

# Angular Arenediethynyl Complexes of Gold(I)

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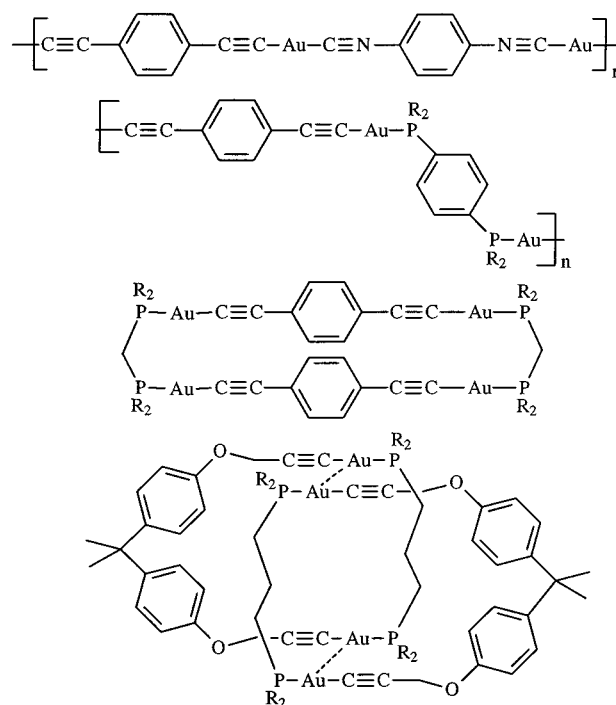
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Alkynylgold(I) complexes have been prepared from the angular bis(alkyne)  $\text{MeC}_6\text{H}_3\text{-3,5-}(\text{CCH})_2$ , in which the alkyne units are rigidly fixed at an angle of  $120^\circ$  to each other. Reaction with  $[\text{AuCl}(\text{SMe}_2)]$  and base yields the shock-sensitive, insoluble compound  $[\{\text{MeC}_6\text{H}_3\text{-3,5-}(\text{CCAu})_2\}_n]$  (**2**), which reacts with isocyanide, phosphine, or phosphite ligands (L) to give  $[\text{MeC}_6\text{H}_3\text{-3,5-}(\text{CCAuL})_2]$  (**3**; L =  $\text{P}(\text{OPh})_3$ ,  $\text{P}(\text{OMe})_3$ ,  $\text{PPh}_3$ ,  $\text{PMePh}_2$ ,  $t\text{-BuNC}$ ,  $\text{MeNC}$ ). The complexes with L =  $\text{P}(\text{OMe})_3$ ,  $\text{PMePh}_2$  exist in the solid state as infinite one-dimensional ribbon structures in which neighboring molecules are associated through secondary gold–gold bonding. Complexes with diisocyanide ligands  $1,4\text{-C}_6\text{R}_4(\text{NC})_2$  (R = H, Me) have the formula  $[\{\text{MeC}_6\text{H}_3\text{-3,5-}(\text{CCAu})_2(\mu\text{-LL})\}_n]$  and are insoluble in organic solvents; they are suggested to have a zigzag polymeric structure. In contrast, complexes with diphosphine ligands  $(\text{CH}_2)_n(\text{PPh}_2)_2$  ( $n = 1\text{--}6$ ) are soluble and are suggested to be the cyclic tetragold(I) complexes of formula  $[\{\text{MeC}_6\text{H}_3\text{-3,5-}(\text{CCAu})_2(\mu\text{-LL})\}_2]$ ; the ring size varies from 24 to 34, depending on  $n$ .

## Introduction

There has been much interest in the use of *p*-diethynylarenes as reagents in forming rigid-rod, organometallic polymers, which may contain square-planar (Ni(II), Pd(II), Pt(II)) or octahedral (Rh(III), Fe(II), Ru(II), Os(II)) metal centers.<sup>1,2</sup> These compounds have interesting nonlinear optical properties, which might lead to materials applications.<sup>1–3</sup> A number of gold(I) polymers, with linear gold(I) centers, have been prepared, and their emission spectra suggest that there is indeed some conjugation present, though the polymers are insoluble.<sup>4,5</sup> Neutral polymers require one alkynylgold group and one other neutral ligand, and examples of known oligomeric or polymeric structures are illustrated in Chart 1. If the dialkyne or supporting ligand is flexible, then rings and even catenated rings rather than polymers may be formed (Chart 1).<sup>5–7</sup>

Chart 1. Polymers and Cyclic Compounds with Bis(alkynylgold(I)) Units



It was of interest to explore the use of rigid, angular diethynylarene ligands in forming gold(I) complexes, polymers, or rings, and this paper reports the results of this study using *m*-diethynylarenes in which the

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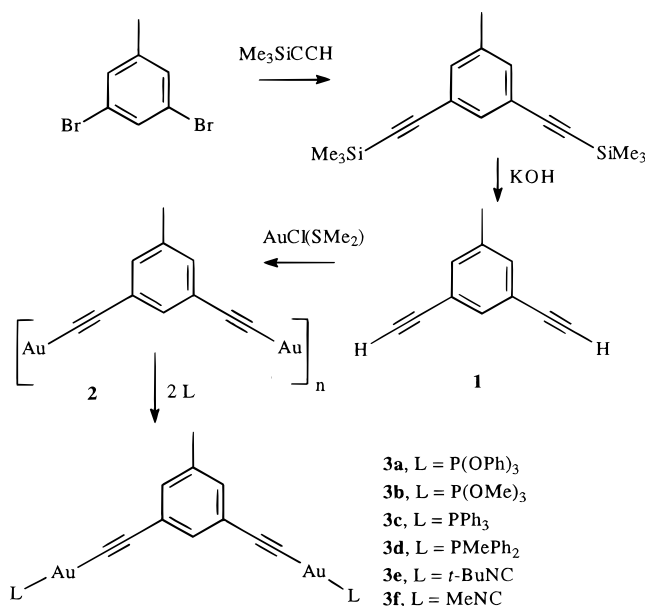
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Scheme 1

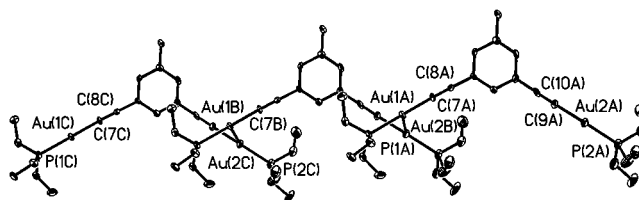


angle between the ethynyl groups is 120°, rather than the more common 180° in rigid-rod ligands. There is limited related work, including a binuclear cationic complex containing octahedral iridium(III) centers bridged by 1,2-diethynylbenzene.<sup>8</sup> Also, 1,3,5-triethynylbenzene has been exploited in forming complexes with platinum, iridium, and gold that may have novel 2-D polymeric structures.<sup>5,9–11</sup>

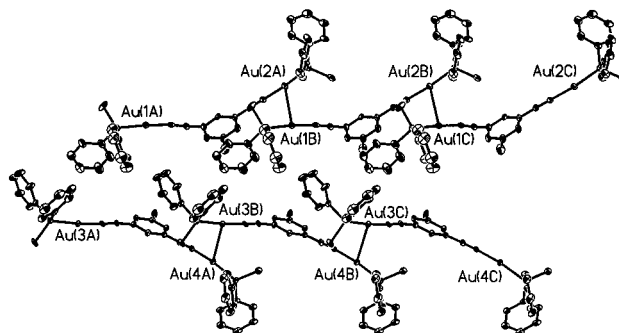
## Results and Discussion

**Synthesis of the Bis(alkyne) and Model Gold(I) Complexes.** The ligand 3,5-diethynyltoluene was prepared by reaction of the protected alkyne (trimethylsilyl)acetylene with 3,5-dibromotoluene, followed by removal of the trimethylsilyl protecting groups with potassium hydroxide (Scheme 1). A similar route has been used to prepare 3,5-diethynylpyridine.<sup>12</sup>

3,5-Diethynyltoluene (**1**) was converted to the polymeric digold(I) diacetylide derivative [ $\text{MeC}_6\text{H}_3\text{-3,5-(C}\equiv\text{CAu)}_2$ ]<sub>n</sub> (**2**) by reaction with  $[\text{AuCl}(\text{SMe}_2)]$  in the presence of sodium acetate (Scheme 1). Complex **2** was isolated as a bright yellow, insoluble powder, and like other gold(I) acetylides, it is presumed to have a polymeric structure in which each acetylide is  $\sigma$ -bonded ( $\eta^1$ ) to one gold atom and  $\pi$ -bonded ( $\eta^2$ ) to another.<sup>13</sup> Some evidence for such a structure is obtained from the IR spectrum of **2**, which exhibits a weak band at 1985  $\text{cm}^{-1}$ ; this band is 132  $\text{cm}^{-1}$  lower than in the precursor **1** and indicates that the alkynyl groups are acting as  $\pi$ -donors, but the insolubility of **2** did not allow characterization by solution NMR.



**Figure 1.** View of the structure of complex **3b**, showing a molecule and its two neighbors connected by Au...Au bonds (25% probability ellipsoids are shown).



**Figure 2.** View of the structure of complex **3d**, showing parallel ribbons formed by the two independent molecules (25% probability ellipsoids are shown).

Complex **2** was converted to more soluble complexes [ $\text{MeC}_6\text{H}_3\text{-3,5-(C}\equiv\text{CAuL)}_2$ ] (**3**) by reaction with monodentate isocyanide or phosphorus-donor ligands as shown in Scheme 1. The pale yellow phosphite, phosphine, and isocyanide complexes were readily characterized by their spectroscopic properties. The IR spectra for these compounds exhibit weak bands near 2120  $\text{cm}^{-1}$  due to  $\nu(\text{C}\equiv\text{C})$  and, for the isocyanide complexes, strong bands at 2230–2260  $\text{cm}^{-1}$  due to  $\nu(\text{N}\equiv\text{C})$ .<sup>14</sup> The  $^1\text{H}$  NMR spectra of **3** contain the expected resonances due to both the alkynyl and neutral ligands, while the phosphine and phosphite complexes each give a single resonance in the  $^{31}\text{P}$  NMR spectra. Details are listed in the Experimental Section. Only **3f** was insufficiently soluble to give a satisfactory NMR spectrum.

Two of the model complexes, **3b** and **3d**, have been characterized crystallographically, and their structures are shown in Figures 1 and 2, while selected bond lengths and angles are presented in Tables 1 and 2.

Molecules of **3b** (L = P(OMe)<sub>3</sub>; Figure 1) have the expected structure with roughly linear C–C≡C–Au–P units held at 120° to each other.<sup>4–6,11,15</sup> The intramolecular distances between the two gold and phosphorus atoms (Au(1)–Au(2) = 10.44 Å, P(1)–P(2) = 14.27 Å) are long, such that common bidentate ligands clearly could not span the two gold(I) centers intramolecularly. In the solid state, the molecules are associated to give a ribbon structure, as shown in Figure 1, by formation

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**Table 1. Selected Bond Distances and Angles for 3b**

Distances (Å)			
Au(1)–P(1)	2.261(4)	Au(2)–P(2)	2.249(4)
Au(1)–C(7)	2.02(1)	Au(2)–C(9)	2.00(2)
O(1)–P(1)	1.55(1)	O(4)–P(2)	1.56(2)
O(2)–P(1)	1.57(1)	O(5)–P(2)	1.55(1)
O(3)–P(1)	1.56(1)	O(6)–P(2)	1.60(2)
C(7)–C(8)	1.19(2)	C(9)–C(10)	1.21(2)
C(8)–C(11)	1.46(2)	C(10)–C(15)	1.45(2)
C(13)–C(17)	1.51(2)	Au(1)–Au(2)#1	3.2196(9)
Angles (deg)			
C(8)–C(7)–Au(1)	176(1)	C(10)–C(9)–Au(2)	178(2)
P(1)–Au(1)–C(7)	175.7(5)	P(2)–Au(2)–C(9)	178.1(5)
Au(1)–P(1)–O(1)	117.9(5)	Au(2)–P(2)–O(6)	117.8(6)
Au(1)–P(1)–O(2)	107.9(4)	Au(2)–P(2)–O(5)	111.7(5)
Au(1)–P(1)–O(3)	118.9(4)	Au(2)–P(2)–O(4)	118.3(6)
C(8)–C(11)–C(12)	120(1)	C(10)–C(15)–C(14)	121(1)
C(8)–C(11)–C(16)	120(1)	C(10)–C(15)–C(16)	119(1)
C(12)–C(13)–C(17)	120(1)	C(14)–C(13)–C(17)	121(1)

**Table 2. Selected Bond Lengths and Angles for 3d**

Distances (Å)			
Au(1)–P(1)	2.275(9)	Au(2)–P(2)	2.267(8)
TAu(1)–C(1)	1.98(4)	Au(2)–C(3)	2.00(3)
C(1)–C(2)	1.24(4)	C(3)–C(4)	1.20(4)
C(2)–C(11)	1.44(4)	C(4)–C(15)	1.43(3)
Au(3)–P(3)	2.298(8)	Au(4)–P(4)	2.290(7)
Au(3)–C(61)	2.04(4)	Au(4)–C(63)	2.09(3)
C(61)–C(62)	1.18(4)	C(63)–C(64)	1.14(3)
C(62)–C(71)	1.43(3)	C(64)–C(75)	1.45(3)
Au(1)–Au(2)#1	3.124(2)	Au(3)–Au(4)#1	3.146(2)
Angles (deg)			
C(2)–C(1)–Au(1)	174(3)	C(4)–C(3)–Au(2)	176(3)
P(1)–Au(1)–C(1)	175.5(8)	P(2)–Au(2)–C(3)	174.1(9)
Au(1)–P(1)–C(36)	114(1)	Au(2)–P(2)–C(46)	113.4(7)
Au(1)–P(1)–C(26)	110(1)	Au(2)–P(2)–C(56)	111.2(9)
Au(1)–P(1)–C(6)	116(2)	Au(2)–P(2)–C(7)	116(1)
C(62)–C(61)–Au(3)	176(3)	C(64)–C(63)–Au(4)	176(3)
C(61)–Au(3)–P(3)	174.6(8)	C(63)–Au(4)–P(4)	171.4(7)
Au(3)–P(3)–C(96)	110.04(9)	Au(4)–P(4)–C(116)	113.3(8)
Au(3)–P(3)–C(86)	111.6(9)	Au(4)–P(4)–C(106)	107.9(7)
Au(3)–P(3)–C(66)	115(1)	Au(4)–P(4)–C(67)	104(1)

of intermolecular Au...Au bonds (Au(1)–Au(2#) (e.g., Au(1A)–Au(2B) in Figure 1, which shows three equivalent molecules designated A–C) = 3.2196(9) Å).

The unit cell for **3d** (L = PMePh<sub>2</sub>, Figure 2) contains two independent but similar molecules. The molecular structure is similar to that of **3b**. Each independent molecule, containing Au(1), Au(2) and Au(3), Au(4), respectively, forms its own independent but parallel ribbon structure as shown in Figure 2. The gold...gold distances, which define the intermolecular auriphilic attraction, are slightly shorter (Au(1)···Au(2#) = 3.124(2) Å; Au(3)···Au(4#) = 3.146(2) Å) than in **3b** (3.2196(9) Å).

**Synthesis of Ring and Zigzag Polymeric Complexes.** Linear, one-dimensional polymers [(Au–C≡C–Ar–C≡C–Au–L–L)]<sub>x</sub> (Ar = linear arene spacer group, L–L = *p*-diisocyanobenzenes or diphosphines) have been prepared by reaction of linear digold(I) diacetylide complexes, [(Au–C≡C–Ar–C≡C–Au)]<sub>x</sub>, with the corresponding bidentate ligand L–L.<sup>4</sup> However, a better procedure when both precursor and product are insoluble is to convert the insoluble gold(I) acetylide to a soluble complex by reaction with *t*-BuNC and then replace the *t*-BuNC with the bidentate ligand. This method was used to prepare the insoluble diisocyanobenzene derivatives **4a,b** shown in Scheme 2.

The products **4a,b** were formed as yellow solids that

were insoluble in common organic solvents. The polymeric compounds have a  $\nu(\text{N}\equiv\text{C})$  value of 2205 cm<sup>−1</sup>, which is similar to the  $\nu(\text{N}\equiv\text{C})$  values of the model compounds.<sup>14</sup> In addition, XPS data shows that the binding energy from these two compounds is 85.0 eV for Au (4f 7/2), which is in agreement with other two-coordinate linear Au atoms in Au(I) complexes that contain alkynyl and isocyanide ligands.<sup>4</sup> The above evidence demonstrates the presence of alkynyl(isocyanide)gold(I) units in **4a,b**, but the overall structures are not defined by the spectroscopic data. Two possible structures are the hexagonal cyclic structure [MeC<sub>6</sub>H<sub>3</sub>-3,5-(C≡CAu)<sub>2</sub>(μ-L-L)]<sub>3</sub> and the zigzag polymeric structure [MeC<sub>6</sub>H<sub>3</sub>-3,5-(C≡CAu)<sub>2</sub>(μ-L-L)]<sub>x</sub>. The insolubility of the compounds suggests, but does not prove, the polymeric structure. We note that the planar hexagonal structure would contain a large cavity (it would be a 102-membered ring) and so interpenetration might still lead to polymer or oligomer formation.

The reaction of the digold(I) diacetylide complex [3,5-MeC<sub>6</sub>H<sub>3</sub>(C≡C–Au)<sub>2</sub>]<sub>n</sub> (**2**) with the diphosphine ligands shown in Scheme 3 yielded the complexes **5a–f**. These complexes were soluble in dichloromethane; therefore, the two-step synthesis procedure used for the diisocyanide complexes was not necessary. Analogous diphosphine complexes of gold acetylides derived from 1,3,5-triethynylbenzene or 1,4-diethynylbenzene are insoluble and almost certainly have polymeric structures.<sup>4,11</sup> The major difference in solubility suggests a nonpolymeric structure for complexes **5**.

The IR spectra show the expected weak peak due to  $\nu(\text{C}\equiv\text{C})$  at ca. 2120 cm<sup>−1</sup>. The <sup>1</sup>H NMR spectra of each complex **5** gave singlet resonances for the methyl and aryl protons of the tolyl group as well as the expected resonances for the diphosphine ligand. In addition, the <sup>31</sup>P NMR spectrum of each complex exhibits one singlet, indicating that there is only one species present and that the phosphine groups are equivalent. The NMR data are not consistent with polymer formation, and a simple digold(I) complex is not possible because the ring strain would be too great. The simplest structure consistent with the spectroscopic data is the "dimer" [MeC<sub>6</sub>H<sub>3</sub>-3,5-(C≡CAu)<sub>2</sub>(μ-L-L)]<sub>2</sub>, but larger rings and even catenanes cannot be ruled out. Most of the complexes failed to give parent ions in the FAB-MS, but **5a** gave a peak at *m/z* 1832 as expected for the dimer formulation.<sup>16</sup> The flexibility of the diphosphine ligands allows formation of the dimers without significant ring strain, as indicated by consideration of molecular models or by molecular mechanics calculations, and, in the absence of a structure determination, we tentatively suggest that all complexes **5** have this structure.

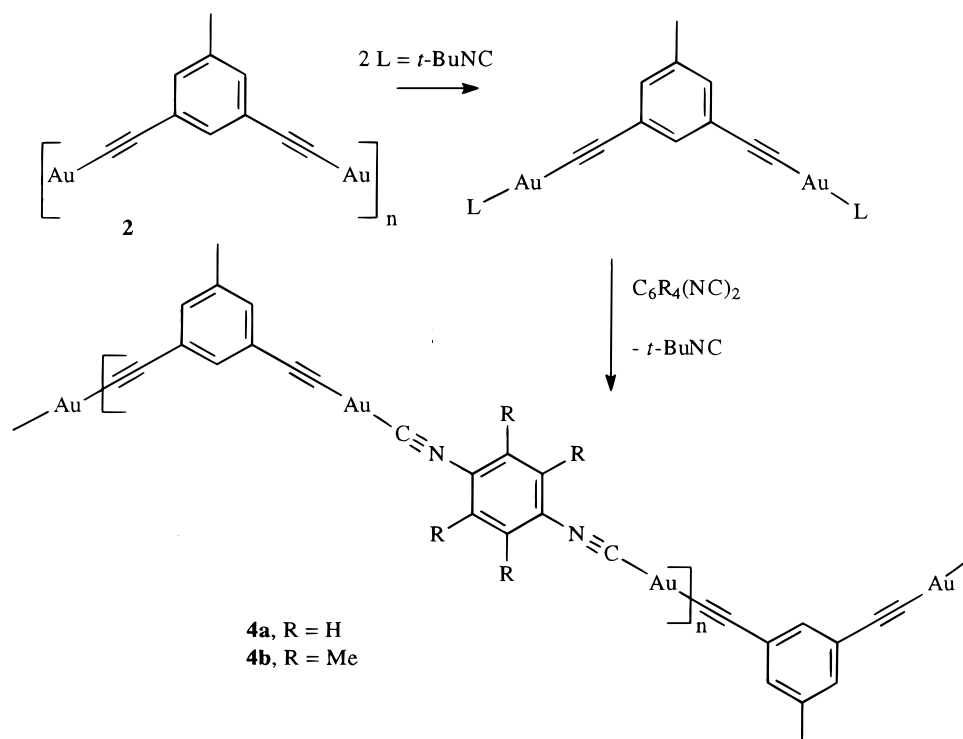
Several conformations of the large rings (ring sizes: **5a**, 24; **5b**, 26; **5c**, 28; **5d**, 30; **5e**, 32; **5f**, 34) that result from dimer formation are possible. A favored conformation, based on molecular mechanics calculations and precedents, is the folded one shown in Scheme 3 for **5a**.<sup>17</sup> However, the <sup>1</sup>H NMR spectrum of **5a** gave only one resonance for the CH<sub>2</sub>P<sub>2</sub> protons, whereas the fixed, folded conformation would give two. No major change

(16) Molecular weights of alkynylgold complexes by FAB-MS can be misleading due to aggregation or fragmentation in the spectrometer: Bruce, M. I.; Liddell, M. J. *J. Organomet. Chem.* **1992**, 427, 263.

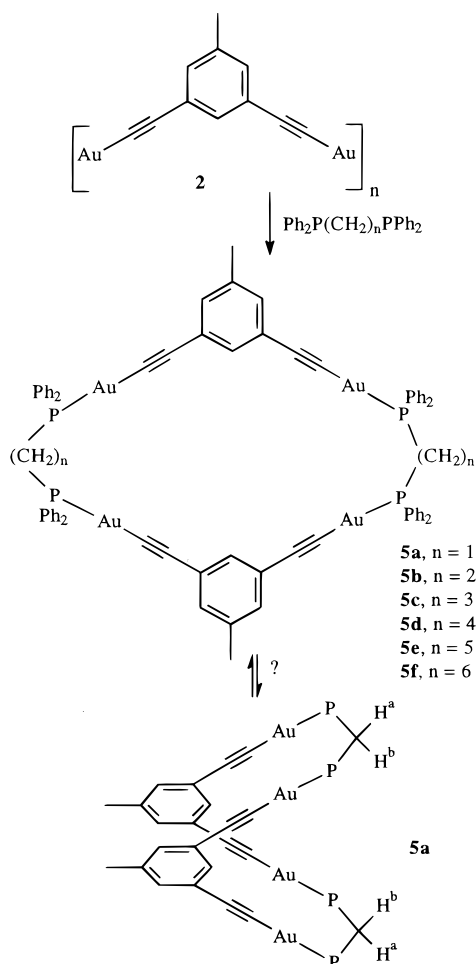
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Scheme 2



Scheme 3

Table 3. Emission Spectra at Room Temperature of Selected Complexes in Solution in Dichloromethane and in the Solid State<sup>a</sup>

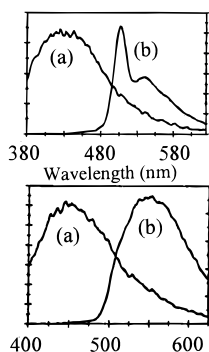
complex	$\lambda_{\text{max}}/\text{nm}$		complex	$\lambda_{\text{max}}/\text{nm}$	
	soln	solid		soln	solid
<b>3a</b>	440	508, 540	<b>4b</b>	<i>b</i>	580
<b>3b</b>	450	575	<b>5a</b>	440	510, 540
<b>3c</b>	430	507, 540	<b>5b</b>	440	510, 540
<b>3d</b>	440	550	<b>5c</b>	440	540
<b>3e</b>	460	508, 560	<b>5d</b>	450	508, 540
<b>3f</b>	<i>b</i>	560	<b>5e</b>	450	510, 540
<b>4a</b>	<i>b</i>	585			

<sup>a</sup> In all cases  $\lambda_{\text{ex}} = 350 \text{ nm}$ . <sup>b</sup> Insufficiently soluble for solution study.

in which there is a plane of symmetry containing the PCP atoms, sufficiently easily that the  $\text{CH}_2$  protons appear equivalent. The  $^1\text{H}$  NMR data of all complexes **5** display similar effective symmetry. Hence, if transannular  $\text{Au}\cdots\text{Au}$  attractions are present in the folded structures, they must be weak.

**Emission Spectra.** A summary of the emission spectra is given in Table 3, and typical spectra are shown in Figure 3. All of the soluble complexes exhibited room-temperature emission as dichloromethane solutions, and all gave a single broad emission in the region 430–460 nm, similar to other alkynylgold(I) complexes.<sup>4,14,15,18</sup> The solid-state emission spectra of these complexes all gave red-shifted bands compared to solution emission (Table 3), perhaps as a result of  $\text{Au}\cdots\text{Au}$  interactions in the solid state.<sup>4,15,18</sup> There were only minor differences in the emission energies or appearance of the emission spectra for the complexes with monodentate phosphite, phosphine, or isocyanide ligands and those containing bidentate phosphines (Table 3, Figure 3). However, in some cases the solid-state

was observed in the low-temperature  $^1\text{H}$  NMR, and so the rings must be able to reach a planar conformation,



**Figure 3.** Typical emission spectra: (top) complex **3c**; (bottom) complex **5c**. In each case, spectrum a is for a solution in dichloromethane and spectrum b is for the solid state.

emission spectra showed resolved fine structure, attributed to vibrational coupling, whereas in other cases they did not (Figure 3). For the phosphine complexes, the resolved bands were separated by ca.  $1100\text{ cm}^{-1}$ , probably indicating coupling to an aryl vibrational mode. Following earlier discussion, the emission is tentatively assigned as arising from a  $\sigma(\text{AuC})-\pi^*$  excited state.<sup>4c</sup> The close similarity between spectra for complexes containing monodentate phosphines (**3c,d**) and bidentate phosphines (**5a–e**) indicates that the methylene bridges in the diphosphine ligands prevent conjugation effects, which might lead to a red shift.<sup>4c</sup> In contrast, the diisocyanide complexes **4a,b** give solid-state emissions that are red shifted compared to the mono-isocyanide complexes **3e,f** (Table 3), indicating that there is extended conjugation in the diisocyanide complexes.<sup>4c</sup>

In summary, the angular 3,5-diethynyltoluene gives complexes with monodentate ligands that form one-dimensional ribbon structures through  $\text{Au}\cdots\text{Au}$  attractions in the solid state. With bidentate ligands, the rigid linear diisocyanides appear to give zigzag polymeric structures, whereas the more flexible diphosphines give ring structures. The emission spectra indicate that intermolecular  $\text{Au}\cdots\text{Au}$  bonding is present in all complexes and that extended conjugation is present in the diisocyanide complexes.

## Experimental Section

NMR spectra were collected by using a Varian Gemini 300 MHz spectrometer, and chemical shifts are referenced to TMS or phosphoric acid. IR spectra were recorded as Nujol mulls on KBr plates using a Perkin-Elmer 2000 FTIR. Mass spectra were recorded by using a Finnigan-MAT 8200 spectrometer.  $[\text{AuCl}(\text{SMe}_2)]$  and diisocyanobenzenes were prepared by literature methods.<sup>19–21</sup>

**$\text{MeC}_6\text{H}_3\text{-3,5-(C}\equiv\text{CH)}_2$  (**1**).** To a mixture of (trimethylsilyl)acetylene (5.89 g, 0.06 mmol) and *m*-dibromotoluene (5.0 g, 0.02 mmol) in piperidine (100 mL) were added  $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$  (0.5 g) and  $\text{CuI}$  (0.2 g). The reaction mixture was stirred for 6 h at  $90^\circ\text{C}$  under an atmosphere of  $\text{N}_2$ . Additional catalyst (as above) and (trimethylsilyl)acetylene (0.02 mmol) were added at this point, and the reaction mixture was heated and stirred

for 6 h. The solvent was removed under reduced pressure, and the residue was then treated with aqueous  $\text{KOH}$  (20 mL, 1 M) and  $\text{MeOH}$  (100 mL) and the mixture refluxed overnight. After removal of methanol, the product was extracted with ether and then purified by chromatography on neutral alumina using hexane as a eluent to afford a clear light yellow oil. Yield: 0.50 g, 18%. NMR in  $\text{CD}_2\text{Cl}_2$ :  $\delta(\text{H})$  2.31 [s, 3H,  $\text{CH}_3$ ]; 3.13 [s, 2H,  $\text{CCH}$ ]; 7.31 [s, 2H, *o*-H]; 7.42 [s, 1H, *p*-H];  $\delta(\text{C})$  133.84, 133.56, 133.38, 133.02 [aryl], 78.16 [ $\text{C}\equiv\text{CH}$ ], 77.89 [ $\text{C}\equiv\text{CH}$ ], 30.18 [ $\text{CH}_3$ ]. IR (Nujol,  $\text{cm}^{-1}$ ):  $\nu(\text{CC}-\text{H})$  3300,  $\nu(\text{C}\equiv\text{C})$  2117(s), 2224.9. MS:  $m/z$  found 140.062 71, calcd for  $\text{C}_{11}\text{H}_8$  140.062 60.

**$[\{\text{MeC}_6\text{H}_3\text{-3,5-(C}\equiv\text{CAu)}_2\}_n]$  (**2**).** *Caution! Shock-sensitive.*  $[\text{AuCl}(\text{SMe}_2)]$  (0.4 g, 1.36 mmol) was suspended in THF (50 mL). A solution of **1** (0.095 g, 0.68 mmol) and  $\text{NaO}_2\text{CMe}$  (0.11 g, 1.36 mmol) in THF (25 mL)/ $\text{MeOH}$  (15 mL) was added, and the resulting mixture was stirred for 3 h, yielding a bright yellow precipitate. The mixture was filtered and the yellow solid washed with THF,  $\text{MeOH}$ , and pentane and dried in vacuo. Yield: 0.32 g, 89%. The solid is insoluble in common organic solvents. IR (Nujol,  $\text{cm}^{-1}$ ):  $\nu(\text{C}\equiv\text{C})$  1985 (w). Anal. Calcd for  $\text{C}_{11}\text{H}_6\text{Au}_2$ : C, 24.8; H, 1.1. Found C, 23.8; H, 1.1. The analysis is poor since the insoluble material cannot be further purified—further characterization is by formation of soluble derivatives described below. A sample of compound **2** exploded on scratching with a metal spatula.

**$[\text{MeC}_6\text{H}_3\text{-3,5-(C}\equiv\text{CAuP(OPh)}_3)_2]$  (**3a**).** A mixture of **2** (0.22 g, 0.41 mmol) and  $\text{P(OPh)}_3$  (0.24 g, 0.83 mmol) in dichloromethane (20 mL) was stirred for 30 min. The mixture was filtered to remove suspended material, and then pentane (100 mL) was added to the filtrate to give the product as a white solid, which was collected by filtration and washed with ether and pentane. Yield: 0.30 g, 63%. NMR in  $\text{CD}_2\text{Cl}_2$ :  $\delta(\text{H})$  2.15 [s, 3H,  $\text{CH}_3$ ], 6.94 [s, 2H, *o*-H], 6.98 [s, 1H, *p*-H], 7.29–7.45 [m, 30H, Ph];  $\delta(\text{P})$  138.18 [s]. IR (Nujol,  $\text{cm}^{-1}$ ):  $\nu(\text{C}\equiv\text{C})$  2115 (w). Anal. Calcd for  $\text{C}_{47}\text{H}_{36}\text{O}_6\text{P}_2\text{Au}_2$ : C, 49.0; H, 3.1. Found: C, 49.3; H, 3.1.

**$[\text{MeC}_6\text{H}_3\text{-3,5-(C}\equiv\text{CAuP(OMe)}_3)_2]$  (**3b**).** This was prepared similarly from **2** (0.20 g, 0.38 mmol) and  $\text{P(OMe)}_3$  (0.081 g, 0.752 mmol). Yield: 0.20 g, 68%. NMR in  $\text{CD}_2\text{Cl}_2$ :  $\delta(\text{H})$  2.22 [s, 3H,  $\text{CH}_3$ ], 7.05 [s, 2H, *o*-H], 7.15 [s, 1H, *p*-H], 3.76 [d, 18H, Ph];  $\delta(\text{P})$  = 16 Hz,  $\text{CH}_3$ ;  $\delta(\text{P})$  150.34 [s]. IR (Nujol,  $\text{cm}^{-1}$ ):  $\nu(\text{C}\equiv\text{C})$  2120 (w). Anal. Calcd for  $\text{C}_{17}\text{H}_{24}\text{O}_2\text{P}_2\text{Au}_2$ : C, 26.2; H, 3.1. Found: C, 26.0; H, 3.1.

**$[\text{MeC}_6\text{H}_3\text{-3,5-(C}\equiv\text{CAuPPh}_3)_2]\cdot 0.5\text{CH}_2\text{Cl}_2$  (**3c**).** This was prepared similarly from **2** (0.20 g, 0.38 mmol) and  $\text{PPh}_3$  (0.20 g, 0.76 mmol). Yield: 0.26 g, 65%. NMR in  $\text{CD}_2\text{Cl}_2$ :  $\delta(\text{H})$  2.23 [s, 3H,  $\text{CH}_3$ ], 7.09 [s, 2H, *o*-H], 7.21 [s, 1H, *p*-H], 7.5 [m, 30H, Ph];  $\delta(\text{P})$  42.80 [s]. IR (Nujol,  $\text{cm}^{-1}$ ):  $\nu(\text{C}\equiv\text{C})$  2120 (w), 2212 (w). Anal. Calcd for  $\text{C}_{47}\text{H}_{36}\text{P}_2\text{Au}_2\cdot 0.5\text{CH}_2\text{Cl}_2$ : C, 51.9; H, 3.4. Found: C, 51.3; H, 3.4. The presence of dichloromethane was confirmed by  $^1\text{H}$  NMR.

**$[\text{MeC}_6\text{H}_3\text{-3,5-(C}\equiv\text{CAuPMePh}_2)_2]$  (**3d**).** This was prepared similarly from **2** (0.20 g, 0.38 mmol) and  $\text{PMePh}_2$  (0.15 g, 0.76 mmol). Yield: 0.24 g, 67%. NMR in  $\text{CD}_2\text{Cl}_2$ :  $\delta(\text{H})$  2.22 [s, 3H,  $\text{CH}_3$ ], 7.06 [s, 2H, *o*-H], 7.18 [s, 1H, *p*-H], 2.05 [d, 6H,  $^2\text{J(PH)} = 9.3\text{ Hz}$ ,  $\text{PMe}$ ], 7.4–7.7 [m, 20H, Ph];  $\delta(\text{P})$  25.17 [s]. IR (Nujol,  $\text{cm}^{-1}$ ):  $\nu(\text{C}\equiv\text{C})$  2120 (w), 2212 (w). Anal. Calcd for  $\text{C}_{37}\text{H}_{32}\text{P}_2\text{Au}_2$ : C, 47.7; H, 3.5. Found: C, 47.9; H, 3.4.

**$[\text{MeC}_6\text{H}_3\text{-3,5-(C}\equiv\text{CAuCN-}t\text{Bu)}_2]$  (**3e**).** This was prepared similarly from **2** (0.10 g, 0.19 mmol) and *t*-BuNC (31.42 mg, 0.38 mmol). Yield: 0.062 g, 47%. NMR in  $\text{CD}_2\text{Cl}_2$ :  $\delta(\text{H})$  2.21 [s, 3H,  $\text{CH}_3$ ], 7.02 [s, 2H, *o*-H], 7.12 [s, 1H, *p*-H], 1.55 [s, 18H, Bu]. IR (Nujol,  $\text{cm}^{-1}$ ):  $\nu(\text{C}\equiv\text{C})$  2120 (w),  $\nu(\text{C}\equiv\text{N})$  2229 (s). XPS:  $\text{BE}(\text{Au } 4f_{7/2}) = 85.0\text{ eV}$ . Anal. Calcd for  $\text{C}_{21}\text{H}_{24}\text{N}_2\text{Au}_2$ : C, 36.1; H, 3.5; N, 4.0. Found: C, 36.0; H, 3.6; N, 3.9.

**$[\text{MeC}_6\text{H}_3\text{-3,5-(C}\equiv\text{CAuCNMe)}_2]$  (**3f**).** This was prepared similarly from **2** (0.10 g, 0.19 mmol) and MeNC (15.52 mg, 0.38 mmol). Yield: 0.080 g, 69%. IR (Nujol,  $\text{cm}^{-1}$ ):  $\nu(\text{C}\equiv\text{N})$  2259 (s),  $\nu(\text{C}\equiv\text{C})$  2120(w). XPS:  $\text{BE}(\text{Au } 4f_{7/2}) = 85.0\text{ eV}$ . Anal.

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Calcd for  $C_{15}H_{12}N_2Au_2$ : C, 29.3; H, 2.0; N, 4.6. Found: C, 29.0; H, 2.0; N, 4.6.

**[MeC<sub>6</sub>H<sub>3</sub>-3,5-(C≡CAu)<sub>2</sub>(μ-1,4-C<sub>6</sub>H<sub>4</sub>(NC)<sub>2</sub>)<sub>2</sub>]<sub>n</sub> (4a).** To a solution of **3e** (0.086 g, 0.12 mmol) in THF (10 mL) was added 1,4-C<sub>6</sub>H<sub>4</sub>(NC)<sub>2</sub> (20.8 mg, 0.16 mmol) in THF (10 mL). The mixture was stirred for 12 h to yield the product as a yellow precipitate, which was collected by filtration, washed with THF, MeOH, and ether, and dried in vacuo. Yield: 0.068 g, 63%. IR (Nujol, cm<sup>-1</sup>): ν(N≡C) 2205 (s), ν(C≡C) 2127 (w). Anal. Calcd for  $C_{19}H_{10}N_2Au_2$ : C, 34.6; H, 1.5; N, 4.2. Found: C, 34.4; H, 1.3; N, 4.2. XPS: BE(Au 4f <sup>7/2</sup>) = 85.0 eV.

**[MeC<sub>6</sub>H<sub>3</sub>-3,5-(C≡CAu)<sub>2</sub>(μ-1,4-C<sub>6</sub>Me<sub>4</sub>(NC)<sub>2</sub>)<sub>2</sub>]<sub>n</sub> (4b).** This was prepared similarly from **3e** (0.08 g, 0.12 mmol) and 1,4-C<sub>6</sub>Me<sub>4</sub>(NC)<sub>2</sub> (27.8 mg, 0.15 mmol). Yield: 0.076 g, 70%. IR (Nujol, cm<sup>-1</sup>): ν(N≡C) 2205 (s), ν(C≡C) 2127 (w). Anal. Calcd for  $C_{23}H_{18}N_2Au_2$ : C, 38.6; H, 2.5; N, 3.9. Found: C, 38.1; H, 2.2; N, 3.6. XPS: BE(Au 4f <sup>7/2</sup>) = 85.0 eV.

**[MeC<sub>6</sub>H<sub>3</sub>-3,5-(C≡CAu)<sub>2</sub>(μ-Ph<sub>2</sub>PCH<sub>2</sub>PPh<sub>2</sub>)<sub>2</sub>] (5a).** A mixture of **2** (0.10 g, 0.19 mmol) and Ph<sub>2</sub>PCH<sub>2</sub>PPh<sub>2</sub> (72.6 mg, 0.19 mmol) in dichloromethane (20 mL) was stirred for 30 min. The mixture was filtered, and pentane (100 mL) was added to the filtrate to precipitate the product as a white solid, which was collected by filtration and washed with ether and pentane. Yield: 0.082 g, 69%. NMR in CD<sub>2</sub>Cl<sub>2</sub>: δ(<sup>1</sup>H) 2.12 [s, 3H, CH<sub>3</sub>], 6.99 [s, 2H, *o*-H], 7.14 [s, 1H, *p*-H], 2.12 [m, 2H, CH<sub>2</sub>], 7.4–7.7 [m, 20H, Ph]; δ(<sup>31</sup>P) 33.61 [s]. IR (Nujol, cm<sup>-1</sup>): ν(C≡C) 2117 (w), 2225 (w). Anal. Calcd for  $C_{36}H_{28}P_2Au_2$ : C, 47.2; H, 3.1. Found: C, 47.4; H, 3.0.

**[MeC<sub>6</sub>H<sub>3</sub>-3,5-(C≡CAu)<sub>2</sub>(μ-Ph<sub>2</sub>P(CH<sub>2</sub>)<sub>2</sub>PPh<sub>2</sub>)<sub>2</sub>] (5b).** This was prepared similarly from **2** (0.20 g, 0.38 mmol) and Ph<sub>2</sub>P(CH<sub>2</sub>)<sub>2</sub>PPh<sub>2</sub> (0.15 g, 0.38 mmol). Yield: 0.20 g, 57%. NMR in CD<sub>2</sub>Cl<sub>2</sub>: δ(<sup>1</sup>H) 2.23 [s, 3H, CH<sub>3</sub>], 7.08 [s, 2H, *o*-H], 7.26 [s, 1H, *p*-H], 2.72 [m, 4H, CH<sub>2</sub>], 7.5–7.7 [m, 20H, Ph]; δ(<sup>31</sup>P) 35.14 [s]. IR (Nujol, cm<sup>-1</sup>): ν(C≡C) 2117 (w), 2225 (w). Anal. Calcd for  $C_{37}H_{30}P_2Au_2$ : C, 47.8; H, 3.2. Found: C, 47.8; H, 3.1.

**[MeC<sub>6</sub>H<sub>3</sub>-3,5-(C≡CAu)<sub>2</sub>(μ-Ph<sub>2</sub>P(CH<sub>2</sub>)<sub>3</sub>PPh<sub>2</sub>)<sub>2</sub>] (5c).** This was prepared similarly from **2** (0.10 g, 0.19 mmol) and Ph<sub>2</sub>P(CH<sub>2</sub>)<sub>3</sub>PPh<sub>2</sub> (78.0 mg, 0.19 mmol). Yield: 0.13 g, 73%. NMR in CD<sub>2</sub>Cl<sub>2</sub>: δ(<sup>1</sup>H) 2.24 [s, 3H, CH<sub>3</sub>], 7.07 [s, 2H, *o*-H], 7.25 [s, 1H, *p*-H], 1.88 [m, 2H, CH<sub>2</sub>], 2.77 [m, 4H, CH<sub>2</sub>], 7.4–7.8 [m, 20H, Ph]; δ(<sup>31</sup>P) 35.27 [s]. IR (Nujol, cm<sup>-1</sup>): ν(C≡C) 2117 (w), 2225 (w). Anal. Calcd for  $C_{38}H_{32}P_2Au_2$ : C, 48.3; H, 3.4. Found: C, 48.0; H, 3.2.

**[MeC<sub>6</sub>H<sub>3</sub>-3,5-(C≡CAu)<sub>2</sub>(μ-Ph<sub>2</sub>P(CH<sub>2</sub>)<sub>4</sub>PPh<sub>2</sub>)<sub>2</sub>] (5d).** This was prepared similarly from **2** (0.05 g, 0.094 mmol) and Ph<sub>2</sub>P(CH<sub>2</sub>)<sub>4</sub>PPh<sub>2</sub> (40.0 mg, 0.094 mmol). Yield: 0.076 g, 84%. NMR in CD<sub>2</sub>Cl<sub>2</sub>: δ(<sup>1</sup>H) 2.22 [s, 3H, CH<sub>3</sub>], 7.06 [s, 2H, *o*-H], 7.25 [s, 1H, *p*-H], 1.67 [m, 4H, CH<sub>2</sub>], 2.46 [m, 4H, CH<sub>2</sub>], 7.4–7.6 [m, 20H, Ph]; δ(<sup>31</sup>P) = 35.39 [s]. IR (Nujol, cm<sup>-1</sup>): ν(C≡C) 2120 (w). Anal. Calcd for  $C_{39}H_{34}P_2Au_2$ : C, 48.9; H, 3.6. Found: C, 49.2; H, 3.5.

**[MeC<sub>6</sub>H<sub>3</sub>-3,5-(C≡CAu)<sub>2</sub>(μ-Ph<sub>2</sub>P(CH<sub>2</sub>)<sub>5</sub>PPh<sub>2</sub>)<sub>2</sub>] (5e).** This was prepared similarly from **2** (0.05 g, 0.094 mmol) and Ph<sub>2</sub>P(CH<sub>2</sub>)<sub>5</sub>PPh<sub>2</sub> (41.4 mg, 0.094 mmol). Yield: 0.078 g, 85%. NMR in CD<sub>2</sub>Cl<sub>2</sub>: δ(<sup>1</sup>H) 2.20 [s, 3H, CH<sub>3</sub>], 7.04 [s, 2H, *o*-H], 7.18 [s, 1H, *p*-H], 1.55 [m, 4H, CH<sub>2</sub>], 1.73 [m, 2H, CH<sub>2</sub>], 2.40 [m, 4H, CH<sub>2</sub>], 7.4–7.7 [m, 20H, Ph]; δ(<sup>31</sup>P) 36.15 [s]. IR (Nujol, cm<sup>-1</sup>): ν(C≡C) 2120 (w). Anal. Calcd for  $C_{40}H_{36}P_2Au_2$ : C, 49.4; H, 3.7. Found: C, 50.0; H, 3.7.

**Table 4. Crystal Data and Structure Refinement**

	<b>3b</b>	<b>3d</b>
formula, fw	C <sub>17</sub> H <sub>24</sub> Au <sub>2</sub> O <sub>6</sub> P <sub>2</sub> , 780.23	C <sub>37</sub> H <sub>32</sub> Au <sub>2</sub> P <sub>2</sub> , 932.50
<i>T</i> /K	298(2)	298(2)
wavelength/Å	0.710 73	0.710 73
system, space group	triclinic, <i>P</i> $\bar{1}$	monoclinic, <i>P</i> 2 <sub>1</sub> / <i>c</i>
cell dimens		
<i>a</i> , Å	7.3441(3)	36.0828(4)
<i>b</i> , Å	10.4689(5)	10.5122(1)
<i>c</i> , Å	15.7477(7)	17.9674(3)
α, deg	93.344(2)	
β, deg	100.786(1)	92.691(1)
γ, deg	103.835(2)	
<i>V</i> /Å <sup>3</sup> , <i>Z</i>	1148.10(9), 2	6807.7(2), 8
<i>d</i> <sub>calc</sub> /Mg m <sup>-3</sup>	2.257	1.820
abs coeff/mm <sup>-1</sup> , <i>F</i> (000)	12.930, 724	8.727, 3536
abs cor	semiempirical	semiempirical
<i>R</i> 1, <i>wR</i> 2 ( <i>I</i> > 2σ( <i>I</i> ))	0.0508, 0.1244	0.0968, 0.1906

**[MeC<sub>6</sub>H<sub>3</sub>-3,5-(C≡CAu)<sub>2</sub>(μ-Ph<sub>2</sub>P(CH<sub>2</sub>)<sub>6</sub>PPh<sub>2</sub>)<sub>2</sub>] (5f).** This was prepared similarly from **2** (0.05 g, 0.094 mmol) and Ph<sub>2</sub>P(CH<sub>2</sub>)<sub>6</sub>PPh<sub>2</sub> (42.7 mg, 0.094 mmol). Yield: 0.075 g, 81%. NMR in CD<sub>2</sub>Cl<sub>2</sub>: δ(<sup>1</sup>H) 2.20 [s, 3H, CH<sub>3</sub>], 7.05 [s, 2H, *o*-H], 7.19 [s, 1H, *p*-H], 1.41 [m, 4H, CH<sub>2</sub>], 1.61 [m, 4H, CH<sub>2</sub>], 2.38 [m, 4H, CH<sub>2</sub>], 7.4–7.7 [m, 20H, Ph]; δ(<sup>31</sup>P) 36.54 [s]. IR (Nujol, cm<sup>-1</sup>): ν(C≡C) 2120 (w). Anal. Calcd for  $C_{41}H_{38}P_2Au_2$ : C, 49.9; H, 3.9. Found: C, 50.4; H, 3.8.

**Structural Determination of 3b and 3d.** Suitable crystals were mounted on thin, glass fibers using paraffin oil. Data were collected using a Bruker AX SMART 1K CCD diffractometer using 0.3° ω-scans at 0, 90, and 180° in φ. Crystal data and structure refinement details are given in Table 4. Unit-cell parameters were determined from 60 data frames collected at different sections of the Ewald sphere. Semiempirical absorption corrections based on ψ scans were applied. Systematic absences in the diffraction data and unit-cell parameters were consistent with *P*1 and *P* $\bar{1}$  and uniquely with *P*2<sub>1</sub>/*c* for **3d**. Solution in the centric space group for **3b** yielded computationally stable and chemically reasonable results of refinement. The structures were solved by direct methods, completed with difference Fourier syntheses, and refined with full-matrix least-squares procedures based on *F*<sup>2</sup>. For complex **3d**, the aromatic groups were treated as rigid hexagons. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were treated as idealized contributions. All scattering factors and anomalous dispersion factors are contained in the SHELXTL 5.10 program library (G. M. Sheldrick, Bruker AXS, Madison, WI, 1997).

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**Supporting Information Available:** Tables of X-ray data for complexes **3b** and **3d**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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