

Transition Metal Complexes of Cyanoisocyanoarenes as Building Blocks for One-, Two-, and Three-Dimensional Molecular Solids

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The complexes *trans*-[M₂(CNC₆H₄-CN-4)₂], (M = Pd and Pt), *trans*-[FeI₂L₄] (L = CNC₆H₄-CN-4 and CNC₆H₂-Me₂-2,6-CN-4), and [Mn(CNC₆H₄-CN-4)₆][SO₃CF₃] were prepared. The compounds are thermally stable up to 230 °C or higher. The molecular structure of *trans*-[FeI₂(CNC₆H₄-CN-4)₄] was determined by X-ray crystallography: monoclinic, space group *P*2₁/*n*, *a* = 11.570(2) Å, *b* = 10.1052(8) Å, *c* = 28.138(7) Å, β = 92.034(9)°, *Z* = 4, 3464 unique reflections, *R* = 0.074, *R*_w = 0.089. The complexes contain the peripheral cyano groups in linear, planar, and octahedral dispositions, respectively. Solids were obtained by combining solutions of [PdI₂(CNC₆H₄-CN-4)₂] and [Cu(hfacac)₂], [FeI₂(CNC₆H₄-CN-4)₄] and AgSO₃CF₃, [FeI₂(CNC₆H₂-Me₂-2,6-CN-4)₄] and [Rh₂(O₂CCF₃)₄], and [Mn(CNC₆H₄-CN-4)₆][SO₃CF₃] and [Rh₂(O₂CCF₃)₄]. [PdI₂(CNC₆H₄-CN-4)₂] and [Cu(hfacac)₂] in a ratio of 1:2 form a crystalline, one-dimensional solid: monoclinic, space group *P*2₁/*c*, *a* = 8.317(2) Å, *b* = 13.541(1) Å, *c* = 22.568(5) Å, β = 100.45(1)°, *Z* = 2, 3279 unique reflections, *R* = 0.037, *R*_w = 0.047.

Introduction

The formation of extended solids by the self-assembly of molecular components is a powerful method in the design of new materials.^{2,3} In such systems, the molecular units are typically held together by weak coordinative bonds^{2,4} or hydrogen bonds.^{3,5} Weak interactions allow the self-assembly processes to proceed under reversible conditions, thus favoring the formation of regular structures. Transition metal complexes of functionalized isocyanides⁶ lend themselves as building blocks for molecular materials for several reasons. Isocyanides are strong ligands, giving rise to stable metal complexes. Isocyanide ligands are also sterically undemanding in the immediate vicinity of the metal centers, accommodating most coordination geometries.⁷ Furthermore, isocyanide ligands can

be functionalized in ways to promote self-assembly. In this work, we are exploring the potential of transition metal isocyanide complexes carrying cyano groups in peripheral sites as building blocks for molecular materials. The expectation that such systems will undergo controlled self-assembly in combination with suitable metal ions or metal complexes is based on the well-known fact that nitriles are weak ligands⁸ and the observation that organic polynitriles can serve as bridging ligands in molecular or extended structures.⁹ Here we report the synthesis of transition metal complexes of isocyanobenzonitriles with linear, square-planar, and octahedral dispositions of the peripheral nitrile groups. These molecular building blocks are designed to combine with suitable metal ions or complexes to form one-, two-, and three-dimensional structures. The viability of the new approach is demonstrated by the formation of a crystalline one-dimensional solid from linear metal diisocyanide building blocks and unsaturated metal complex linking units.

Results and Discussion

The cyanoisocyanobenzene **1a** reacts with suspensions of [PdI₂] and [PtI₂] in THF to afford the complexes **2** and **3**, respectively (eq 1). Compound **2** forms orange crystals from THF/hexane; compound **3** precipitates as a yellow solid from the same solvent mixture. Treatment of [FeI₂·4H₂O] with the cyanoisocyanobenzenes **1a** and **1b** in THF gives the complexes **4a** and **4b**, respectively (eq 2). Both **4a** and **4b** form dark green

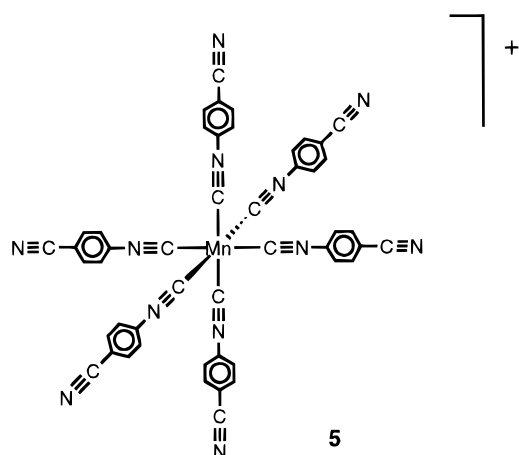
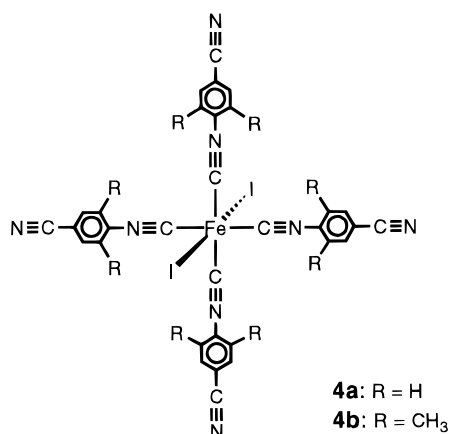
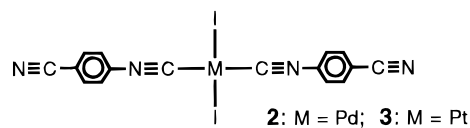
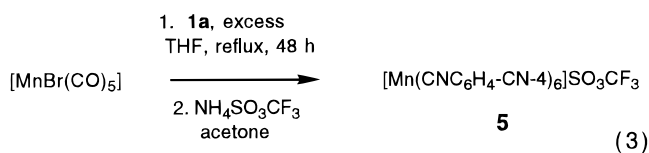
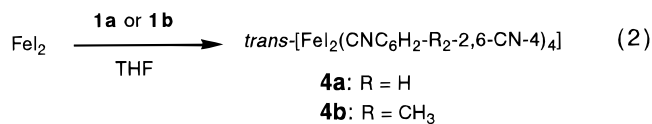
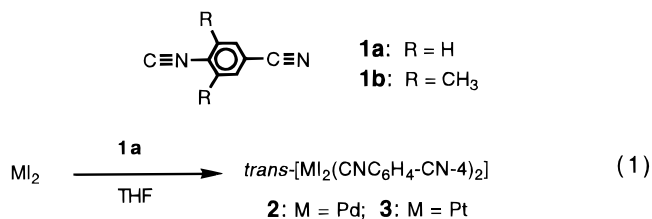
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crystals from methylene chloride/ether. The manganese complex **5** is obtained by heating a mixture of $[\text{MnBr}(\text{CO})_5]$ and excess **1a** in THF to reflux for 2 days, followed by metathesis with $\text{NH}_4\text{SO}_3\text{CF}_3$ in acetone (eq 3). Complex **5** forms orange-yellow crystals from acetone/hexane. The isocyanide complexes **2–5** are thermally very stable. Complexes **2**, **3**, **4b**, and **5** show no signs of decomposition up to 230 °C. Complex **4a** begins to melt and decompose at 230 °C.

Table 1. Crystallographic Data for **4a** and **6**

	4a	6
formula	C ₃₂ H ₁₆ FeI ₂ N ₈	C ₃₆ H ₁₂ Cu ₂ F ₂₄ I ₂ N ₄ O ₈ Pd
fw	822.19	1571.80
space group	P2 ₁ /n (No. 14)	P2 ₁ /c (No. 14)
a, Å	11.570(2)	8.317(2)
b, Å	10.1052(8)	13.541(1)
c, Å	28.138(7)	22.568(5)
β, deg	92.034(9)	100.45(1)
V, Å ³	3280.5(1)	2499.5(8)
Z	4	2
T, °C	25	25
λ, Å	0.710 73	0.710 73
linear abs coeff, cm ⁻¹	23.543	25.568
R ^a	0.074	0.037
R _w ^b	0.089	0.047
goodness of fit	2.067	2.067

^a $R = \sum ||F_o| - |F_c|| / \sum |F_o|$ (quantity minimized $(\sum w(|F_o| - |F_c|)^2)$); weight $w = 1/(\sigma(F_o) + 0.0016F_o^2)$. ^b $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum wF_o^2]^{1/2}$.

Complexes **2** and **3** exist as the trans isomers. The IR spectra exhibit only a single sharp absorption for the isocyanide groups at 2199 and 2191 cm⁻¹ (CH₂Cl₂ solution), respectively. Weak signals at 2236 and 2231 cm⁻¹ are observed for the nitrile groups. The meridional arrangement of the four isocyanide ligands in **4a** and **4b** is evident from the IR and NMR data. The isocyanide groups of complexes **4a** and **4b** in methylene chloride solution give rise to absorptions at 2119 and 2117 cm⁻¹, respectively. The nitrile stretching frequencies of **4a** and **4b** are found at 2234 and 2230 cm⁻¹. The ¹H and ¹³C NMR spectra of **4a** and **4b** show only single sets of signals for the isocyanide ligands. The IR spectrum of a CH₂Cl₂ solution of **5** exhibits a strong signal at 2089 cm⁻¹ with a shoulder at 2120 cm⁻¹ and a weak peak at 2037 cm⁻¹ for the isocyanide groups, and a weak absorption at 2233 cm⁻¹ for the nitrile groups. The ¹H and ¹³C NMR spectra of **5** show only single sets of signals for the six isocyanide ligands, indicating a regular octahedral coordination geometry.

The structure of **4a** was determined by X-ray crystallography. The crystal data are collected in Table 1; selected bond distances and bond angles are listed in Table 2. Figure 1 shows the structure of one of two independent molecules in the unit cell. The two iodide ligands are mutually trans, and the four isocyanide ligands are in meridional arrangement. The bond distances and angles are within the expected range, except for one symmetry-related pair of bent nitrile groups in the second independent molecule (not shown in Figure 1).

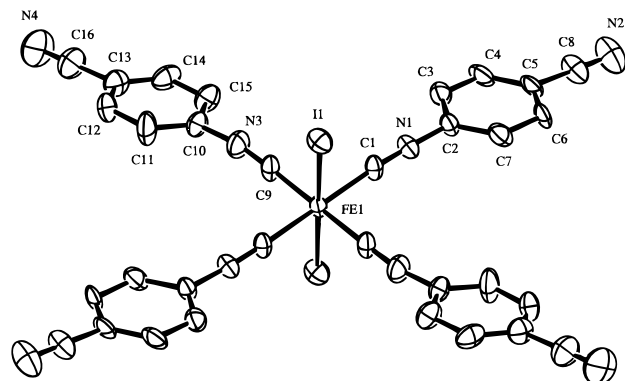
Complexes of the types $[\text{MX}_2(\text{CNR})_2]$ (M = Pd, Pt; X = halogen) and $[\text{MX}_2(\text{CNR})_4]$ (M = Fe, Co; X = halogen) are well established.⁷ They exist as cis and trans isomers. With the heavier halogens the trans isomers are preferred. Octahedral complexes of the type $[\text{M}(\text{CNR})_6]^+$ (M = Mn, Tc, Re) have been studied intensively in recent years, primarily because of the use of technetium complexes as radioimaging agents.¹⁰ Isocyanobenzonitriles have received attention as components in nonlinear optical devices.¹¹

On the basis of the spectroscopic and structural studies, the peripheral nitrile groups of complexes **2/3**, **4**, and **5** are in linear, square-planar, and octahedral dispositions, respectively. If these nitrile groups are connected in an oriented fashion, e.g. by coordination to suitable metal centers, then one-, two-, and three-

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Table 2. Selected Bond Lengths (Å) and Angles (deg) for Complex **4a**

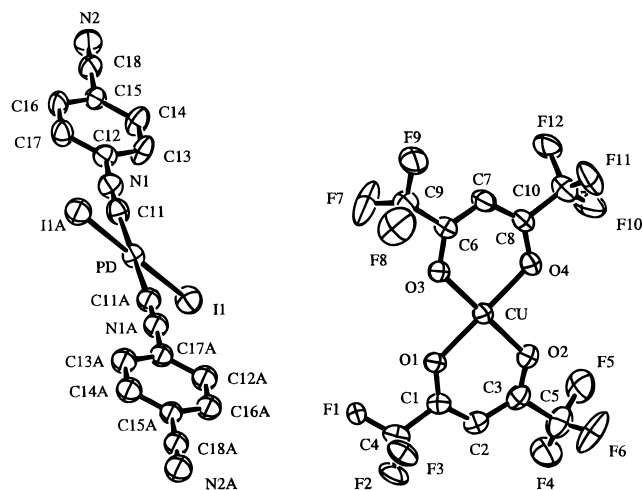
molecule 1		molecule 2	
(a) Bond Lengths			
Fe(1)–I(1)	2.619(1)	Fe(2)–I(2)	2.637(1)
Fe(1)–C(1)	1.92(1)	Fe(2)–C(17)	1.86(2)
Fe(1)–C(9)	1.84(2)	Fe(2)–C(25)	1.91(2)
N(1)–C(1)	1.13(2)	N(5)–C(17)	1.16(2)
N(1)–C(2)	1.35(2)	N(5)–C(18)	1.38(2)
N(2)–C(8)	1.15(2)	N(6)–C(24)	1.10(2)
N(3)–C(9)	1.18(2)	N(7)–C(25)	1.11(2)
N(3)–C(10)	1.38(2)	N(7)–C(26)	1.35(2)
N(4)–C(16)	1.11(2)	N(8)–C(32)	1.20(4)
C(5)–C(8)	1.43(2)	C(21)–C(24)	1.51(3)
C(13)–C(16)	1.49(2)	C(29)–C(32)	1.45(4)
(b) Bond Angles			
I(1)–Fe(1)–I(1A)	180.00	I(2)–Fe(2)–I(2A)	180.00
I(1)–Fe(1)–C(1)	88.6(4)	I(2)–Fe(1)–C(17)	93.8(5)
I(1)–Fe(1)–C(9)	92.7(4)	I(2)–Fe(2)–C(25)	92.3(4)
C(1)–Fe(1)–C(1A)	180.00	C(17)–Fe(2)–C(17A)	180.00
C(1)–Fe(1)–C(9)	91.1(6)	C(17)–Fe(2)–C(25)	88.5(7)
C(9)–Fe(1)–C(9A)	180.00	C(25)–Fe(2)–C(25A)	180.00
Fe(1)–C(1)–N(1)	176(1)	Fe(2)–C(17)–N(5)	177(1)
Fe(1)–C(9)–N(3)	178(1)	Fe(2)–C(25)–N(7)	177(2)
N(1)–C(2)–C(3)	120(1)	N(5)–C(18)–C(19)	119(2)
N(2)–C(8)–C(5)	178(2)	N(6)–C(24)–C(21)	177(3)
N(3)–C(10)–C(11)	121(2)	N(7)–C(26)–C(27)	121(2)
N(4)–C(16)–C(13)	177(3)	N(8)–C(32)–C(29)	155(6)
C(1)–N(1)–C(2)	175(1)	C(17)–N(5)–C(18)	177(2)
C(9)–N(3)–C(10)	172(1)	C(25)–N(7)–C(26)	168(2)

**Figure 1.** ORTEP drawing of **4a**. Only one of the two independent molecules is shown. The thermal ellipsoids are shown at the 35% probability level.

dimensional extended structures should result. To test the feasibility of this approach, solutions of the complexes **2**–**5** were treated with several metal reagents which are known to link organic nitriles or metal cyanide complexes, e.g. $[\text{Cu}(\text{hfacac})_2]$ (hfacac = hexafluoroacetylacetonate), $\text{Ag}(\text{I})$, and $[\text{Rh}_2(\text{O}_2\text{-CCF}_3)_4]$.^{8,9c,e} When a solution of equimolar amounts of **2** and $[\text{Cu}(\text{hfacac})_2]$ in CH_2Cl_2 is slowly evaporated to dryness, a mixture of solids results. One of the components is the starting material **2**. However, when the palladium building block and the copper linker are combined in the same manner in a 1:2 ratio, a residue of apparently homogeneous green crystals, solid **6**, is obtained. Large dark green crystals of **6** form when the solvent is allowed to evaporate very slowly. Attempts to obtain solids from **3** with $[\text{Cu}(\text{hfacac})_2]$ or other linking units have not yet given satisfactory results, presumably due to the low solubility of the platinum complex. Addition of $[\text{AgSO}_3\text{CF}_3]$ to a THF solution of **4a** affords solid **7**. It contains the components in a ratio close to 1:2. When benzene solutions of **4b** and $[\text{Rh}_2(\text{O}_2\text{CCF}_3)_4]$ are combined, solid **8** forms with a relative ratio of about 1:2.6 of the components. Solid **9**, which results by combining THF solutions of **5** and $[\text{Rh}_2(\text{O}_2\text{CCF}_3)_4]$, contains the manganese building block and the rhodium linker

Table 3. (a) Selected Bond Lengths (Å) and Angles (deg) for Solid **6**

Pd component		Cu component	
Bond Lengths			
Pd–I(1)	2.5795(6)	Cu–O(1)	1.933(3)
Pd–C(11)	1.944(6)	Cu–O(2)	1.921(4)
N(1)–C(11)	1.147(7)	Cu–O(3)	1.933(4)
N(1)–C(12)	1.403(7)	Cu–O(4)	1.944(3)
N(2)–C(18)	1.131(7)	Cu–N(2)	2.669(6)
C(12)–C(13)	1.360(8)	Cu–I(1)	3.1929(9)
C(12)–C(17)	1.385(8)	O(1)–C(1)	1.253(6)
C(13)–C(14)	1.372(8)	O(2)–C(3)	1.247(7)
C(14)–C(15)	1.364(8)	O(3)–C(6)	1.263(6)
C(15)–C(16)	1.385(8)	O(4)–C(8)	1.253(6)
C(15)–C(18)	1.441(8)	C(1)–C(2)	1.378(8)
C(16)–C(17)	1.373(8)	C(2)–C(3)	1.392(9)
		C(6)–C(7)	1.369(7)
		C(7)–C(8)	1.368(8)
(b) Bond Angles			
I(1)–Pd–I(1A)	180.00	O(1)–Cu–O(2)	92.3(2)
I(1)–Pd–C(11)	88.4(2)	O(1)–Cu–O(3)	87.3(1)
C(11)–Pd–C(11A)	180.00	O(1)–Cu–O(4)	179.7(2)
Pd–C(11)–N(1)	177.2(5)	O(2)–Cu–O(3)	177.3(2)
C(11)–N(1)–C(12)	175.5(6)	O(2)–Cu–O(4)	87.9(2)
N(1)–C(12)–C(13)	118.4(5)	O(3)–Cu–O(4)	92.5(1)
C(13)–C(12)–C(17)	122.9(5)	Cu–N(2)–C(18)	108.4(5)
C(12)–C(13)–C(14)	119.0(5)	Cu–I(1)–Pd	99.81(2)
C(12)–C(17)–C(16)	117.1(5)	Cu–O(1)–C(1)	124.6(4)
C(13)–C(14)–C(15)	119.8(5)	Cu–O(2)–C(3)	125.3(4)
C(14)–C(15)–C(16)	120.5(5)	Cu–O(3)–C(6)	124.5(3)
C(14)–C(15)–C(18)	119.7(5)	Cu–O(4)–C(8)	124.1(3)
C(15)–C(16)–C(17)	120.6(5)	O(1)–C(1)–C(2)	128.2(5)
		O(2)–C(3)–C(2)	127.3(5)
		O(3)–C(6)–C(7)	127.7(5)
		O(4)–C(8)–C(7)	127.5(5)
		C(1)–C(2)–C(3)	121.2(5)
		C(6)–C(7)–C(8)	122.7(5)

**Figure 2.** ORTEP drawing of the molecular components $[\text{PdI}_2(\text{CNC}_6\text{H}_4\text{-CN-4})_2]$ and $[\text{Cu}(\text{hfacac})_2]$ of solid **6**. The thermal ellipsoids are shown at the 35% probability level.

in a ratio of about 1:2. This ratio suggests that only four isocyanide ligands per manganese complex are involved in the formation of the extended framework.

The crystal structure of solid **6** was determined by X-ray crystallography. The crystal data are collected in Table 1; selected bond distances and bond angles are listed in Table 3. An ORTEP drawing of the molecular components is shown in Figure 2. The $[\text{PdI}_2(\text{CNC}_6\text{H}_4\text{-CN-4})_2]$ building blocks and the $[\text{Cu}(\text{hfacac})_2]$ linker units are arranged to form one-dimensional chains. A short section of a single chain is shown in Figure 3. Each copper atom achieves an octahedral coordination geometry by interacting with one nitrile group and one iodine atom of

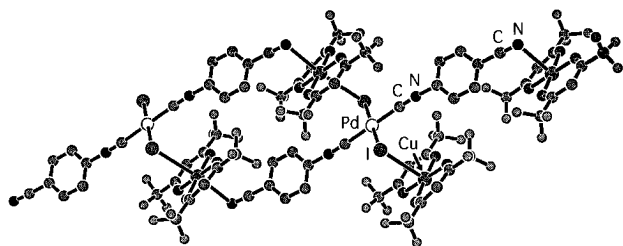


Figure 3. Portion of a chain of $[\text{PdI}_2(\text{CNC}_6\text{H}_4\text{-CN-4})_2]$ building blocks linked by $[\text{Cu}(\text{hfacac})_2]$ units in solid **6**.

complex **2**. Thus, two copper linkers are accommodated per palladium building block. The nitrile groups are coordinated to the copper atoms in a bent fashion (Cu-N(2)-C(18) , $108.4(5)^\circ$). The Cu-N(2) distance of $2.669(6)$ Å is longer by about 0.1 Å than in the "linear" links of the one-dimensional solid $[\text{Cu}(\text{hfacac})_2][\text{TCNE}]$ (Cu-N-C , $164.7(3)^\circ$; Cu-N , $2.563(3)$ Å; TCNE = tetracyanoethylene). Apparently, a π orbital of the CN triple bond acts as the donor site rather than the lone pair of the nitrile group.

The results demonstrate that metal complexes of 4-cyano-1-isocyanobenzenes can serve as building blocks for the assembly of extended molecular solids. An interesting fact, which hints at electronic communication between the linked metal centers across the 4-cyano-1-isocyanobenzenes, is the observation that the colors of some solids differ significantly from those of the building blocks and linking groups. For example, solid **8**, formed from deep green **3b** and blue $[\text{Rh}_2(\text{O}_2\text{CCF}_3)_4]$, is brown and solid **9**, formed from yellow **5** and blue $[\text{Rh}_2(\text{O}_2\text{CCF}_3)_4]$, is dark yellow. We therefore expect that solids containing metal complexes of cyanoisocyanobenzenes as structural components will exhibit novel materials properties.

1,4-Diisocyanobenzene, an isomer of **1a**, and other diisocyanobenzenes have previously been used as bridging ligands in organometallic polymers.¹² Extended solids have also been obtained with 1,4-dicyanobenzene.^{3b} Electronic communication between metal centers across the 1,4-diisocyanobenzene ligand has been studied.¹³ The linear 4-cyanoisocyanobenzenes may also be considered as elongated neutral analogues of the cyanide ion. Cyanide forms stable mononuclear complexes by coordination to metal centers via the carbon atom and polynuclear assemblies or extended solids upon further coordination of the nitrogen atom.^{6a,14} The solids obtained from the new building blocks **2–5** may thus be viewed as expanded analogues of metal cyanides. Considering the large number of possible cyanoisocyanobenzenes, the rich coordination chemistry of isocyanides and nitriles, and the formal analogy between metal complexes of cyanoisocyanobenzenes and cyanometal complexes, the molecular

solid-state chemistry based on cyano-substituted isocyanide complexes as building blocks can be expected to be quite extensive.

Experimental Section

Standard inert-atmosphere techniques were used in the execution of the experiments. The solvents methylene chloride (CaH_2), tetrahydrofuran, ether (Na/benzophenone), and hexane (CaH_2) were dried and distilled prior to use. **1a**¹⁵ and **1b**,^{15,16} $[\text{MnBr}(\text{CO})_5]$,¹⁷ and $[\text{Rh}_2(\text{O}_2\text{CCF}_3)_4]$ ¹⁸ were prepared on the basis of literature procedures. $[\text{FeI}_2 \cdot 4\text{H}_2\text{O}]$ and $[\text{PtI}_2]$ were obtained from commercial sources. The NMR spectra were measured at 250 or 300 MHz (for ^1H NMR) in CDCl_3 at room temperature unless otherwise noted. Solvent peaks were used as internal reference; the chemical shifts are reported in δ relative to TMS.

Synthesis of $[\text{PdI}_2(\text{CN-C}_6\text{H}_4\text{-CN})_2]$ (2**).** Black $[\text{PdI}_2]$ (100 mg, 0.277 mmol) is suspended in CH_2Cl_2 (20 mL), and $\text{CN-C}_6\text{H}_4\text{-CN-4}$ (78 mg, 0.61 mmol) in 10 mL of CH_2Cl_2 is added. An orange solution forms immediately. After the mixture is stirred for 1 h at room temperature, the solvent is removed under vacuum and the residue is washed with ether to remove excess ligand. The residue is recrystallized from CH_2Cl_2 to give orange crystals (0.111 g, 65%), mp >230 °C. ^1H NMR (CD_2Cl_2): δ 7.70 (d, 2H, $J = 8.7$ Hz, C_6H_4), 7.84 (d, 2H, $J = 8.4$ Hz, C_6H_4). IR (CH_2Cl_2 , cm^{-1}): $\nu(\text{-C}\equiv\text{N})$ 2236 m, $\nu(\text{-N}\equiv\text{C})$ 2199 s. Anal. Calcd for $\text{C}_{16}\text{H}_8\text{I}_2\text{N}_4\text{Pd}$: C, 31.17; H, 1.31; N, 9.09; I, 41.17. Found: C, 30.98; H, 1.17; N, 8.86; I, 41.39.

Synthesis of $[\text{PtI}_2(\text{CN-C}_6\text{H}_4\text{-CN})_2]$ (3**).** Black $[\text{PtI}_2]$ (200 mg, 0.446 mmol) is suspended in THF (25 mL), and $\text{CN-C}_6\text{H}_4\text{-CN-4}$ (114 mg, 0.89 mmol) is added. A green-brown solution forms immediately. The solution is filtered, and the solvent is removed under vacuum. The residue is washed with ether and reprecipitated from THF/hexane to give a yellow noncrystalline solid (0.172 g, 55%), mp >230 °C. ^1H NMR (d_6 -THF): δ 7.87 (d, 2H, $J = 8.51$ Hz, C_6H_4), 7.99 (d, 2H, $J = 8.52$ Hz, C_6H_4). $^{13}\text{C}\{^1\text{H}\}$ NMR (d_6 -THF): δ 134.8, 128.7, 117.7, 116.2 (C_6H_4). IR (THF, cm^{-1}): $\nu(\text{-C}\equiv\text{N})$ 2231 m, $\nu(\text{-N}\equiv\text{C})$ 2191 s. Anal. Calcd for $\text{C}_{16}\text{H}_8\text{I}_2\text{N}_4\text{Pt}$: C, 27.25; H, 1.14; N, 7.95. Found: C, 27.48; H, 1.21; N, 7.99.

Synthesis of $[\text{FeI}_2(\text{CN-C}_6\text{H}_4\text{-CN})_4]$ (4a**).** $[\text{FeI}_2 \cdot 4\text{H}_2\text{O}]$ (1.0 g, 2.6 mmol) is first dried under vacuum for 1 h at room temperature and then dissolved in THF (200 mL) to give a dark purple solution. Upon addition of $\text{CN-C}_6\text{H}_4\text{-CN-4}$ (1.34 g, 10.47 mmol), the solution turns greenish brown immediately. After the mixture is stirred for 2 h at room temperature, the solvent is removed under vacuum, and the residue is washed with ether to remove excess ligand. Recrystallization from CH_2Cl_2 /ether gives a dark green crystalline solid (0.90 g, 39%). Crystals suitable for X-ray crystallography were grown by diffusion of pentane into a CH_2Cl_2 solution of **4a**, mp 230 – 270 °C dec. ^1H NMR (CDCl_3): δ 7.63 (d, 2H, $J = 8.50$ Hz, C_6H_4), 7.78 (d, 2H, $J = 8.50$ Hz, C_6H_4). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 176.1 (Fe-CN), 133.5, 131.3, 127.4, 117.2, 113.4 (C_6H_4 , -CN). IR (CH_2Cl_2 , cm^{-1}): $\nu(\text{-C}\equiv\text{N})$ 2234 w, $\nu(\text{-N}\equiv\text{C})$ 2119 vs, 2039 vw. Anal. Calcd for $\text{C}_{32}\text{H}_{16}\text{FeI}_2\text{N}_8$: C, 46.75; H, 1.96; N, 13.63. Found: C, 46.55; H, 1.95; N, 13.45.

Synthesis of $[\text{FeI}_2(\text{CN-C}_6\text{H}_8\text{-Me}_2\text{-2,6-CN-4})_4]$ (4b**).** The procedure for the synthesis of **4a** was followed. Reaction of $[\text{FeI}_2 \cdot 4\text{H}_2\text{O}]$ (200 mg, 0.524 mmol) and **2** (327 mg, 2.10 mmol) in THF and recrystallization from CH_2Cl_2 /ether gives dark green crystals (202 mg, 41%), mp >230 °C. ^1H NMR (CDCl_3): δ 7.42 (s, 2H, C_6H_2), 2.61 (s, 6H, CH_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): 178.1 (Fe-CN), 137.5, 131.7, 131.0, 117.5, 112.3 (C_6H_2 , -CN), 19.0 (CH_3). IR (CH_2Cl_2 , cm^{-1}): $\nu(\text{-C}\equiv\text{N})$ 2230 m, $\nu(\text{-N}\equiv\text{C})$ 2117 vs. Anal. Calcd for $\text{C}_{40}\text{H}_{32}\text{FeI}_2\text{N}_8$: C, 51.42; H, 3.45; N, 11.99. Found: C, 50.74; H, 4.20; N, 11.41. On the basis of ^1H NMR, the crystals include a small amount of ether.

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Synthesis of [Mn(CN-C₆H₄-CN)₆SO₃CF₃] (5). A mixture of [Mn(CO)₅Br] (1.50 g, 5.5 mmol) and CN-C₆H₄-CN-4 (5.59 g, 43.7 mmol) in THF (150 mL) is refluxed for 2 days. During this time the solution turns from orange to dark red and an orange precipitate forms, which is collected by filtration and washed with ether. The solid is transferred into a flask and treated with acetone and NH₄SO₃CF₃. The resulting suspension is stirred at room temperature for 1 h to give an orange-yellow solution and a pale yellow precipitate, which is removed by filtration. The solvent is removed from the filtered solution to give an orange yellow solid. The solid is redissolved in CH₂Cl₂, the resulting solution is filtered, and the solvent is removed again under vacuum. The product is recrystallized from acetone/hexane to give orange yellow microcrystals (2.16 g, 40%), mp > 230 °C. ¹H NMR (CD₂Cl₂): δ 7.63 (d, 2H, J = 7.15 Hz, C₆H₄), 7.76 (d, 2H, J = 7.16 Hz, C₆H₄). ¹³C{¹H} NMR (CD₂Cl₂): δ 134.4, 131.8, 128.0, 118.0, 113.4 (C₆H₄ and -CN, isocyanide signal not found). IR (CH₂Cl₂, cm⁻¹): ν(-C≡N) 2233 w, ν(-N≡C) 2120 sh, 2088 vs, 2037 m. Anal. Calcd for C₄₉H₂₄F₃MnN₁₂SO₃: C, 60.50; H, 2.49; N, 17.28. Found: C, 59.91; H, 2.12; N, 17.37.

Formation of Solid 6 from 2 and [Cu(hfacac)₂]. A green solution of [Cu(hfacac)₂] (15 mg, 0.031 mmol) in 0.5 mL of CH₂Cl₂ is slowly added to an orange solution of [PdI₂(CN-C₆H₄-CN)₂] (10 mg, 0.016 mmol) in 1 mL of CH₂Cl₂. Green crystals form when the solvent slowly evaporates. IR (KBr, cm⁻¹): ν(-C≡N) 2228 m, ν(-N≡C) 2213 s. Anal. Calcd for [PdI₂(CN-C₆H₄-CN)₂] + 2[Cu(hfacac)₂]: C, 27.46; H, 0.80; N, 3.55. Found: C, 27.51; H, 0.77; N, 3.56.

Formation of Solid 7 from 4a and AgSO₃CF₃. A solution of [AgSO₃CF₃] (31 mg, 0.12 mmol) in 1 mL of THF is added to a solution of 4a (50 mg, 0.061 mmol) in 8 mL of THF. A lime green precipitate forms immediately. The solid is separated from the light yellow solution by centrifugation. After removal of the supernatant, the precipitate is washed with THF and dried under vacuum. IR (KBr, cm⁻¹): ν(-C≡N) 2244 w, 2233 w, ν(-N≡C) 2182 sh, 2145 s. Anal. Found: C, 30.03; H, 1.35; N, 8.02; Ag, 17.08. Calcd for 4a + 2.24AgSO₃CF₃: C, 29.43; H, 1.15; N, 8.02; Ag, 17.29. Calcd for 1Fe + 2Ag: C, 30.58; H, 1.21; N, 8.39; Ag, 16.15.

Formation of Solid 8 from 4b and [Rh₂(O₂CCF₃)₄]. A blue solution of [Rh₂(O₂CCF₃)₄] (14 mg, 0.021 mmol) in 0.5 mL of benzene is slowly added to a green solution of 4b (10 mg, 0.011 mmol) in 5 mL of benzene. A brown precipitate forms immediately. The mixture is stirred for several minutes and then allowed to stand overnight. The nearly colorless supernatant is decanted; the precipitate is washed with ether and then dried under vacuum. IR (KBr, cm⁻¹): ν(-N≡C) 2124 sh, 2117 s, 2110 sh. Anal. Found: C, 27.82; H, 1.09; N, 4.23. Calcd for 4b + 2.61[Rh₂(O₂CCF₃)₄]: C, 27.58; H, 1.22; N, 4.23.

Formation of Solid 9 from 5 and Rh₂(O₂CCF₃)₄]. A blue solution of [Rh₂(O₂CCF₃)₄] (50 mg, 0.076 mmol) in CH₂Cl₂ is added to a yellow solution of 5 (25 mg, 0.026 mmol) in CH₂Cl₂. A dark yellow precipitate forms immediately. It is allowed to stand for 2 days and then separated by filtration. The solid is washed with CH₂Cl₂ and dried under vacuum. IR (KBr, cm⁻¹): ν(-C≡N) 2260 w, 2234 w, ν(-N≡C) 2120 sh, 2083 s, 2042 m, 1667 s. Anal. Found: C, 34.14; H, 1.17; N, 7.31; F, 22.93. Calcd for 5 + 2[Rh₂(O₂CCF₃)₄]: C, 34.11; H, 1.06; N, 7.34; F, 22.41.

X-ray Structure Determination. The general procedures for unit cell determination, data collection, and structure solution have been previously described in detail.¹⁹ All intensity measurements were made on an Enraf-Nonius CAD4A automated diffractometer, using a variable-rate, ω-2θ scan technique. Empirical absorption corrections (DIFABS) were applied. All calculations were performed using the TEXRAY programs. The structures were solved by direct methods and difference Fourier methods. The positions of the hydrogen atoms were calculated and used in the least-squares calculations but were not refined. Selected crystallographic data are listed in Table 1.

The asymmetric unit of compound 4a contains two centrosymmetric molecules. The terminal CN group (C(32), N(8)) of one ligand in molecule 4a(2) shows very large thermal parameters. The entire C₆ ring also shows large thermal parameters. All attempts to refine models with a disordered CN group or with a disordered C₆ ring and CN group were unsuccessful. The final model has unrealistic metrical parameters concerning these fragments. The high values of R (R_w) reflect the unresolved disorder.

The CF₃ groups in compound 6 show significant disorder. An acceptable refinement was achieved using a model in which the fluorine atoms of each CF₃ group were 2-fold disordered. The structural diagram in Figure 2 shows only one set of fluorine atoms for each CF₃ group.

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Supporting Information Available: Tables of crystallographic data, positional parameters, U values, bond lengths, and bond angles 4a and of crystallographic data, positional parameters, U values, bond lengths, bond angles, and intermolecular distances for 6 (16 pages). Ordering information is given on any current masthead page.

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