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Cyanometalate Cages with Exchangeable Terminal Ligands

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The coordination chemistry of the unusual metallo-ligand $Cs\subset[CpCo(CN)_3]_4[Cp^*Ru]_3$ ($Cs\subset Co_4Ru_3$) is described with attention to the behavior of the ligand itself, its binding to Lewis-acidic metal cations, and its ability to stabilize catalytically relevant $Ru–PPh_3$ fragments. A series of tests demonstrate that the "rim" $[CpCo(CN)_3]^-$ groups in $Cs\subset Co_4Ru_3$ are exchangeable. Upon treatment with $[(MeC_5H_4)Co(CN)_3]^-$ (Co′) $Cs\subset Co_4Ru_3$ undergoes vertex exchange to give $Cs\subset Co_{4-x}Co'_xRu_3$. Similarly the cage is degraded by CO. Most convincing, $Cs\subset Co_4Ru_3$ reacts with $PhNH_3OTf$ to precipitate the polymer $PhNH_3CpCo(CN)_3$ and form the molecular box $[Cs\subset Co_4Ru_4]^+$. Treatment of $Cs\subset Co_4Ru_3$ with $[M(NCMe)_x]PF_6$ (M = Cu, Ag) gave the Lewis acidic cages $\{Cs\subset[CpCo(CN)_3]_4[Cp^*Ru]_3M(NCMe)\}PF_6$, which reacted with tertiary phosphane ligands to give adducts $[Cs\subset Co_4Ru_3M(PPh_3)]PF_6$. Lewis acidic octahedral vertices were installed using Fe, Ni, and Ru reagents. The boxes $[Cs\subset Co_4Ru_3M(NCMe)_3]^{2+}$ (M = Ni, Fe) formed readily from the reaction $Cs\subset Co_4Ru_3$ with $[Ni(NCMe)_6](BF_4)_2$ and $[Fe(NCMe)_6](PF_6)_2$. Displacement of the MeCN ligands gives $[Cs\subset Co_4Ru_3Ni(9\text{-ane-S3})](BF_4)_2$. A series of boxes were prepared by the reaction of $Cs\subset Co_4Ru_3$ and $RuCl_2(PPh_3)_3$, $RuHCl(PPh_3)_3$, and $[(C_6H_6)Ru(NCMe)_3](PF_6)_2$. The derivative of the hydride, $[Cs\subset Co_4Ru_3Ru(NCMe)(PPh_3)_2](PF_6)_2$, was characterized crystallographically.

Introduction

The centuries old field of metal cyanide chemistry[1] has experienced a renaissance due the zeolitic,[2,3] magnetic,[4] and electronic properties[5] of cyanometalate materials. Parallel to these application-driven studies, we have focused on synthetic methodologies leading to discrete molecular architectures that can be characterized in solution. In recent years we have developed families of molecular cyanometalate ensembles that are synthesized analogously to Prussian Blue (PB), except that our molecular building blocks are tricyanometalates.[6] Half of the coordination sphere of these tricyanometalates is occupied by a strongly coordinating, non-displaceable co-ligand such as $C_5H_5^-$. The face-capping co-ligand inhibits the formation of polymers, by minimizing cross-linking, but still allows the formation of three-dimensional structures, which resemble subunits of PB.[7,8]

Our first attempt at molecular cyanometalate cages afforded the cationic cage $[CpCo(CN)_3]_4[Cp^*Rh]_4^{4+}$.[7] Replacing the dicationic tritopic Lewis acid with a monocationic analog results in charge-neutral ionophilic molecular cages.[9] Specifically, the reaction $[CpCo(CN)_3]^-$, $[Cp^*Ru(NCMe)_3]^+$, and CsOTf at the ratio of 4:4:1 produces the molecular box $\{Cs\subset[CpCo(CN)_3]_4[Cp^*Ru]_4\}^+$ ($Cs\subset Co_4Ru_4^+$).[10] By changing the ratio of the reactants to 4:3:1, one obtains instead the violet-colored "defect" box $Cs\subset[CpCo(CN)_3]_4[Cp^*Ru]_3$ ($Cs\subset Co_4Ru_3$).[10] Aside from its novel structure, an exciting aspect of $Cs\subset Co_4Ru_3$ is its potential as a well-defined building block for the assembly of novel molecular cages via $Cs\subset Co_4Ru_3 + ML_n^z \rightarrow Cs\subset Co_4Ru_3ML_n^z$, a box-completion process. Proof-of-concept was provided by the finding that $Cs\subset Co_4Ru_3$ reacts with one equiv. of $[Cp^*M(NCMe)_3](PF_6)_n$ to give the completed box $Cs\subset Co_4Ru_3M^z$ (M = Cp*Ru, Cp*Rh, z = 1, 2) in high yield.[10]

All previously synthesized cyanometalate boxes and defect boxes possessed non-displaceable ligands such as Cp and Cp*. Isolable cyanometalate cages with *displaceable* ligands L, e.g. $Cs\subset[CpCo(CN)_3]_4[Cp^*Ru]_3ML_n^z$ (L = MeCN, n = 1, 3), represent intriguing targets, which would enable the generation of ensembles of greater complexity and enhanced reactivity. For example, one could envision a modular approach to the preparation of "boxes-of-boxes." Few cyanometalates of nuclearity >8 have been well-characterized *in solution*.[11] We previously described the "double boxes" $\{[Cs\subset Co_4Ru_3]_2M\}^z$, and we anticipate that still higher nuclearity cages can be achieved. The construction of such oligo-cages will require boxes with one or more vertices that contain labile terminal ligands. This paper outlines our initial efforts toward this goal (Scheme 1).

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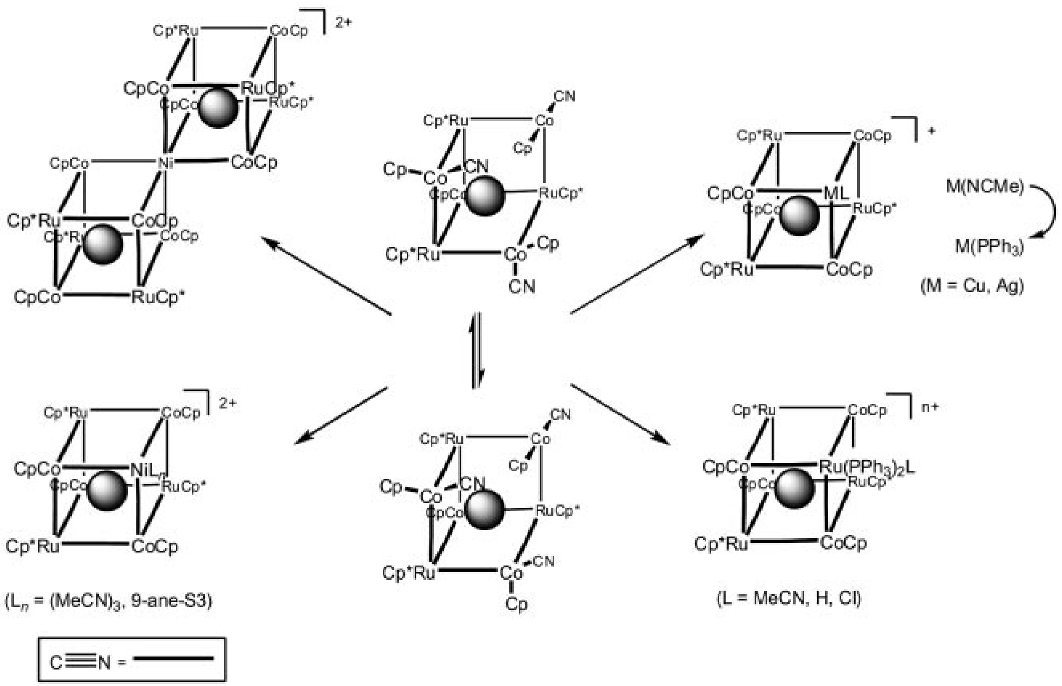
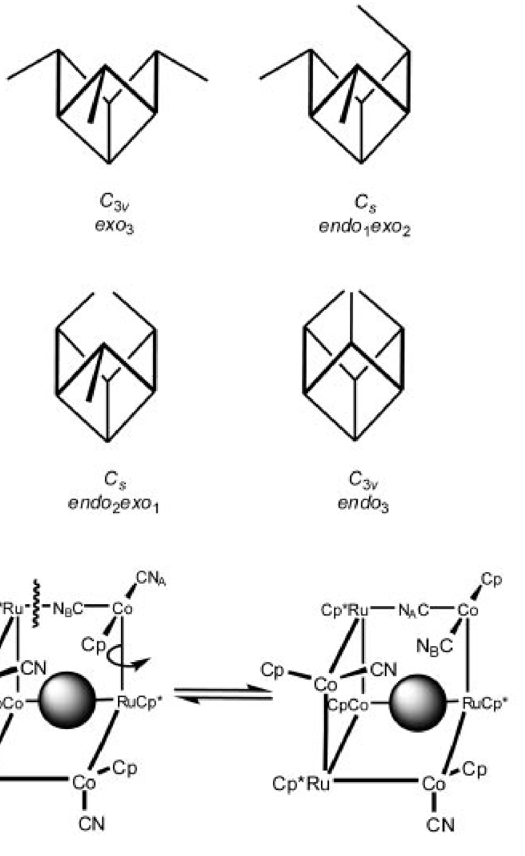


Scheme 1. Box-completion reactions of $Cs\subset Co_4Ru_3$ described in this report.

Results and Discussion

Solution Properties of the $Cs\subset Co_4Ru_3$ Metallo-Ligand



Scheme 2. Schematic depiction of isomers for the M_7 defect cages (top), and pathway that interconverts the two C_s isomers (bottom).

Prior to examining the complexation properties of $Cs\subset Co_4Ru_3$, we conducted experiments aimed at elucidating the solution behavior of this "defect box." Four isomers are possible, depending on the relative stereochemistry of the three $CpCo(CN)_3$ units situated on the "rim" (Scheme 2). Two C_s isomers are observed by ^1H NMR spectroscopy.[10] The interconversion of these two C_s isomers is hypothesized to occur through the scission of one Ru–N bond, rotation of the unidentate $[CpCo(CN)_3]^-$ subunit, and reformation of the Ru–N bond to a different cyano group of the same $[CpCo(CN)_3]^-$ subunit (Scheme 2).

The stereochemical nonrigidity of the rim $[CpCo(CN)_3]^-$ groups is indicated by the effect of solvent on the *endo*$_2$*exo*$_1$/*endo*$_1$*exo*$_2$ isomer ratio. In THF solution, the ratio is 3:1, whereas addition of 10% MeCN shifts this ratio to 9:1 (Figure 1). The presence of MeCN favors the C_s isomer with two *endo* CN_t ligands (see Scheme 2). Furthermore, small amount of MeCN cause the chemical shifts of the Cp signals to shift downfield, possibly due an apparent interaction of the Cp protons with the triple bond of the MeCN. The interaction between the MeCN protons and the cyanide linkers of the cage framework was previously indicated with the solid-state structure of $Cs\subset Co_4Ru_3$.[2]

Labeling studies provided further evidence that the $Cs\subset Co_4Ru_3$ cage undergoes partial disassembly in solution. Two Ru–N bonds must break to dissociate a "rim" $CpCo(CN)_3^-$ subunit. As monitored by ESI-MS, $Cs\subset Co_4Ru_3$ was shown to exchange with $K[(MeC_5H_4)Co(CN)_3]$ (Co′) to give $Cs\subset Co_{4-x}Co'_xRu_3$ over the course of days. Altering the amount of Co′ from one to four equiv. did not increase the rate vertex exchange, suggesting that vertex exchange is dissociative, being dependent only on $[Cs\subset Co_4Ru_3]$. In a similar experiment, we found that the

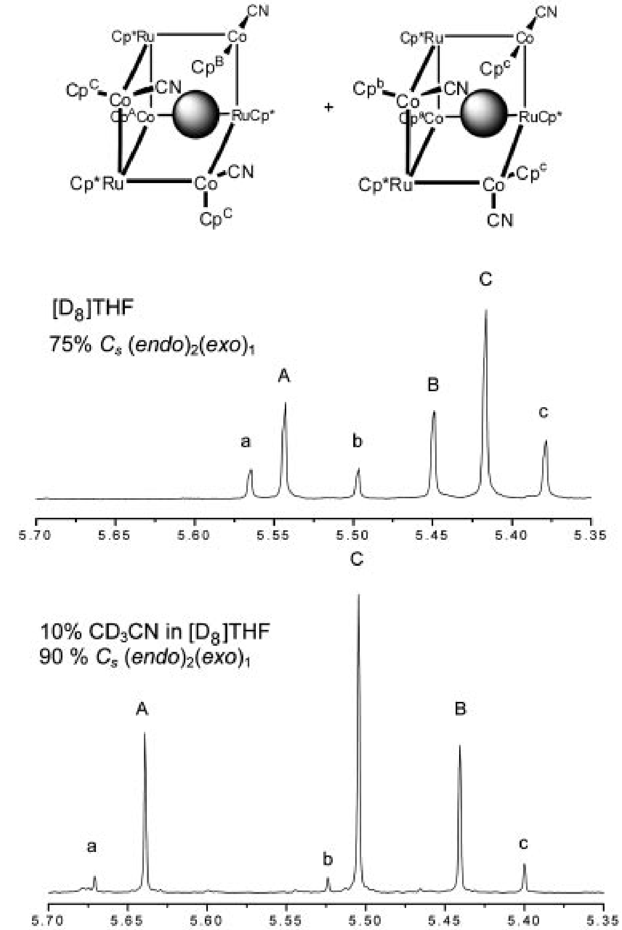


Figure 1. Schematic of the two detected isomers of $Cs\subset Co_4Ru_3$ (top), ^1H NMR spectra of $Cs\subset Co_4Ru_3$ in various solvents (bottom).

defect box $[CpCo(CN)_3]_4[Cp^*Rh]_3^{2+}$ ($Co_4Rh_3^{2+}$) underwent rapid exchange with Co′ to give $Co_{4-x}Co'_xRh_3^{2+}$ in under 5 h.

Treatment of a solution of $Cs\subset Co_4Ru_3$ with CO resulted in rapid degradation as indicated by the appearance of a ν_{CO} band at 1943 cm^{-1}. ESI-MS of the reaction mixture featured peaks corresponding to $\{[CpCo(CN)_3]_2[Cp^*Ru(CO)]_3\}^+$. We propose $\{[CpCo(CN)_3]_2[Cp^*Ru(CO)]_3\}^+$ is a trigonal-bipyramidal cage, other examples of which are known in cyanometalate chemistry.[12]

Further evidence for the mobility of the $CpCo(CN)_3^-$ vertices in $Cs\subset Co_4Ru_3$ came from vertex extraction reactions involving ammonium ions. Thus treatment of this cage with $PhNH_3OTf$ afforded the coordination polymer $PhNH_3CpCo(CN)_3$ [Equation (1)].

$$4\ Cs\subset Co_4Ru_3 + 4\ PhNH_3^+ \rightarrow 4\ PhNH_3CpCo(CN)_3 + 3\ [Cs\subset Co_4Ru_4]^+ + Cs^+ \qquad (1)$$

This polymeric species was independently synthesized by treating an MeCN solution of $PPN[CpCo(CN)_3]$ with $PhNH_3OTf$ ($PPN^+ = Ph_3PNPPh_3^+$). The yellow solid was soluble only in polar solvents, i.e. those expected to compete for hydrogen bonds. The polymer adopts a “folded tape” motif, constructed from strong hydrogen bonds connecting the acidic protons and the basic cyanide ligands (Figure 2). The ammonium cyanide distances (*N*···*N*C–Co) range from 2.747 to 2.999 Å indicating strong hydrogen bonds.[13]

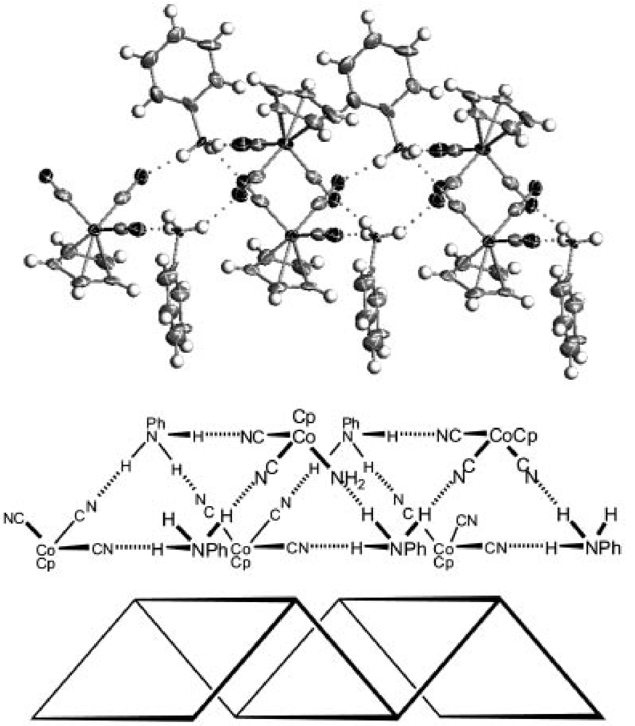


Figure 2. Structure of the hydrogen-bonded polymer $PhNH_3CpCo(CN)_3$ (top). Schematic illustrating the bonding in the tape polymer (bottom).

Although the defect box $Cs\subset Co_4Ru_3$ does undergo partial disassembly in solution, it displayed greater stability than the analogous $Co_4Rh_3^{2+}$, which lacks a centrally “gluing” Cs^+ center. The $Co_4Rh_3^{2+} + [Cp^*Ru(NCMe)_3]^+$ reaction afforded a mixture of $Co_4Rh_4^{4+}$, $Co_4Rh_3Ru^{3+}$, and $Co_4Rh_2Ru_2^{2+}$. These products, especially $Co_4Rh_4^{4+}$, indicate that the starting $Co_4Rh_3^{2+}$ disassembles followed by reassembly of $[Cp^*Rh(NCMe)_3]^{2+}$, $[Cp^*Ru(NCMe)_3]^+$, and $[CpCo(CN)_3]^-$ in a nearly statistical manner. Slightly different products are obtained when the $Co_4Rh_3^{2+} + [Cp^*Ru(NCMe)_3]^+$ reaction was conducted in the presence of Cs^+. Again, the main products are $Co_4Rh_4^{4+}$ and $Co_4Rh_3Ru^{3+}$, but we also obtained small amounts of $Cs\subset Co_4Rh_2Ru_2^{3+}$ and $Cs\subset Co_4Rh_3Ru^{4+}$. These latter two species are unprecedented examples of cationic receptors binding Cs^+. In contrast to the behavior of the Cs-free cages, $Cs\subset Co_4Ru_3$ remained intact upon complexation to $[Cp^*Rh(NCMe)_3]^{2+}$ to produce $Cs\subset Co_4Ru_3Rh^{2+}$ quantitatively.

Boxes with Lewis-Acidic Tetrahedral Vertices: Copper(I) and Silver(I)

Treatment of a MeCN solution of $[Cu(NCMe)_4]PF_6$ with a THF solution of $Cs\subset Co_4Ru_3$ at 0 °C gave red

$\{Cs\subset[CpCo(CN)_3]_4[Cp^*Ru]_3Cu(NCMe)\}PF_6$ ($[Cs\subset Co_4Ru_3Cu(NCMe)]PF_6$). The ^1H NMR spectrum confirmed the C_{3v} symmetry with two Cp resonances in a 3:1 ratio and single resonance for Cp*. The IR spectrum of $[Cs\subset Co_4Ru_3Cu(NCMe)]PF_6$ featured a single broad ν_{CN} band at 2144 cm^{-1}, which is higher in energy vs. ν_{CN} for the terminal cyanides of $Cs\subset Co_4Ru_3$ (2129 cm^{-1}). The ESI-MS of the product solution supported the formulation. The red-colored silver derivative $[Cs\subset Co_4Ru_3Ag(NCMe)]^+$ was prepared analogously from $AgPF_6$ and $Cs\subset Co_4Ru_3$.

The MeCN ligands in $[Cs\subset Co_4Ru_3M(NCMe)]^+$ (M = Ag, Cu) exchange readily. Treatment of these cages with PPh_3 yielded the expected adducts $[Cs\subset Co_4Ru_3MPPh_3]PF_6$, which were characterized spectroscopically. We attempted to generate higher nuclearity cyanometalates by exploiting the Lewis acidities of $[Cs\subset Co_4Ru_3M(NCMe)]^+$ by their condensation with $(18\text{-crown-}6\,K)_3[Co(CN)_6]$ or Et_4NCN. Such reactions only regenerated $Cs\subset Co_4Ru_3$, suggesting that the metallo-ligand $Cs\subset Co_4Ru_3$ is only weakly bound to the coinage metal.

Boxes with Lewis-Acidic Octahedral Vertices: Nickel

Condensation of $Cs\subset Co_4Ru_3$ with $[Ni(NCMe)_6](BF_4)_2$ gave the trimetallic cage $\{Cs[CpCo(CN)_3]_4[Cp^*Ru]_3Ni(NCMe)_3\}^{2+}$ ($[Cs\subset Co_4Ru_3Ni(NCMe)_3]^{2+}$). To prevent the generation of the $\{\{Cs[CpCo(CN)_3]_4[Cp^*Ru]_3\}_2Ni\}^{2+}$ by-product, the $Cs\subset Co_4Ru_3$ cage was added as an MeCN slurry to a concentrated solution of $[Ni(NCMe)_6](BF_4)_2$. The ^1H NMR spectrum of the red product indicated C_{3v} symmetry. The signals, especially those of the "rim" CpCo centers, are broadened due to their adjacency to the paramagnetic octahedral Ni^{II} center. The IR spectrum of $[Cs\subset Co_4Ru_3Ni(NCMe)_3](BF_4)_2$ featured a single broad ν_{CN} band at 2170 cm^{-1}; absent was the ν_{CNt} band at 2129 cm^{-1} for $Cs\subset Co_4Ru_3$. The ESI-MS of the product solution supported the formation of $[Cs\subset Co_4Ru_3Ni(NCMe)_3]^{2+}$ (m/z = 855); signals corresponding to $\{(Cs\subset Co_4Ru_3)_2Ni\}^{2+}$ were not detected. The metalation route enjoys some generality: a slurry of $Cs\subset Co_4Ru_3$ was found to react with $[Fe(NCMe)_6](PF_6)_2$ to afford $[Cs\subset Co_4Ru_3Fe(NCMe)_3](PF_6)_2$, which was identified by ESI-MS.

The MeCN ligands of $[Cs\subset Co_4Ru_3Ni(NCMe)_3]^{2+}$ exchange with a variety of Lewis bases. Qualitative tests using ESI-MS showed that 9-ane-S3 formed adducts (9-ane-S3 is 1,4,7-trithiacyclononane). Preparative-scale reaction gave the red crystalline species $[Cs\subset Co_4Ru_3Ni(9\text{-ane-S3})](BF_4)_2$, which was characterized crystallographically (see below).

Attempts were made to generate higher nuclearity cages by exploiting the Lewis acidity of $[Cs\subset Co_4Ru_3Ni(NCMe)_3]^{2+}$. Treatment of these cages, however, with $K[(C_5R_5)M(CN)_3]$ [$(C_5R_5)M$ = Cp*Rh, CpCo] or Et_4NCN generated the double box $\{(Cs\subset Co_4Ru_3)_2Ni\}^{2+}$, as indicated by ESI-MS analysis. Apparently, scission of the Ni–N(cage) bonds is facile. A sample $\{[Cs\subset Co_4Ru_3]_2Ni\}(BF_4)_2$ was generated independently by treatment of $Cs\subset Co_4Ru_3$ with 0.5 equiv. of $[Ni(NCMe)_6](BF_4)_2$ and characterized by ^1H NMR and IR spectroscopy, as well as ESI-MS.

Boxes Completed with Lewis-Acidic Octahedral Vertices: Ruthenium

The metallo-ligand $Cs\subset Co_4Ru_3$ was shown to bind a variety of ruthenium PPh_3 complexes. Thus, $RuCl_2(PPh_3)_3$ and $RuHCl(PPh_3)_3$ afforded the corresponding eight-vertex cages (Scheme 1). The ^1H NMR spectra of $[Cs\subset Co_4Ru_3Ru(PPh_3)_2Cl]Cl$ and $[Cs\subset Co_4Ru_3Ru(PPh_3)_2H]Cl$ are consistent with C_s symmetry (Figure 3). Treatment of $[Cs\subset Co_4Ru_3Ru(PPh_3)_2H]Cl$ with an MeCN solution of $AgPF_6$ gave $[Cs\subset Co_4Ru_3Ru(PPh_3)_2(NCMe)](PF_6)_2$, concomitant with formation of Ag. This MeCN-containing product was characterized by proton NMR spectroscopy and X-ray crystallography.

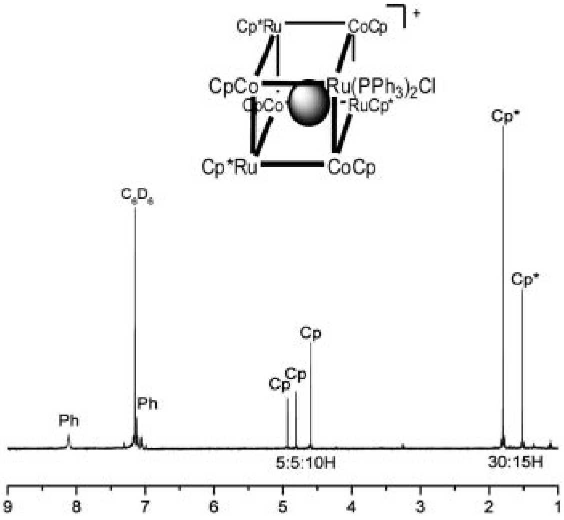


Figure 3. ^1H NMR spectrum of $\{Cs\subset[CpCo(CN)_3]_4[Cp^*Ru]_3[Ru(PPh_3)_2Cl]\}Cl$ in C_6D_6 solution.

A cage containing one $Ru(C_6H_6)^{2+}$ vertex was prepared from the reaction of $Cs\subset Co_4Ru_3$ and $[(C_6H_6)Ru(NCMe)_3](PF_6)_2$. Photolysis of $[Cs\subset Co_4Ru_3Ru(C_6H_6)](PF_6)_2$ was anticipated to afford the corresponding $[Ru(NCMe)_3]$ derivative, which would be promising building block. Unfortunately, photolysis of $[Cs\subset Co_4Ru_3Ru(C_6H_6)](PF_6)_2$ was a slow process. Only 30% conversion to $[Cs\subset Co_4Ru_3Ru(NCMe)_3](PF_6)_2$ was observed after four days.[14]

X-ray Crystallographic Results on New Molecular Boxes

Single crystal X-ray structure of $[Cs\subset Co_4Ru_3Ni(9\text{-ane-}S_3)](BF_4)_2$ confirmed the structure of the completed box. The $Cs\subset Co_4Ru_3$ subunit remains intact and binds the Ni(9-ane-S3) subunit in a tridentate fashion forming the trimetallic cube framework, analogous to previously reported completed boxes (Figure 4).[15] In the case of $[Cs\subset Co_4Ru_3Ru(PPh_3)_2(NCMe)](PF_6)_2$, the dicationic cage consists of a $Co_4Ru_4(\mu\text{-}CN)_{12}$ cube with a $Ru(PPh_3)_2(NCMe)^{2+}$ vertex and three Cp*Ru vertices. The cyanide linkages in both the

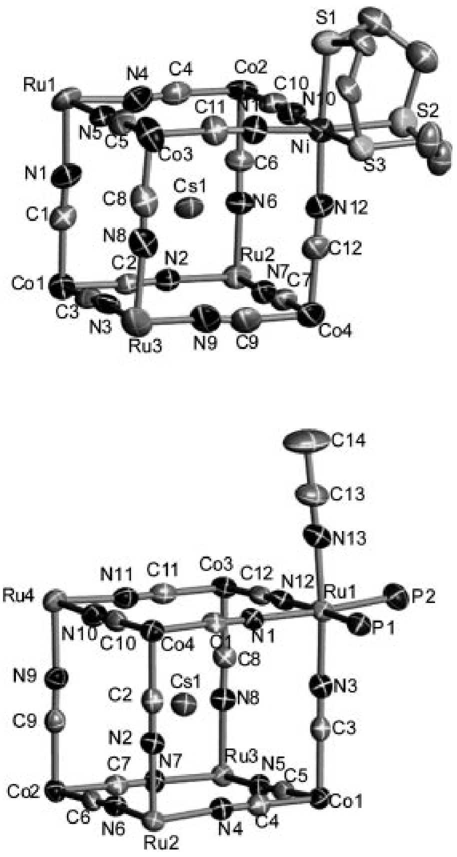


Figure 4. Molecular structures from left to right: $\{Cs\subset[CpCo(CN)_3]_4[Cp^*Ru]_3Ni(9\text{-ane-S3})\}(BF_4)_2$ and $\{Cs\subset[CpCo(CN)_3]_4[Cp^*Ru]_3[Ru(NCMe)(PPh_3)_2]\}(PF_6)_2$. Cp and Cp* rings, phenyl groups, and counterions were omitted for clarity. Thermal ellipsoids are set at the 50% level.

Table 1. Selected bond lengths [Å] and angles [°] for $[Cs\subset Co_4Ru_3Ni(9\text{-ane-S}_3)](BF_4)_2$.

Ni–N(10)	2.0035	N(10)–Ni–N(11)	93.97
Ni–N(11)	2.0786	N(10)–Ni–N(12)	93.68
Ni–N(12)	2.0005	N(11)–Ni–N(12)	92.33
Ru(2)–N(2)	2.0963	N(2)–Ru(2)–N(6)	88.10
Ru(2)–N(6)	2.0698	N(2)–Ru(2)–N(7)	85.53
Ru(2)–N(7)	2.0409	N(6)–Ru(2)–N(7)	83.34
Co(2)–C(4)	1.8224	C(4)–Co(2)–C(6)	88.27
Co(2)–C(6)	1.8830	C(4)–Co(2)–C(10)	92.99
Co(2)–C(10)	1.9023	C(6)–Co(2)–C(10)	87.48

Table 2. Selected bond lengths [Å] and angles [°] for $\{Cs\subset[CpCo(CN)_3]_4[Cp^*Ru]_3[Ru(NCMe)(PPh_3)_2]\}(PF_6)_2$.

Ru(2)–N(2)	2.0920	N(2)–Ru(2)–N(4)	85.72
Ru(2)–N(4)	2.0954	N(2)–Ru(2)–N(6)	85.81
Ru(2)–N(6)	2.0829	N(4)–Ru(2)–N(6)	87.81
Co(1)–C(3)	1.8644	C(3)–Co(1)–C(4)	91.23
Co(1)–C(4)	1.8833	C(3)–Co(1)–C(5)	92.62
Co(1)–C(5)	1.8739	C(4)–Co(1)–C(5)	89.96
Ru(1)–N(1)	2.0841	N(1)–Ru(1)–N(3)	88.49
Ru(1)–N(3)	2.0423	N(1)–Ru(1)–N(12)	86.94
Ru(1)–N(12)	2.0781	N(3)–Ru(1)–N(12)	87.22
Ru(1)–N(13)	2.0841		
Ru(1)–P(1)	2.3403		
Ru(1)–P(2)	2.3475		

$[Cs\subset Co_4Ru_3Ni(9\text{-ane-S}_3)](BF_4)_2$ and $[Cs\subset Co_4Ru_3Ru(PPh_3)_2(NCMe)](PF_6)_2$ cages are ordered, as indicated by characteristically short Co-C distances. The cage frameworks conform well to the geometry of a cube with ca. 90° N–M–N and C–M–C angles (Table 1 and Table 2).

Conclusions

The cage $Cs\subset Co_4Ru_3$ is a versatile metallo-ligand, despite its stereochemical complications. Neither of the two isomers of this cage are poised to serve as a tridentate ligand: reorientation of the terminal cyanide ligands is required. Metalation of $Cs\subset Co_4Ru_3$ is complete upon addition of the electrophile. The isomerization of the terminal cyanides would appear to require the scission of at least one intra-cage Ru–NC–Co linkage, which allows it to exchange sites with the terminal cyanide ligand. Various chemical tests – cage degradation with CO and $PhNH_3^+$, as well as quasi-degenerate exchange reactions – show that vertex exchange occurs, however, more slowly than complexation.

The metallo-ligand $Cs\subset Co_4Ru_3$ exhibits exceptional affinity for binding to diverse metal centers. This work substantially extends this range to include a range of metal centers that bear reactive ligands. We show that these site-differentiated cages can undergo selective substitution reactions without disruption of the $M_8(\mu\text{-CN})_{12}$ framework. It appears that this first generation of reactive cages are insufficiently robust, so further work is merited on the design of new cyanometalate cage-ligands. The $Cs\subset Co_4Ru_3$ ligand functions as a facially capping tridentate ligand akin to tris(pyrazolyl)borate (Tp) and triazacyclononane (TACN). Complexes of the type Tp_2M^z and $(TACN)_2M^z$ are common, whereas the half-sandwich complexes are rarer.[16]

Experimental Section

Reactions and manipulations were performed under nitrogen, using standard Schlenk-line techniques. Solvents were dried and deoxygenated prior to use $K(MeC_5H_4)Co(CN)_3$,[17] $[Cu(NCMe)_4]PF_6$,[18] $[Ni(NCMe)_6](BF_4)_2$,[19] $[Fe(NCMe)_6](PF_6)_2$,[20] $Ru(PPh_3)_3Cl_2$,[21] $[(C_6H_6)Ru(NCMe)_3](PF_6)_2$[22] and $\{Cs\subset[CpCo(CN)_3]_4[Cp^*Ru]_3\}$[10] were prepared according to literature methods. Elemental analyses were conducted by the School of Chemical Sciences Microanalytical Laboratory. ^1H and ^{31}P NMR spectra were acquired with Varian Unity 400 and 500. Electrospray ionization-mass spectra (ESI-MS) and MS-MS measurements were acquired with a Micromass Quattro QHQ quadrupole-hexapole-quadrupole instrument. Infrared spectra were obtained with a Mattson Galaxy Series FT-IR 3000 on pressed KBr pellets.

Crystallography: Crystals were mounted to a thin glass fiber using oil (Paratone-N, Exxon). Data were filtered to remove statistical outliers. The integration software (SAINT) was used to test for crystal decay as a bilinear function of X-ray exposure time and sine (θ). Data were collected with a Siemens Platform/CCD automated diffractometer. Crystal and refinement details are given in supplementary material. The structures were solved using SHELXTL by direct methods; correct atomic positions were deduced from an E map or by an unweighted difference Fourier synthesis. H atom U values were assigned as 1.2 times the U_{eq} values of adjacent C atoms. Non-H atoms were refined with anisotropic thermal coefficients. Successful convergence of the full-matrix least-squares refinement of F^2 was indicated by the maximum shift/error for the last cycle.

CCDC-632474 for $\{Cs\subset[CpCo(CN)_3]_4[Cp^*Ru]_3Ni(9\text{-}ane\text{-}S3)\}(BF_4)_2$, -632475 for $PhNH_3CpCo(CN)_3$, and -632476 for $\{Cs\subset[CpCo(CN)_3]_4[Cp^*Ru]_3Ru(NCMe)(PPh_3)_2\}(PF_6)_2)$ contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre at www.ccdc.cam.ac.uk/data_request/cif.

^{1}H NMR Properties of $Cs\subset Co_4Ru_3$: *THF (Cp signals only)*: δ = 5.43 [s, 10 H, Cp, for $(endo)_2(exo)_1$], 5.45 [s, 5 H, Cp, for $(endo)_2(exo)_1$], 5.59 [s, 5 H, Cp, for $(endo)_2(exo)_1$], 5.38 [s, 10 H, Cp, for $(endo)_1(exo)_2$], 5.50 [s, 5 H, Cp, for $(endo)_1(exo)_2$], 5.62 [s, 5 H, Cp, for $(endo)_1(exo)_2$] ppm. *THF/MeCN, 9:1 (Cp signals only)*: δ = 5.51 [s, 10 H, Cp, for $(endo)_2(exo)_1$], 5.44 [s, 5 H, Cp, for $(endo)_2(exo)_1$], 5.64 [s, 5 H, Cp, for $(endo)_2(exo)_1$], 5.40 [s, 10 H, Cp, for $(endo)_1(exo)_2$], 5.53 [s, 5 H, Cp, for $(endo)_1(exo)_2$], 5.67 [s, 5 H, Cp, for $(endo)_1(exo)_2$] ppm.

Vertex Exchange in $Cs\subset Co_4Ru_3$: A mixture of $K[MeC_5H_4Co(CN)_3]$ (20.5 mg, 0.08 mmol) and $Cs\subset[CpCo(CN)_3]_4[Cp^*Ru]_3$ (33 mg, 0.02 mmol) was stirred in MeCN (5 mL) and THF (5 mL) for 5 h. A 0.1-mL sample of reaction mixture was diluted with 3 mL MeCN/THF (1:1) and analyzed by ESI-MS over the course of 96 h.

43 h: *m/z* (%) = 1678 (100) $[\{Cs[CpCo(CN)_3]_2[MeC_5H_4Co(CN)_3]_2[Cp^*Ru]_3\}^+]$.

67 h: *m/z* (%) = 1678 (74) $[\{Cs[CpCo(CN)_3]_2[MeC_5H_4Co(CN)_3]_2[Cp^*Ru]_3\}^+]$, 1692 (100) $[\{Cs[CpCo(CN)_3][MeC_5H_4Co(CN)_3]_3[Cp^*Ru]_3\}^+]$ and 1706 (28) $[\{Cs[MeC_5H_4Co(CN)_3]_4[Cp^*Ru]_3\}^+]$.

96 h: *m/z* (%) = 1678 (56) $[\{Cs[CpCo(CN)_3]_2[MeC_5H_4Co(CN)_3]_2[Cp^*Ru]_3\}^+]$, 1692 (100) $[\{Cs[CpCo(CN)_3][MeC_5H_4Co(CN)_3]_3[Cp^*Ru]_3\}^+]$ and 1706 (52) $[\{Cs[MeC_5H_4Co(CN)_3]_4[Cp^*Ru]_3\}^+]$.

Vertex Exchange in $Co_4Rh_3^{2+}$: A mixture of $PPN[MeC_5H_4Co(CN)_3]$ (59.8 mg, 0.08 mmol) and $\{[CpCo(CN)_3]_4[Cp^*Rh]_3\}(PF_6)_2$ (35.9 mg, 0.02 mmol) was stirred in MeCN (10 mL) for 5 h. A 0.1-mL sample of the reaction mixture was diluted with 3 mL MeCN and analyzed by ESI-MS.

5 h: *m/z* (%) = 761 $[\{[CpCo(CN)_3]_4[Cp^*Rh]_3\}^{2+}]$, 768 $[\{[CpCo(CN)_3]_3[MeC_5H_4Co(CN)_3][Cp^*Rh]_3\}^{2+}]$, 775 $[\{[CpCo(CN)_3]_2[MeC_5H_4Co(CN)_3]_2[Cp^*Rh]_3\}^{2+}]$, 782 $[\{[CpCo(CN)_3][MeC_5H_4Co(CN)_3]_3[Cp^*Rh]_3\}^{2+}]$, 789 $[\{[MeC_5H_4Co(CN)_3]_4[Cp^*Rh]_3\}^{2+}]$.

Degradation of $Cs\subset Co_4Ru_3$ with CO: A solution of $Cs\subset[CpCo(CN)_3]_4[Cp^*Ru]_3$ (50.3 mg, 0.031 mmol) in CH_2Cl_2 (20 mL) was purged with CO for 7 h. The solvent was then removed in vacuo and the red residue was extracted into MeCN and CH_2Cl_2 and analyzed by mass spectrometry and IR spectroscopy, respectively ESI-MS: (*m/z*) = 1198 $[\{[CpCo(CN)_3]_2[Cp^*RuCO]_3\}^+]$. IR ($CH_2Cl_2$): $\tilde{\nu}$ = 1947 (ν_{CO}), 2165 (ν_{CN}), 2126 cm^{-1}.

Degradation with $PhNH_3^+$. Generation of $PhNH_3CpCo(CN)_3$: A THF stock solution of $PhNH_3OTf$ (1 mL, 0.004 mM) was added to 7.4 mg (0.004 mmol) of $Cs\subset[CpCo(CN)_3]_4[Cp^*Ru]_3$. After 7 d, a yellow-colored precipitate, $PhNH_3[CpCo(CN)_3]$, formed. This species was independently prepared by addition of a solution of $PhNH_3OTf$ (97.2 mg, 0.4 mmol) in MeCN (50 mL) to a solution of $PPN[CpCo(CN)_3]$ (294.7 mg, 0.4 mmol) in MeCN (20 mL) to afford yellow microcrystals. Yield: 0.0761 g (64%). IR (KBr): $\tilde{\nu}$ = 2129 (ν_{CN}) cm^{-1}, 2603 (ν_{NH}) cm^{-1}. $C_{14}H_{13}CoN_4$ (296.05): calcd. C 56.75, H 4.43, N 18.92; found C 56.38, H 4.36, N 18.53. The salt was insoluble in acetone, CH_2Cl_2, THF, MeCN but dissolved in EtOH and DMSO. Single crystals were grown by vapor diffusion of Et_2O into an EtOH solution.

$\{Cs\subset[CpCo(CN)_3]_4[Cp^*Ru]_3[Cu(NCMe)]\}PF_6$, $[Cs\subset Co_4Ru_3Cu(NCMe)]PF_6$: A solution of $Cs\subset[CpCo(CN)_3]_4[Cp^*Ru]_3$ (413 mg, 0.25 mmol) in THF (30 mL) was added dropwise to a stirred solution of $[Cu(MeCN)_4]PF_6$ (93 mg, 0.25 mmol) in MeCN (15 mL) at 0 °C over 1 h. The resulting dark red solution was stirred for 5 h, and the solvent was removed under vacuum. Yield: 394 mg (83%). ^{1}H NMR (CD_3CN): δ = 1.68 (s, 45 H, Cp*), 5.53 (s, 15 H, Cp), 5.60 (s, 5 H, Cp) ppm. ESI-MS: *m/z* = 1714 [M$^+$ – MeCN]. IR (KBr): $\tilde{\nu}$ = 2144 (ν_{CN}) cm^{-1}. $C_{64}H_{68}Co_4CsCuF_6N_{13}PRu_3$ (1898.94): calcd. C 40.46, H 3.61, N 9.59; found C 40.93, H 3.75, N 10.07.

$\{Cs\subset[CpCo(CN)_3]_4[Cp^*Ru]_3Cu(PPh_3)\}PF_6$, $[CsCo_4Ru_3Cu(PPh_3)]PF_6$: An MeCN stock solution of PPh_3 (1 mL, 0.0012 mM) was added dropwise to a stirred solution of $[Cs\subset Co_4Ru_3Cu(NCMe)]PF_6$ (2.2 mg, 0.0012 mmol) in MeCN (5 mL). ^{1}H NMR (CD_3CN): δ = 1.68 (s, 45 H), 5.51 (s, 15 H), 5.61 (s, 5 H), 7.55 (m, 15 H) ppm. ^{31}P NMR (CD_3CN): δ = 21.89 ppm. ESI-MS: *m/z* = 1977 $[\{Cs[CpCo(CN)_3]_4[Cp^*Ru]_3[CuPPh_3]\}^+]$.

$\{Cs\subset[CpCo(CN)_3]_4[Cp^*Ru]_3Ag(NCMe)\}PF_6$, $[Cs\subset Co_4Ru_3Ag(NCMe)]PF_6$: A solution of $AgPF_6$ (33.4 mg, 0.13 mmol) in MeCN (10 mL) was added dropwise to a slurry of $Cs\subset Co_4Ru_3$ (218 mg, 0.13 mmol) in MeCN (15 mL) at 0 °C. The deep red solution was warmed to room temperature. After stirring for 1 h, the solvent was evaporated. Yield: 87% (220 mg). ^{1}H NMR (CD_3CN): δ = 1.68 (s, 45 H, Cp*), 1.96 (s, 3 H, MeCN), 5.54 (s, 15 H, Cp), 5.62 (s, 5 H, Cp) ppm. ESI-MS: *m/z* = 1758 $[\{Cs[CpCo(CN)_3]_4[Cp^*Ru]_3Ag\}^+]$. IR (KBr): $\tilde{\nu}$ = 2141 (ν_{CN}) cm^{-1}. $C_{64}H_{68}AgCo_4CsN_{13}F_6PRu_3$ (1943.26): calcd. C 39.52, H 3.53, N 9.37; found C 39.13, H 3.55, N 9.60.

$\{Cs\subset[CpCo(CN)_3]_4[Cp^*Ru]_3Ag(PPh_3)\}PF_6$, $[Cs\subset Co_4Ru_3Ag(PPh_3)]PF_6$: A solution of PPh_3 (12.8 mg, 0.05 mmol) in MeCN (10 mL) was added dropwise to a stirred solution of $[Cs\subset Co_4Ru_3Ag(NCMe)]PF_6$ (95.2 mg, 0.05 mmol) in MeCN (20 mL). The solvent was removed under vacuum. ^{1}H NMR (CD_3CN): δ = 1.68 (s, 45 H, Cp*), 5.51 (s, 15 H, Cp), 5.62 (s, 5 H, Cp), 7.54–7.53 (m, 15 H, Ph) ppm. ^{31}P NMR (CD_3CN): δ = 10.7 [d, ^1J(P, ^{107}Ag) = 577 Hz], 10.70 [d, ^1J(P, ^{109}Ag) = 651.9 Hz] ppm. ESI-MS: *m/z* = 2021 $[\{Cs[CpCo(CN)_3]_4[Cp^*Ru]_3AgPPh_3\}^+]$.

$\{Cs\subset[CpCo(CN)_3]_4[Cp^*Ru]_3Ni(NCMe)_3\}(BF_4)_2$, $[Cs\subset Co_4Ru_3Ni(NCMe)_3](BF_4)_2$: A slurry of $Cs\subset Co_4Ru_3$ (224 mg, 0.14 mmol) in MeCN (90 mL) was added dropwise to a solution of $[Ni(NCMe)_6](BF_4)_2$ (65.2 mg, 0.14 mmol) in MeCN (10 mL) at 0 °C. The deep red solution was warmed to room temperature. After stirring for 1 h, the solvent was removed in vacuo. Yield: 227 mg (85%). ^{1}H NMR (CD_3CN): δ = 1.70 (s, 45 H, Cp*), 1.96 (s, 9 H, MeCN), 4.99 (br. s, 15 H, Cp), 5.63 (s, 5 H, Cp) ppm. IR (KBr): $\tilde{\nu}$ = 2170 (ν_{CN}) cm^{-1}. ESI-MS: *m/z* = 855 $[\{Cs[CpCo(CN)_3]_4[Cp^*Ru]_3Ni\}^{2+}]$, 1796 $[\{Cs[CpCo(CN)_3]_4[Cp^*Ru]_3Ni\}BF_4^+]$. $C_{68}H_{74}B_2Co_4CsF_8N_{15}NiRu_3$ (2005.16): calcd. C 40.69, H 3.72, N 10.48; found C 41.05, H 3.96, N 10.77.

$[\{Cs\subset[CpCo(CN)_3]_4[Cp^*Ru]_3\}_2Ni](BF_4)_2$: A solution of $Cs\subset Co_4Ru_3$ (197.1 mg, 0.12 mmol) in CH_2Cl_2/MeCN (40 mL, 1:1) was treated with a solution of $[Ni(NCMe)_6](BF_4)_2$ (28.6 mg, 0.06 mmol) in MeCN (10 mL). The solvent was removed in vacuo. Yield: 169 mg (80%). ^{1}H NMR (CD_3CN): δ = 1.68 (s, 90 H, Cp*), 5.09 (br. s, 30 H, Cp), 5.62 (s, 10 H, Cp) ppm. ESI-MS: *m/z* = 1680 $[[\{Cs[CpCo(CN)_3]_4[Cp^*Ru]_3\}_2Ni]^{2+}]$. $C_{124}H_{130}B_2Co_{88}Cs_2N_{24}NiRu_6$ (3531.48): calcd. C 42.14, H 3.71, N, 9.52; found C 42.56, H 3.74, N 9.80.

$\{Cs\subset[CpCo(CN)_3]_4[Cp^*Ru]_3Fe(NCMe)_3\}(PF_6)_2$: A slurry of $Cs\subset Co_4Ru_3$ (168.5 mg, 0.1 mmol) in MeCN (70 mL) was added dropwise to a stirred solution of $[Fe(NCMe)_6](PF_6)_2$ (60.5 mg, 0.1 mmol) in MeCN (8 mL) at 0 °C. The deep red solution was warmed to room temperature. After a further 1 h, the solvent was removed in vacuo. Yield: 170 mg (80%). IR (KBr): $\tilde{\nu}$ = 2153 (ν_{CN}) cm^{-1}. ESI-MS: *m/z* = 854 $[\{Cs[CpCo(CN)_3]_4[Cp^*Ru]_3Fe\}^{2+}]$. $C_{68}H_{74}Co_4CsF_{12}FeN_{15}P_2Ru_3$ (2118.26): calcd. C 38.52, H, 3.52, N, 9.92; found C 39.03, H 3.56, N 9.81.

$\{Cs\subset[CpCo(CN)_3]_4[Cp^*Ru]_3Ni(9\text{-ane-S3})\}(BF_4)_2$, $[CsCo_4Ru_3Ni(9\text{-ane-S3})](BF_4)_2$: A solution of 9-ane-S3 (7.3 mg, 0.04 mmol) in MeCN (10 mL) was added to a solution of $[Cs\subset Co_4Ru_3Ni(NCMe)_3](BF_4)_2$ (81.5 mg, 0.04 mmol) in of MeCN (10 mL). The red solution was stirred for 1 h, and the solvent was removed in vacuo. ESI-MS: *m/z* = 945 $[\{Cs[CpCo(CN)_3]_4[Cp^*Ru]_3Ni(9\text{-ane-S3})\}^{2+}]$. Single crystals were grown by vapor diffusion of Et_2O into a CH_2Cl_2/acetone solution of $[Cs\subset Co_4Ru_3Ni(9\text{-ane-S3})](BF_4)_2$.

$\{Cs\subset[CpCo(CN)_3]_4[Cp^*Ru]_3RuCl(PPh_3)_2\}Cl$: A solution of $Cs\subset Co_4Ru_3$ (440 mg, 0.266 mmol) in THF (40 mL) was added dropwise to a stirred solution of $RuCl_2(PPh_3)_3$ (256 mg, 0.266 mmol) in THF (40 mL) at 0 °C over the course of 1 h. After stirring the resulting dark red solution for 16 h, the solvent was removed under vacuum. The residue was extracted with Et_2O (60 mL), and this extract was concentrated under vacuum. Addition of hexane gave a dark red solid. Yield: 390 mg (63%). ^1H NMR ($[D_8]$THF): δ = 1.69 (s, 15 H, Cp*), 1.73 (s, 30 H, Cp*), 4.83 (s, 5 H, Cp), 4.96 (s, 10 H, Cp), 5.54 (s, 5 H, Cp), 7.08 (m, 12 H, Ph), 7.45 (m, 6 H, Ph), 7.73 (m, 12 H, Ph) ppm. ESI-MS: *m/z* = 2312 $[M^+, (Cs\subset\{[CpCo(CN)_3]_4[Cp^*Ru]_3RuCl(PPh_3)_2\})^+]$. $C_{98}H_{95}Cl_2Co_4CsN_{12}P_2Ru_4$ (2345.56): calcd. C 50.16, H 4.08, N 7.16; found C 50.33, H 3.21, N 7.27.

$\{Cs\subset[CpCo(CN)_3]_4[Cp^*Ru]_3RuH(PPh_3)_2\}Cl$: A solution of $Cs\subset Co_4Ru_3$ (330 mg, 0.2 mmol) in THF (30 mL) was added dropwise to a stirred solution of $RuHCl(PPh_3)_3$ (185 mg, 0.2 mmol) in THF (30 mL) at 0 °C over the course of 1 h. After stirring the dark red solution for 16 h, it was concentrated under vacuum to ca. 10 mL. Addition of 50 mL of hexane gave a dark red precipitate, which was washed with hexane, dried under vacuum to give a dark red solid. Yield: 348 mg (75%). ^1H NMR (CD_3CN): δ = –15.24 (t, $J_{Ru\text{-}H}$ = 27 Hz, 1 H, Ru-H), 1.68 (s, 15 H, Cp*), 1.73 (s, 30 H, Cp*), 4.83 (s, 10 H, Cp), 5.01 (s, 5 H, Cp), 5.60 (s, 5 H, Cp), 7.20 (m, $J_{H\text{-}H}$ = 7 Hz, 12 H, Ph), 7.27 (m, $J_{H\text{-}H}$ = 7 Hz, 6 H, Ph), 7.52 (m, $J_{H\text{-}H}$ = 7 Hz, 12 H, Ph) ppm. ESI-MS: *m/z* = 2278 $[M^+, (Cs\subset\{[CpCo(CN)_3]_4[Cp^*Ru]_3RuH(PPh_3)_2\})^+]$. $C_{98}H_{96}ClCo_4CsN_{12}P_2Ru_4$ (2311.12): calcd. C 50.91, H, 4.18, N, 7.27; found C 51.03, H 4.23, N 8.62.

$\{Cs\subset[CpCo(CN)_3]_4[Cp^*Ru]_3Ru(NCMe)(PPh_3)_2\}(PF_6)_2$: A mixture of $\{Cs\subset[CpCo(CN)_3]_4[Cp^*Ru]_3RuH(PPh_3)_2\}Cl$ (46 mg, 0.02 mmol) and $AgPF_6$ (5 mg, 0.0.02 mmol) in THF (5 mL) was stirred overnight. After the solvent was removed under vacuum, the residue was extracted with MeCN (5 mL), which was concentrated to ca. 1 mL. Dilution of this extract with Et_2O (5 mL) gave a red-colored solid. The product was crystallized by dissolution in MeCN followed by the slow addition of Et_2O. Crystals were grown by liquid diffusion of diethyl ether into acetonitrile solution. ESI-MS: *m/z* = 1139 $[M^+, \{Cs\subset[CpCo(CN)_3]_4[Cp^*Ru]_3Ru(NCMe)(PPh_3)_2\}^{2+}]$.

$\{Cs\subset[CpCo(CN)_3]_4[Cp^*Ru]_3Ru(C_6H_6)\}(PF_6)_2$: A solution of $Cs\subset Co_4Ru_3$ (330 mg, 0.2 mmol) in THF (15 mL) was added dropwise to a solution of $[(C_6H_6)Ru(NCMe)_3](PF_6)_2$ (119 mg, 0.2 mmol) in MeCN (25 mL) at 0 °C over 1 h. After stirring for 16 h, the resulting dark red solution was evaporated. Yield: 340 mg (80%). ^1H NMR (CD_3CN): δ = 1.66 (s, 45 H, Cp*), 5.58 (s, 5 H, Cp), 5.73 (s, 15 H, Cp), 6.17 (s, 6 H, C_6H_6) ppm. ESI-MS: *m/z* = 915 $[M^{2+}, \{Cs\subset[CpCo(CN)_3]_4[Cp^*Ru]_3Ru(C_6H_6)\}^{2+}]$. $C_{98}H_{96}ClCo_4CsN_{12}P_2Ru_4\cdot CH_3CN\cdot Et_2O$: calcd. C 39.78, H 3.79, N 8.15; found C 40.42, H 3.64, N 8.36. A solution of $\{Cs\subset[CpCo(CN)_3]_4[Cp^*Ru]_3Ru(C_6H_6)\}(PF_6)_2$ (9 mg) in CD_3CN (0.7 mL) in a NMR tube was subjected to photolysis using a mercury lamp. After 96 h, the ESI-MS and NMR spectra of the reaction mixture showed a 30% conversion to $\{Cs\subset[CpCo(CN)_3]_4[Cp^*Ru]_3Ru(NCCD_3)_3\}(PF_6)_2$.

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