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Cyanoisocyanoarene Metal Complexes as Building Blocks for Coordination Polymers: Structural Nonrigidity of a Metal−Nitrile Linkage[1]

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The complexes *trans*-[$PdI_2(CNR)_2$], **1a**−**1e**, (CNR = 3-CN−C_6H_4−CN (**1a**), 4-CN−3−C_2H_5−C_6H_3−CN (**1b**), **c**: 4-CN−3−Cl−C_6H_3−CN (**1c**), 4-CN−1,2-$(NC)_2$−C_6H_3 (**1d**), 4-CN−C_6H_4−CH_2CN (**1e**)), have been prepared. Complex **2a** forms a coordination polymer, **3**, with copperbis(hexafluoroacetylacetonate) in the ratio of 1:2. The crystal structures of compounds **2b**, **2c**, **2e**, and **3** have been determined by X-ray crystallography. **2b**: $C_{20}H_{16}I_2N_4$-Pd, monoclinic space group, $P1$ (no. 2), $a = 4.630(2)$ Å, $b = 8.365(4)$ Å, $c = 14.835(5)$ Å, $\beta = 98.03(2)°$, $Z =$ 1 1964 unique reflections, $R = 0.038$, $R_w = 0.036$. **2c**: $C_{16}H_6Cl_2I_2N_4Pd$, monoclinic space group, $P1$ (no. 2), $a = 7.569(1)$ Å, $b = 8.229(1)$ Å, $c = 9.114(2)$ Å, $\beta = 77.21(1)°$, $Z = 1$, 1633 unique reflections, $R = 0.030$, $R_w = 0.028$. **2e**: $C_{18}H_{12}I_2N_4Pd$, monoclinic space group, $C2/c$ (no. 15), $a = 14.171(3)$ Å, $b = 8.3781(7)$ Å, $c = 18.096(4)$ Å, $\beta = 103.41(1)°$, $Z = 4$, 2198 unique reflections, $R = 0.036$, $R_w = 0.023$. **3**: $C_{36}H_{12}Cu_2F_{24}I_2N_4O_8$-Pd, monoclinic space group, $P1$ (no. 2), $a = 10.946(2)$ Å, $b = 11.315(3)$ Å, $c = 12.261(3)$ Å, $\beta = 99.39(1)°$, $Z = 1$, 2698 unique reflections, $R = 0.049$, $R_w = 0.057$.

Introduction

Organic and organometallic polynitriles[3] are representatives of a growing class of polytopic organic ligands for the self-assembly of coordination polymers and supramolecular metal complexes.[4] We have recently demonstrated that transition metal complexes of arylisocyanides bearing nitrile groups in peripheral locations can be employed in a similar fashion.[5] The presence of the isocyanide transition metal complex cores[6] offers special opportunities concerning the control of the structural and electronic properties of coordination polymers and molecular aggregates,[7] via independent variation of the metal center and the isocyanide ligands.[8] In the previous study, we have developed metal complexes of 4-isocyanobenzonitriles with linear, square planar, and octahedral dispositions of the isocyanide ligands and demonstrated the formation of coordination polymers with these building blocks.[5] The solid formed from *trans*-diiodobis(4-isocyanobenzonitrile)palladium and 2 equiv of bis(hexafluoroacetylacetonate)copper, compound **4**, was found to possess a one-dimensional structure, which can be described as a string of 20-membered rings, each consisting of two I−Pd−CN−C_6H_4−CN subunits that are joined by copper bridges, whereby the palladium atoms are shared by adjacent rings. As a consequence of the linear nature of the Pd−CN−C_6H_4−CN-4 portion within the rings, the copper−nitrile linkages are strongly bent. The small C−N−Cu bond angle of only 105° indicates that the nitrile π electrons are involved in the nitrile−

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(1) Dedicated to Prof. Herbert D. Kaesz on the occasion of his 65th birthday.

(2) On leave at The University of Hong Kong.

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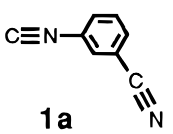
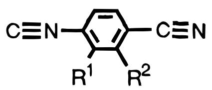
Cu σ bond. The unusual nature of the nitrile−copper interaction prompted us to determine the effect of introducing a bent isocyanobenzonitrile ligand into the system. As reported here, the analogous solid, **3**, formed from *trans*-diiodobis(3-isocyanobenzonitrile)palladium and bis(hexafluoroacetylacetonate)copper contains the same type of rings but with linear copper−nitrile linkages. The observation of end-on- and side-on-bonded nitrile ligands in the two isomeric coordination polymers **3** and **4** suggests that metal−nitrile bonds may not generally be relied upon as rigid structural links in coordination polymers.

Results and Discussion

The isocyanides **1a**−**1e** were prepared in the established fashion by sequential treatment of the corresponding anilines with formic acetic anhydride and triphosgene/NEt_3.[9] The characteristic IR stretching frequencies for the isocyanide groups are observed in the range of 2122−2141 cm^{-1} and those for the aromatic nitrile functionalities at about 2230−2240 cm^{-1}. The IR stretching frequency of the CH_2CN group in **1e** appears at 2255 cm^{-1}. The syntheses of the *trans*-diiodobis(isocyanide)palladium complexes **2a**−**2e** are achieved by addition of the ligands to stirred suspensions of PdI_2 in CH_2Cl_2. Upon coordination to the Pd(II) center, the stretching vibrations of the isocyanide groups shift to higher frequencies by about 70 cm^{-1}, as expected,[6] while those of the free nitrile groups remain almost unaffected. Solid **3** was obtained by slow evaporation of a solution of **2a** and $Cu(hfacac)_2$ (hfacac = hexafluoroacetylacetonate) in CH_2Cl_2. Upon formation of solid **3**, the stretching frequency of the nitrile group of **2a** experiences a shift of 25 cm^{-1} to higher frequencies, which is consistent with the formation of a linear coordinative bond to a Lewis acidic metal center, i.e., the copper atom of $Cu(hfacac)_2$.[10] In contrast, the nitrile stretching frequency of *trans*-$[PdI_2(CNC_6H_4{-}CN\text{-}4)_2]$ decreases by 8 cm^{-1} upon formation of solid **4**.[11] This shift of the nitrile stretching frequency to lower energy is similar in magnitude to that observed upon coordination of 8-cyanoquinoline to $CuCl_2$ and $PdCl_2$.[12] In the complexes of the type $[MCl_2(\text{8-cyanoquinoline})_2]$, the side-on coordination of the nitrile groups is enforced by the steric properties of the 8-cyanoquinoline ligands. In this situation, the shift of the nitrile stretching frequency was attributed primarily to the effects of the interactions of the π_{CN} orbital with the metal center. The isocyanide stretching frequency of **2a** experiences a small yet distinct shift of 12 cm^{-1} to higher frequencies upon formation of solid **3**. A similar shift has been observed in the case of solid **4**. This shift to higher frequencies suggests that in the coordination polymers there is an increase of σ donation by the isocyanide group to the palladium center and possibly some decrease in π back-bonding compared with that in the free metal complexes. The removal of electron density from the palladium centers is probably caused by the interaction of the iodide ligands with the copper centers.



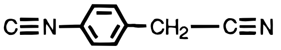
1a



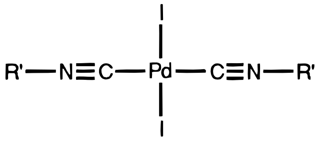
1b: R^1 = Et; R^2 = H

1c: R^1 = Cl; R^2 = H

1d: R^1 = H; R^2 = CN



1e



2a-e: CNR' = **1a-e**

The solid-state structures of the complexes **2b**, **2c**, and **2e** and of solid **3** were determined by X-ray crystallography. The crystallographic data are listed in Table 1, selected bond distances and bond angles are collected in Table 2, and the molecular structures are shown in Figure 1. The bond distances and bond angles of the $PdI_2(CN)_2$ core in complexes **2b**, **2c**, and **2e** are very similar to those found in other *trans*-diiodobis(arylisocyanide)palladium complexes.[13] The structures of complexes **2b** and **2c** serve as reference points for a comparison of the structural parameters of a “free” isocyanide palladium complex building block with those of the “coordinated” building block in solid **4**, *trans*-$[PdI_2(CNC_6H_4CN\text{-}4)_2{\cdot}2Cu(hfacac)_2]$. Previously, we had not been able to obtain suitable crystals to determine the structure of the isolated building block *trans*-$[PdI_2(CNC_6H_4CN\text{-}4)_2]$. The values for the Pd−I, Pd−C, and C−N(nitrile) distances of complexes **2b** and **2c** are virtually indistinguishable from the corresponding values of the “coordinated” building blocks in solid **4** (2.5795(6), 1.944(6), and 1.131(7) Å). The I−Pd−C and C−C−N(nitrile) bond angles of **2b** and **2c** are also very similar to those of **4** (88.4(2)° and 177.6(6)°). Thus, the interactions of the nitrile groups and the

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(11) Based on IR measurements of the “free” building blocks **2a** and *trans*-$[PdI_2(CNC_6H_4CN\text{-}4)_2]$ in CH_2Cl_2 solution and of the solids **3** and **4** in KBr.

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Table 1. Crystallographic Data for Compounds **2b**, **2c**, **2e**, and **3**

compd	**2b**	**2c**	**2e**	**3**
formula	$C_{20}H_{16}I_2N_4Pd$	$C_{16}H_6Cl_2I_2N_4Pd$	$C_{18}H_{12}I_2N_4Pd$	$C_{36}H_{12}Cu_2F_{24}I_2N_4O_8Pd$
cryst size (mm)	0.1 × 0.3 × 0.4	0.2 × 0.1 × 0.3	0.2 × 0.2 × 0.3	0.1 × 0.2 × 0.3
a (Å)	4.630(2)	7.569(1)	14.171(3)	10.946(2)
b (Å)	8.365(4)	8.229(1)	8.3781(7)	11.315(3)
c (Å)	14.835(5)	9.114(2)	18.096(4)	12.261(3)
α (deg)	103.25(2)	82.78(1)		109.21(1)
β (deg)	98.03(2)	77.21(1)	103.41(1)	99.39(1)
γ (deg)	94.64(3)	64.18(1)		111.21(1)
V (Å^3)	550.0(4)	499.7(2)	2090.0(6)	1266.5(3)
Z	1	1	4	1
space group	$P1$ (no. 2)	$P1$ (no. 2)	$C2/c$ (no. 15)	$P1$ (no. 2)
ρ calc (g cm^{-3})	2.031	2.277	2.048	2.061
temp	ambient	ambient	ambient	ambient
radiation (graphite monochromator)	M*o* Kα (λ = 0.710 73 Å)	M*o* Kα (λ = 0.710 73 Å)	M*o* Kα (λ = 0.710 73 Å)	M*o* Kα (λ = 0.710 73 Å)
linear abs coeff (cm^{-1})	36.63	42.93	38.51	25.225
scan mode	$\theta-2\theta$	$\theta-2\theta$	$\omega-2\theta$	$\theta-2\theta$
2θ range (deg)	$0 < 2\theta < 59.9$	$0 < 2\theta < 52.0$	$0 < 2\theta < 51.9$	$0 < 2\theta < 50$
total no. of reflns collected	3567	2112	2294	4797
unique reflns ($I > 3\sigma(I)$)	1964	1633	2198	2698
final no. of variables	124	115	115	332
$R^a = \sum\|\|F_o\| - \|F_c\|\|/\sum\|F_o\|$	0.038	0.030	0.036	0.049
$R_w = [\sum w(\|F_o\| - \|F_c\|)^2/\sum w\|F_o{}^2\|]^{1/2}$	0.036	0.028	0.023	0.057
goodness of fit	3.02	4.26	2.82	2.098

[a] Quantity minimized ($\sum w(|F_o| - |F_c|)^2$); weight, $w = 1/(\sigma^2 + 0.0016F_o{}^2)$.

Table 2. Selected Bond Lengths (Å) and Bond Angles (deg) for Compound 2b

	Compound **2b**		
Pd(1)−I(1)	2.583(1)	Pd(1)−C(1)	1.941(6)
N(1)−C(1)	1.150(7)	N(1)−C(2)	1.401(7)
N(2)−C(8)	1.129(8)	C(5)−C(8)	1.448(8)
I(1)−Pd(1)−C(1)	90.1(2)	Pd(1)−C(1)−N(1)	178.1(6)
C(1)−N(1)−C(2)	179.0(7)	N(1)−C(2)−C(3)	119.0(6)
N(2)−C(8)−C(5)	178.6(8)	C(4)−C(5)−C(8)	119.9(6)
	Compound **2c**		
Pd(1)−I(1)	2.5779(7)	Pd(1)−C(1)	1.965(6)
N(1)−C(1)	1.126(6)	N(1)−C(2)	1.390(6)
N(2)−C(8)	1.140(7)	C(5)−C(8)	1.440(7)
Cl(1)−C(3)	1.708(5)		
I(1)−Pd(1)−C(1)	90.4(2)	Pd(1)−C(1)−N(1)	179.3(5)
C(1)−N(1)−C(2)	176.3(6)	N(1)−C(2)−C(3)	119.7(5)
N(2)−C(8)−C(5)	178.4(7)	C(4)−C(5)−C(8)	119.4(5)
Cl(1)−C(3)−C(2)	120.2(4)		
	Compound **2e**		
Pd(1)−I(1)	2.5718(7)	Pd(1)−C(1)	1.960(6)
N(1)−C(1)	1.137(6)	N(1)−C(2)	1.410(6)
N(2)−C(8)	1.119(7)	C(8)−C(9)	1.466(8)
I(1)−Pd(1)−C(1)	91.2(2)	Pd(1)−C(1)−N(1)	177.9(6)
C(1)−N(1)−C(2)	172.4(7)	N(1)−C(2)−C(3)	119.9(6)
N(2)−C(9)−C(8)	178.7(9)	C(5)−C(8)−C(9)	115.3(5)
	Compound **3**		
Pd component		Cu component	
Pd(1)−I(1)	2.584(1)	Cu(1)−O(1)	1.946(6)
Pd(1)−C(11)	1.942(8)	Cu(1)−O(2)	1.941(6)
N(1)−C(11)	1.15(1)	Cu(1)−O(3)	1.930(6)
N(1)−C(12)	1.428(9)	Cu(1)−O(4)	1.939(6)
N(2)−C(18)	1.14(1)	Cu(1)−N(2)	2.317(8)
C(14)−C(18)	1.46(1)	Cu(1)−I(1)	3.506(2)
I(1)−Pd−I(1A)	180.00	O(1)−Cu(1)−O(2)	91.6(3)
I(1)−Pd−C(11)	88.0(3)	O(1)−Cu(1)−O(3)	176.9(3)
C(11)−Pd−C(11A)	180.00	O(1)−Cu(1)−O(4)	87.2(3)
Pd−C(11)−N(1)	177.5(8)	O(2)−Cu(1)−O(3)	87.9(2)
C(11)−N(1)−C(12)	175.2(9)	O(2)−Cu(1)−O(4)	170.1(3)
N(1)−C(12)−C(13)	117.6(7)	O(3)−Cu(1)−O(4)	92.7(3)
C(13)−C(14)−C(18)	118.3(7)	Cu(1)−N(2)−C(18)	174.9(8)
N(2)−C(18)−C(14)	179(1)	Pd(1)−I(1)−Cu(1)	84.37(4)

iodine atoms of *trans*-[$PdI_2(CNC_6H_4CN\text{-}4)_2$] with the copper atoms in solid **4** do not induce any distinct changes of the geometric parameters within the isocyanide palladium complex building block. A comparison of the relevant bond distances and bond angles of solid **3** with those of complexes **2b** and **2c** as well as solid **4** suggests that the interaction of complex **2a** with $Cu(hfacac)_2$ also causes no significant structural changes within the palladium building block.

Figure 2 shows small portions of the one-dimensional structures of solids **3** (part a) and **4** (part b) as well as a superimposition of the two fragments (part c), which illustrates the close structural relationship between solids **3** and **4**. The superimposition shows that the "reorientation" of the nitrile group of the isocyanide ligands in **3** versus **4**, by changing the position on the arene ring from the para to the metaposition, leaves the large ring structure intact. The transannular Pd−Pd separation is almost the same in both solids (**3**, 13.68 Å; **4**, 13.54 Å). The ring structure in **3** is free of the steric constraints that caused the nitrile groups in **4** to employ π electrons to establish the connections with the copper centers. In solid **3**, the nitrile groups form "normal" linear links with the bridging copper units. The reorientation of the nitrile groups is accompanied by a pronounced adjustment of the Cu−N and Cu−I bond lengths. The Cu(1)−N(2) distance of 2.669(6) Å in **4** shrinks to 2.317(8) Å in **3**. At the same time, the Cu(1)−I(1) distance lengthens from 3.1929(9) Å in **4** to 3.506(2) Å in **3**. Since the Cu(1)−N(2) distance shortens by about the same amount as the Cu(1)−I(1) distance lengthens, the sum of the Cu(1)−N(2) and Cu(1)−I(1) distances remains almost constant (5.82 Å for **3**, 5.86 Å for **4**). This suggests that the bonding capabilities of $Cu(hfacac)_2$ as a linking unit are fully utilized in both solids. The different Cu(1)−N(2) bond lengths in solids **3** and **4** may be considered to reflect the different donor strengths of the nitrile σ versus π electrons, while the changes in the Cu(1)−I(1) bond lengths may be attributed to the different trans influences of the nitrile σ and π electrons.

The π(CN) → Cu interaction in **4** is presumably weaker than the σ(CN) → Cu interaction in **3**. Nevertheless, since the respective arrangements of the coordinative bonds in **3** and **4** are ultimately stabilized by relatively weak crystal packing forces, it may be concluded that the cost in energy for the "migration" of the copper atom from the tip of the nitrile group to its side is not high. Concerning the use of polytopic nitriles

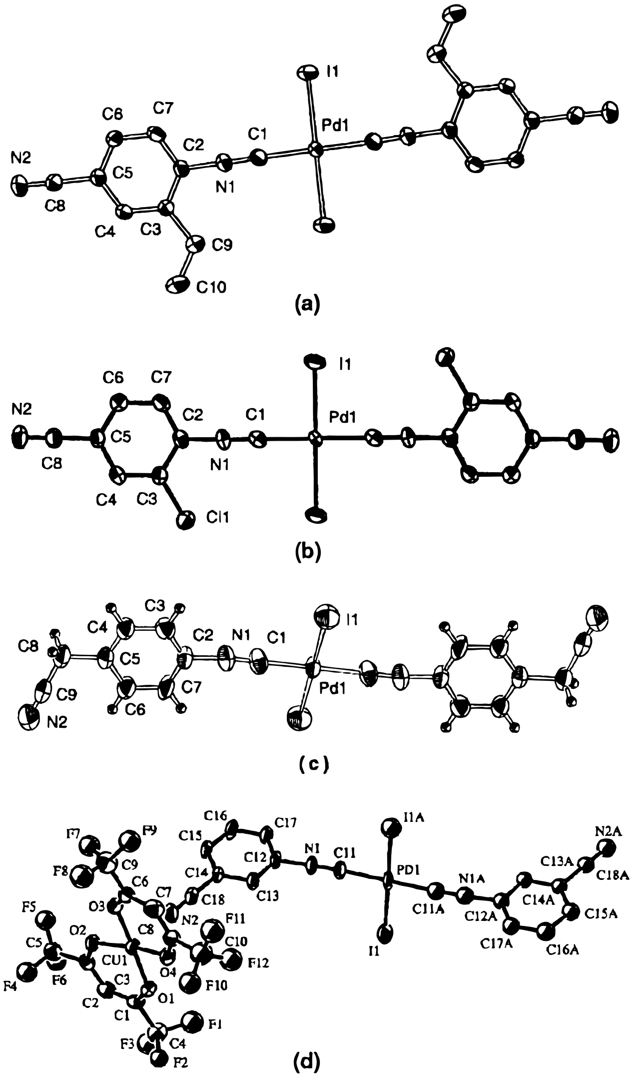

Figure 1. Molecular structures of **2b** (a), **2c** (b), **2e** (c), and **3** (d).

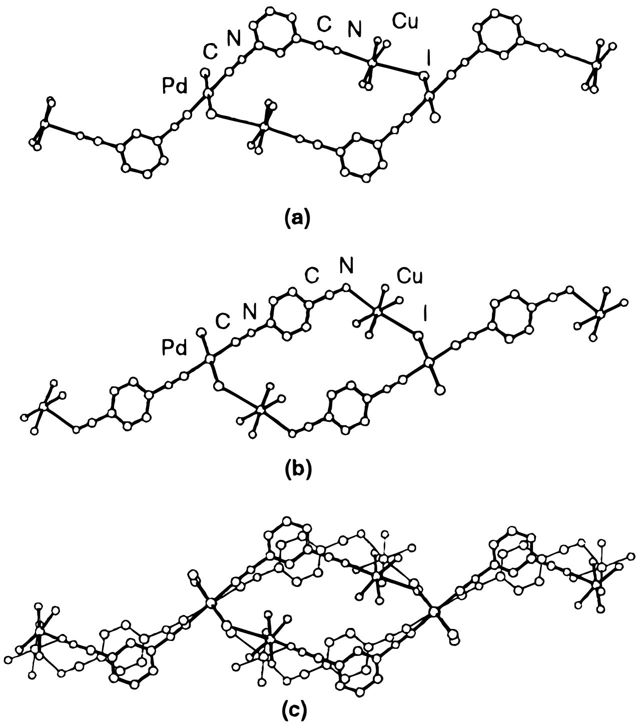

Figure 2. (a) Short segment of the chain structure of **3**. (b) Short segment of the chain structure of **4**. (c) Superimposition of the structural segments shown in (a) and (b). The Cu(hfacac)$_2$ units are truncated to show only the CuO$_4$ cores.

as building blocks for coordination polymers, these results consequently imply that metal−nitrile linkages may not in all situations be relied upon as stereochemically rigid connections. In this sense, the bent metal−nitrile linkage of solid **4** may be viewed as a "collapsed" structural unit.

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. 3-H$_2$N−C$_6$H$_4$−CN, 4-H$_2$N−3-C$_2$H$_5$−C$_6$H$_3$−CN, 4-H$_2$N−3-Cl−C$_6$H$_3$−CN, 4-H$_2$N−1,2-(CN)$_2$−C$_6$H$_3$, 4-H$_2$N−C$_6$H$_4$−CH$_2$CN, [Cu(hfacac)$_2$], and [PdI$_2$] were obtained from commercial sources. The NMR spectra were measured at 250 or 300 MHz (for ^{1}H NMR) in CDCl$_3$ at room temperature unless otherwise noted; solvent peaks were used as internal references, and the chemical shifts are reported in δ relative to TMS.

Synthesis of 3-CN−C$_6$H$_4$−CN (1a). Formic acid (3.72 mL, 102 mmol) and acetic anhydride (8.67 mL, 95 mmol) are mixed and stirred at 50−60 °C for 2 h. The solution is cooled to room temperature, and 3-aminobenzonitrile (5.00 g, 42.3 mmol) is added slowly. Then, ether (100 mL) is added, and the mixture is allowed to stir for about 60 h at room temperature. The product is separated by filtration and washed with ether (3 × 30 mL). Yield 4.99 g (80.7%). The product is used in the next step without further purification.

3-Formamidobenzonitrile (2.34 g, 16.0 mmol), triethylamine (5.20 mL, 37.2 mmol), and CH$_2$Cl$_2$ (150 mL) are placed in a reaction flask and cooled to 0 °C. Phosgene (8.70 mL, 16.8 mmol), as a solution in toluene, is added dropwise. CAUTION: Phosgene is a highly toxic gas. Even when used as a dilute solution, all operations must be executed in a well-ventilated fume hood. After the solution is stirred for about 2 h at room temperature, ammonia gas is bubbled into the solution for 15 min. The white precipitate is filtered off. The pale-yellow filtrate is concentrated under a vacuum. After being chromatographed on silica gel/CH$_2$Cl$_2$, the product is isolated as a white solid (1.65 g, 80.6%), mp 128 °C, dec. ^{1}H NMR (CDCl$_3$): δ 7.72−7.53 (m, 4H, C$_6$H$_4$). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 167.7 (−NC), 132.9, 130.8, 130.7, 129.8, 116.8, 114.0 (C$_6$H$_4$, −CN). IR (CH$_2$Cl$_2$, cm^{-1}): ν(−CN) 2238 m, ν(−NC) 2141 s, 2121 s. HRMS (EI) *m*/*e*: calcd for C$_8$H$_4$N$_2$, 128.0375; found, 128.0371 (M+).

Synthesis of 4-CN−3-C$_2$H$_5$−C$_6$H$_3$−CN (1b). By use of the procedure described for **1a**, 4-H$_2$N−3-C$_2$H$_5$−C$_6$H$_3$−CN (2.00 g, 13.68 mmol) is converted to 4-CHONH−3-C$_2$H$_5$−C$_6$H$_3$−CN (1.85 g, 77.5%) and **1b** (1.48 g, 89.1%), a white solid, mp 80−81 °C. ^{1}H NMR (CDCl$_3$): δ 7.60 (d, 1H, J = 1.20 Hz, C$_6$H$_3$), 7.53 (dd, 1H, J = 8.05, 1.39 Hz, C$_6$H$_3$), 7.44 (d, 1H, J = 8.15 Hz, C$_6$H$_3$), 2.81 (q, 2H, J = 7.58 Hz, CH$_2$), 1.28 (t, 3H, J = 7.53 Hz, CH$_3$). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 170.4 (−NC), 142.1, 132.9, 130.6, 127.6, 117.6, 113.4 (C$_6$H$_3$, −CN), 25.3, 13.3 (C$_2$H$_5$). IR (CH$_2$Cl$_2$, cm^{-1}): ν(−CN) 2234 m, ν(−NC) 2122 s. HRMS (EI) *m*/*e*: calcd for C$_{10}$H$_8$N$_2$, 156.0688; found, 156.0681 (M+).

Synthesis of 4-CN−3-Cl−C$_6$H$_3$−CN (1c). By use of the procedure described for **1a**, 4-H$_2$N−3-Cl−C$_6$H$_3$−CN (2.00 g, 13.13 mmol) is converted to 4-CHONH−3-Cl−C$_6$H$_3$−CN (2.02 g, 85.3%) and then to **1c** (1.60 g, 88.0%), a white solid, mp 116−117 °C. ^{1}H NMR (CDCl$_3$): δ 7.82 (d, 1H, J = 1.46 Hz, C$_6$H$_3$), 7.63 (dd, 1H, J = 8.25, 1.50 Hz, C$_6$H$_3$), 7.57 (d, 1H, J = 8.25 Hz, C$_6$H$_3$). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 174.0 (−NC), 133.7, 132.2, 131.3, 128.7, 116.1, 114.4 (C$_6$H$_3$, −CN). IR (CH$_2$Cl$_2$, cm^{-1}): ν(−CN) 2237 w, ν(−NC) 2125 s. Anal. Calcd for C$_8$H$_3$N$_2$Cl: C, 59.10; H, 1.86; N, 17.23. Found: C, 59.02; H, 1.92; N, 17.04.

Synthesis of 4-CN−1,2-(CN)$_2$−C$_6$H$_3$ (1d). By use of the procedure described for **1a**, 4-H$_2$N−1,2-(CN)$_2$−C$_6$H$_3$ (1.00 g, 6.99 mmol) is converted to 4-CHONH−1,2-(CN)$_2$−C$_6$H$_3$ (1.10 g, 92.0%) and **1d** (0.78 g, 87.2%) a white solid, mp 89−90 °C. ^{1}H NMR (CDCl$_3$): δ 7.92 (d, 1H, $J = 8.34$ Hz, C_6H_3), 7.84 (d, 1H, $J = 1.74$ Hz, C_6H_3), 7.76 (dd, 1H, $J = 8.24$, 1.93 Hz, C_6H_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 172.6 (−NC), 135.1, 131.2, 131.1, 117.9, 116.7, 114.1, 113.6 (C_6H_3, −CN). IR (CH_2Cl_2, cm^{-1}): ν(−CN) 2240 w, ν(−NC) 2126 s, 2116 sh. HRMS (EI) *m*/*e*: calcd for $C_9H_3N_3$, 153.0328; found, 153.0330 (M+).

Synthesis of 4-CN−C_6H_4−CH_2CN (1e). By use of the procedure described for **1a**, 4-H_2N−C_6H_4−CH_2CN (3.30 g, 25.0 mmol) is converted to 4-CHONH−C_6H_4−CH_2CN (3.40 g, 84.9%). Then, 1.28 g of 4-CHONH−C_6H_4−CH_2CN (8.00 mmol) is converted to **1e** (1.0 g, 88%) a white solid, mp 72−73 °C. ^1H NMR ($CDCl_3$): δ 7.37 (s, 4H, C_6H_4), 3.78 (s, 2H, CH_2). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 165.8 (−NC), 131.6, 129.2, 127.1, 117.6 (C_6H_4, −CN), 23.4 (CH_2). IR (CH_2Cl_2, cm^{-1}): ν(−CN) 2255 vw, ν(−NC) 2129 s. HRMS (EI) *m*/*e*: calcd for $C_9H_6N_2$, 142.0532; found, 142.0528 (M+).

Synthesis of [PdI_2(3-CN−C_6H_4−CN)$_2$] (2a). [PdI_2] (250 mg, 0.693 mmol) is suspended in CH_2Cl_2(50 mL), and **1a** (190 mg, 1.48 mmol) in 20 mL of CH_2Cl_2 is added. An orange solution forms 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, yielding an orange solid (340 mg, 80%), mp > 230 °C. ^1H NMR ($CDCl_3$): δ 7.62−7.86 (m, 4H, C_6H_4). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 134.7, 131.1, 130.7, 129.9, 114.7 (C_6H_4, −CN). IR (CH_2Cl_2, cm^{-1}): ν(−CN) 2239 vw, ν(−NC) 2205 s. IR (KBr, cm^{-1}): ν(−CN) 2237 w, ν(−NC) 2211 s. Anal. Calcd for $C_{16}H_8I_2N_4Pd$: C, 31.17; H, 1.31; N, 9.09. Found: C, 31.04; H, 1.42; N, 8.88.

Synthesis of [PdI_2(4-CN−3−C_2H_5−C_6H_3−CN)$_2$] (2b). Following the procedure described for **2a**, **2b** was prepared from [PdI_2] (250 mg, 0.693 mmol) and **1b** (230 mg, 1.47 mmol) as an orange solid (396 mg, 84.9%). Crystals suitable for X-ray crystallography were grown by diffusion of pentane into a CH_2Cl_2 solution of the compound. mp 230 °C. ^1H NMR(CD_2Cl_2): δ 7.80−7.60 (m, 3H, C_6H_3), 2.98 (q, 2H, $J = 6.26$ Hz, C_2H_5), 1.35 (t, 3H, 6.26 Hz, C_2H_5). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 144.4, 134.0, 131.5, 128.4, 117.8, 115.9 (C_6H_3, −CN), 26.0, 14.4 (C_2H_5). IR (CH_2Cl_2, cm^{-1}): ν(−CN) 2234 vw, ν(−NC) 2196 s. Anal. Calcd for $C_{20}H_{16}I_2N_4Pd$: C, 35.72; H, 2.40; N, 8.33. Found: C, 35.80; H, 2.27; N, 8.38.

Synthesis of [PdI_2(4-CN−3−Cl−C_6H_3−CN)$_2$] (2c). By use of the procedure described for **2a**, **2c** was prepared from PdI_2 (250 mg, 0.693 mmol) and **1c** (240 mg, 1.48 mmol) as an orange solid (368 mg, 77.4%). Crystals suitable for X-ray crystallography were grown by diffusion of pentane into a CH_2Cl_2 solution of the compound. mp > 230 °C. ^1H NMR (CD_2Cl_2): δ 7.90 (d, 1H, $J = 1.10$ Hz, C_6H_3), 7.78 (d, 1H, $J = 6.85$ Hz, C_6H_3), 7.73 (dd, 1H, $J = 6.85$, 1.10 Hz, C_6H_3). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 134.7, 133.8, 132.3, 129.6, 116.8, 116.4 (C_6H_3, −CN). IR (CH_2Cl_2, cm^{-1}): ν(−CN) 2238 vw, ν(−NC) 2194 s. Anal. Calcd for $C_{16}H_6Cl_2I_2N_4Pd$: C, 28.04; H, 0.88; N, 8.17. Found: C, 28.21; H, 0.85; N, 8.03.

Synthesis of [PdI_2(4-CN−1,2-(CN)$_2$−C_6H_3)$_2$] (2d). By use of the procedure described for **2a**, **2d** was prepared from [PdI_2] (250 mg, 0.693 mmol) and **1d** (230 mg, 1.46 mmol) as an orange solid (350 mg, 75.5%), mp > 230 °C. ^1H NMR (acetone-d_6): δ 8.62 (s, 1H, C_6H_3), 8.47 (s, 2H, C_6H_3). $^{13}C\{^1H\}$ NMR (acetone-d_6): δ 136.8, 132.9, 132.7, 130.0, 119.2, 118.7, 115.5, 115.0 (C_6H_3, −CN). IR (CH_2Cl_2, cm^{-1}): ν(−NC) 2195 s. Anal. Calcd for $C_{18}H_6I_2N_6Pd$: C, 32.44; H, 0.91; N, 12.61. Found: C, 32.78; H, 0.80; N, 12.55.

Synthesis of [PdI_2(4-CN−C_6H_4−CH_2CN)$_2$] (2e). By use of the procedure described for **2a**, **2e** was prepared from [PdI_2] (250 mg, 0.693 mmol) and **1e** (210 mg, 1.48 mmol) as an orange solid (380 mg, 85%), mp 177 °C, dec. ^1H NMR($CDCl_3$): δ 7.59 (d, 2H, $J = 8.45$ Hz, C_6H_4), 7.49 (d, 2H, $J = 8.43$ Hz, C_6H_4), 3.84 (s, 2H, CH_2). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 141.8, 133.6, 129.4, 127.4, 125.4, 116.4 (C_6H_4, −CN), 23.6 (CH_2). IR (CH_2Cl_2, cm^{-1}): ν(−CN) 2253 vw, ν(−NC) 2203 s. Anal. Calcd for $C_{18}H_{12}I_2N_4Pd$: C, 33.54; H, 1.88; N, 8.69. Found: C, 33.70; H, 1.93; N, 8.57.

Formation of Solid 3 from 2a and [Cu(hfacac)$_2$]. A green solution of [Cu(hfacac)$_2$] (16 mg, 0.032 mmol) in 0.5 mL of CH_2Cl_2 is slowly added to an orange solution of **2a** (10 mg, 0.016 mmol) in 1 mL of CH_2Cl_2. Green crystals form when the solvent slowly evaporates. IR (KBr, cm^{-1}): ν(−CN) 2264 m, ν(−NC) 2217 s. Anal. Calcd for [PdI_2-(3-CN−C_6H_4−CN)$_2$] + 2[Cu(hfacac)$_2$]: C, 27.51; H, 0.77; N, 3.56. Found: C, 27.65; H, 0.50; N, 3.57.

Crystallographic Studies.[14] **Crystal Structure Analysis of 2b**. An orange block crystal of **2b** having approximate dimensions of 0.10 × 0.30 × 0.40 mm^3 was mounted on a glass fiber. Diffraction data were measured on an Enraf-Nonius CAD4 diffractometer with graphite monochromated Mo Kα radiation ($\lambda = 0.710\,73$ Å). Cell constants and an orientation matrix for data collection were obtained from a least-squares refinement based on the setting angles of 25 carefully centered reflections in the range of $20° < 2\theta < 22°$. The data were collected at room temperature, using the $\theta-2\theta$ scan technique to a maximum value of 60°. Of the 3567 reflections that were collected, 3199 were unique ($R_{int} = 0.016$). The linear absorption coefficient, μ, for Mo Kα radiation is 36.6 cm^{-1}. An empirical absorption correction using the program DIFABS[15] was applied. The structure was solved and expanded using Fourier techniques.[16] The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. The final cycle of full-matrix least-squares refinement was based on 1964 observed reflections ($I > 3\sigma(I)$) and 124 variable parameters and converged with unweighted and weighted agreement factors of $R = 0.038$ and $R_w = 0.036$. The standard deviation of an observation of unit weight was 3.02. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.83 and −0.93 e/Å^3, respectively. All calculations were performed using the teXsan[17] crystallographic software package of Molecular Structure Corporation.

The crystal analyses of **2c** and **3** were performed following the same general procedure.[14] The CF_3 groups in **3** showed significant disorder. An acceptable refinement was achieved using a model in which the fluorine atoms of each CF_3 group were 2-fold disordered. The structural diagram in Figure 1d shows only one set of fluorine atoms for each CF_3 group.

Acknowledgment. We thank Prof. Stephen A. Koch and Hua-Fen Hsu for performing the crystal structure analyses of **2b**, **2c**, **2e**, and **3**. Financial support by the National Science Foundation is gratefully acknowledged.

Supporting Information Available: Positional parameters, *U* values, bond lengths, and bond angles for **2b**, **2c**, **2e**, and **3** (16 pages). Ordering information is given on any current masthead page.

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