Metal Complexes of Pyridylphenylisocyanides and Pyridylethynylphenylisocyanides as Building Blocks for Coordination Polymers and Supramolecular Assemblies

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The isocyanides 3-(4-pyridylethynyl)phenylisocyanide, **3**, 4-(4-pyridylethynyl)phenylisocyanide, **6**, 2,6-diisopropyl-4-(4-pyridylethynyl)phenylisocyanide, **9**, and 2,6-diisopropyl-4-(4-pyridyl)phenylisocyanide, **11**, were prepared. With PdI_2 and PtI_2, these isocyanides form the complexes *trans*-$[MI_2(CNR)_2]$, **12**−**19** (M = Pd, Pt; CNR = **3**, **6**, **9**, **11**). The previously prepared complex *trans*-$[PdI_2(CNC_5H_4N\text{-}3)_2]$ and *trans*-$[PdI_2(CNC_6H_2\text{-}(i\text{-}Pr)_2\text{-}2,6\text{-}(CC\text{-}C_5H_4N\text{-}4)\text{-}4)_2]$, **16**, combine with copper bis(trifluoroacetylacetonate) in the ratio of 1:2 to form the adducts *trans*-$[PdI_2(CNC_5H_4N\text{-}3)_2]\cdot 2[Cu(tfacac)_2]\cdot 2CH_2Cl_2$, **20**, and *trans*-$[PdI_2(CNC_6H_2\text{-}(i\text{-}Pr)_2\text{-}2,6\text{-}(CC\text{-}C_5H_4N\text{-}4)\text{-}4)_2]\cdot 2[Cu(tfacac)_2]$, **21**, respectively. The complexes *trans*-$[MI_2(CNC_6H_2\text{-}(i\text{-}Pr)_2\text{-}2,6\text{-}(C_5H_4N\text{-}4)\text{-}4)_2]$, **19** (M = Pd) and **20** (M = Pt), react with $[Pd(SO_3CF_3)_2(dppp)]$ (dppp = bisdiphenylphosphinopropane) to form the molecular squares $[Pd(dppp)(trans\text{-}[MI_2(CNC_6H_2\text{-}(i\text{-}Pr)_2\text{-}2,6\text{-}(C_5H_4N\text{-}4)\text{-}4)_2]_4(SO_3CF_3)_8$, **22** (M = Pd) and **23** (M = Pt). The crystal structure of **20** has been determined by X-ray crystallography. **20**: $C_{34}H_{28}Cl_4Cu_2F_{12}I_2N_4O_8Pd$, monoclinic space group, $P2_1/n$ (No. 14), $a = 10.899(3)$ Å, $b = 13.903(1)$ Å, $c = 17.827(6)$ Å, $\beta = 105.50(2)°$, $Z = 2$, 2618 unique reflections, $R = 0.093$, $R_w = 0.091$.

Introduction

The molecular self-assembly of coordination polymers and supramolecules is a promising route to novel molecular materials.[1] The general expectations associated with this methodology rest on the possibility to modify the materials properties via the steric and electronic features of the individual molecular components. In several design strategies, organic molecules which have specifically tailored shapes and are fitted with directional donor sites are allowed to self-assemble with metal ions or unsaturated metal complexes.[2] In a similar fashion, transition metal complexes can be utilized to encode the steric information.[3] In this context, isocyanide metal complexes[4] are particularly attractive as molecular building blocks, since all major coordination geometries can be realized and the intrinsic coordination geometries of the metal centers can be extended directly along the axes of the isocyanide ligands toward the periphery of the molecules. Since pyridine and other nitrogen heterocyclic donors are among the most commonly used donor groups in coordination polymers[5] and supramolecular coordination compounds,[6] isocyanide metal complexes bearing these types of donors can be expected to combine the advantages of metal−pyridine type interactions with the comprehensive steric flexibility of the metal isocyanide system. Moreover, the presence of partial metal−carbon multiple bonds in metal isocyanides is likely to foster the appearance of long-range electronic effects. We have recently prepared several transition metal complexes of pyridylisocyanides[7] and other functionalized

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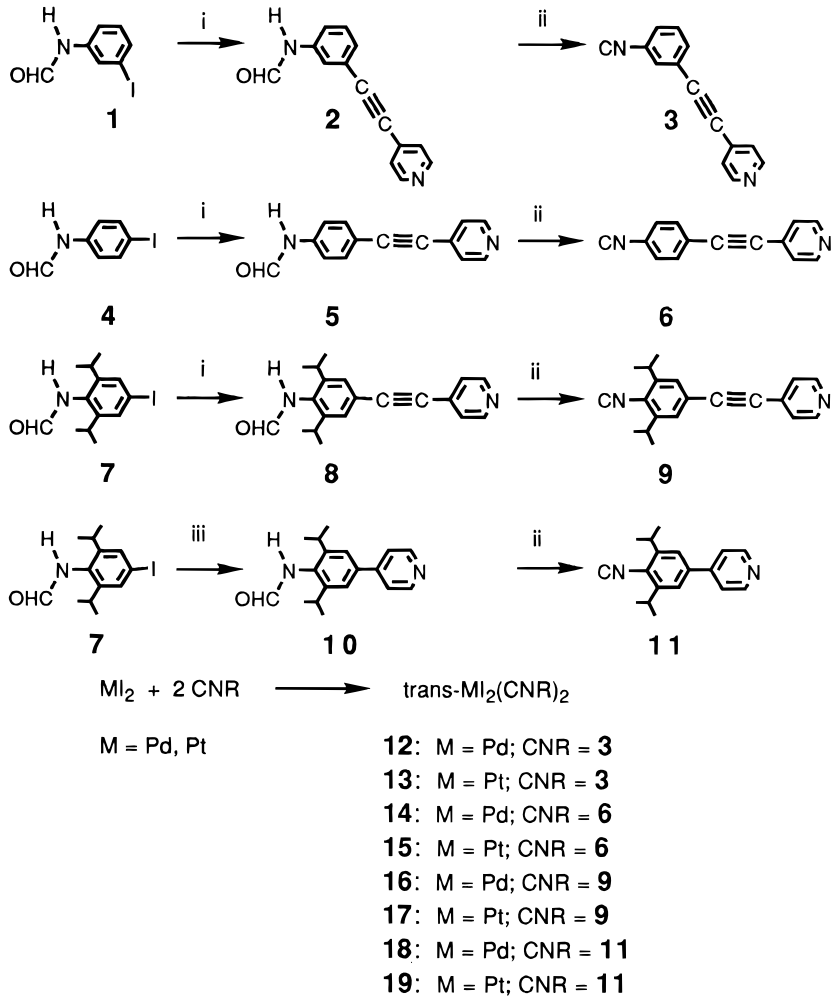
Scheme 1



[a] Legend: (i) 4-HCCC$_5$H$_4$N/Pd(dba)$_2$/PPh$_3$/CuI/NEt$_3$; (ii) phosgene/triethylamine; (iii) 4-Me$_3$SnC$_5$H$_4$N/PdCl$_2$(PPh$_3$)$_2$/LiCl/toluene or 4-Me$_3$SnC$_5$H$_4$N/Pd(PPh$_3$)$_4$/THF.

isocyanides[8] as potential building blocks for molecular materials. In continuation of this work, we have now synthesized analogous comlexes of spacially extended pyridylisocyanides and explored molecular self-assembly processes with this type of metal complex.

Results and Discussion

The synthesis of the pyridylethynylphenylisocyanides **3**, **6**, and **9** (Scheme 1) is accomplished by palladium-catalyzed cross-coupling[9] of the aryl iodides **1**, **4**, and **7** with 4-pyridylacetylene, followed by dehydration of the formamides **2**, **5**, and **8** with triphosgene/NEt$_3$.[10] The pyridylphenylisocyanide **11** was obtained by palladium-catalyzed cross-coupling of the formamidophenyl iodide **7**[11] with 4-trimethylstannylpyridine,[12] followed by dehydration of the formamide group. The pure isocyanides **3**, **6**, and **9** are not stable at room temperature, although **9** is significantly more stable than **3** and **6**. These compounds can, if necessary, be stored in solution at low temperature. Compound **11** appears to be stable at room temperature for longer periods of time.

The isocyanides **3**, **6**, **9**, and **11** exhibit strong single IR absorptions in the range of 2116−2134 cm^{-1} for the N≡C triple bonds. The ^{13}C NMR resonances of isocyanide groups are generally of low intensity.[4] For arylisocyanides, these signals typically occur near δ 170 and were detected for the compounds **6** and **9**. The alkynyl groups in the compounds **2**, **3**, **5**, **6**, **8**, and **9** give rise to characteristic ^{13}C NMR signals for the alkynyl carbon atoms in the range of δ 80−100.

All new isoycanides readily react with PdI$_2$ and PtI$_2$ in CH$_2$Cl$_2$ solution to form stable isocyanide metal complexes of the type *trans*-[MI$_2$(CNR)$_2$] (M = Pd, Pt), **12**−**19**. The trans arrangement of the two isocyanide ligands is indicated by the appearance of only a single stretching frequency for the metal-coordinated isocyanide groups. The stretching frequencies of the free isocyanide groups shift by about 70−90 cm^{-1} to higher

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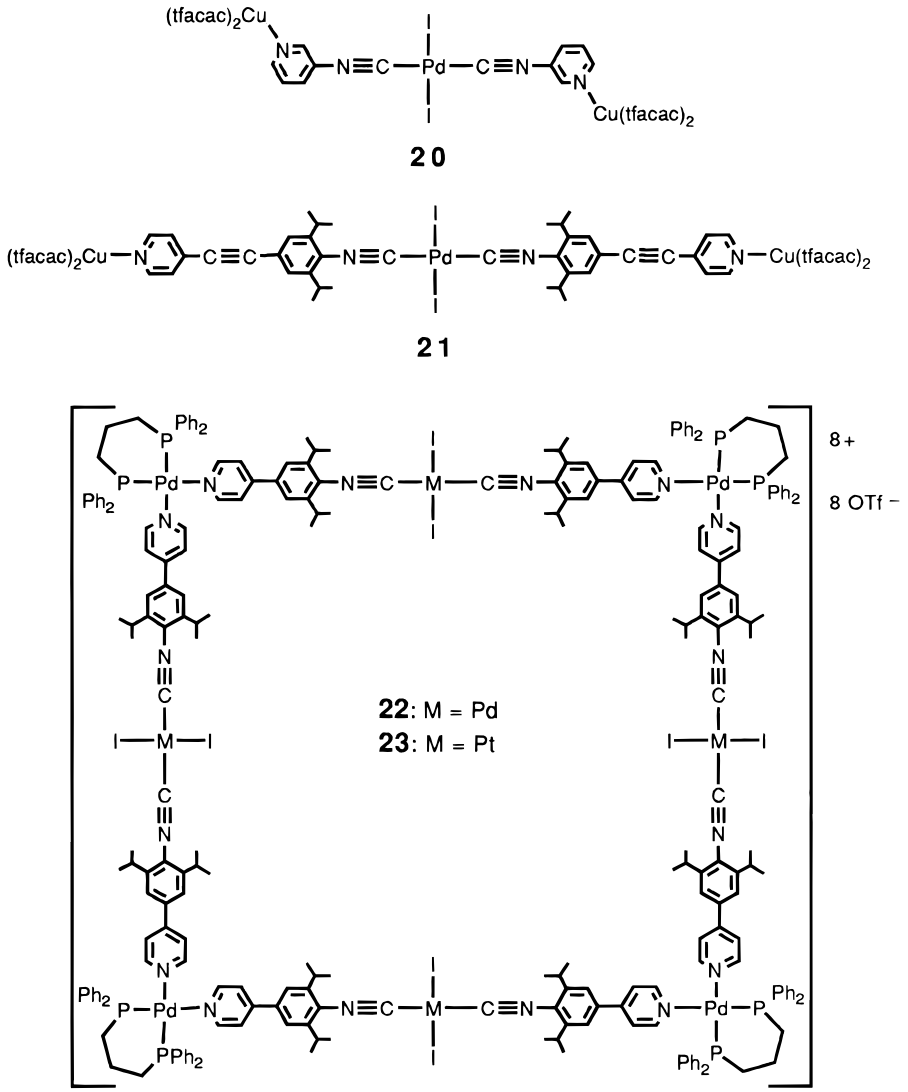
Chart 1



frequencies upon coordination to the metal centers. Due to this shift, the weak absorptions of the alkynyl groups of the coordinated ligands are no longer obstructed by the more intensive absorptions of the isocyanide groups. For the complexes **12** and **13**, weak absorptions between 2130 and 2140 cm^{-1} were assigned to the C≡C-stretching frequencies.

Complexes **12**−**19** are extended analogues of the metal complexes of the corresponding simple pyridylisocyanide metal complexes which we have described recently.[7] They bear pyridyl groups in defined orientations at peripheral locations, and it appears reasonable to expect that they will serve as building blocks for the self-assembly of molecular solids or supramolecular structures in a similar manner as is established for organic polypyridyl compounds.[5,6] An analogy may also be drawn between the pyridylethynylisocyanide ligands of this work and some pyridylethynylphenylacetylide ligands, which have recently been demonstrated to serve as versatile ligands for the synthesis of metal complexes with interesting electronic properties.[13] In first attempts to utilize the new metal complexes as molecular building blocks, we combined several representative examples with $[Cu(tfacac)_2]$ (tfacac = trifluoroacetylacetonate) and $[Pd(SO_3CF_3)_2(dppp)]$ (dppp = bisdiphenylphosphinopropane), both of which belong to established types of linking groups.[14,15]

When pentane or hexane is allowed to diffuse slowly into methylene chloride or chloroform solutions containing the previously prepared complex $[PdI_2(CNC_5H_4N\text{-}3)_2]$ or compound **16**, and $[Cu(tfacac)_2]$ in a relative molar ratio of 1:2, then the green crystalline solids of the relative composition $[PdI_2(CNC_5H_4N\text{-}3)_2]\cdot 2[Cu(tfacac)_2]\cdot 2CH_2Cl_2$, **20**, and *trans*-$[PdI_2(CNC_6H_2\text{-}(i\text{-}Pr)_2\text{-}2,6\text{-}(CC\text{-}C_5H_4N\text{-}4)\text{-}4)_2]\cdot 2[Cu(tfacac)_2]$, **21**, are obtained. Solid **20** is a two-dimensional coordination polymer in which the copper units are connecting the palladium building blocks via Cu−N and Cu−I interactions (Chart 1). The solid-state structure of **21** is not yet known, since we have been unsuccessful in growing single crystals of this compound, but it appears likely that the two copper units in **21** are coordintated to the pyridyl groups of **16**. Upon combining the complexes **18** or **19** with $[Pd(SO_3CF_3)_2(dppp)]$ in a 1:1 molar ratio in methylene chloride solution, the new molecular species **22** and **23** form. The formulation of compounds **22** and **23** as molecular squares is based on the ^1H, ^{13}C, and ^{31}P NMR spectroscopic

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Table 1. Crystallographic Data for Compound **20**

chemical formula $C_{34}H_{28}Cl_4Cu_2F_{12}I_2N_4O_8Pd$	fw 1477.2
$a = 10.899(3)$ Å	space group $P2_1/n$ (No. 14)
$b = 13.903(1)$ Å	temperature 25 °C
$c = 17.827(6)$ Å	$\lambda = 0.710\ 73$ Å
$\beta = 105.50(2)°$	$\rho_{calcd} = 2.03$ g cm^{-3}
$V = 2603.2(1)$ Å^3	$\mu = 28.38$ cm^{-1}
$Z = 2$	$R^a = 0.093$
	$R_w{}^b = 0.091$

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

Table 2. Selected Bond Lengths (Å) and Bond Angles (deg) for Compound **20**

Pd component		Cu component	
Pd(1)−I(1)	2.580(2)	Cu(1)−O(1)	1.93(1)
Pd(1)−C(1)	2.20(2)	Cu(1)−O(2)	1.93(1)
N(1)−C(1)	1.11(2)	Cu(1)−O(3)	1.93(1)
N(1)−C(2)	1.36(2)	Cu(1)−O(4)	1.96(1)
N(2)−C(3)	1.36(2)	Cu(1)−N(2)	2.28(1)
N(2)−C(4)	1.31(3)	Cu(1)−I(1)	3.568(3)
I(1)−Pd−C(1)	92.0(6)	O(1)−Cu(1)−O(2)	93.6(5)
Pd−C(1)−N(1)	172(3)	O(1)−Cu(1)−O(3)	171.7(6)
C(1)−N(1)−C(2)	177(2)	O(1)−Cu(1)−O(4)	86.3(6)
Pd(1)−I(1)−Cu(1)	93.65(6)	O(2)−Cu(1)−O(3)	87.0(5)
		O(2)−Cu(1)−O(4)	174.1(6)
		O(3)−Cu(1)−O(4)	92.5(6)
		Cu(1)−N(2)−C(3)	118(1)
		I(1)−Cu(1)−N(2)	171.97 (4)

results, which show only single sets of signals for the [Pd(dppp)]$^{2+}$ "corners", as well as the precedent in the literature[16] for the facile formation of molecular squares from *cis*-palladium metal complex fragments and linear bipyridine-type organic ligands.

The solid-state structure of compound **20** was established by X-ray crystallography. The crystallographic information is collected in Table 1. Probably as a consequence of the disorder of the copper bistrifluoroacetylacetonate units, *R* and *Rw* have relatively high values. Nevertheless, since the important aspect of the structure is the spatial arrangement of the molecular units in the crystal, not the precise intramolecular metric parameters, the X-ray crystallographic study does provide valuable structural information. Selected bond distances and bond angles are listed in Table 2. The structure of the molecular components of **20** is shown in Figure 1. The palladium building blocks connect with the copper linking units via the nitrogen atoms of the pyridyl groups *and* the iodide ligands to form a two-dimensional network, a portion of which is represented in Figure 2. The intramolecular bond distances and bond angles of both molecular components are normal. The Pd(1)−I(1) and Pd(1)−C(1) distances as well as the I(1)−Pd(1)-C(1) bond angle are not significantly different from the corresponding values of "free" diiodobis(isocyanide)palladium complexes.[8,17] The lengths of the intermolecular Cu−N(1) and Cu(1)−I(1) contacts are 2.28(2) and 3.568(3) Å, respectively. The molecules are arranged to form infinite [I-Pd-I-Cu-3-py-NCPdCNpy-Cu]$_n$ chains which are crossing each other at the palladium atoms, thereby forming a two-dimensional network of 32-membered rings.

Solid **20** is related to the coordination polymers $[PdI_2(CNC_6H_4$-CN-4)$_2]\cdot 2[Cu(hfacac)_2]$, **24**,[8a] and $[PdI_2(CNC_6H_4CN$-3)$_2]\cdot 2[Cu(hfacac)_2]$, **25**[18] (hfacac = hexafluoroacetylacetonate). As shown in Figure 3, in these coordination polymers, the copper units also connect the palladium building blocks via Cu−N and Cu−I interactions to form large rings which are joined at the palladium atoms. Because of the longer dimensions of the cyanophenylisocyanide ligands, the 20-membered rings in these solids are of sufficient size to accommodate the sterically bulky copper linking groups. Due to the linear nature of the 4-isocyanobenzonitrile ligand in **24**, the nitrile group coordinates only weakly in a bent fashion to the copper atom, with a rather long Cu−N distance (Table 3). Because of the small C−N−Cu bonding angle of 108.4(5)° in **24**, the nitrile−copper interaction was described as a π(CN)→Cu σ bond, i.e. a coordinative bond in which the nitrile acts as a sigma donor ligand via its π electrons.[19] The nitrile−copper interaction in **25** is linear and apparently unstrained. The Cu−N distance in **25** is significantly shorter than in **24**, by about 0.35 Å. On the other hand, the Cu−I distance is longer by about 0.31 Å. Since a pyridine group is a stronger donor than a nitrile group, one would expect the Cu−N bond in **20** to be even shorter than in **25**. This appears to be the case, although the difference is only about 0.04 Å. At the same time, the Cu−I distance is longer by about 0.06 Å in **20** than in **25**. While these differences are statistically barely significant, especially considering the large R factor for the structure of compound **20**, they follow the expected trend. As is evident from the data in Table 3, the sum of the Cu−I and Cu−N bond lengths, i.e., the separation of the building blocks across the copper linking groups, remains almost constant in all three solids and the I−Cu−N arrangement does not deviate strongly from linearity. Thus the copper atom of the linking group is shifting along the I−N vector and its location appears to be determined by the donor strength of the nitrogen atom ($N_{pyridyl} > N_{\sigma(CN)} > N_{\pi(CN)}$) while the Cu−I distance is adjusting in response to the respective trans influences.

Conclusion

Several "extended" ligands of the pyridylisocyanide type have been prepared. These ligands form stable transition metal complexes with a defined spacial arrangement of the peripheral pyridyl groups. The potential of these metal complexes to serve as building blocks for the assembly of molecular solids and supramolecular structures has been demonstrated.

Experimental Section

All experiments were carried out using standard Schlenk techniques under nitrogen atmosphere. THF, Et_2O (Na/benzophenone), CH_2Cl_2, $CHCl_3$, and hexane (CaH_2) were dried and distilled prior to use. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AC-250 spectrometer at room temperature. Solvent peaks were used as internal reference; the chemical shifts are reported in δ relative to TMS. IR spectra were recorded on a Perkin-Elmer 1600 spectrometer. Elemental analyses were carried out by M-H-W Laboratories. 3-Iodoaniline, 4-iodoaniline, PdI_2, PtI_2, and $Cu(tfacac)_2$ (tfacac = trifluoroacetylacetonate) were obtained from commercial sources. 4-Ethynylpyridine,[20] 4-trimethyltinpyridine,[12] $Pd(SO_3CF_3)_2(dppp)$[15] (dppp = bis-diphenylphosphinopropane), and compound **7**[11] were prepared according to literature methods. Compounds **1** and **4** were prepared by treatment of the corresponding anilines with formic acetic anhydride.[10a]

Synthesis of *N*-(3-(4-Pyridylethynyl)phenyl)formamide (2). Compound **1**, (988 mg, 4 mmol), $Pd(dba)_2$ (46 mg, 0.08 mmol), CuI (16 mg, 0.08 mmol), and PPh_3 (106 mg, 0.4 mmol) are put into a flask. The flask is evacuated and back-filled with nitrogen three times. NEt_3

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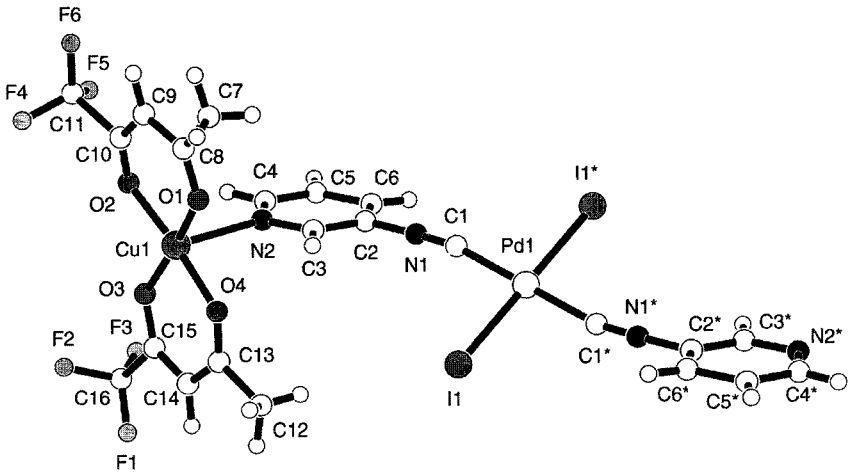

Figure 1. Molecular structure of compound **20**. One of the symmetry-related Cu(tfacac)$_2$ units has been omitted for clarity.

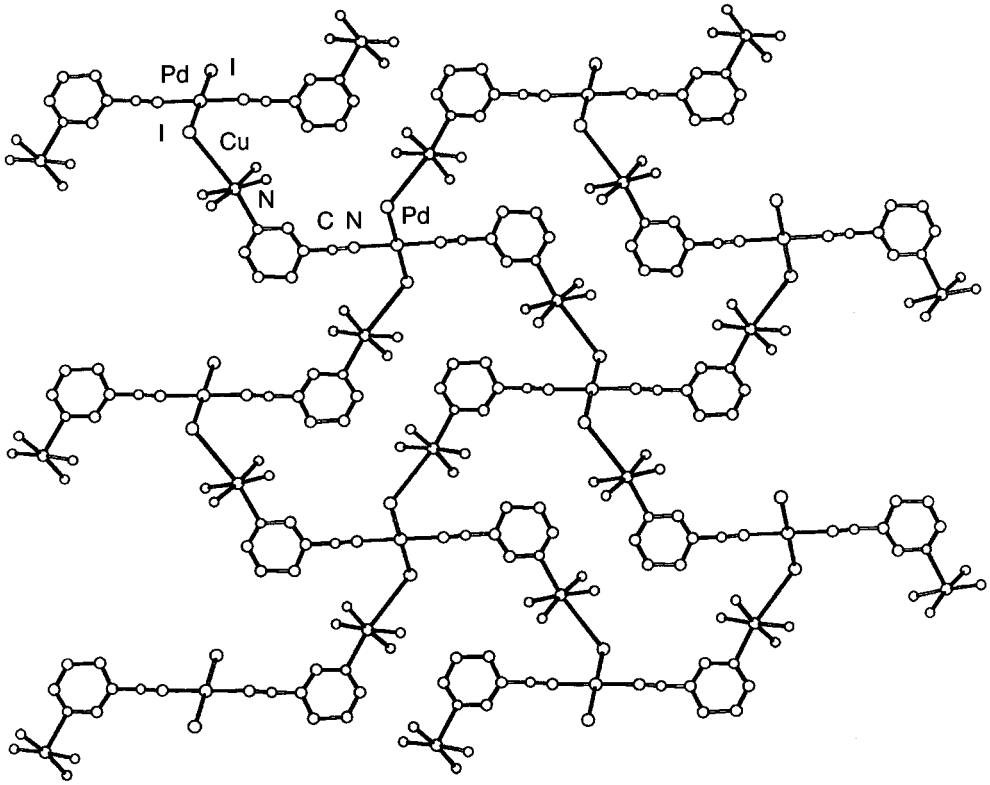

Figure 2. Segment of the two-dimensional network of solid **20**. The molecules of methylene chloride included in the crystal structures are not shown, and the Cu(tfacac)$_2$ units are truncated to show only the CuO_4 cores.

(50 mL) and 4-ethynylpyridine (413 mg, 4 mmol) are then added, and the mixture is stirred at 50−60 °C for about 24 h. The solvent is removed under reduced pressure. The solid residue is dissolved in CH_2Cl_2, filtered through a plug of silica gel, and washed with AcOEt and acetone. The filtered solution is evaporated to dryness, and the residue is redissolved in CH_2Cl_2. The solution is washed with water, dried over $MgSO_4$, and evaporated to produce a pale yellow powder which is purified by column chromatography (hexane/acetone, 5:1 to 1:1). A 630 mg (71%) amount of a pale yellow solid is obtained, mp 165 °C (dec). ^{1}H NMR ($CDCl_3$), two isomers: δ 8.73 (s) and 8.41 (m) (2H, CHO, py), 7.85 (1H, s, py), 7.54−7.32 (m) and 7.12 (m) (7H, py, C_6H_4, NH). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 158.9, 152.0, 149.7, 130.5, 129.3, 128.7, 128.3, 123.0, 121.7, 120.6, 119.5, 87.5. IR (CH_2Cl_2, cm^{-1}): ν(−NH) 3414 w, ν(−CC−) 2218 w, ν(CO) 1704 vs. Anal. Calcd for $C_{14}H_{10}N_2O$: C, 75.66; H, 4.54; N, 12.60. Found: C, 75.46; H, 4.59; N, 12.40.

Synthesis of 3-(4-Pyridylethynyl)phenylisocyanide (3). Compound **2** (430 mg, 1.93 mmol), Et_3N (445 mg, 4.4 mmol), and 50 mL of CH_2Cl_2 are placed in a reaction flask and cooled to 0 °C. Phosgene (198 mg, 2 mmol) as a solution in toluene is added dropwise. After the solution is stirred for about 2 h at 0 °C, water is added. The nonaqueous layer is separated and dried with $MgSO_4$. The solution is reduced to a small volume, and the product is purified by column chromatography on silica gel (hexane/AcOEt, 2:1 to 1:2). A 305 mg (yield: 77%) amount of a yellow solid is obtained. The solid is unstable at room temperature. The compound can be stored for longer periods in solution at low temperature, e.g. in CH_2Cl_2 at −30 °C. ^{1}H NMR ($CDCl_3$): δ 8.64−8.61 (2H, m), 7.57−7.55 (2H, m), 7.45−7.37 (4H, m). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 149.8, 132.6, 129.8, 126.9, 125.6, 91.5. IR (CH_2Cl_2, cm^{-1}): ν(−NC) 2134 s. HRMS calcd for $C_{14}H_8N_2$: 204.0688 (M^+). Found: 204.0693.

Synthesis of *N*-(4-(4-Pyridylethynyl)phenyl)formamide (5). Following the procedure for **2**, a mixture of **4** (988 mg, 4 mmol), 4-ethynylpyridine (413 mg, 4 mmol), Pd(dba)$_2$ (46 mg, 0.08 mmol), CuI (16 mg, 0.08 mmol), and PPh_3 (106 mg, 0.4 mmol) is stirred at 50−60 °C for about 24 h. A 613 mg (yield: 69%) amount of a pale

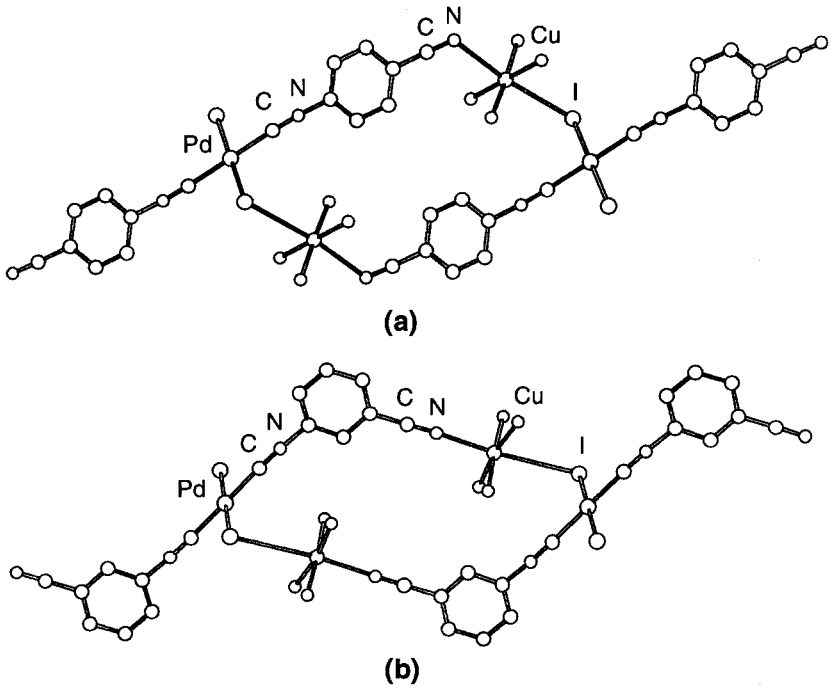

Figure 3. Ring structures of the coordination polymers **24** (a) and **25** (b). The Cu(hfacac)$_2$ units are truncated to show only the CuO_4 cores.

Table 3. Interatomic Distances (Å) and Angles (deg) within the I−Cu−N Bridge in **20**, **24**, and **25**

	20	**24**	**25**
Cu−N	2.28(1)	2.669(6)	2.317(8)
Cu−I	3.568(3)	3.1929(9)	3.506(2)
(Cu−I) + (Cu−N)	5.85	5.86	5.82
I−Cu−N	172	174	168

yellow solid is obtained, mp 165 °C (dec). ^{1}H NMR ($CDCl_3$), two isomers: δ 8.77 (d) and 8.36 (s)(1H), 8.60 (2H, bs), 7.69−7.38 (m) and 7.09 (m) (7H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 161.8, 159.2, 149.6, 138.1, 133.5, 132.8, 132.1, 131.4, 128.7, 128.5, 125.6, 119.7, 118.1, 117.9, 87.0. IR (CH_2Cl_2, cm^{-1}): ν(−NH) 3416 w, ν(CO), 1705 vs. HRMS calcd for $C_{14}H_{10}N_2O$: 223.0871 ([M + H]$^+$). Found: 223.0874.

Synthesis of 4-(4-pyridylethynyl)phenylisocyanide (6). Following the procedure for **3**, **5** (315 mg, 1.4 mmol) is converted to **6** by reaction with phosgene (148 mg, 1.5 mmol) and Et_3N (333 mg, 3.3 mmol) in CH_2Cl_2. A 210 mg (yield: 73%) amount of a yellow solid is obtained. The solid is unstable at room temperature but can be stored in CH_2Cl_2 solution at −30 °C, mp 85 °C (dec). ^{1}H NMR ($CDCl_3$): δ 8.62 (2H, m), 7.58−7.53 (2H, m), 7.40−7.36 (4H, m). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 166.5, 149.8, 132.9, 126.6, 125.5, 89.8. IR (CH_2Cl_2, cm^{-1}): ν(−NC) 2126 s. HRMS calcd for $C_{14}H_8N_2$: C, 204.0688 (M$^+$). Found: 204.0686.

Synthesis of *N*-(2,6-Diisopropyl-4-(4-pyridylethynyl)phenyl)formamide (8). Compound **7** (663 mg, 2 mmol), $Pd(dba)_2$ (23 mg, 0.04 mmol), CuI (0.04 mmol), and PPh_3 (0.2 mmol) are put into a flask. The flask is evacuated and back-filled with nitrogen three times. Et_3N (40 mL) and 4-ethynylpyridine (207 mg, 2 mmol) are added to the mixture under nitrogen. The mixture is stirred at 50−60 °C for about 10 h. The solvent is removed under reduced pressure. The solid residue is dissolved in CH_2Cl_2, filtered through a plug of silica gel, and washed with AcOEt and acetone. The filtrate is evaporated to dryness, and the residue is redissolved in CH_2Cl_2. The solution is washed with water, dried over $MgSO_4$, and evaporated to produce a pale yellow powder which is recrystallized in CH_2Cl_2/hexane to produce 517 mg (84%) of a pale yellow solid, mp 157 °C (dec). ^{1}H NMR ($CDCl_3$), two isomers: δ 8.60 (2H, m), 8.48 (s) and 8.03 (d) (1H), 7.41−7.37 (4H, m), 7.20 (d) and 7.02 (s) (1H), 3.26−3.05 (2H, m), 1.24−1.21 (12H, m). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 164.9, 160.6, 149.6, 149.5, 147.1, 146.7, 132.1, 132.0, 128.6, 128.4, 127.6, 127.4, 125.7, 94.6, 86.9, 28.8, 28.5, 23.5. IR (CH_2Cl_2, cm^{-1}): ν(−NH) 3406 w, ν(−CC−) 2214 w, ν(CO), 1697 vs. Anal. Calcd for $C_{20}H_{22}N_2O\cdot 0.5\ H_2O$: C, 76.16; H, 7.35; N, 8.88. Found: C, 76.70; H, 7.49; N, 8.73.

Synthesis of 2,6-Diisopropyl-4-(4-pyridylethynyl)phenylisocyanide (9). The procedure for **3** is followed, using 517 mg (1.7 mmol) of **8**. The product is purified by column chromatography on silica gel (hexane/AcOEt, 5:1 to 1:1). A 437 mg (90%) amount of a white solid is obtained. The compound is unstable at room temperature but can be stord in CH_2Cl_2 solution at −30 °C, mp 107−110 °C. ^{1}H NMR ($CDCl_3$): δ 8.62 (2H, m), 7.39 (2H, m), 7.34 (2H, s), 3.38 (2H, h, J = 6.77 Hz), 1.30 (12H, d, J = 6.77 Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 170.5, 149.8, 145.4, 131.0, 127.0, 125.5, 123.1, 93.2, 88.0, 29.8, 22.5. IR (CH_2Cl_2, cm^{-1}): ν(−NC) 2116 vs. Anal. Calcd for $C_{20}H_{20}N_2$: C, 83.30; H, 6.99; N, 9.71. Found: C, 83.16; H, 7.07; N, 9.89.

Synthesis of *N*-(2,6-Diisopropyl-4-(4-pyridyl)phenyl)formamide (10). Method A. $PdCl_2(PPh_3)_2$ (70 mg, 0.1 mmol) and LiCl (212 mg, 5.0 mmol) are added to a suspension of **7** (285 mg, 1.0 mmol) and 4-trimethyltinpyridine (266 mg, 1.1 mmol) in toluene. The mixture is stirred for 72 h under reflux. The solvent is removed under reduced pressure. Purification of the solid residue by column chromatography on silica gel (hexane/AcOEt, 5:1 to 1:1) affords 160 mg (yield: 57%) of a pale yellow solid, mp 150 °C (dec). ^{1}H NMR ($CDCl_3$), two isomers: δ 8.67 (2H, bs), 8.51 (s) and 8.06 (d) (1H), 7.54 (2H, m), 7.43 (2H, m), 7.35 (d) and 7.22 (s) (1H), 3.24 (2H, m), 1.27 (12H, m). $^{13}C\{^1H\}$ NMR ($CDCl_3$), two isomers: δ 164.9, 160.6, 149.8, 149.3, 147.7, 147.2, 138.6, 131.0, 122.7, 122.6, 122.1, 121.9, 29.0, 28.6, 23.6. IR (CH_2Cl_2, cm^{-1}): ν(−NH) 3407 w, ν(CO) 1696 vs. HRMS calcd for $C_{18}H_{22}N_2O$: 282.1733. Found: 282.1735.

Method B. $Pd(PPh_3)_4$ (58 mg, 0.05 mmol) is added to a THF solution of **7** (332 mg, 1.0 mmol) and 4-trimethyltinpyridine (266 mg, 1.1 mmol). The mixture is stirred for 72 h under reflux. The solvent is removed under reduced pressure. Purification of the solid residue by column chromatography on silica gel (hexane/AcOEt, 5:1 to 1:1) afford 167 mg (yield: 59%) of pale yellow solid.

Synthesis of 2,6-Diisopropyl-4-(4-pyridy)phenylisocyanide (11). Following the procedure for **3**, compound **10** (384 mg, 1.4 mmol) is converted to **11**. The compound is purified by column chromatography on silica gel (hexane/acetone, 5:1 to 1:1). 275 mg (yield 76%) of a yellow solid is obtained, mp 90−93 °C. ^{1}H NMR ($CDCl_3$): δ 8.69 (2H, m), 7.50 (2H, m), 7.39 (2H, s), 3.44 (2H, h, J = 6.86 Hz), 1.33 (12H, d, J = 6.86 Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 149.9, 146.5, 122.2, 121.9, 30.0, 22.6. IR (CH_2Cl_2, cm^{-1}): ν(−NC) 2118 vs. Anal. Calcd for $C_{20}H_{20}N_2$: C, 81.78; H, 7.62; N, 10.60. Found: C, 81.63; H, 7.51; N, 10.42.

Synthesis of Diiodobis(3-(4-pyridylethynyl)phenylisocyanide)-palladium (12). A mixture of **3** (70 mg, 0.34 mmol) and PdI_2 (54 mg, 0.15 mmol) in CH_2Cl_2 is stirred at room temperature for 2 h. 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 an orange solid (88 mg, 76%), mp > 230 °C. ^{1}H NMR ($CDCl_3$): δ 8.66 (4H, bs), 7.75−7.68 (4H, m), 7.60−7.50 (4H, m), 7.42 (4H, d, J = 5.42 Hz). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 149.9, 134.5, 130.3, 130.1, 129.6, 126.9, 125.6, 124,4, 90.7, 89.2. IR (CH_2Cl_2, cm^{-1}): ν(−NC) 2204 s, ν(−CC−) 2133 w. Anal. Calcd for $C_{28}H_{16}I_2N_4Pd$: C, 43.75; H, 2.10; N, 7.29. Found: C, 43.71; H, 2.00; N, 7.20.

Synthesis of Diiodobis(3-(4-pyridylethynyl)phenylisocyanide)-platinum (13). Following the procedure for **12**, PtI_2 (67 mg, 0.15 mmol) and **3** (70 mg, 0.34 mmol) are converted to a yellow solid (115 mg, 90%), mp > 230 °C. ^{1}H NMR ($CDCl_3$): δ 8.65 (4H, m), 7.74−7.68 (4H, m), 7.59−7.49 (m, 4H), 7.41 (4H, m). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 149.8, 134.4, 130.1, 129.7, 127.1, 125.6, 124.4, 90.8, 89.2. IR (CH_2Cl_2, cm^{-1}): ν(−NC) 2197 s, ν(−CC−) 2136 w. Anal. Calcd for $C_{28}H_{16}I_2N_4Pd$: C, 39.23; H, 1.88; N, 6.53. Found: C, 39.29; H, 2.00; N, 6.45.

Synthesis of Diiodobis(4-(4-pyridylethynyl)phenylisocyanide)-palladium (14). Following the procedure for **12**, PdI_2 (60 mg, 0.17 mmol) and **6** (78 mg, 0.38 mmol) are converted to an orange solid (114 mg, 89%), mp > 230 °C. ^{1}H NMR ($CDCl_3$): δ 8.65 (4H, d, J = 5.69 Hz), 7.66 (4H, d, J = 8.59 Hz), 7.58 (4H, d, J = 8.59 Hz), 7.40 (4H, d, J = 5.91 Hz). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 150.0, 133.1, 130.3, 126.9, 125.6, 125.5, 91.4, 90.4. IR (CH_2Cl_2, cm^{-1}): ν(−NC) 2199 s. Anal. Calcd for $C_{28}H_{16}I_2N_4Pd$: C, 43.75; H, 2.10; N, 7.29. Found: C, 43.80; H, 2.26; N, 7.18.

Synthesis of Diiodobis(4-(4-pyridylethynyl)phenylisocyanide)-platinum (15). Following the procedure for **12**, PtI_2 (76 mg, 0.17 mmol) and **6** (78 mg, 0.38 mmol) are converted to a yellow solid (106 mg, 73%), mp > 230 °C. ^{1}H NMR ($CDCl_3$): δ 8.65 (4H, d, J = 5.63 Hz), 7.66 (4H, d, J = 8.59 Hz), 7.57 (4H, d, J = 8.59 Hz), 7.40 (4H, d, J = 5.95 Hz). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 149.9, 133.1, 130.3, 127.0, 125.5, 125.4, 91.5, 90.4. IR (CH_2Cl_2, cm^{-1}): ν(−NC) 2193 s. Anal. Calcd for $C_{28}H_{16}I_2N_4Pt$: C, 39.23; H, 1.88; N, 6.53. Found: C, 39.44; H, 1.81; N, 6.28.

Synthesis of Diiodobis(2,6-diisopropyl-4-(4-pyridylethynyl)phenylisocyanide)palladium (16). Following the procedure for **12**, **9** (84 mg, 0.29 mmol) and PdI_2 (48 mg, 0.13 mmol) are converted to an orange solid (111 mg, 89%), mp > 230 °C. ^{1}H NMR ($CDCl_3$): δ 8.65 (4H, bs), 7.41 (8H, m), 3.56 (4H, h, J = 6.75 Hz), 1.36 (24H, d, J = 6.91 Hz). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 149.9, 147.4, 127.4, 125.5, 125.1, 92.7, 89.5, 29.7, 22.9. IR (CH_2Cl_2, cm^{-1}): ν(−NC) 2192 s. Anal. Calcd for $C_{40}H_{40}I_2N_4Pd$: C, 51.27; H, 4.30; N, 5.98. Found: C, 51.41; H, 4.49; N, 5.90.

Synthesis of Diiodobis(2,6-diisopropyl-4-(4-pyridylethynyl)phenylisocyanide)platinum (17). Following the procedure for **12**, a mixture of **9** (120 mg, 0.42 mmol) and PtI_2 (90 mg, 0.2 mmol) is converted to an orange solid (175 mg, 85%), mp > 230 °C. ^{1}H NMR ($CDCl_3$): δ 8.64 (4H, m), 7.41 (8H, m), 3.56 (4H, h, J = 6.79 Hz), 1.36 (24H, d, J = 6.79 Hz). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 149.9, 147.3, 130.7, 127.4, 125.5, 125.0, 92.8, 29.6, 22.8. IR (CH_2Cl_2, cm^{-1}): ν(−NC) 2187 s. Anal. Calcd for $C_{40}H_{40}I_2N_4Pt\cdot 2H_2O$: C, 45.25; H, 4.18; N, 5.28. Found: C, 45.16; H, 4.52; N, 5.19.

Synthesis of Diiodobis(2,6-diisopropyl-4-(4-pyridyl)phenylisocyanide)palladium (18). Following the procedure for **12**, PdI_2 (60 mg, 0.17 mmol) and **11** (100 mg, 0.38 mmol) are converted to an orange solid (114 mg, 77%), mp > 230 °C. ^{1}H NMR ($CDCl_3$): δ 8.72 (4H, m), 7.50 (4H, m), 7.44 (4H, s), 3.62 (4H, h, J = 6.80 Hz), 1.39 (24H, d, J = 6.77 Hz). ^{13}C{1H} NMR ($CDCl_3$): δ 150.4, 147.9, 147.3, 141.1, 122.6, 121.9, 29.9, 23.0. IR (CH_2Cl_2, cm^{-1}): ν(−NC) 2195 s. Anal. Calcd for $C_{36}H_{40}I_2N_4Pd$: C, 48.64; H, 4.54; N, 6.30. Found: C, 48.83; H, 4.68; N, 6.17.

Synthesis of Diiodobis(2,6-diisopropyl-4-(4-pyridyl)-phenylisocyanide)platinum (19). Following the procedure for **12**, PtI_2 (60 mg, 0.13 mmol) and **11** (79 mg, 0.30 mmol) are converted to a yellow solid (81 mg, 62%), mp > 230 °C. ^{1}H NMR ($CDCl_3$): δ 8.71 (4H, m), 7.51 (4H, m), 7.44 (4H, s), 3.63 (4H, h, J = 6.75 Hz), 1.40 (24H, d, J = 6.88 Hz). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 150.3, 147.9, 147.5, 141.0, 122.7, 121.9, 29.8, 23.0. IR (CH_2Cl_2, cm^{-1}): ν(−NC) 2188 s. Anal. Calcd for $C_{36}H_{40}I_2N_4Pt$: C, 44.23; H, 4.12; N, 5.73. Found: C, 44.23; H, 4.34; N, 5.67.

Preparation of 20 from Cu(tfacac)$_2$ and Diiodobis(3-isocyanopyridine)palladium. A solution of diiodobis(3-isocyanopyridine)palladium (57 mg, 0.1 mmol) in $CHCl_3$ is added to a $CHCl_3$ solution of Cu(tfacac)$_2$ (75 mg 0.2 mmol). Hexane is slowly allowed to diffused into the green solution at room temperature. After several days, 95 mg (yield: 73%) of green crystals is separated and dried under vacuum, mp 163 °C (dec). IR (KBr, cm^{-1}): ν(−NC) 2201 s. Anal. Calcd for $C_{32}H_{24}F_{12}I_2N_4O_8Cu_2Pd\cdot 2CHCl_3$: C, 27.40; H, 1.76; N, 3.76. Found: C, 27.58; H, 1.83; N, 3.50. Single crystals of **20**$\cdot 2CH_2Cl_2$ were grown as described above, using CH_2Cl_2 instead of $CHCl_3$.

Preparation of 21 from Cu(tfacac)$_2$ and 16. A solution of **16** (30 mg 0.03 mmol) in CH_2Cl_2 is added to a CH_2Cl_2 solution of Cu(tfacac)$_2$ (24 mg 0.06 mmol). Pentane is allowed to diffuse slowly into the green solution at room temperature. After several days, 40 mg (yield: 74%) of green crystals is separated and dried under vacuum, mp 180 °C (dec). IR (CH_2Cl_2, cm^{-1}): ν(−NC) 2192 s. Anal. Calcd for $C_{60}H_{56}F_{12}I_2N_4O_8Cu_2Pd$: C, 42.99; H, 3.37; N, 3.34. Found: C, 43.09; H, 3.45; N, 3.15.

Preparation of 22 from (dppp)Pd(OTf)$_2$ and 18. (dppp)Pd(OTf)$_2$ (55 mg, (0.07 mmol) is added to a solution of **18** (60 mg, 0.07 mmol) in 30 mL of CH_2Cl_2. The mixture is stirred overnight at room temperature. The solution is then filtered, and the solvent is reduced to about 5 mL under vacuum. A 30 mL amount of Et_2O is added, and orange solid precipates immediately. The solid is washed with Et_2O several times and dried under vacuum. A 93 mg (yield: 81%) amount of orange solid is obtained, mp > 230 °C. ^{1}H NMR (CD_2Cl_2): δ 9.10 (16H, m), 7.72−7.21 (112H, m), 3.55 (16H, h, J = 6.69 Hz), 3.23 (16H, bs), 2.31(8H, m), 1.34 (106H, d, J = 6.90 Hz). ^{13}C{^{1}H} NMR (CD2Cl2): δ 151.2, 150.1, 148.5, 139.0, 133.5, 132.4, 129.8, 126.1, 125.0, 124.5, 123.0, 30.2, 22.9. ^{31}P NMR (CD_2Cl_2): δ 9.73. ^{19}F NMR (CD_2Cl_2): δ −76. IR (KBr, cm^{-1}): ν(−NC) 2192 s. Anal. Calcd for $C_{65}H_{66}F_6I_2N_4O_6P_2S_2Pd_2$: C, 45.76; H, 3.90; N, 3.28. Found: C, 45.49; H, 4.04; N, 3.26.

Preparation of 23 from (dppp)Pd(OTf)$_2$ and 19. (dppp)Pd(OTf)$_2$ (25 mg, (0.03 mmol) is added to a solution of **19** (30 mg, 0.03 mmol) in 30 mL of CH_2Cl_2. The mixture is stirred overnight at room temperature. The solution is then filtered and the solvent is reduced to about 5 mL under vacuum. 30 mL of Et_2O is added and an orange solid precipates immediately. The solid is washed with Et_2O several times and dried under vacuum. A 42 mg (yield: 81%) amount of a pale yellow solid is obtained, mp 228 °C (dec). ^{1}H NMR (CD_2Cl_2): δ 9.10 (16H, bs), 7.72−7.22 (112H, m), 3.58 (16H, h, J = 6.74 Hz), 3.24 (16H, bs), 2.30 (8H, m), 1.35 (106H, d, J = 6.73 Hz). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 169.3, 151.0, 150.1, 148.4, 138.8, 133.5, 132.4, 131.1, 129.8, 126.1, 125.7, 125.2, 124.9, 124.5, 123.0, 30.1, 22.9. ^{31}P NMR (CD_2Cl_2): δ 9.72. ^{19}F NMR (CD_2Cl_2): δ −76. IR (KBr, cm^{-1}): ν(−NC) 2183 s. Anal. Calcd for $C_{65}H_{66}F_6I_2N_4O_6P_2S_2PdPt$: C, 43.50; H, 3.71; N, 3.12. Found: C, 43.37; H, 3.51; N, 3.06.

Crystallographic Studies

The crystal structure analysis of **20** was performed following the general procedure described previously.[21] Information on data collection and treatment is collected in Table 1. Diffraction data were measured on an Enraf-Nonius CAD4 diffractometer with graphite monochromated Mo Kα radiation (λ = 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° < 2θ < 22°. The data were collected at room temperature, using the $\theta-2\theta$ scan technique to a maximum value of 50°. An empirical absorption correction using the program DIFABS[22] was applied. The structure was solved by and expanded using Fourier techniques.[23] The non-hydrogen atoms were refined anisotropically.

(21) Lincoln, S.; Koch, S. A. *Inorg. Chem.* **1986**, *25*, 1594.
(22) Walker, N.; Stuart, D. *Acta Crystallogr. A* **1983**, *39*, 158.
(23) Beurskens, P. T., Admiraal, G.; Beurskens, G.; Bosman, W. P.; Garcia-Granda, S.; Gould, R. O.; Smits, J. M. M.; Smykalla, C. *DIRDIF92: The DIRDIF program system*; Technical Report of the Crystallography Laboratory; University of Nijmegen: The Netherlands, 1992.

Hydrogen atoms were included but not refined. All calculations were performed using the teXsan[24] crystallographic software package of Molecular Structure Corporation.

The relatively high values for R and R_w are probably a consequence of positional disorder of the CF_3 groups of the copper bistrifluoroacetylacetonate units. 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 1 shows only one set of fluorine atoms for each CF_3 group.

(24) *teXsan: Crystal Structure Analysis Package*; Molecular Structure Corporation: The Woodlands, TX, 1985 and 1992.

Acknowledgment. We thank Prof. Stephen A. Koch and Hua-Fen Hsu for performing the crystal structure analysis of **20**. Financial support by the National Science Foundation is gratefully acknowledged.

Supporting Information Available: Positional parameters, U values, bond lengths, and bond angles for **20**. This material is available free of charge via the Internet at http://pubs.acs.org.

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