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36. TRICYANOMETALATE BUILDING BLOCKS AND ORGANOMETALLIC CYANIDE CAGES

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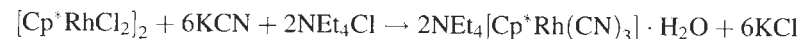
Tricyanometalate complexes are useful building blocks for the construction of molecular cage compounds¹⁻⁶ and coordination solids.^{7,8} One class of tricyanometalates that has proved especially useful are those with the formula $[\text{M}(\text{C}_5\text{R}_5)(\text{CN})_3]^-$, since the cyclopentadienyl coligand limits the degree of polymerization and facilitates the formation of molecular cages. The tricyanides of the monocyclopentadienyl complexes with middle transition series metals were not well studied until the early 1970s. Pauson and Dineen reported the preparation of $[\text{K}[\text{CpCo}(\text{CN})_3]]$ and $[\text{PPH}_3\text{CH}_2\text{Ph}][\text{CpCo}(\text{CN})_3]$ via the reaction of cyanide with $\text{CpCoI}_2(\text{CO})$.⁹ We have obtained the former compound using a

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slightly modified procedure and have been able to convert it to the organic solvent soluble $[\text{K}(18\text{-crown-6})]^+$ salt. The related tricyanides $[\text{Cp}^*\text{Rh}(\text{CN})_3]^-$, $[\text{Cp}^*\text{Ir}(\text{CN})_3]^-$, and $[\text{Cp}^*\text{Ru}(\text{CN})_3]^{2-}$ are readily prepared from commercially available $[\text{Cp}^*\text{MCl}_2]_2$,⁹ and the related $[\text{Cp}^*\text{Fe}(\text{CN})_3]^{2-}$ can be obtained from the photolysis of $[\text{Cp}^*\text{Fe}(\text{CO})(\text{CN})_2]^-$.¹⁰ Of these, $[\text{Cp}^*\text{Co}(\text{CN})_3]^-$, $[\text{Cp}^*\text{Rh}(\text{CN})_3]^-$, and $[\text{Cp}^*\text{Ir}(\text{CN})_3]^-$ are useful in the synthesis of molecular cages. Of particular note is the condensation between $[\text{Cp}^*\text{Co}(\text{CN})_3]^-$ and $[\text{Cp}^*\text{Rh}(\text{NCMe})_3]^{2+}$ ¹¹ to give a molecular cube of formula $[\{\text{Cp}^*\text{Co}(\text{CN})_3\}_4\{\text{Cp}^*\text{Rh}\}_4]^{4+}$ or a molecular bowl of formula $[\{\text{Cp}^*\text{Co}(\text{CN})_3\}_4\{\text{Cp}^*\text{Rh}\}_3]^{2+}$, depending on the stoichiometric ratio of the reactants used.

■ **Caution.** Because of the toxic nature of cyanide, special care should be exercised in these preparations. We make amylnitrite available in the laboratory as an antidote to acute cyanide poisoning. Organic soluble salts of cyanide (and potentially cyanometallates) are especially hazardous contact poisons because they are transported intravenously through the skin.

A. TETRAETHYLAMMONIUM TRICYANO(PENTAMETHYL CYCLOPENTADIENYL)RHODATE(III) MONOHYDRATE, $[\text{NEt}_4][\text{Cp}^*\text{Rh}(\text{CN})_3] \cdot \text{H}_2\text{O}$



Procedure

A 250-mL round-bottomed flask containing a stirring bar is covered with aluminum foil (to exclude light) and then charged with 0.30 g (0.485 mmol) of $(\text{Cp}^*\text{RhCl}_2)_2$ and 50 mL of H_2O . To the resulting slurry, 0.329 g (1.94 mmol) of AgNO_3 is added. Over the course of 40 min, the color of the solution becomes yellow and a white precipitate of AgCl appears. The slurry is filtered through Celite. To the filtered solution of $[\text{Cp}^*\text{Rh}(\text{H}_2\text{O})_3]^{2+}$ is added 0.284 g (4.36 mmol) of KCN . This solution is allowed to stir overnight. The resulting colorless solution is treated with 0.161 g (0.970 mmol) of Et_4NCl . After a further 20 min, the solvent is evaporated. The pale yellow solid residue is extracted into 30 mL of CH_2Cl_2 , and the solution is filtered through a medium-porosity frit to remove a white solid consisting of KCl , KCN , and KNO_3 . The product, $[\text{Et}_4\text{N}][\text{Cp}^*\text{Rh}(\text{CN})_3]$, is precipitated by the addition of 50 mL Et_2O to the filtered extract. The precipitate is collected by filtration, washed with 10 mL of Et_2O , and dried under vacuum. Yield: 0.401 g (93%).*

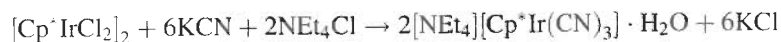
*The checkers' yield was 73–76%.

Anal. Calcd. for $C_{21}H_{37}N_4ORh$: C, 54.31; H, 8.03; N, 12.06. Found: C, 53.93; H, 8.20; N, 11.97.

Properties

The product is a pale yellow crystalline solid. It is air-stable both as a solid and in solutions. It is soluble in polar solvents such as water, acetone, and acetonitrile as well as CH_2Cl_2 and is insoluble in ether and hexanes. The 1H NMR spectrum (CD_3CN) exhibits a triplet at δ 3.16 [$N(CH_2CH_3)_4$, 8H], a singlet at 1.86 (Cp^+ , 15H), and a quartet at 1.20 [$N(CH_2CH_3)_4$, 12H]. The 1H NMR spectrum in $CDCl_3$ is similar: δ 1.36, 1.93, and 3.40. The $^{13}C\{^1H\}$ NMR spectrum ($CDCl_3$) shows signals at δ 128.9 (d, $J_{C-Rh} = 51$ Hz, CN), 100.59 (d, $J_{C-Rh} = 4.6$ Hz, Me_5C_5), 52.7 [s, $(CH_3CH_2)_4N$], 9.9 [s, $(CH_3)_5C_5$] 7.7 [$(CH_3CH_2)_4N$]. The molecular ion is evident in the negative-ion FAB mass spectrum at m/z 316.0. The infrared spectrum of the solid (KBr pellet) exhibits the typical two-band pattern for pseudo- C_{3v} symmetry at 2110 and 2122 cm^{-1} in the cyanide region.

B. TETRAETHYLAMMONIUM TRICYANO (PENTAMETHYLCYCLOPENTADIENYL)IRIDATE(III) MONOHYDRATE, $[NEt_4][Cp^*Ir(CN)_3] \cdot H_2O$



Procedure

A 250-mL round-bottomed flask containing a stirring bar is charged with 0.300 g (0.377 mmol) of $(Cp^*IrCl_2)_2$ and 100 mL of H_2O . To this slurry is added 0.150 g (2.30 mmol) of KCN. The resulting mixture is heated at reflux for 3 h under N_2 to give a clear, colorless solution. To the solution is added 0.150 g (0.905 mmol) of $[Et_4N]Cl$, and then the solvent is removed under vacuum. The pale yellow solid residue is extracted into 50 mL CH_2Cl_2 , and the volume of the resulting colorless solution is reduced under vacuum to ~ 5 mL. The product, $[Et_4N][Cp^*Ir(CN)_3]$, is precipitated by the addition of 50 mL Et_2O . The precipitate is collected by filtration, washed with 10 mL of Et_2O , and dried under vacuum. Yield: 0.293 g (73%).*

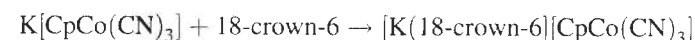
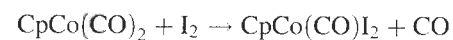
Anal. Calcd. for $C_{21}H_{37}IrN_4O$: C, 45.55; H, 6.73; N, 10.12. Found: C, 45.63; H, 6.66; N, 10.22.

The checkers' yield was 85–87%.

Properties

The product is a colorless crystalline solid. It is air stable both as a solid and in solutions. It is soluble in polar solvents such as water, acetone, and acetonitrile as well as CH_2Cl_2 and is insoluble in ether and hexanes. The 1H NMR spectrum (CD_2Cl_2) exhibits a quartet at δ 3.35 [8H, $(CH_3CH_2)_4N$], a singlet at δ 1.99 [15H, $(CH_3)_5C_5$], and a triplet at δ 1.34 [12H, $(CH_3CH_2)_4N$]. The 1H NMR spectrum in CD_3CN is similar, with signals at δ 3.15, 1.95, and 1.20, respectively. The cyanide region in the infrared spectrum of the solid (KBr pellet) shows a typical two-band pattern at 2107 and 2124 cm^{-1} .

C. (18-CROWN-6)POTASSIUM TRICYANO(CYCLOPENTADIENYL) COBALTATE(III), $[K(18-CROWN-6)][CpCo(CN)_3]$



Procedure

■ **Caution.** The procedure involves the formation of gaseous CO and should be conducted in a well-ventilated hood.

The synthesis of $CpCo(CO)I_2$ is performed by using a modification of literature methods.¹² A tared syringe is used to weigh out 3.0 g (17.0 mmol) $CpCo(CO)_2$ in air. The compound is then dissolved in 50 mL of MeOH to give a red-brown solution. Then 4.23 g (17.0 mmol) I_2 is added to the stirred solution in 0.1–0.2 g portions over 20 min. The addition occurs with evolution of gas and formation of a black precipitate. The resulting mixture is stirred for 2 h, and then the solvent is removed under vacuum. The residue is extracted with four 100-mL portions of CH_2Cl_2 (or until further extracts are colorless), and the extracts are evaporated to dryness to give black microcrystals. The crystals are washed with two 10-mL portions of Et_2O and dried in air on the frit for 20 min. Yield: 6.1 g $CpCo(CO)I_2$ (88%).

Under a nitrogen atmosphere, a solution of 2.41 g (37 mmol) of KCN in 80 mL of MeOH is added to a solution of 5.0 g (12 mmol) of $CpCo(CO)I_2$ in 20 mL of MeOH, and the resulting solution is heated under reflux for 3 days. The reaction mixture is allowed to cool, and then it is filtered in air. The filtrate is evaporated to dryness and the residue is washed with 800 mL of MeCN in 50-mL portions until the washings contain no KI (as indicated by the failure to obtain a

precipitate on addition of Et₂O to the washings). The solid K[CpCo(CN)₃] is washed with two 10-mL portions of Et₂O and dried under vacuum for 2 h. Yield: 1.16 g (41%).

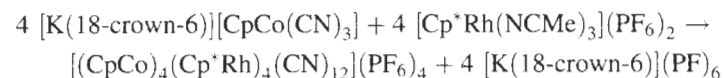
Then 1.16 g (4.81 mmol) of K[CpCo(CN)₃] is suspended in a solution containing 1.28 g (4.84 mmol) of 18-crown-6 in 250 mL of MeCN, and the suspension is stirred for 3 h. During this time the K[CpCo(CN)₃] dissolves to give a golden yellow solution. The solution is filtered to remove a small quantity of an insoluble brown impurity, and then the solvent is reduced in volume to ~100 mL under vacuum. Addition of 150 mL Et₂O precipitates the product as yellow microcrystals. The product is collected by filtration, washed with two 10-mL portions of Et₂O, and finally dried under vacuum for 1 h. Yield: 2.31 g (91% from K[CpCo(CN)₃]; 33% overall).

Anal. Calcd. for C₂₀H₂₉CoKN₃O₆: C, 47.52; H, 5.78; N, 8.31. Found: C, 47.50; H, 5.82; N, 8.36.

Properties

The compound is a golden yellow microcrystalline solid. It is stable in air both as a solid and in solution. It is soluble in water, methanol, and acetonitrile and is insoluble in ether and hexanes. The ¹H NMR spectrum (CD₃CN) shows two singlets at δ 3.56 (24H, [K(C₁₂H₂₄O₆)]) and 5.23 (5H, C₅H₅). The infrared spectrum of the solid (KBr) shows a single band in the cyanide region at 2119 cm⁻¹.

D. DODECACYANOTETRAKIS {CYCLOPENTADIENYL} COBALT(III)} TETRAKIS{PENTAMETHYL CYCLOPENTADIENYL RHODIUM(III)} TETRAKIS (HEXAFLUOROPHOSPHATE), [(CpCo(CN)₃)₄(Cp^{*}Rh)₄](PF₆)₂



Procedure

A solution of 50 mg (0.10 mmol) of [K(18-crown-6)][CpCo(CN)₃] in 15 mL of MeCN is added dropwise to a stirred solution of 65 mg (0.1 mmol)

The checkers' yields were 88–90% and 25–30% overall.

[Cp^{*}Rh(NCMe)₃](PF₆)₂,¹³ in 15 mL MeCN. The resulting solution is allowed to stand for 36 h, and then the product is precipitated as a yellow powder by addition of 100 mL of Et₂O. The product is collected by filtration, washed with two 10-mL portions of Et₂O, and dried under vacuum for 1 h. Yield: 58 mg (99%).

Anal. Calcd. for C₇₂H₉₆Co₄F₂₄N₁₂P₄Rh₄: C, 36.95; H, 3.44; N, 7.18. Found: C, 37.29; H, 3.73; N, 7.24.

Properties

The compound, a golden yellow powder, is stable in air both as a solid and in solutions. It is soluble in acetonitrile and slightly so in dichloromethane. It is insoluble in water, ether, and hexanes. The ¹H NMR spectrum (CD₃CN) shows two singlets at δ 1.762 [60H, C₅(CH₃)₅] and 5.720 (20H, C₅H₅). The ESI-MS shows peaks at *m/z* = 2195 amu corresponding to [(CpCo)₄(Cp^{*}Rh)₄(CN)₁₂]-[PF₆]₃⁺ and at *m/z* = 1025 amu (atomic mass units) due to [(CpCo)₄(Cp^{*}Rh)₄(CN)₁₂][PF₆]₂²⁺. The infrared spectrum of the solid (KBr) shows a single band in the cyanide region at 2180 cm⁻¹.

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The checkers' yield was 86–91%.