

Synthesis of organometallic solids by protonation of $\text{Cp}^*\text{M}(\text{CN})_3^{n-}$ ($\text{M} = \text{Rh}, \text{Ir}, \text{Ru}$)

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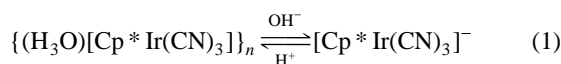
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Protonation of aqueous acetone solutions of $[\text{Cp}^*\text{Ir}(\text{CN})_3]^-$ produces the two-dimensional organometallic solid $(\text{H}_3\text{O})[\text{Cp}^*\text{Ir}(\text{CN})_3]\cdot\text{Me}_2\text{CO}$ wherein 14 Å diameter channels ($\text{Ir}_4\text{C}_8\text{N}_8\text{O}_4$) contain exchangeable solvent molecules; the analogous Ru and Rh tricyanide complexes are also susceptible to proton-induced polymerization.

The synthesis of solids based on organic¹ and metal organic subunits² from molecular precursors is a mature but still growing theme.³ Organometallic solids are less well developed,⁴ although the face-capping C_5R_5 ligands should be convenient for limiting the degrees of freedom in condensation processes. Molecular cages have been prepared by the reaction of *fac*-octahedral tritopic Lewis base $\text{CpM}(\text{CN})_3^-$ with *fac*-octahedral tritopic Lewis acids Cp^*M^{2+} and $\text{Mo}(\text{CO})_3$.^{5–7} The complementary interaction of $\text{Cp}^*\text{M}(\text{CN})_3^-$ with the pyramidal tritopic receptor⁸ H_3O^+ is now shown to afford extended structures featuring two-dimensional net structures⁹ (Scheme 1).

Aqueous solutions of $\text{NEt}_4[\text{Cp}^*\text{Ir}(\text{CN})_3]$ **1** react upon mixing with protic acids (HOTf, HCl, HOTs) to produce the colorless solid $(\text{H}_3\text{O})[\text{Cp}^*\text{Ir}(\text{CN})_3]$ **2** in 82% isolated yield.† The yield is proportional to the stoichiometry of the acid, consistent with a cooperative process vs. formation of species of intermediate degrees of condensation (e.g. $[\text{Cp}^*\text{Ir}(\text{CN})_3]_2^-$). Base reverses the polymerization process, affording intact $[\text{Cp}^*\text{Ir}(\text{CN})_3]^-$ [eqn. (1)].



IR measurements on **2** show two ν_{CN} bands (2156 and 2137 cm^{-1}) in the region for hydrogen bonded (or bridging) CN ligands. Compound **2** is completely insoluble in common solvents except methanol, wherein it dissociates to give free $[\text{Cp}^*\text{Ir}(\text{CN})_3]^-$, as indicated by ¹H NMR measurements (δ 1.945, as for **1**). Conductivity measurements on 10^{-3} M MeOH solutions confirm that **2** is a 1:1 electrolyte (A_M of 96 $\Omega \text{ cm}^2 \text{ mol}^{-1}$).

Crystals of **2** were obtained by layering an acetone solution of HOTf (10 mM) over an (10 mM) CHCl_3 solution of $\text{NEt}_4[\text{Cp}^*\text{Ir}(\text{CN})_3]$ for 48 h.‡ The resulting crystals readily desolvate to give powders, even at 0 °C. The crystallographic analysis reveals a layered structure of formula $[\text{Cp}^*\text{Ir}(\text{CN})_3]\text{H}_3\text{O}\cdot\text{Me}_2\text{CO}$. The corrugated sheets consist of $[\text{Cp}^*\text{Ir}(\text{CN})_3]^-$ ions triply bridged *via* hydrogen bonds to H_3O^+ ions (Fig. 1). As in

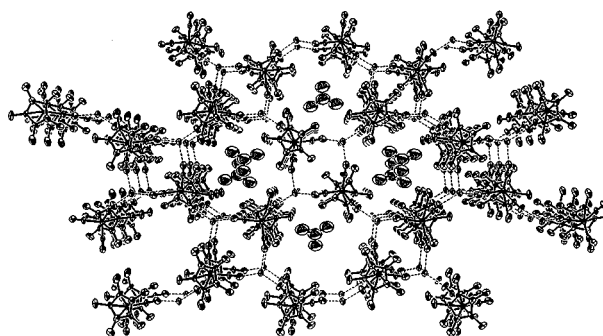


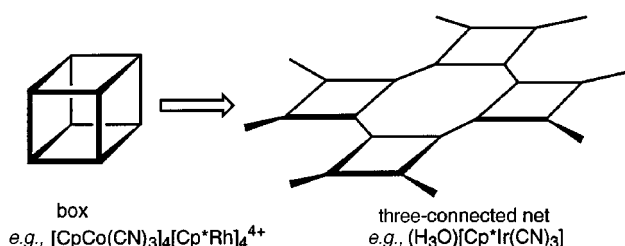
Fig. 1 Fragment of one layer of $(\text{H}_3\text{O})[\text{Cp}^*\text{Ir}(\text{CN})_3]\cdot\text{Me}_2\text{CO}$ viewed down the *a* axis. The acetone molecules occupy the octagonal channels (thermal ellipsoids set at the 50% probability level).

the previously described molecular boxes,^{13,14} there is complementary connectivity of the Lewis base $[\text{M}(\text{CN})_3]$ and Lewis (in this case Brønsted) acid (H_3O^+). The layers feature alternating 24- and 12-membered rings composed, respectively, of $\text{Ir}_4\text{C}_8\text{N}_8\text{O}_4$ and $\text{Ir}_2\text{C}_4\text{N}_4\text{O}_2$ atoms (ignoring H atoms). Owing to the linearity of the $\text{Ir}-\text{C}-\text{N}\cdots\text{O}$ linkages, the 24-membered rings are approximately octagonal and the 12 membered rings are approximately square. The 'cross window' distances in the 24-membered rings are *ca.* 14 ($\text{Ir}\cdots\text{Ir}$) and *ca.* 13 Å ($\text{O}\cdots\text{O}$). The 12- and 24-membered rings are eclipsed, leaving large channels that extend through the solid along the *a* axis (interlayer distance of 6.976 Å).

The octagonal channels in **2** are filled with acetone molecules that are subject to large thermal motion. It is thus understandable that this material easily desolvates. The lability of the solvent in **2** was examined by thermogravimetry, which confirms that acetone evolution reversibly occurs in the range 25–65 °C. Solvent exchange also occurs readily for *solid 2*. To prove this point, samples of **2**· Me_2CO were exposed to the vapor of fluoroacetone, which is virtually isosteric with acetone (Fig. 2). The TGA curves of the resultant material show an increase in the solvent weight loss from *ca.* 12% (*vs.* 12.0% theoretical) to *ca.* 15% (14.8% theoretical for **2**· $(\text{CH}_2\text{F})\text{MeCO}$).

While the synthesis, spectroscopy, and solubility properties of $(\text{H}_3\text{O})[\text{Cp}^*\text{Rh}(\text{CN})_3]$ **3** are virtually identical to that of **2**, the rhodium species is significantly less stable. Thus **3** decomposes after several hours in refluxing CHCl_3 with evolution of HCN to produce, *inter alia*, $\{[\text{Cp}^*\text{Rh}]_7(\text{CN})_{12}\}^{2+}$; the analogous decomposition of **2** requires 3 weeks.⁶ This reaction illustrates the potential utility of the acid-catalysed condensation, somewhat analogous to the decarbonylation route used to prepare polynuclear metal carbonyls.

Hydrogen bonding interactions also play a significant role in the chemistry of $\text{Cp}^*\text{Ru}(\text{CN})_3^{2-}$, which is of interest as a precursor to electroactive solids and cages. This species was readily prepared from the reaction of $\text{Cp}^*\text{Ru}(\text{MeCN})_3^+$ with 3 equiv. of NaCN but it is difficult to separate the product from contaminating salts. Treatment of the crude product with HOTf (2 equiv) produced the polymer $\text{H}_2[\text{Cp}^*\text{Ru}(\text{CN})_3]$ **4** as a white



Scheme 1

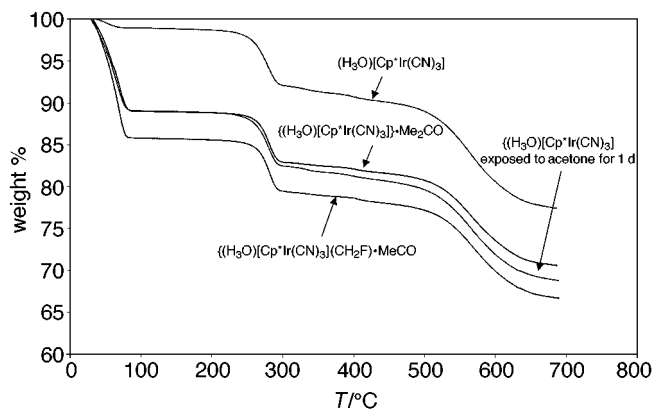


Fig. 2 TGA results for solvent exchange of $(\text{H}_3\text{O})[\text{Cp}^*\text{Ir}(\text{CN})_3]$ -derived solids. From the top: $(\text{H}_3\text{O})[\text{Cp}^*\text{Ir}(\text{CN})_3]$, $(\text{H}_3\text{O})[\text{Cp}^*\text{Ir}(\text{CN})_3]\cdot\text{Me}_2\text{CO}$, vacuum-dried $(\text{H}_3\text{O})[\text{Cp}^*\text{Ir}(\text{CN})_3]$ after exposure to acetone vapor (24 h, 298 K), $(\text{H}_3\text{O})[\text{Cp}^*\text{Ir}(\text{CN})_3]\cdot\text{Me}_2\text{CO}$ that had been exposed to $(\text{CH}_2\text{F})\text{MeCO}$ vapor (24 h, 298 K).

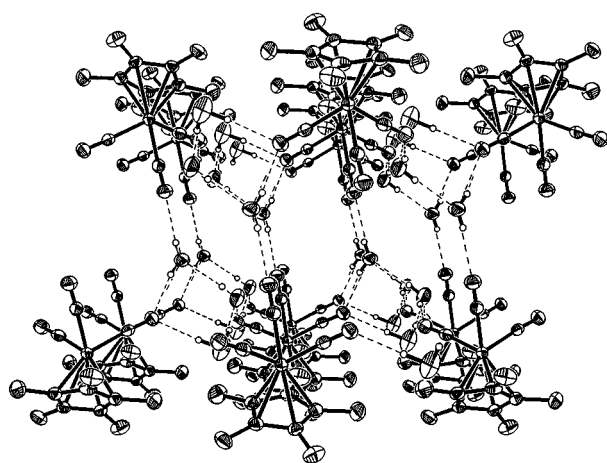


Fig. 3 Side view of one layer of hydrated anions in $[\text{NEt}_4]_2[\text{Cp}^*\text{Ru}(\text{CN})_3]\cdot 3\text{H}_2\text{O}$ (thermal ellipsoids at the 50% probability level). Selected average bond lengths and angles: Ru–CN 1.995 Å, C–N 1.165 Å, Ru–C–N 176.8°, NC–Ru–CN 89.3°.

precipitate. Depolymerization was effected by treatment of aqueous suspensions of **4** with aqueous NEt_4OH to give analytically pure CH_2Cl_2 -soluble $[\text{NEt}_4]_2[\text{Cp}^*\text{Ru}(\text{CN})_3]$ **5** ($E_{1/2} = -729 \text{ mV vs. Fc/Fc}^+$). Crystallographic characterization[‡] of the beige crystals of **5** revealed a hydrate with a layered

structure wherein the hydrophobic and hydrophilic subunits are segregated (Fig. 3).

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Notes and references

[†] *Data for new compounds:* $(\text{H}_3\text{O})[\text{Cp}^*\text{Ir}(\text{CN})_3]$ **2**: 82% yield; ν_{CN} 2162, 2128 cm^{-1} ; $^1\text{H NMR}$ (CD_3OD): δ_{Cp^*} 2.040. Anal. CHN. $(\text{H}_3\text{O})[\text{Cp}^*\text{Rh}(\text{CN})_3]$ **3**: 84% yield, ν_{CN} 2156, 2137 cm^{-1} . $^1\text{H NMR}$ (CD_3OD): δ_{Cp^*} = 1.945; Anal. CHN. $\text{H}_2[\text{Cp}^*\text{Ru}(\text{CN})_3]$ **4**: 80% yield; Anal. CHN; $^1\text{H NMR}$ (CD_3OD): δ_{Cp^*} 1.90; ν_{CN} 2096, 2057, 2001 cm^{-1} . $[\text{NEt}_4]_2[\text{Cp}^*\text{Ru}(\text{CN})_3]\cdot 3\text{H}_2\text{O}$ **5**: 63% yield. Anal. CHN; $^1\text{H NMR}$: δ_{Cp^*} 1.90; ν_{CN} 2052, 2019 cm^{-1} . CV (MeCN): quasi-reversible oxidation at $-729 \text{ mV vs. Fc/Fc}^+$.

[‡] *Crystal data:* $(\text{H}_3\text{O})[\text{Cp}^*\text{Ir}(\text{CN})_3]\cdot 3\text{H}_2\text{O}$ ($M = 482.58$), monoclinic, space group $P2_1/c$, $0.06 \times 0.05 \times 0.05 \text{ mm}$, $a = 6.9764(2)$, $b = 15.9021(5)$, $c = 16.7178(6)$ Å, $\beta = 90.8730(10)^\circ$, $V = 1854.45(10)$ Å³, $Z = 4$, $D_c = 1.728 \text{ g cm}^{-3}$, $T = 198(2)$ K; $\lambda(\text{Mo-K}\alpha) = 0.71073$ Å, 9590 reflections, 3268 independent ($R_{\text{int}} = 0.1555$), $R1 = 0.0854$, $wR2$ (on F^2) = 0.1397.

$[\text{NEt}_4]_2[\text{Cp}^*\text{Ru}(\text{CN})_3]\cdot 3\text{H}_2\text{O}$ ($M = 628.90$), monoclinic, space group $P2_1/c$, $0.22 \times 0.34 \times 0.38 \text{ mm}$, $a = 15.7795(7)$, $b = 14.8677(7)$, $c = 15.2447(7)$ Å, $\beta = 109.4830(10)^\circ$, $V = 3371.7(3)$ Å³, $Z = 4$; $D_c = 1.239 \text{ g cm}^{-3}$, $T = 173(2)$ K; $\lambda(\text{Mo-K}\alpha) = 0.71073$ Å; 21890 reflections, 8054 independent ($R_{\text{int}} = 0.0338$), $R1 = 0.0312$, $wR2$ (on F_2) = 0.0763. CCDC 182/1263.

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