The Synthesis and Reactivity of Organometallic Cyanometallates

Stephen M. Contakes Final Seminar April 26, 2001

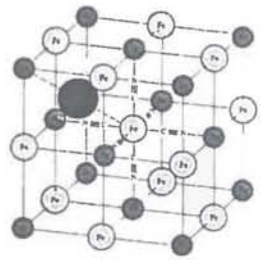
The synthesis of soluble cyanometallate cages is of interest in the context of providing molecular analogues of Prussian Blue and related solids[1-3] as well as for elucidating new structure types in cyanometallate chemistry.[4] The development of rational synthetic methods in this area of chemistry will serve to open this field to studies by other researchers. At the beginning of this work, one prominent review of cyanometallate chemistry characterized the rational synthesis of cyanometallate cages as follows:

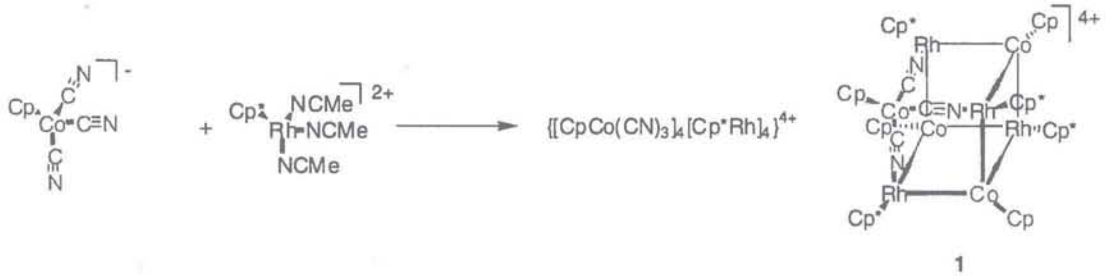
> "...the construction of cages requires trifunctional building blocks and a lot of luck. Cyanometal cages are known but more often three-dimensional polymers have been obtained. One cannot say at the moment how to design the right building blocks for cyanometal cages, but Mother Nature helps sometimes with the self-assembly."[5]

This talk will present several methods for the design of rational building blocks for and the synthesis of no less than five distinct types of cyanometal cages, all of which were unknown at the start of this project.

The synthesis of soluble ordered organometallic cyanometallate cages is analagous to the synthesis of Prussian Blue developed by Diesbach nearly three hundred years ago (Equation 1).[6,7] The precursors are modified by the addition of *fac*-capping organic end groups, such as Cp, Cp*, or 3 CO ligands, to octahedral cyanometallate precursors with kinetically inert M-CN bonds (Equation 2).[8] The face capping ligands inhibit the formation of three-dimensional networks. This is similar to the use of en ligands bound to Pd^{2+} ions in the synthesis of metal organic polygons and cages.[9]

$$4\,[Fe(CN)_6]^{2-} \quad + \quad 3\,Fe^{3+} \longrightarrow Fe_3[Fe(CN)_6]_4 \qquad (1)$$





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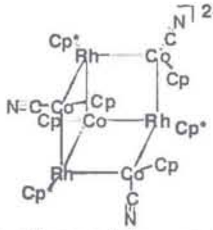
Cages prepared using this method possess ordered m-CN linkages and contain square faces.[3,10,11] If the synthesis in equation 2 is modified so that $CpCo(CN)_3^-$ and $Cp^*Rh(NCMe)_3^{2+}$ are combined in a 4:3 ratio the "defect box" $\{[CpCo(CN)_3]_4[Cp^*Rh]_3\}^{2+}$ (**2**) with a $Co_4Rh_3(CN)_{12}$ framework is obtained (Scheme 1).

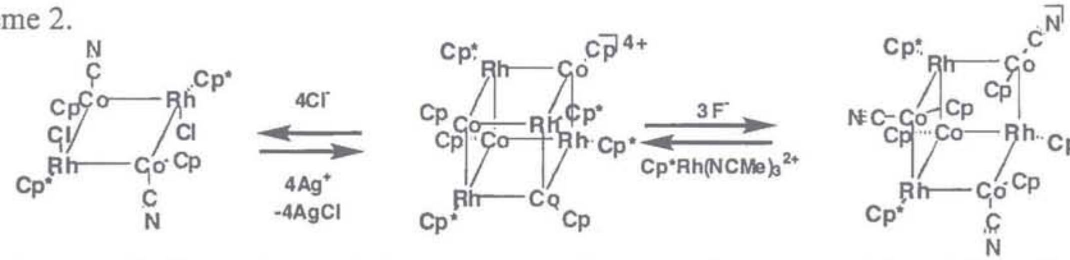
This can be converted to **1** by addition of one equivalent of $[Cp^*Rh(CNMe)_3]^{2+}$. The reverse reaction of **2** with 1.33 equiv of $[CpCo(CN)_3]^-$ does not occur.

Scheme 1.



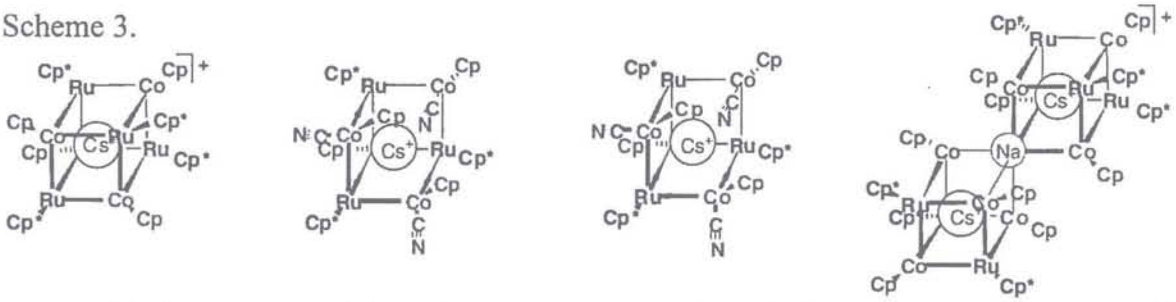
The M-NC bonds in these cages can be cleaved by nucleophiles such as Cl^-, F^-, CN^- to give a variety of products as shown in Scheme 2.

Scheme 2.



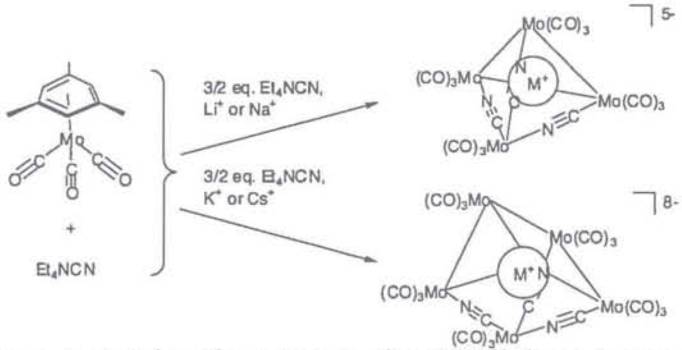
A variety of alkali metal containing cyanometallates can be prepared by adding alkali metal salts to the reaction mixture, as has previously been done for anionic boxes.[11] The most stable boxes and defect boxes of this type contain Cs^+ ion. Favorable CN-Cs interactions in these species allow for the synthesis of a variety of defect box isomers and the double box, $[Na\{Cs\subset[CpCo(CN)_3]_4[Cp^*Ru]_3\}_2]^+$, as shown in Scheme 3.

Scheme 3.



Alkali-metal containing trigonal prismatic and tetrahedral cyanometallate cages of formula $\{M\subset[Mo(CO)_3]_x(CN)_{1.5x}\}^{(1.5x-1)-}$ were prepared in a multicomponent synthesis involving mixing the an alkali metal salt, (mesitylene)$Mo(CO)_3$, and Et_4NCN in the appropriate ratio as shown in Scheme 4.[12,13]

Scheme 4.



The cages were shown to consist of a mixture of m-CN linkage isomers using ^{13}C NMR spectroscopy. The size of the cage is determined by the size of the alkali metal cation:

trigonal prismatic cages are obtained with Cs^+ and K^+ and tetrahedral cages are obtained with Na^+ and Li^+. The tetrahedral cages can be converted to trigonal prismatic cages by addition of Cs^+ or K^+.

In an attempt to prepare edge expanded cyanometallate boxes, $Cp^*M(CN)_3^-$ (M = Rh, Ir) was allwed to react with ditopic and tritopic Lewis acids such as $Rh_2(O_2CCX_3)_4$ (X = H, F), $Ni(en)_2^{2+}$, H_3O^+ and Ag^+. These reactions resulted in the formation of 1-D, 2-D, and 3-D coordination solids.[14,15]

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