

# Systematic assembly of the double molecular boxes: $\{\text{Cs}[\text{C}[\text{CpCo}(\text{CN})_3]_4[\text{Cp}^*\text{Ru}]_3\}$ as a tridentate ligand

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**Cubic cage compounds composed of Co-CN-Ru linkages have been prepared which illustrate the following features: (i) new motifs for alkali metal ion complexation (i.e., cationic receptors for cations), (ii) a new family of triaza-metalloligands, and (iii) a double box-like cage. The cages are synthesized by the condensation of  $[\text{CpCo}(\text{CN})_3]^-$  and  $[\text{Cp}^*\text{Ru}(\text{NCMe})_3]^+$  (cyclopentadienyl, Cp; pentamethylcyclopentadienyl, Cp\*) the presence of  $\text{Cs}^+$ . The species  $\{\text{Cs}[\text{C}[\text{CpCo}(\text{CN})_3]_4[\text{Cp}^*\text{Ru}]_4\}^+$  and  $\{\text{Cs}[\text{C}[\text{CpCo}(\text{CN})_3]_4[\text{Cp}^*\text{Ru}]_3[\text{Cp}^*\text{Rh}]_2\}^{2+}$  illustrate the box-completion reaction  $\text{Cs}[\text{C}[\text{CpCo}(\text{CN})_3]_4[\text{Cp}^*\text{Rh}]_2\}^{2+} + \text{M}$  ( $\text{M} = \text{Cp}^*\text{Rh}^{2+}$ ,  $\text{Cp}^*\text{Ru}^+$ ). With the naked ion precursors  $[\text{Na}(\text{NCMe})_6]^-$  and  $[\text{Fe}(\text{NCMe})_6]^{2+}$ , the box-completion reactions afforded  $\{\text{Na}[\text{Cs}[\text{C}[\text{CpCo}(\text{CN})_3]_4[\text{Cp}^*\text{Ru}]_3]_2\}^+$  and  $\{\text{Fe}[\text{Cs}[\text{C}[\text{CpCo}(\text{CN})_3]_4[\text{Cp}^*\text{Ru}]_3]_2\}^{2+}$ . These cages provide the first examples, to our knowledge, of the double-box motif.**

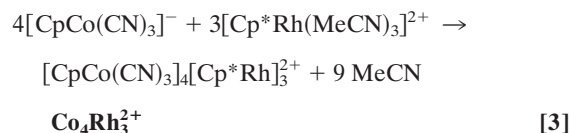
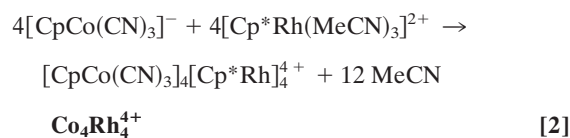
The design of molecular containers represents an important component of nanotechnology and has attracted intense interest from synthetic chemists (1–4). Research on molecular containers can realistically be expected to provide highly selective sensors, sorters, and catalysts for numerous applications. A significant challenge in this area is the development of containers that are stereochemically rigid, because rigidity is the basis of sterically governed selectivity. Rigidity, however, is incompatible with much of organic chemistry, and this dichotomy is problematic because organic (and organometallic) chemistry provides the most versatile construction tools for the synthesis of molecular containers. In this contribution, we address this dichotomy, i.e., the incorporation of organic motifs into rigid frameworks. Our approach involves a hybridization of organometallic chemistry and well established precedents in the chemistry of metal cyanides.

Cyanometallates are metal complexes with the general formula  $\text{L}_m\text{M}_n(\text{CN})_n$ . The most important cyanometallate is Prussian blue (PB), an inorganic polymer with the formula  $\text{Fe}_7(\text{CN})_{18}(\text{H}_2\text{O})_x$  ( $x \sim 15$ ) (5). The synthesis of this useful solid arises from the condensation of  $[\text{Fe}(\text{CN})_6]^{4-}$  and Fe(III) salts (Eq. 1).



The structure of PB may be roughly described as interconnected cubic cage subunits with Fe vertices linked by cyanide. The PB structure is in fact complicated because the otherwise idealized cubic framework is interrupted by vacancies at the metal positions, these vacancies being occupied by water molecules (6). A building block approach is inherent in Eq. 1, i.e., the use of preassembled  $[\text{Fe}(\text{CN})_6]^{4-}$  units that remain intact throughout their condensation with the labile  $\text{Fe}^{3+}$  precursors. Recognition of this building block aspect has spawned intense exploratory studies by using variations of the original PB synthesis, especially focused on other polycyanometallates (e.g.,  $[\text{Mo}(\text{CN})_7]^{4-}$ ,  $[\text{V}(\text{CN})_6]^{3-}$ , and  $[\text{Ni}(\text{CN})_4]^{2-}$ ) (7–9) and, in place of Fe(III) in Eq. 1, coordination complexes containing some nondisplaceable ligands (e.g.,  $[\text{Ni}(\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2)_2]^{2+}$  as a bridging, doubly Lewis-acidic metal center) (10). The PB analogues are of continuing interest as sources of molecular magnets, solid sorbents, and electrode materials.

In recent years we have developed families of molecular cyanometallate ensembles that are synthesized analogously to PB, except that our molecular building blocks are tricyanometallates wherein the three cyanide ligands are mutually cis. Half of the coordination sphere of these tricyanometallates is occupied by a strongly coordinating nondisplaceable coligand. The face-capping coligand inhibits the formation of polymers by minimizing crosslinking but still promotes the formation of three-dimensional structures, which resemble subunits of PB. Particularly effective as face-capping ligands are cyclopentadienyl,  $\text{C}_5\text{H}_5$  (Cp), and its pentamethyl analogue,  $\text{C}_5\text{Me}_5$  (pentamethylcyclopentadienyl, Cp\*). In a proof of concept experiment, we showed that  $[\text{CpCo}(\text{CN})_3]^-$  and  $[\text{Cp}^*\text{Rh}(\text{MeCN})_3]^{2+}$  condense with displacement of MeCN to give  $\text{M}_8(\text{CN})_{12}$  and related  $\text{M}_7(\text{CN})_{12}$  cages, which we refer to as cyanometallate boxes and bowls, respectively (Eqs. 2 and 3; refs. 11 and 12).



The organometallic approach is powerful because numerous CpM and Cp\*M precursor reagents are available, which enable investigations of diverse collections of cages that differ in charge, steric properties, and kinetic lability. Furthermore, one can use ligands in place of  $\text{C}_5\text{R}_5$ , such as 1,4,7-triazaacyclononane (13). In this report, we explore the impact of the seemingly subtle replacement of  $\text{Cp}^*\text{Rh}^{2+}$  in  $\text{Co}_4\text{Rh}_4^{4+}$  and  $\text{Co}_4\text{Rh}_3^{2+}$  (Eqs. 2 and 3) by  $\text{Cp}^*\text{Ru}^+$ . Both  $\text{Cp}^*\text{Rh}^{2+}$  and  $\text{Cp}^*\text{Ru}^+$  are  $12e^-$  fragments that are in common use in organometallic chemistry. The structural and host-guest properties of the resulting Co-Ru cages are not only rich but also predictable, and the latter behavior has allowed the synthesis of an example of a molecular double box.

## Materials and Methods

**General.** Standard Schlenk techniques were used in all syntheses. The precursors  $[\text{Cp}^*\text{Rh}(\text{NCMe})_3](\text{PF}_6)_2$  (14) and  $[\text{Fe}(\text{NCMe})_6](\text{PF}_6)_2$  (15) were prepared according to published procedures. Because the purity of  $[\text{Cp}^*\text{Ru}(\text{NCMe})_3]\text{PF}_6$  (16) proved critical, the as-synthesized salt (4) was further recrystallized from  $\text{CH}_2\text{Cl}_2\text{-Et}_2\text{O}$ .  $^{133}\text{Cs}$  NMR spectra were obtained at 78

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Abbreviations: ESI-MS, electrospray ionization MS; THF, tetrahydrofuran; Cp, cyclopentadienyl; Cp\*, pentamethylcyclopentadienyl; PB, Prussian blue; OTf, trifluoromethanesulfonate.

Data deposition: The atomic coordinates have been deposited with the Cambridge Structural Database, Cambridge Crystallographic Data Centre, Cambridge CB2 1EZ, United Kingdom (CSD reference nos. CCDC-174664 and -174665).

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MHz, and the chemical shift of CsOTf (OTf, trifluoromethanesulfonate) (MeCN solution) was referenced at  $\delta 34.362$ .

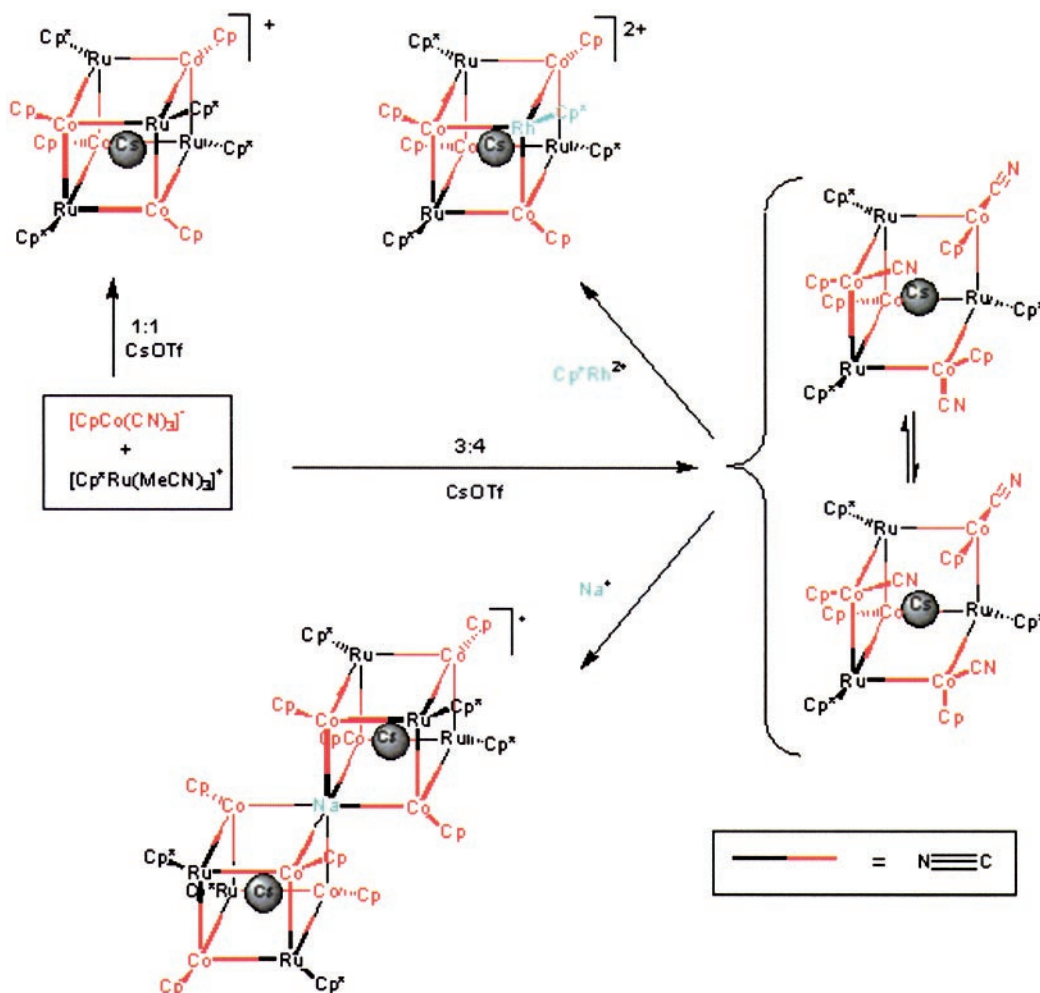
**{CsC[CpCo(CN)<sub>3</sub>]<sub>4</sub>[Cp\**Ru*]<sub>4</sub>}PF<sub>6</sub>·2H<sub>2</sub>O.** A solution of 102 mg (0.202 mmol) of [Cp\**Ru*(NCMe)<sub>3</sub>]PF<sub>6</sub> in 20 ml of MeCN was added dropwise to a solution of 14 mg (0.051 mmol) of CsOTf and 102 mg (0.202 mmol) of [K(18-crown-6)][CpCo(CN)<sub>3</sub>] in 20 ml of MeCN. The resulting red solution was stirred for 1 h, and then solvent was reduced to about 5 ml under vacuum. The concentrate was diluted with 20 ml of Et<sub>2</sub>O to precipitate the product as a dark red powder, which was collected by filtration, washed with 5:1 Et<sub>2</sub>O/MeCN (vol/vol) and Et<sub>2</sub>O, and dried under vacuum. Yield: 96 mg (93%). IR (KBr, cm<sup>-1</sup>):  $\nu_{\text{CN}} = 2174, 2119$ . <sup>1</sup>H NMR (CD<sub>3</sub>CN):  $\delta 1.679$  (s, 15H), 5.568 (s, 5H). <sup>133</sup>Cs NMR (CD<sub>3</sub>CN):  $\delta 1.33$ . Electrospray ionization (ESI)-MS (*m/z*): 1887 ({CsC[CpCo(CN)<sub>3</sub>]<sub>4</sub>[Cp\**Ru*]<sub>4</sub>}<sup>+</sup>). Anal. Calcd for C<sub>72</sub>H<sub>84</sub>Co<sub>4</sub>CsF<sub>6</sub>N<sub>12</sub>O<sub>2</sub>PRu (Found): C, 41.83 (41.98); H, 4.27 (4.10); N, 8.13 (8.02).

**{CsC[CpCo(CN)<sub>3</sub>]<sub>4</sub>[Cp\**Ru*]<sub>3</sub>}**. A solution of 100 mg (0.198 mmol) of [Cp\**Ru*(NCMe)<sub>3</sub>]PF<sub>6</sub> in 15 ml MeCN was added dropwise to a solution of 133.6 mg (0.264 mmol) of [K(18-crown-6)][CpCo(CN)<sub>3</sub>] and 18.6 mg (0.066 mmol) of CsOTf in 5 ml of MeCN. Immediately, the solution became deep red, and a violet-brown solid precipitated over the course of 30 min. The solid was collected, washed with Et<sub>2</sub>O, and recrystallized from 5 ml of CH<sub>2</sub>Cl<sub>2</sub> by the addition of 20 ml of Et<sub>2</sub>O. Yield of

violet-brown microcrystals: 86 mg (79%). (Note: CsCCo<sub>4</sub>Ru<sub>3</sub> is soluble in tetrahydrofuran (THF), insoluble in MeCN, and unstable in CH<sub>2</sub>Cl<sub>2</sub>.) <sup>1</sup>H NMR ( $\delta$ , THF-*d*<sub>8</sub>) indicates a mixture of two isomers in a 4:1 ratio. Major isomer: 1.663 (s, 30H), 1.689 (s, 15H), 5.430 (s, 10 H), 5.452 (s, 5H), 5.593 (s, 5H); minor isomer: 1.636 (s, 15H), 1.679 (s, 30H), 5.384 (s, 10 H), 5.505 (s, 5H), 5.624 (s, 5H). 78 MHz <sup>133</sup>Cs NMR (THF):  $\delta 41.462$  (major isomer),  $\delta 89.321$  (minor isomer). IR (KBr): 2163, 2124 cm<sup>-1</sup>. ESI-MS: *m/z* = 1649 (Cs[CpCo(CN)<sub>3</sub>]<sub>4</sub>[Cp\**Ru*]<sub>3</sub>). Anal. Calcd for C<sub>62</sub>H<sub>65</sub>Co<sub>4</sub>CsN<sub>12</sub>Ru<sub>3</sub>·4.5CH<sub>2</sub>Cl<sub>2</sub> (Found): C, 39.30 (39.23); H, 3.67 (3.65), N, 8.27 (8.27).

**{CsC[CpCo(CN)<sub>3</sub>]<sub>4</sub>[Cp\**Ru*]<sub>3</sub>[Cp\**Rh*]}(PF<sub>6</sub>)<sub>2</sub>.** A solution of 19 mg (0.03 mmol) of [Cp\**Rh*(NCMe)<sub>3</sub>](PF<sub>6</sub>)<sub>2</sub> in 25 ml of 5:1 CH<sub>2</sub>Cl<sub>2</sub>:MeCN was added dropwise to a solution of 49 mg (0.03 mmol) of CsCCo<sub>4</sub>Ru<sub>3</sub> in 20 ml of CH<sub>2</sub>Cl<sub>2</sub>. The resulting solution was stirred for 1 h, allowed to stand for 24 h, and finally diluted with 60 ml of Et<sub>2</sub>O to precipitate a dark red powder, which was collected by filtration, washed with THF and Et<sub>2</sub>O, and dried under vacuum. Yield: 43 mg (66%). <sup>1</sup>H NMR (CD<sub>3</sub>CN):  $\delta 1.675$  (s, 45H), 1.805 (s, 15H), 5.616 (s, 5H), and 5.687 (s, 15H). 78 MHz <sup>133</sup>Cs NMR (CD<sub>3</sub>CN):  $\delta 10.225$ . ESI-MS (*m/z*): 944.4 ({CsC[CpCo(CN)<sub>3</sub>]<sub>4</sub>[Cp\**Ru*]<sub>3</sub>[Cp\**Rh*]}<sup>2+</sup>). Anal. Calcd for C<sub>72</sub>H<sub>80</sub>Co<sub>4</sub>CsF<sub>12</sub>N<sub>12</sub>P<sub>2</sub>RhRu<sub>3</sub>·2CH<sub>2</sub>Cl<sub>2</sub> (found): C, 37.85 (37.83); H, 3.61 (3.75); N, 7.16 (7.29).

**{Na[CsC[CpCo(CN)<sub>3</sub>]<sub>4</sub>[Cp\**Ru*]<sub>3</sub>]}PF<sub>6</sub>.** Ether was allowed to vapor-diffuse into a solution of 20 mg (0.012 mmol) of



Scheme 1.

**Table 1. Crystallographic data for {Na[C<sub>s</sub>C<sub>o</sub>Co<sub>4</sub>Ru<sub>3</sub>]<sub>2</sub>}PF<sub>6</sub> and {Fe[C<sub>s</sub>C<sub>o</sub>Co<sub>4</sub>Ru<sub>3</sub>]<sub>2</sub>}(PF<sub>6</sub>)<sub>2</sub>**

Parameter	{Na[C <sub>s</sub> C <sub>o</sub> Co <sub>4</sub> Ru <sub>3</sub> ] <sub>2</sub> }PF <sub>6</sub> ·13MeCN·2CH <sub>2</sub> Cl <sub>2</sub>	{Fe[C <sub>s</sub> C <sub>o</sub> Co <sub>4</sub> Ru <sub>3</sub> ] <sub>2</sub> }(PF <sub>6</sub> ) <sub>2</sub> ·12MeCN
Chemical formula	C <sub>152</sub> H <sub>173</sub> N <sub>37</sub> Cl <sub>4</sub> Co <sub>8</sub> CS <sub>2</sub> F <sub>6</sub> PNaRu <sub>6</sub>	C <sub>148</sub> H <sub>166</sub> N <sub>36</sub> Co <sub>8</sub> CS <sub>2</sub> F <sub>12</sub> P <sub>2</sub> FeRu <sub>6</sub>
Temp. (K)	153 (2)	193 (2)
Crystal size, mm	0.16 × 0.10 × 0.02	0.30 × 0.24 × 0.06
Space group	P $\bar{1}$	P2 <sub>1</sub> /c
a (Å)	15.330 (4)	22.335 (7)
b (Å)	15.788 (4)	15.936 (5)
c (Å)	21.255 (6)	26.402 (8)
$\alpha$ (deg)	69.696 (4)	90
$\beta$ (deg)	71.320 (4)	111.558 (5)
$\gamma$ (deg)	80.682 (5)	90
V (Å <sup>3</sup> )	4563 (2)	8740 (5)
Z	1	2
D <sub>calcd</sub> (Mg m <sup>-3</sup> )	1.518	1.573
$\mu$ (Mo K $\alpha$ , mm <sup>-1</sup> )	1.710	1.815
Minimum and maximum transmission	0.6982/0.9996	0.4527, 0.8942
Reflections measured/independent	33399/8512	65622/64364
Data/restraints/parameters	8512/13/362	64364/0/336
Goodness of fit	0.999	1.017
R <sub>1</sub> [I > 2 $\sigma$ ] (all data)*	0.1225 (0.2903)	0.1469 (0.3783)
wR <sub>2</sub> [I > 2 $\sigma$ ] (all data) <sup>†</sup>	0.2824 (0.3787)	0.1935 (0.4063)
Maximum peak/hole (e <sup>-</sup> /Å <sup>3</sup> )	1.329/-1.015	3.506/-3.579

\*R<sub>1</sub> =  $\sum ||F_o| - |F_c|| / \sum |F_o|$ .

<sup>†</sup>wR<sub>2</sub> =  $\{\sum [w(F_o^2 - F_c^2)]^2 / \sum [w(F_o^2)]^2\}^{1/2}$ .

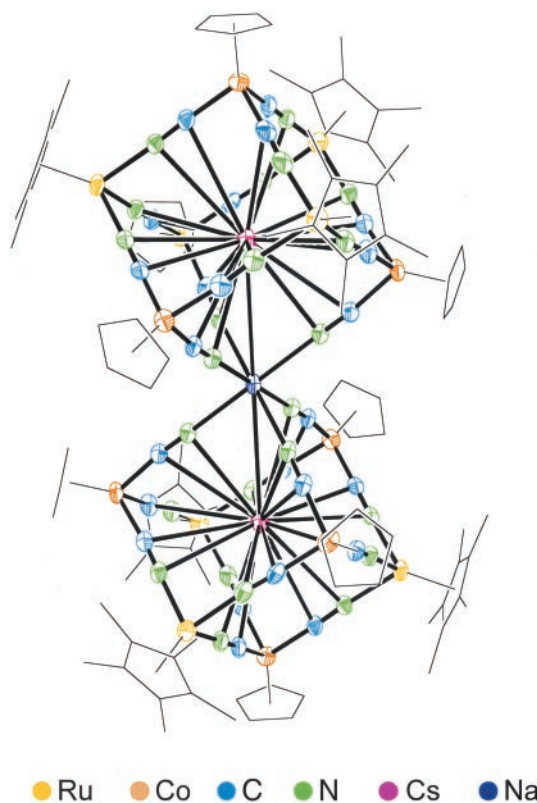
**CsC<sub>o</sub>Co<sub>4</sub>Ru<sub>3</sub>** and 1.0 mg (0.0061 mmol) of NaPF<sub>6</sub> in 5 ml of 1:1 CHCl<sub>3</sub>/MeCN at 0°C. After 72 h, red crystals were collected by decantation and dried under vacuum for 6 h. The crystals were dissolved in 5 ml of CHCl<sub>3</sub> and reprecipitated by allowing Et<sub>2</sub>O to vapor-diffuse into the solution at 0°C over the course of 72 h. <sup>1</sup>H NMR (CD<sub>3</sub>CN):  $\delta$ 1.681 (s, 90H), 5.485 (s, 30H), and 5.610 (s, 10H).

**{Fe[C<sub>s</sub>C[CpCo(CN)<sub>3</sub>]<sub>4</sub>[Cp\*Ru]<sub>3</sub>]<sub>2</sub>}(PF<sub>6</sub>)<sub>2</sub>.** A solution of 13 mg (0.024 mmol) of [Fe(NCMe)<sub>6</sub>](PF<sub>6</sub>)<sub>2</sub> in 2 ml of MeCN was added dropwise to a solution of 79 mg (0.048 mmol) of **CsC<sub>o</sub>Co<sub>4</sub>Ru<sub>3</sub>** in 12 ml of 1:1 MeCN:CH<sub>2</sub>Cl<sub>2</sub>. After 24 h, a dark red powder was precipitated by the addition of 30 ml of Et<sub>2</sub>O. The powder was collected by filtration, washed with 10-ml portions of THF and Et<sub>2</sub>O, and dried under vacuum for 24 h. Yield: 69 mg (79%). <sup>1</sup>H NMR (CD<sub>3</sub>CN):  $\delta$ 1.684 (s, 90H), 4.952 (s, 30H), and 5.687 (s, 10H). ESI-MS (*m/z*): 1678.4. ([Fe{Cs[C[CpCo(CN)<sub>3</sub>]<sub>4</sub>[Cp\*Ru]<sub>3</sub>]<sub>2</sub>}<sup>2+</sup>). Anal. Calcd for C<sub>124</sub>H<sub>130</sub>Co<sub>8</sub>CS<sub>2</sub>F<sub>12</sub>FeN<sub>24</sub>P<sub>2</sub>Ru<sub>6</sub>·3CH<sub>2</sub>Cl<sub>2</sub> (found): C, 39.10 (39.06); H, 3.51 (3.40); N, 8.62 (8.93).

**Crystallography.** Crystals of {Na[C<sub>s</sub>C<sub>o</sub>Co<sub>4</sub>Ru<sub>3</sub>]<sub>2</sub>}PF<sub>6</sub>·13MeCN·2CH<sub>2</sub>Cl<sub>2</sub> were grown by vapor diffusion of Et<sub>2</sub>O into a MeCN-CH<sub>2</sub>Cl<sub>2</sub> solution (2:1 ratio) of **CsC<sub>o</sub>Co<sub>4</sub>Ru<sub>3</sub>** and NaPF<sub>6</sub>. Crystals of {Fe[C<sub>s</sub>C<sub>o</sub>Co<sub>4</sub>Ru<sub>3</sub>]<sub>2</sub>}(PF<sub>6</sub>)<sub>2</sub> grew over the course of 1 week by vapor diffusion of Et<sub>2</sub>O into a solution in CH<sub>2</sub>Cl<sub>2</sub>-MeCN. The crystals were mounted on thin glass fibers with oil (Paratone N, Exxon, Annandale, NJ) before being transferred to a Siemens (Iselin, NJ) Platform/CCD automated diffractometer. Data processing was performed with the integrated program package SHELXTL. All structures were solved with direct methods and refined by using full matrix least squares on F<sup>2</sup> with the program SHELXL-93. Hydrogen atoms were fixed in idealized positions with thermal parameters 1.5× those of the attached carbon atoms. The data were corrected for absorption on the basis of  $\Psi$ -scans. Specific details for each crystal are given in Table 1. Full crystallographic details have been deposited with the Cambridge Crystallographic Data Center (nos. CCDC-174664 and -174665). (See Tables 3–12, which are published as supporting information on the PNAS web site, www.pnas.org.)

## Results and Discussion

**{Cs[C[CpCo(CN)<sub>3</sub>]<sub>4</sub>[Cp\*Ru]<sub>3</sub>]<sub>2</sub>}<sup>(x-3)+</sup> (x = 3, 4).** The reaction between [K(18-crown-6)][CpCo(CN)<sub>3</sub>] and [Cp\*Ru(NCMe)<sub>3</sub>]<sup>+</sup> in the presence of CsOTf produces the molecular box {Cs[C[CpCo(CN)<sub>3</sub>]<sub>4</sub>[Cp\*Ru]<sub>3</sub>]<sub>2</sub>}<sup>+</sup>, **CsC<sub>o</sub>Co<sub>4</sub>Ru<sub>3</sub>**<sup>+</sup>. The structural assignment (Scheme 1) was inferred from its <sup>1</sup>H NMR spectrum,



**Fig. 1.** Molecular structure of the cation {Na[C<sub>s</sub>C[CpCo(CN)<sub>3</sub>]<sub>4</sub>[Cp\*Ru]<sub>3</sub>]<sub>2</sub>}<sup>+</sup> with thermal ellipsoids drawn at the 35% probability level.

**Table 2. Selected bond distances (Å) and angles (°) for the cations in {Na[C<sub>5</sub>C<sub>4</sub>Ru<sub>3</sub>]<sub>2</sub>}PF<sub>6</sub>·13MeCN·2CH<sub>2</sub>Cl<sub>2</sub>, and {Fe[C<sub>5</sub>C<sub>4</sub>Ru<sub>3</sub>]<sub>2</sub>}(PF<sub>6</sub>)<sub>2</sub>·12MeCN**

Parameter	{Na[C <sub>5</sub> C <sub>4</sub> Ru <sub>3</sub> ] <sub>2</sub> } <sup>+</sup>	{Fe[C <sub>5</sub> C <sub>4</sub> Ru <sub>3</sub> ] <sub>2</sub> } <sup>2+</sup>
C(1)-Cs(1)	3.95 (3)	3.657 (10)
C(2)-Cs(1)	3.93 (3)	3.666 (11)
C(3)-Cs(1)	3.89 (3)	3.676 (10)
C(4)-Cs(1)	3.67 (3)	3.620 (11)
C(5)-Cs(1)	3.73 (3)	3.689 (14)
C(6)-Cs(1)	3.73 (3)	3.778 (10)
C(7)-Cs(1)	3.73 (3)	3.661 (13)
C(8)-Cs(1)	3.78 (3)	3.626 (11)
C(9)-Cs(1)	3.73 (3)	3.850 (12)
C(10)-Cs(1)	3.72 (3)	3.624 (10)
C(11)-Cs(1)	3.70 (3)	3.607 (10)
C(12)-Cs(1)	3.76 (3)	3.792 (10)
N(1)-Cs(1)	3.85 (2)	3.588 (8)
N(2)-Cs(1)	3.84 (2)	3.527 (9)
N(2)-Cs(1)	3.86 (2)	3.572 (9)
N(4)-Cs(1)	3.67 (2)	3.554 (8)
N(5)-Cs(1)	3.66 (2)	3.604 (11)
N(6)-Cs(1)	3.66 (2)	3.863 (11)
N(7)-Cs(1)	3.76 (2)	3.594 (11)
N(8)-Cs(1)	3.66 (2)	3.503 (8)
N(9)-Cs(1)	3.61 (3)	3.893 (10)
N(10)-Cs(1)	3.57 (2)	3.551 (8)
N(11)-Cs(1)	3.68 (2)	3.592 (8)
N(12)-Cs(1)	3.64 (2)	3.813 (10)
Na(1)/Fe(1)-N(6)	2.49 (3)	2.207 (8)
Na(1)/Fe(1)-N(12)	2.58 (3)	2.218 (9)
Na(1)/Fe(1)-N(9)	2.65 (3)	2.169 (9)
N(6)-Na(1)/Fe(1)-N(12)	88.6 (8)	87.0 (3)
N(6)-Na(1)/Fe(1)-N(9)	86.7 (7)	88.2 (3)
N(12)-Na(1)/Fe(1)-N(9)	87.4 (8)	88.9 (3)

which exhibits one signal each for Cp and Cp\* in the appropriate 1:3 intensity ratio. The ESI-MS spectrum ( $M^+$  at  $m/z = 1887$  atomic mass units) provided evidence for the inclusion of the  $Cs^+$  at the center of the cage, which is further supported by its  $^{133}Cs$  NMR spectrum (MeCN solution) that shows a single peak at  $\delta 1.33$  vs.  $\delta 34.36$  for CsOTf. The IR spectrum features  $\nu_{CN}$  bands at 2174 and 2119  $cm^{-1}$ , which are shifted to higher frequencies relative to free  $[CpCo(CN)_3]^-$  (2119  $cm^{-1}$ ), consistent with all cyano ligands serving as bridges. The synthesis of  $CsC_5C_4Ru_4^+$  is modeled after that for the related  $\{[CpCo(CN)_3]_4[Cp^*Rh]_4\}^{4+}$ , except that the formation of Ru-containing cages requires the presence of a templating cation. Attempted synthesis of neutral  $Co_4Ru_4$  cage in the absence of alkali metal salts afforded mainly insoluble, apparently polymeric products.

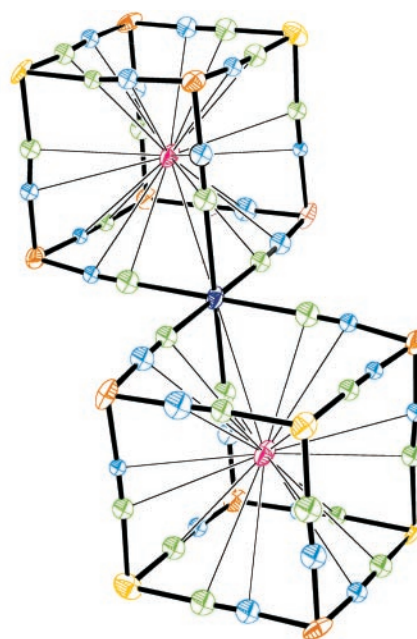
When the synthesis of  $CsC_5C_4Ru_4^+$  is attempted with a deficiency of  $[Cp^*Ru(NCMe)_3]PF_6$ , one obtains the corresponding  $CsC_5C_4Ru_3$  cage,  $CsC[CpCo(CN)_3]_4[Cp^*Ru]_3$ . The violet-colored “defect box” precipitates in excellent yield when  $[Cp^*Ru(NCMe)_3]PF_6$  was added to an MeCN solution of  $CsO_3SCF_3$  and  $[CpCo(CN)_3]_4$  in 3:1:4 molar ratio, respectively. In contrast to the ionic cages that we have previously prepared,  $CsC_5C_4Ru_3$  is insoluble in MeCN but soluble in Et<sub>2</sub>O and THF. Initial characterization of  $CsC_5C_4Ru_3$  is based on ESI-MS measurements, with  $M^+$  at  $m/z = 1649$  and no signals for the box  $CsC_5C_4Ru_4^+$ .

The  $^1H$  NMR spectrum of  $CsC_5C_4Ru_3$  indicates that it exists as a mixture of two isomers. Each isomer exhibits three singlets in the Cp region and two singlets in the Cp\* region with the expected relative intensities of 5:10:5:30:15, respectively. The

$^{133}Cs$  NMR spectrum (THF) also confirms the presence of two isomers characterized by singlets at  $\delta 41.46$  and  $\delta 89.32$ . The two isomers are proposed to differ in terms of the relative stereochemistry of the Cp and CN<sub>t</sub> (terminal) ligands of the cage (see Scheme 1). In contrast, the three CN<sub>t</sub> ligands in the cationic bowl  $Co_4Rh_3^{2+}$  are oriented toward the exterior of the cage ( $C_{3v}$  symmetry). Because Cp\*<sub>2</sub>Ru and Cp\*<sub>2</sub>Rh are isosteric, the differing stereochemistry of  $Co_4Rh_3^{2+}$  and  $CsC_5C_4Ru_3$  must be attributed to the influence of the included (denoted by  $\subset$ )  $Cs^+$ . We propose that the  $Cs^+$  ion influences the orientation of the CN<sub>t</sub> ligands in  $CsC[CpCo(CN)_3]_4[Cp^*Ru]_3$  via a  $\pi$ -bonding interaction. Preliminary crystallographic analysis (M.L.K., unpublished results) on a weakly diffracting crystal confirms that two CN<sub>t</sub> groups are side-bonded to the  $Cs^+$ .

**Box-Completion Reactions:  $CsC_5C_4Ru_3$  Is a Building Block for Molecular Boxes.** Aside from its novel structure, an exciting aspect of  $CsC_5C_4Ru_3$  is its potential as a well defined building block for the assembly of novel molecular cages via  $CsC_5C_4Ru_3 + M \rightarrow CsC_5C_4Ru_3M$ , a box-completion process. Proof of concept was provided by the finding that  $CsC_5C_4Ru_3$  reacts with one equivalent of  $[Cp^*Ru(NCMe)_3]PF_6$  to give the completed box  $CsC_5C_4Ru_4^+$  in high yield. No information is presently available on the mechanism by which the CN<sub>t</sub> ligands in  $CsC_5C_4Ru_3$  rearrange to allow the box-completion process, which results in all three formerly CN<sub>t</sub> ligands being related by  $C_3$  symmetry.

The box-completion reaction was extended to the synthesis of the dicationic box  $\{CsC[CpCo(CN)_3]_4[Cp^*Ru]_3[Cp^*Rh]\} (PF_6)_2$ . This synthesis was accomplished by treatment of a solution of  $CsC_5C_4Ru_3$  with an equimolar quantity of the dication  $[Cp^*Rh(NCMe)_3](PF_6)_2$  (Scheme 1). The transformation occurred at room temperature over the course of 24 h to give  $CsC_5C_4Ru_3Rh^{2+}$  in 66% isolated yield. The product was characterized by ESI-MS (molecular ion  $M^{2+}$  at  $m/z = 944.4$ ).  $^1H$  NMR spectra showed two Cp signals with relative intensities of 3:1 ratio



● Ru ● Co ● C ● N ● Cs ● Na

**Fig. 2.** View of the M-C-N framework in  $\{Na[C_5C_4Ru_3]_2\}^+$  with organic ligands removed for clarity.

and two Cp\* signals, which also integrate in a 3:1 ratio, a pattern consistent with the expected  $C_{3v}$  symmetry. The  $^{133}\text{Cs}$  NMR spectrum (MeCN) of  $\text{CsC}\text{Co}_4\text{Ru}_3\text{Rh}^{2+}$  exhibits a singlet at  $\delta 10.23$ .

It is instructive to contrast the  $\text{CsC}\text{Co}_4\text{Ru}_3 + [\text{Cp}^*\text{Rh}(\text{NCMe})_3]^{2+}$  box-completion reaction with the complementary reaction of  $\text{Co}_4\text{Rh}_3^{2+} + [\text{Cp}^*\text{Ru}(\text{NCMe})_3]^+$ . The products of these reactions can be identified by ESI-MS by both molecular ions for the cage cations and the ion-paired species containing one or two  $\text{PF}_6^-$  counterions. The  $\text{Co}_4\text{Rh}_3^{2+} + [\text{Cp}^*\text{Ru}(\text{NCMe})_3]^+$  reaction afforded a mixture of both  $\text{Co}_4\text{Rh}_4^{4+}$  and  $\text{Co}_4\text{Rh}_3\text{Ru}^{3+}$ , together with trace amounts of  $\text{Co}_4\text{Rh}_2\text{Ru}_2^{2+}$ . The complexity of the product mixture, especially the formation of substantial amounts of  $\text{Co}_4\text{Rh}_4^{4+}$ , shows that  $\text{Co}_4\text{Rh}_3^{2+}$  undergoes significant disassembly during the conversion. The difference in the product mixture (vs. that derived from  $\text{CsC}\text{Co}_4\text{Ru}_3 + [\text{Cp}^*\text{Rh}(\text{NCMe})_3]^{2+}$ ) is attributed to the absence of  $\text{Cs}^+$ , which in the Co-Ru cages glues together the  $\text{M}_7(\text{CN})_9$  framework.

**The Double Molecular Boxes  $[\text{M}\{\text{CsC}[\text{CpCo}(\text{CN})_3]_4[\text{Cp}^*\text{Ru}]_3\}_2]^{n+}$ .** In the preceding examples,  $\text{CsC}\text{Co}_4\text{Ru}_3$  was deployed as a ligand toward the “half-sandwich” cations  $\text{Cp}^*\text{M}^{n+}$  ( $\text{M} = \text{Rh}, \text{Ru}$ ), which feature three coordination sites. The use of metal centers with six labile ligands should therefore allow the synthesis of double boxes. Indeed, treatment of solutions of  $\text{CsC}\text{Co}_4\text{Ru}_3$  with  $\text{NaPF}_6$  afforded pale red crystals of  $\{\text{Na}\{\text{CsC}[\text{CpCo}(\text{CN})_3]_4[\text{Cp}^*\text{Ru}]_3\}_2\}\text{PF}_6$  ( $\text{Na}[\text{CsC}\text{Co}_4\text{Ru}_3]_2^+$ ) (Scheme 1). The  $^1\text{H}$  NMR spectrum of this salt indicates that the cage has high symmetry, as signals for two types of Cp (relative intensities 1:3) and one type of Cp\* are observed.

The structure of  $\{\text{Na}[\text{CsC}\text{Co}_4\text{Ru}_3]_2\}\text{PF}_6$ , confirmed crystallographically, consists of two  $\{\text{CsC}[\text{CpCo}(\text{CN})_3]_4[\text{Cp}^*\text{Ru}]_3\}$  cages conjoined at an  $\text{Na}^+$  (Fig. 1, Table 2). The  $\text{Cs}^+$  ions are situated at the center of each of the two box-like fragments, similar to other Cs-intercalated boxes (17). The smaller  $\text{Na}^+$  ion is octahedrally coordinated by the six terminal CN ligands from the two defect box fragments. The double cage has idealized  $D_{3d}$  symmetry. The species provides a relatively rare example of an alkali metal ion receptor that contains different alkali metal cations. The Na-N distances are 2.56 Å vs. the Ru-N distances of 2.09 Å; consequently, each  $\text{Co}_4\text{NaRu}_3$  box is slightly distorted. The extent of this distortion is indicated by the  $\text{Na}^+\text{Co}$  edge distance of 5.55 Å vs. the  $\text{Co}^+\text{Ru}$  edge distances of 5.12 Å. The  $\text{Cs}^+\text{-C/N}$  distances occur over the range (3.95(3) – 3.66(2) Å, the broad range due to the fact that  $\text{Cs}^+$  is displaced by 0.27 Å

along the Co-Na body diagonal toward the Na. The perspective shown in Fig. 2 shows that the conjoined boxes retain their nearly idealized box-like architectures.

The formation of double boxes seems to be a general property of  $\text{CsC}\text{Co}_4\text{Ru}_3$  as demonstrated by its reaction with  $\text{Fe}^{2+}$  sources to give  $\text{Fe}\{\text{CsC}[\text{CpCo}(\text{CN})_3]_4[\text{Cp}^*\text{Ru}]_3\}_2(\text{PF}_6)_2$ ,  $\{\text{Fe}[\text{CsC}\text{Co}_4\text{Ru}_3]_2\}(\text{PF}_6)_2$ . Definitive characterization followed from mass spectrometric and crystallographic analyses (Table 1). The geometries of the Na and Fe double boxes are very similar. The Fe double box is more compact, as reflected in the contracted C/N-Cs and  $\text{Fe}\cdots\text{N}$  distances, which reflect the smaller radius of  $\text{Fe}^{2+}$  vs.  $\text{Na}^+$ . The corresponding  $\{\text{Co}[\text{CsC}\text{Co}_4\text{Ru}_3]_2\}(\text{PF}_6)_2$  was also prepared, further demonstrating the generality of the double-box motif.

## Summary

Previous work had established the affinity of alkali metal cations for anionic cages, e.g.,  $\{\text{CsC}[(\text{CO})_3\text{Mo}(\text{CN})_3]_4[\text{Cp}^*\text{Rh}]_4\}^{3-}$  and  $\{\text{CsC}[(\text{CO})_3\text{Mo}]_6(\text{CN})_9\}^{8-}$  (17, 18). The formation of  $\text{CsC}\text{Co}_4\text{Ru}_3^+$  significantly extends this host-guest behavior to a neutral  $\text{M}_8(\text{CN})_{12}$  host for  $\text{Cs}^+$ . Even more remarkable is the stability of the corresponding  $\text{CsC}\text{Co}_4\text{Ru}_3\text{Rh}^{2+}$ , which is a  $\text{Cs}^+$  complex of a cationic receptor  $\text{Co}_4\text{Ru}_3\text{Rh}^+$ . Mass spectral data points to the existence of  $\text{CsC}\text{Co}_4\text{Ru}_2\text{Rh}_2^{3+}$ , the  $\text{Cs}^+$  complex of a dicationic host.

The species  $\text{CsC}\text{Co}_4\text{Ru}_3$  represents a  $\text{Cs}^+$  complex of the anionic molecular bowl  $\{[\text{CpCo}(\text{CN})_3]_4[\text{Cp}^*\text{Ru}]_3\}^-$ , which seems to be unstable in the absence of an encapsulated cation. We propose that the bowl is stabilized by  $\text{Cs}^+\cdots\text{CN}$  interactions involving the  $\pi$  bond of cyanide, analogous to the recently observed interaction between  $\text{Cs}^+$  and the triple bond in MeCN (19). Such  $\pi$ -bonding interactions provide the basis for the design of new complexants for  $\text{Cs}^+$ , which is relevant to radio-waste remediation (20, 21). The species  $\text{CsC}\text{Co}_4\text{Ru}_3$  is of further interest as a face-capping tridentate ligand, which should allow it to be deployed broadly. Face-capping  $\text{N}_3$  ligands have played a significant role in coordination chemistry, and catalysis as exemplified by extensive work on 1,4,7-triazacyclonane (22, 23) and tris(pyrazolyl)borate (24).

The double boxes described in this report are the largest known molecular subunits of a cubic cyanometallate framework. The stability and easy formation of these double boxes suggest the feasibility of synthesizing even larger multicages.

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