−N(2)−Rh(3). Rh−C−N angles range from 173.0(3)° to 178.5(5)°. Rh−N distances range from 2.065(5) to 2.109(7) Å, while Rh−C(N) distances range from 1.985(7) to 2.033(8) Å.

Rh(*N*C)$_3$ (∼δ 1.7) centers. Mixing MeCN solutions of **1** and **2** (4:3 ratio) results in the rapid (1 min) consumption of **2** and the formation of a complex mixture. After 1 day, $[Cp^*_7Rh_7(CN)_{12}](PF_6)_2$ (**3**) is the dominant species (89% isolated yield). Consistent with its crystallographically verified structure (see below), **3** has three ^{1}H NMR signals with relative intensities of 1:3:3, the first two of which fall in the Cp*Rh(CN)$_3$ region, while the other signal is in the Cp*Rh(NC)$_3$ region.

The rate of assembly of **3** is comparable to that for the box $Cp_4Cp^*_4Co_4Rh_4(CN)_{12}{}^{4+}$ from [K(18-crown-6)]-[CpCo(CN)$_3$] and $[Cp^*Rh(NCMe)_3](PF_6)_2$.[11] It is striking, however, that the all-Cp* box is never observed. Instead, equimolar quantities of **1** and **2** react to produce **3**, leaving some unreacted **2**. We suggest that the formation of $Cp^*_8Rh_8(CN)_{12}{}^{4+}$ is prevented by repulsive Cp*−Cp* interactions.[12] Solvent also strongly affects the assembly process: in CH_2Cl_2 solution, compounds **1** and **2** (4:3 ratio) react, but **3** is not formed until the solution is diluted with an equal volume of MeCN.

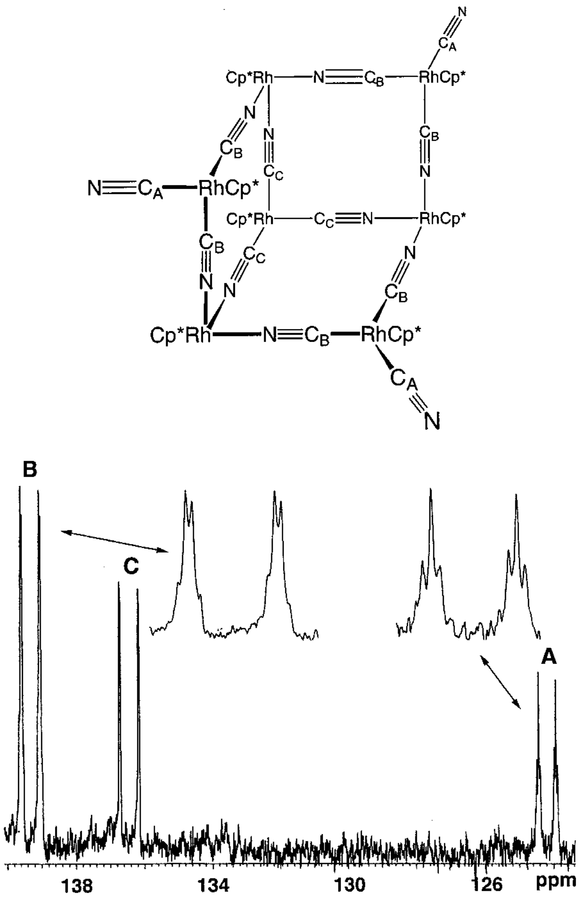

Figure 2. 125 MHz ^{13}C NMR spectrum of a MeCN solution of **3** (33% ^{13}C-enriched in *C*N region).

The formulation of **3** as $[Cp^*_7Rh_7(CN)_{12}](PF_6)_2$[13] was confirmed by electrospray mass spectrometry on MeCN solutions, which showed peaks for the dicationic cage at $m/z = 2128$ ($z = 1$) and 991 ($z = 2$). The solid-state structure of **3** was deduced by X-ray crystallographic analysis of crystals grown from MeCN/Et$_2$O (Figure 1). The dicationic cage has idealized C_{3v} symmetry with three types of Cp*Rh centers.[14] Nine of the 12 CN ligands bridge between Rh atoms; the remaining three CN groups are terminal. The C−Rh−C and N−Rh−N angles range from 87.1° to 94°, i.e., **3** is well described as three conjoined $Rh_4(\mu\text{-}CN)_4$ squares. Thus, the $Rh_7(CN)_9$ core is a fragment of a $M_8(CN)_{12}$ box, which cannot form from **3** because three CN$_{\text{term}}$ groups are oriented away from the cage interior. This change in stereochemistry, versus that of the cubic mixed Cp-Cp* cage $Cp_4Cp^*_4Co_4Rh_4(CN)_{12}{}^{4+}$, minimizes inter-Cp* steric repulsions which would prevail in a $Cp^*_8Rh_8(CN)_{12}{}^{4+}$

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[12] Reaction of $Et_4N[(C_5Me_4H)Rh(CN)_3]$ and $[(C_5Me_4H)Rh(NCMe)_3](PF_6)_2$ in a 1:1 ratio also fails to give molecular boxes. However, use of a 4:3 ratio of reactants affords $[(C_5Me_4H)_7Rh_7(CN)_{12}](PF_6)_2$ as the exclusive product.

[13] $[Cp^*_7Rh_7(CN)_{12}](PF_6)_2$: ^{1}H NMR (CD$_3$CN soln): 2.14 (s, 15H), 1.98 (s, 45H), and 1.70 (s, 45H). ^{13}C{^{1}H} NMR (CD$_3$CN soln, see Figure 2). ESI MS: *m/z* 991.2 (M^{2+}) 2128 (M^{2+} PF$_6{}^-$) (mass spect. sample was prepared with 33% ^{13}CN). IR (KBr, cm^{-1}): 2126 (ν_{CN_t}) and 2169 ($\nu_{\mu\text{-}CN}$). Anal. CHN.

box. The solid-state structure of **3** features a MeCN molecule inserted into the cage.[15] The inclusion capability of the cage is thus demonstrated, although the scope and energetics of this process will require further study.

As the connectivity of the CN ligands is highly relevant to the assembly process, we sought confirmatory evidence for the proposed structure beyond that afforded by the crystallographic analysis. To this end, we conducted one- and two-dimensional ^{13}C NMR measurements on samples of **3** prepared from 33% ^{13}C-enriched cyanide.[16] Observed were three sets (6:3:3) of *C*N signals, all of which showed strong coupling (51−56 Hz) to ^{103}Rh as well as additional longer range $^{2}J(^{13}C,^{13}C)$ and $^{2}J(^{13}C,^{103}Rh)$ fine structure (Figure 2). The three terminal CN groups absorb at δ 125, while the two types of μ-CN groups, which can be assigned on the basis of their intensities, absorb in the region δ 136−140. These results prove that the cage assembles without cleavage of Rh−C bonds. This proposal is further supported by the synthesis of heterometallic analogues of **3**: the reaction of $(Et_4N)[Cp^*Ir(CN)_3]$ (**4**) with **2** (4:3 ratio) afforded $[Cp^*_7Ir_4Rh_3(CN)_{12}](PF_6)_2$ (**5**) in 69% isolated yield.[17]

In summary, this paper demonstrates the considerable potential of organometallic cyanometalates as precursors to novel cage structures. The formation of the new $M_7(CN)_9$ cages results from a balance between inter-Cp* steric repulsions and attractive M···N interactions.

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Supporting Information Available: Synthetic and characterization details for **1**, **3**, **4**, and **5**; details of the crystal structure analysis of **3** including tables of positions, displacement parameters, and bond angles and distances (22 pages). Ordering and Internet access information is given on any current masthead page.

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[14] $C_{90}H_{123}F_{12}N_{16}O_3P_2Rh_7$: fw = 2487.35; T = 175 K.; λ = 0.710 73 Å; crystal size = 0.15 × 0.08 × 0.08 mm; Siemens CCD detector; orthorhombic (*Pnma*); a = 24.7243(6) Å, b = 16.8342(5) Å, c = 27.1790(7) Å; $\alpha = \beta = \gamma = 90°$; V = 11 312.3(5) Å^3; Z = 4; ρ = 1.460 Mg/m^3; 7232 reflns ($2 \leq \theta \leq 22$); rflns = 44 725 [$R_{int} = 0.1883$] (indep rflns = 7232 [2169 obs, $I > 2\sigma(I)$]); direct methods; data/restraints/parameters = 7227/457/578; GOF on F^2 = 1.100; R1 (obs data) = 0.0871, wR2 = 0.1917; R1 (all data) = 0.1597, wR2 = 0.2393; largest diff peak and hole = 1.030 and −0.910 e·Å^{-3}. The deposition number with the Cambridge Crystallographic Data Centre is 101195.

[15] In the solid state, the cages in **3** are solvated by two molecules of H_2O per formula unit; these water molecules are situated near (3.05 Å) two CN_{term} ligands. In addition to the MeCN that is inside the cage, two other MeCN molecules/formula unit are positioned near two of the three $Rh_4(CN)_4$ faces (in $Cp_4Cp^*_4Co_4Rh_4(CN)_{12}{}^{4+}$ each of the six faces is solvated by MeCN. See ref 5).

[16] ^{125} MHz ^{13}C NMR in *C*N region (*J*'s in Hz): 139.3 ($J_{C-Rh} = 54$, $^{2}J_{C-Rh} = 3.6$), 136.5 ($J_{C-Rh} = 56$, $^{2}J_{C-Rh} \sim 2$), 124.1 ($J_{C-Rh} = 50$, $^{2}J_{C-C} = 10$). These assignments are consistent with the results of a ^{13}C COSY experiment.

[17] A solution of 107 mg (0.20 mmol) of $Et_4N[(Cp^*)Ir(CN)_3]$ in 10 mL of MeCN was added to a solution of 98 mg (0.15 mmol) of $[(Cp^*)Rh(MeCN)_3](PF_6)_2$ in 10 mL of MeCN. After 24 h, the reaction solution was concentrated to ca. 5 mL and diluted with 50 mL of Et_2O to precipitate the product **5** as a yellow powder. Yield: 206 mg (69%). $\{[Cp^*Ir(CN)_3]_4[Cp^*Rh]_3\}(PF_6)_2$. ^{1}H NMR (500 MHz, MeCN): δ 1.68 (s, 45*H*); 2.07 (s, 45*H*); 2.12 (s, 15*H*). ^{13}C NMR (125 MHz, MeCN): δ 9.92, 9.97, 10.40, 15.47, 66.14, 98.00, 98.20, 98.72, 99.23, 109.31, 112.86. ESI MS: m/z 2480.9 ($M - PF_6$) 1168.3 (M^{2+}). IR (KBr, cm^{-1}): 2247 ($\nu_{\mu-CN}$) and 2170 (ν_{CN_t}). Anal. CHN.