

Synthesis and characterization of the hexagonal prismatic cage $\{ \text{THF} \subset [\text{PhB}(\text{CN})_3]_6 [\text{Cp}^* \text{Rh}]_6 \}^{6+}$

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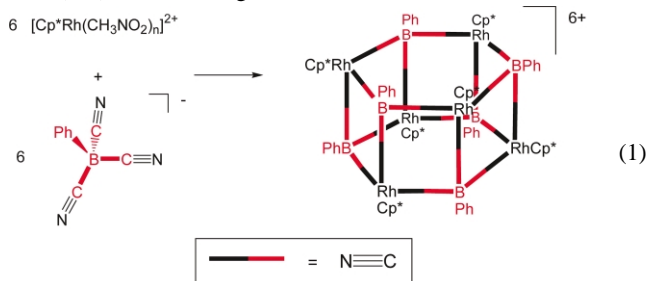
Condensation of $[\text{Cp}^* \text{Rh}(\text{CH}_3\text{NO}_2)_n]^{2+}$ and the tricyanoborate $[\text{PhB}(\text{CN})_3]^-$ affords the hexagonal bipyramidal cage $\{ [\text{PhB}(\text{CN})_3]_6 [\text{Cp}^* \text{Rh}]_6 \}^{6+}$, demonstrating that tetrahedral tricyanide building blocks can lead to novel cage structures.

Cages based on coordination frameworks with substantial interior volumes are of topical interest for their potential in host-guest behavior.^{1–5} The continuing, critical requirement in this area is for predictable synthetic routes, and key here are modular precursors – sometimes called tectons or building blocks that have geometrically well-defined bridging tendencies.^{6–8} Through systematic modification of these subunits, one can optimize conditions that favor cage formation. Within this context, cyanide has long been recognized as a particularly useful linking group, and cyanometallates are useful building blocks for the synthesis of polymeric coordination solids. These binary cyanometallates have not proven suitable for the synthesis of molecular cages, but related mixed-ligand tricyanometallates are reliable precursors to molecular cages,^{9–11} some of which exhibit highly selective host-guest behavior.^{12,13} Characteristically, the tricyanometallate approach gives rise to cuboidal or box-like cages (Scheme 1). The box-like structures are a natural consequence of the $\sim 90^\circ$ NC–M–CN angles in the tricyanometallates. In an effort to develop new families of cyanometallate cages, we sought tricyano building blocks where the NC–M–CN angles are $> 90^\circ$. Preliminary results described below demonstrate the promise of this approach.

Our attention was drawn to the recently reported coordination solid $\{ \text{Ag}[\text{FB}(\text{CN})_3] \}$, formed serendipitously *via* the reaction of AgNO_3 , NaF, and $\text{K}[\text{B}(\text{CN})_4]$.¹⁴ In our initial approach we examined the reaction of $[\text{Cp}^* \text{Rh}(\text{NCMe})_3]^{2+}$ with $\text{HB}(\text{CN})_3^-$,¹⁵ which gave the adduct $[\text{H}(\text{CN})_2\text{BCN}–\text{RhCp}^*(\text{NCMe})_2]^{2+}$ characterized by ESI-MS (molecular ions for $[\text{H}(\text{CN})_2\text{B}–\text{CN}–\text{RhCp}^*(\text{NCMe})_x]^{2+}$, where $x = 0, 1, 2$). The inability of the cyanoborate to compete with the MeCN solvent encouraged us to modify the tricyanoborate and to avoid coordinating solvents. To this end we prepared the new cyanoborate $[\text{K}(18\text{-c-6})][\text{PhB}(\text{CN})_3]$, *via* the reaction of PhBCl_2 and three equiv. of $[\text{K}(18\text{-crown-6})]\text{CN}$ in THF solution. This air stable, colorless salt was obtained in analytically pure form after chromatographic purification on alumina and was further characterized by ESI-MS, ^1H , and

^{11}B NMR spectroscopy. Preliminary studies suggest that numerous cyanoborate ligands can be prepared analogously.

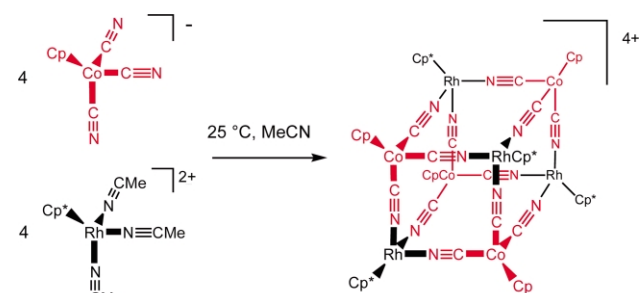
The reaction of $[\text{PhB}(\text{CN})_3]^-$ and MeNO_2 solutions of $[\text{Cp}^* \text{Rh}(\text{CH}_3\text{NO}_2)_n]^{2+}$ (generated *in situ* from four equiv. AgOTf and $\text{Cp}^* \text{Rh}_2\text{Cl}_4$) afforded a single major product, **1** (eqn. (1)). The ^1H NMR spectrum consisted of one Cp^* signal as well as one set of multiplets for the phenyl region, with Ph/ Cp^* ratio $\sim 1 : 1$. ESI-MS analysis of fresh CH_3NO_2 solutions indicated that **1** (404 m/z) undergoes fragmentation to numerous $[\text{PhB}(\text{CN})_3]_x[\text{Cp}^* \text{Rh}]_y^{z+}$ species such as $[\text{PhB}(\text{CN})_3]_6[\text{Cp}^* \text{Rh}]_5^{4+}$ (547 m/z), $[\text{PhB}(\text{CN})_3]_4[\text{Cp}^* \text{Rh}]_3^{2+}$ (689 m/z), and $[\text{PhB}(\text{CN})_3]_6[\text{Cp}^* \text{Rh}]_4^{2+}$ (974 m/z) although solvento adducts (*e.g.*, $\{ \text{PhB}(\text{CN})_3 : \text{RhCp}^*(\text{NCMe})_x \}^+$) were not observed. The IR spectrum of **1** revealed ν_{CN} at 2253 and 2207 cm^{-1} , *vs.* 2134 cm^{-1} for $[\text{PhB}(\text{CN})_3]^-$, indicating all three CN units are coordinated.



The aforementioned data support the formation of a cage but it remained unclear if in fact the cage structure was cuboidal. X-ray crystallographic analysis on crystals obtained from THF– MeNO_2 established that **1** consists of the hexacationic cage $\{ [\text{PhB}(\text{CN})_3]_6 [\text{Cp}^* \text{Rh}]_6 \}^{6+}$ (Fig. 1)†. The $\text{Rh}_6\text{B}_6(\text{CN})_{18}$ framework in **1** is hexagonal prismatic. Two 18-membered $\text{Rh}_3\text{B}_3(\text{CN})_6$ rings are inter-connected by six cyanides. The resulting cage has idealized D_{3d} symmetry. The structural results explain the observation of two bands for ν_{CN} , 12 of the cyanide ligands form the hexagonal faces and the other six cyanides connect the two hexagonal faces. The edge dimension (B–C–N–Rh) of the hexagonal prism is 4.8 \AA yielding a volume of 287 \AA^3 , whereas the free volume or van der Waals' volume of the hexagonal prism is calculated (Cerius² version 4.9) at 173 \AA^3 , considerably large than our previously described molecular boxes¹¹ (free volume of *ca.* 57 \AA^3).

Both NMR spectroscopy and crystallography indicate the presence of a molecule of THF at the interior of the cage, which demonstrates its considerable volume. We have verified by ^1H NMR spectroscopy that THF can be removed from crystalline **1** in vacuum; space-filling models suggests the THF can easily escape through the hexagonal face (Fig. 2). THF is not however required for the formation of the cage, **1** can be synthesized in neat MeNO_2 solution.

Hexagonal prisms are ideally composed of 90° and 120° angles, whereas the molecular building blocks feature 90° (N–Rh–N) and 109° (C–B–C) angles. The resulting strain is accommodated in a number of ways. A slight chair-like ruffling of the two $\text{Rh}_3\text{B}_3(\text{CN})_6$ hexagons results in diamondoid distortions of the four-sided $\text{Rh}_2\text{B}_2(\text{CN})_4$ rings (Fig. 1B.). The angles of C–B–C and N–Rh–N that compose the hexagonal face have values typical for tetrahedral and octahedral geometries, $109\text{--}106^\circ$ and $93\text{--}85^\circ$, respectively, *vs.*



Scheme 1

† Electronic supplementary information (ESI) available: experimental details for syntheses and crystallographic analyses. See <http://www.rsc.org/suppdata/cc/b4/b401505c/>

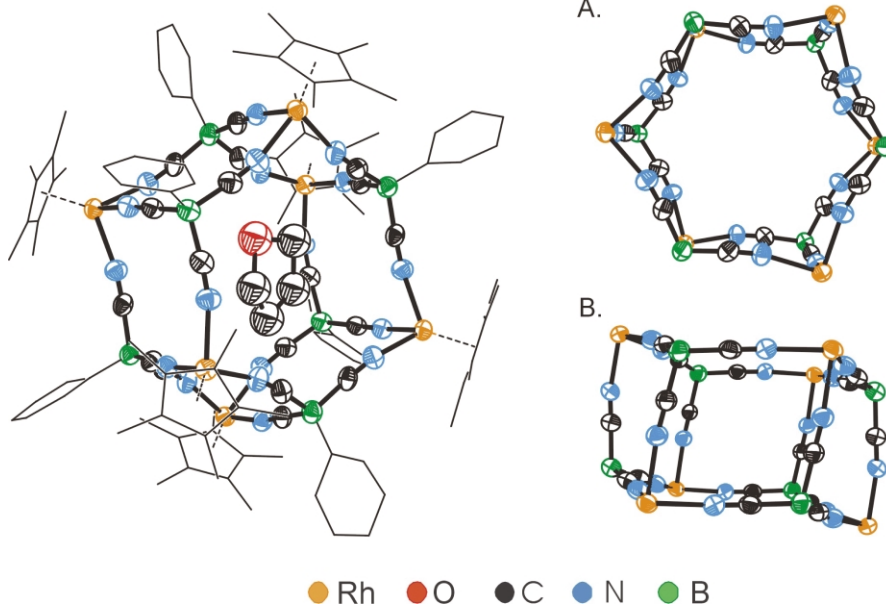


Fig. 1 Molecular structure of the cation in $\{\text{THFC}[\text{PhB}(\text{CN})_3]_6[\text{Cp}^*\text{Rh}]_6\}(\text{OTf})_6$ and two perspectives of the inorganic framework. Thermal ellipsoids are drawn at the 50% level.

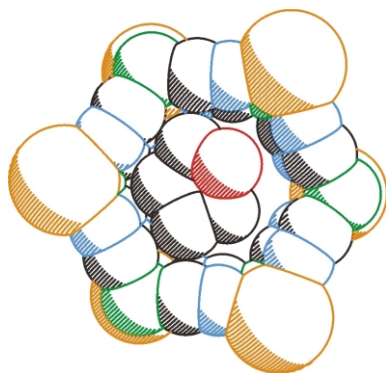


Fig. 2 Space-filling model of $\{\text{THFC}[\text{PhB}(\text{CN})_3]_6[\text{Cp}^*\text{Rh}]_6\}(\text{OTf})_6$. The hydrocarbon ligands have been omitted.

120° for an idealized hexagon. The large difference is absorbed by distortions in the B–C–N and especially Rh–N–C angles, which are 175° and 167° , respectively. The B–CN and Rh–NC distances of 1.61 Å and 2.09 Å, respectively, are typical.

The present work demonstrates that tricyanometallate building blocks with C–M–C angles more open than 90° enable the formation of a new generation of molecular cages. The potential to vary the organic substituent in the organotricyano-borate building block lends further scope to this area.

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Notes and references

‡ Crystal data: for **1** (yellow hexagon prism $0.36 \times 0.20 \times 0.14$ mm): $\text{C}_{118}\text{H}_{128}\text{B}_6\text{N}_{18}\text{ORh}_6^6\text{OTf}\cdot\text{THF}$, $M = 3463.23$, trigonal, $a = 18.325(6)$,

$b = 18.325(6)$, $c = 13.871(9)$ Å, $V = 4034(3)$ Å³, $T = 193(2)$ K, space group $\text{P}\bar{3}\text{m}1$, $Z = 1$, $\mu(\text{MoK}\alpha)$, $\lambda = 0.71073$ Å, $\mu = 0.760$ mm⁻¹, 31922 data collected, 2741 unique ($R_{\text{int}} = 0.069$). Final $R_1 [I > 2\sigma(I)] = 0.0406$, wR_2 (all data) = 0.1362. CCDC 230644. See <http://www.rsc.org/suppdata/cc/b4/b401505c/> for crystallographic data in .cif or other electronic format.

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