

# Binuclear Gold(I) and Mercury(II) Derivatives of Diethynylfluorenes

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Received July 12, 2001

A new series of bis(alkynyl) gold(I) and mercury(II)  $d^{10}$  complexes incorporating fluorenyl-based linking units are reported. The binuclear complexes  $[LAuC\equiv CRC\equiv CAuL]$  and their isoelectronic mercury(II) congeners  $[R'HgC\equiv CRC\equiv CHgR']$  ( $L$  = tertiary phosphines;  $R$  = fluorene-2,7-diyl, dihexylfluorene-2,7-diyl, 9-((ferrocenylphenylene)methylene)fluorene-2,7-diyl, fluoren-9-one-2,7-diyl, 9-(dicyanomethylene)fluorene-2,7-diyl;  $R'$  = Me, Ph) were prepared in very good yields by the base-catalyzed dehydrohalogenation reaction of the corresponding metal chloride precursors with the appropriate diethynylfluorene derivatives  $HC\equiv CRC\equiv CH$  at room temperature. All the compounds have been fully characterized by FTIR, NMR and electronic absorption spectroscopies and FAB mass spectrometry. The solid-state molecular structures of  $[Ph_3PAuC\equiv CRC\equiv CAuPPh_3]$  ( $R$  = 9,9-dihexylfluorene-2,7-diyl, fluoren-9-one-2,7-diyl) and  $[MeHgC\equiv CRC\equiv CHgMe]$  ( $R$  = fluoren-9-one-2,7-diyl) have been determined crystallographically, the last of which represents the first dimercury diacetylide to be structurally characterized. Absorption studies suggest that it is possible to fine-tune the optical gap of this class of materials by modifying the electronic properties of the substituent at the 9-position of the central fluorene spacer. The solution redox chemistry of these fluorene-linked binuclear complexes as revealed by cyclic voltammetry indicates some degree of electronic communication between the 9-substituent of the fluorenyl ring and the terminal metal groups via the conjugated alkynyl bridge. Most of the complexes in this study have been shown to exhibit rich photophysical behavior, and a discussion on their emission properties in terms of the nature of metal groups and their auxiliary ligands as well as the fluorene spacer was made.

## Introduction

There is a rapidly growing interest in the study and design of rigid-rod metal acetylide materials due to the potential applications of these compounds in many areas of materials science.<sup>1</sup> Among these, the chemistry of alkynylgold(I) complexes has received much current attention.<sup>2,3</sup> The preference of  $d^{10}$  gold(I) to form linear two-coordinate species, along with the linearity of the  $C\equiv C$  bond in alkynyl ligands, make the  $-(AuC\equiv C)-$  moiety an attractive and promising candidate for the

design of linear-chain metal-containing materials with extensive electronic conjugation.<sup>2,3</sup> It has been shown that some of these gold(I) complexes show liquid-crystalline properties<sup>4</sup> or nonlinear optical behavior.<sup>5</sup> In addition, many alkynylgold(I) derivatives exhibit diverse and interesting luminescent properties.<sup>3,6</sup> In particular, alkynylgold(I) compounds with tertiary phosphine ligands are well-known for their rich photochemistry and belong to a class of luminophores that may find applications in electronic devices.<sup>6,7</sup> In view of the fact that the

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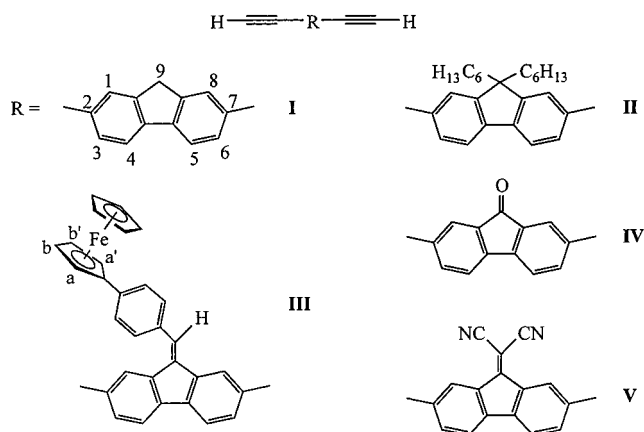
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[R'Hg]<sup>+</sup> unit (R' = alkyl, aryl) is isoelectronic and isolobal with the [Ph<sub>3</sub>PAu]<sup>+</sup> fragment,<sup>8</sup> a comparative study of the alkynylmercury(II) complexes to their gold(I) counterparts represents a challenging area of research. Despite a vast number of works on the chemistry of alkynylgold(I) species, much less is known for the mercury(II) congeners and related studies on the isoelectronic mercury(II) systems are still sparse. Organomercurials, particularly methyl- and arylmercury(II) compounds, are the most deleterious mercury contaminant agents that take part in the biogeochemical cycle of mercury.<sup>9</sup> Considerable effort has been devoted to the search for rapid and sensitive separation and detection methods for these toxic mercury species.<sup>10,11</sup> With the recent reports on the successful development of new derivatization procedures which convert Hg(II) and MeHg(II) species into organometallic compounds suitable for chromatographic analyses<sup>11</sup> and the recent efforts by us and others in employing fluorene-based spacers to make luminescent bimetallic and organometallic polymeric materials,<sup>12</sup> it seemed an attractive goal to us to synthesize new d<sup>10</sup> metal complexes with electronically tunable fluorenyl linkers, I–V (Chart 1). Here we report the first synthesis, characterization, and redox and luminescence behavior of a series of novel bis-(alkynyl)gold(I) and -mercury(II) complexes [LAuC≡CRC≡CAuL] and [R'HgC≡CRC≡CHgR'] (L = tertiary phosphines; R = fluorenyl groups; R' = Me, Ph) with electron-rich and electron-deficient fluorene moieties,

Chart 1



and the first structurally characterized dimercury(II) diacetylde complex is also presented. Their luminescent behavior will be discussed in terms of the electronic, geometric, and steric properties of L, R, and R'.

## Results and Discussion

**Synthesis.** The ligand precursors I and IV were prepared by previously reported procedures.<sup>12a</sup> 9,9-Dihexyl-2,7-bis(trimethylsilyl)ethynylfluorene was prepared as a white crystalline solid by the Sonogashira coupling reaction of Me<sub>3</sub>SiC≡CH with 9,9-dihexyl-2,7-dibromofluorene.<sup>13</sup> The ferrocenyl species 9-(ferrocenylphenylene)methylene-2,7-bis(trimethylsilyl)ethynylfluorene was made by condensing 2,7-bis(trimethylsilyl)ethynylfluorene<sup>12a</sup> with 4-ferrocenylbenzaldehyde<sup>14</sup> in the presence of <sup>1</sup>Pr<sub>2</sub>NLi and isolated as an orange solid. 9-(Dicyanomethylene)-2,7-bis(trimethylsilyl)ethynylfluorene was obtained as a dark brown powder from the reaction of the fluorene-9-one derivative with malononitrile in DMSO at 110 °C.<sup>15</sup> Conversion of these Me<sub>3</sub>Si-substituted compounds into the diterminal H derivatives II, III, and V was accomplished by desilylation with K<sub>2</sub>CO<sub>3</sub> in MeOH (for II and III) or Bu<sub>4</sub>NF (for V) at room temperature. The yields of these reactions are high.

Scheme 1 outlines the reactions leading to the new fluorene-linked digold(I) and dimercury(II) complexes. The precursors I–V can be used to form binuclear alkynyl complexes of Au(I) and Hg(II) by the classical dehydrohalogenation reaction between alkynes and

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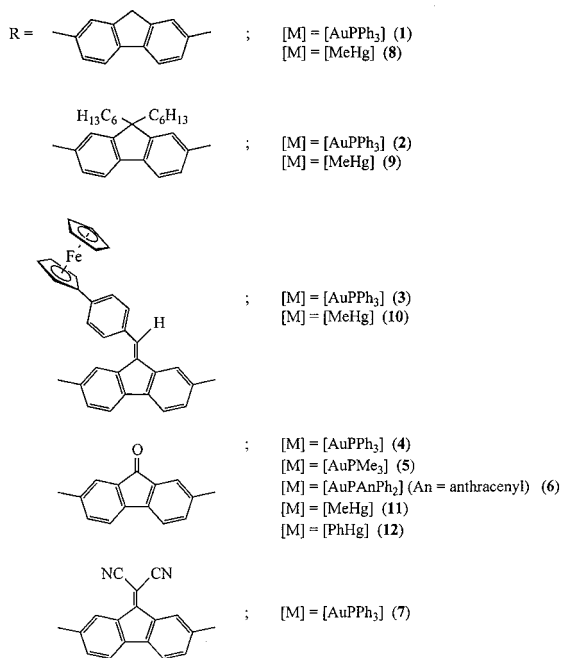
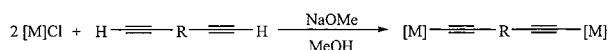
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Scheme 1



chlorogold(I) phosphine complexes or alkylmercury(II) chlorides in the presence of a base.<sup>11c,16</sup> Treatment of 2 equiv of [AuCl(L)] with each of the bifunctional diethynylfluorene ligands HC≡CRC≡CH in an excess of basic MeOH afforded the digold(I) diacetylide complexes [LAuC≡CRC≡CAuL] (L = PPh<sub>3</sub>, R = fluorene-2,7-diyl (**1**), 9,9-dihexylfluorene-2,7-diyl (**2**), 9-((ferrocenylphenylene)methylene)fluorene-2,7-diyl (**3**), fluoren-9-one-2,7-diyl (**4**), 9-(dicyanomethylene)fluorene-2,7-diyl (**7**); L = PMe<sub>3</sub>, R = fluoren-9-one-2,7-diyl (**5**); L = PAnPh<sub>2</sub>, An = anthracenyl, R = fluoren-9-one-2,7-diyl (**6**)) in very good yields, which readily precipitated from the solution mixture. Likewise, we were able to isolate the isoelectronic Hg(II) compounds [R'HgC≡CRC≡CHgR'] (R' = Me, R = fluorene-2,7-diyl (**8**), 9,9-dihexylfluorene-2,7-diyl (**9**), 9-((ferrocenylphenylene)methylene)fluorene-2,7-diyl (**10**), fluoren-9-one-2,7-diyl (**11**); R' = Ph, R = fluoren-9-one-2,7-diyl (**12**)) from MeHgCl or PhHgCl under similar experimental conditions.<sup>11c</sup> Once again, the product yields of **8–12** are very high (80–95%). All the new complexes were obtained as air-stable solids in high purity and found to be soluble in chlorinated solvents such as CH<sub>2</sub>Cl<sub>2</sub>. They all gave satisfactory analytical data and were characterized by fast atom bombardment mass spectrometry (FAB-MS) and IR and NMR spectroscopy. The X-ray structures of compounds **2**, **4**, and **11** were also determined. However, all attempts to prepare the bis(mercurial) analogue of **7**, [MeHgC≡CRC≡CHgMe] (R = 9-(dicyanomethylene)fluorene-2,7-diyl), failed. The direct reaction of MeHgCl and **V** in basic MeOH only led to the isolation of compound **11**, probably due to the attack of MeO<sup>-</sup> on the C=C(CN)<sub>2</sub> group. Using the CuI/Pr<sub>2</sub>NH system, no

Table 1. Selected Bond Lengths (Å) and Angles (deg) for 2·0.5C<sub>6</sub>H<sub>14</sub>

Au(1)–C(19)	2.003(5)	Au(1)–P(1)	2.281(1)
Au(2)–C(47)	1.985(6)	Au(2)–P(2)	2.270(1)
C(19)–C(20)	1.181(7)	C(20)–C(21)	1.448(7)
C(46)–C(47)	1.202(8)	C(27)–C(46)	1.443(7)
C(19)–Au(1)–P(1)	175.9(2)	Au(1)–C(19)–C(20)	172.6(6)
C(19)–C(20)–C(21)	178.4(6)	C(47)–Au(2)–P(2)	177.1(2)
Au(2)–C(47)–C(46)	175.8(6)	C(27)–C(46)–C(47)	179.1(7)

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

Au(1)–C(19)	1.99(1)	Au(1)–P(1)	2.273(3)
Au(2)–C(35)	2.022(9)	Au(2)–P(2)	2.276(3)
C(19)–C(20)	1.23(2)	C(20)–C(21)	1.37(2)
C(34)–C(35)	1.16(2)	C(27)–C(34)	1.48(2)
C(19)–Au(1)–P(1)	175.3(4)	Au(1)–C(19)–C(20)	167(1)
C(19)–C(20)–C(21)	175(1)	C(35)–Au(2)–P(2)	170.6(3)
Au(2)–C(35)–C(34)	165(1)	C(27)–C(34)–C(35)	174(2)

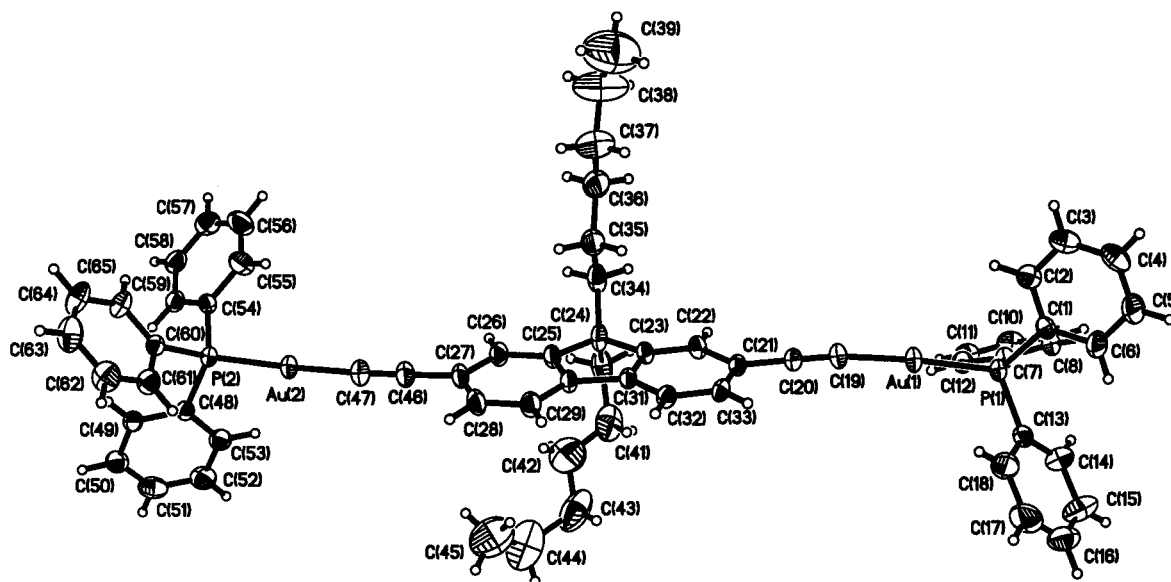
sign of the formation of bis(mercurial) species could be detected and the reaction only occurred with partial decomposition to metallic mercury. The reaction between **11** and malononitrile in DMSO has also been attempted and seemed to produce a complex mixture which we could not separate.

### Spectroscopic and Structural Characterization.

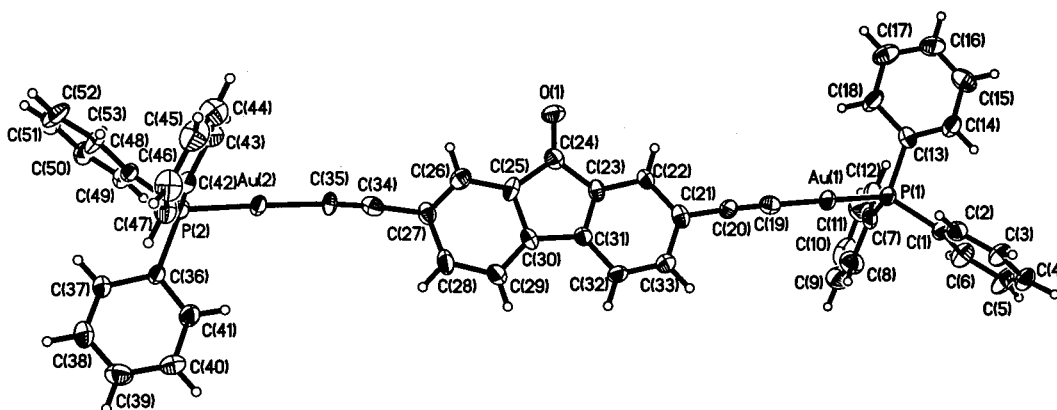
All the new complexes in this study display weak IR  $\nu(\text{C}\equiv\text{C})$  absorptions at ca. 2095–2113 cm<sup>-1</sup> (for Au(I)) and 2121–2130 cm<sup>-1</sup> (for Hg(II)). The C≡CH stretching mode in the starting material is absent in each case. The characteristic IR vibration due to  $\nu(\text{C}=\text{O})$  is apparent in all fluorenone-containing alkynyl complexes at ca. 1712–1717 cm<sup>-1</sup>, whereas complex **7** also gave  $\nu(\text{C}\equiv\text{N})$  2224 cm<sup>-1</sup>. In the <sup>1</sup>H NMR spectra, proton signals arising from the aromatic and other organic groups were observed. Except for **3** and **10**, the symmetrical nature of all other complexes was evident from the NMR spectral pattern. The room-temperature <sup>31</sup>P NMR spectrum of **3** displays two sharp singlets in close proximity at  $\delta$  43.46 and 43.70, indicating an unsymmetrical arrangement of PAuC≡C groups in solution. The ferrocenyl moieties in **3** and **10** show the expected pattern where the unsubstituted C<sub>5</sub>H<sub>5</sub> ring appears as a strong singlet and the monosubstituted C<sub>5</sub>H<sub>4</sub> ring gives an unsymmetrical pair of “pseudo” triplets corresponding to the A<sub>2</sub>B<sub>2</sub> spectrum with  $J(\text{adjacent}) \cong J(\text{cross})$ . In each case, we can locate an intense molecular ion peak in the respective mass spectrum.

Although a slight difficulty in growing single crystals of these bis(alkynyl)gold(I) and -mercury(II) complexes was encountered, X-ray structure determinations were successfully carried out for three of them. We are aware that there are only a few structurally characterized examples of digold(I) diacetylide complexes in the literature,<sup>3c–e</sup> the first one being [Me<sub>3</sub>PAuC≡CC<sub>6</sub>H<sub>2</sub>Me<sub>2</sub>C≡CAuPMe<sub>3</sub>], reported by Puddephatt and co-workers.<sup>3c</sup> The perspective drawings of **2** and **4** with atomic numberings are shown in Figures 1 and 2, respectively. Selected bond lengths and angles are presented in Tables 1 and 2. There is a half hexane solvate in the unit cell of compound **2**. In contrast to many Au(I) compounds, where there frequently exist short Au···Au intermolecular contacts,<sup>6</sup> no such weak interactions are observed in **2** and **4** in the solid state, as the sterically bulky phenyl groups of the phosphine

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**Figure 1.** Perspective drawing of compound **2**.



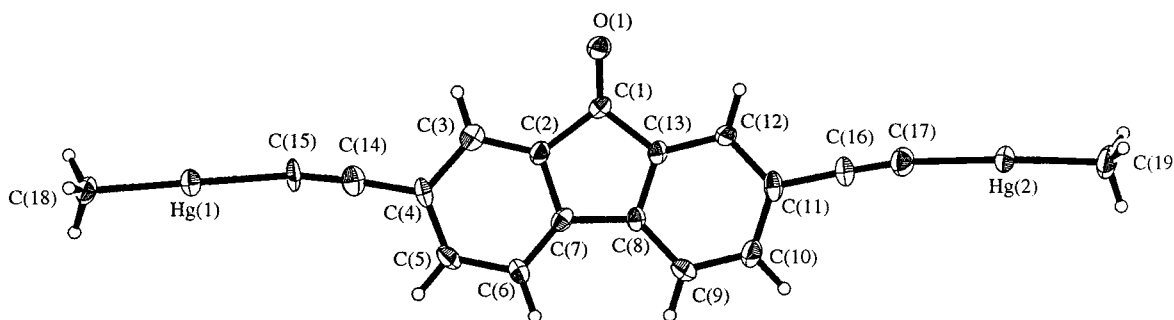
**Figure 2.** Perspective drawing of compound **4**.

ligands and the long hexyl chains (for **2**) probably prevent their close approach.<sup>2c</sup> The closest intramolecular nonbonded contact in **2** is due to an Au(2)⋯H(55A) interaction (3.022 Å), and the nearest intermolecular contact arises from an Au(1)⋯H(10A) interaction (3.072 Å). For **4**, the nearest intermolecular contact is attributed to the hydrogen-bonding interaction between O(1) and H(49A) on C(49) of the phenyl ring (O(1)⋯H(49A) = 2.399 Å), and an intermolecular Au(1)⋯H(17A) interaction (3.004 Å) is also observed. Although the fluorenyl ring system is almost planar in **2** and **4** (mean deviations 0.024 and 0.014 Å, respectively), no indication of the presence of  $\pi$ -stacking of the aromatic rings is apparent. The C=C bond distances of 1.192(8) Å (**2**) and 1.20(2) Å (**4**) are characteristic of terminal acetylides. Variation of the fluorenyl group does not have a significant influence on the bonding in the central PAuC≡C unit. The average Au–P bond lengths of 2.276(1) Å in **2** and 2.275(3) Å in **4** are similar to those observed in other alkynylgold(I) phosphines<sup>3a,c,d,6</sup> but longer than those of the chlorogold(I) phosphine complexes,<sup>17</sup> in line with the higher trans influence of the alkynyl group. The Au–C bond distances lie in the narrow range 1.985(6)–2.022(9) Å. The geometry about the Au(I) center is essentially linear, and the mean P–Au–C angles of 176.5(2)° (**2**) and 172.8(4)° (**4**) and

Au–C–C angles of 174.2(6)° (**2**) and 166(1)° (**4**) are indicative of  $sp$  hybridization in Au(I) and acetylenic carbon necessary for a rigid-rod molecule. However, we observe a slight bending of the AuPPh<sub>3</sub> fragments away from the mean plane of the diacetylenic fluorene moiety in the structure of **4**, presumably due to crystal-packing effects, and the distances of Au(1) and Au(2) from the mean plane are –0.858 and 0.651 Å, respectively. All of these structural parameters are comparable to those found for other crystal structures of mononuclear, binuclear, and oligomeric alkynylgold(I) complexes.<sup>3a,c,d,6</sup>

The molecular structure of **11** is depicted in Figure 3, and some important bond distances and angles are given in Table 3. The crystal structure shows a binuclear molecule in which two MeHg<sup>II</sup> units are linked by a diacetylenic fluorene-9-one-2,7-diyl moiety in a rigid-rod manner. This is the first example of a dimercury(II) diacetylide complex to be characterized crystallographically. Reported structures of mononuclear Hg(II) acetylides are also limited.<sup>18</sup> There are no apparent short intermolecular interactions between the fluorenyl rings

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**Figure 3.** Perspective drawing of compound **11**.**Table 3. Selected Bond Lengths (Å) and Angles (deg) for **11****

Hg(1)–C(15)	2.03(1)	Hg(1)–C(18)	2.06(2)
Hg(2)–C(17)	2.05(2)	Hg(2)–C(19)	2.06(2)
C(14)–C(15)	1.19(2)	C(4)–C(14)	1.42(2)
C(16)–C(17)	1.16(2)	C(11)–C(16)	1.46(2)
C(15)–Hg(1)–C(18)	178.0(7)	Hg(1)–C(15)–C(14)	170(1)
C(4)–C(14)–C(15)	175(1)	C(17)–Hg(2)–C(19)	176.5(8)
Hg(2)–C(17)–C(16)	171(1)	C(11)–C(16)–C(17)	177(2)

as well as the Hg(II) centers. The Hg–C(alkyne) bond (Hg(1)–C(15) = 2.03(1) Å, Hg(2)–C(17) = 2.05(2) Å) is slightly longer than the Au–C(alkyne) bond in **4** but comparable to those in other Hg(II) acetylide compounds.<sup>18</sup> The fluorenediyl unit does not deviate significantly from planarity, and the C≡C bonds in the ethynyl bridge are fairly typical at 1.19(2) and 1.16(2) Å. Reminiscent of the PAuC≡C fragment, the isoelectronic MeHgC≡C entity displays similar structural motifs and geometry in **11**. The angles C–Hg–C (C(15)–Hg(1)–C(18) = 178.0(7)°, C(17)–Hg(2)–C(19) = 176.5(8)°) and Hg–C–C (Hg(1)–C(15)–C(14) = 170(1)°, Hg(2)–C(17)–C(16) = 171(1)°) are close to linearity. The Hg–CH<sub>3</sub> bond (2.06(2) Å) is slightly shorter than those observed in some methylmercury(II) complexes with thiol ligands such as [(MeHg)<sub>2</sub>(S<sub>2</sub>C<sub>6</sub>H<sub>10</sub>)] (2.08(2)–2.12(2) Å)<sup>10b</sup> and [MeC(CH<sub>2</sub>SHgMe)<sub>3</sub>] (2.09(3)–2.13(3) Å).<sup>10c</sup>

**Absorption and Emission Properties.** The electronic absorption and emission data of our compounds in CH<sub>2</sub>Cl<sub>2</sub> are presented in Table 4. The absorption spectra of the digold(I) and dimercury(II) complexes display intense ligand-localized  $\pi \rightarrow \pi^*$  transitions in the near-UV region (ca. 231–389 nm) and, in most cases, at the low-energy regime of the visible spectrum (ca. 422–579 nm). We note that the absorption bands show bathochromic shifts when the d<sup>10</sup> metal fragments are introduced at the terminal groups, and the red shift is more pronounced with the gold(I) species. These observations are consistent with the increased  $\pi$ -delocalization through the metal groups due to metal to ligand back-donation to  $\pi^*(C\equiv CR)$ .<sup>2c,3a</sup> In this study, the energy gap between the highest occupied (HOMO) and lowest unoccupied (LUMO) molecular orbitals follows the order **1** > **2** > **3** > **4**  $\approx$  **5**  $\approx$  **6** > **7** and **8** > **9** > **10** > **11**  $\approx$  **12**. Replacing the unsubstituted fluorene spacer as in **1** by a 9-(dicyanomethylene)fluorene unit lowers

the HOMO–LUMO gap substantially by 1.51 eV. For each spacer unit, there is a sequential lowering in the energy gap from the ligand to the Hg(II) complex and the Au(I) counterpart, indicative of the metal to ligand  $\pi$  back-bonding, and the stronger interaction at the gold center with a +1 formal oxidation state gives a smaller optical gap. This agrees with the molecular orbital calculations on **2**, **4**, and **11**. Figure 4 depicts the contour plots<sup>19</sup> of the HOMO and LUMO for **4**, showing the common bonding feature in the frontier molecular orbitals of these three complexes. The calculated HOMO–LUMO gap follows the order **2** > **11** > **4**, consistent with the experimental observations (Table 4). It is obvious that the LUMO has  $\pi^*$  character involving the carbonyl unit. By virtue of the accessible low-lying  $\pi^*$  orbitals of CO, the fluorenone-based organometallic complexes give smaller energy gaps. We expect that metal fragments at both ends of **4** and **11** affect more the HOMO and less the LUMO. Indeed, the LUMOs of **4** and **11** are similar in energy (–0.079 04 and –0.080 55 au, respectively). Because of the greater electronegativity and higher formal oxidation state, Hg(II) in **11** pulls down the HOMO's orbital energy more significantly when compared to Au(I), leading to a larger HOMO–LUMO gap.

With reference to spectroscopic studies on [Me<sub>3</sub>PAuC≡CRC≡CAuPMe<sub>3</sub>] (R = C<sub>6</sub>H<sub>4</sub>, C<sub>6</sub>H<sub>2</sub>Me<sub>2</sub>) and other similar alkynylgold(I) complexes, we can tentatively assign the emissive bands to triplet  $\pi\text{--}\pi^*$  or triplet  $\sigma\text{--}\pi^*$  excited states or a combination of both associated with the metal acetylide groups.<sup>3</sup> At 290 K, the emission energies of the complexes roughly follow the same order as the absorption maxima. Within each metal class, the emission energy was found to change upon variation of both the fluorene moieties R and the auxiliary groups L and R'. Figure 5 shows the solution emission spectra of **IV**, **4**, and **12** at 290 K. Their similar spectral patterns are suggestive of the ligand-dominant emissive state, and the spectra display featureless luminescence peaks centered at ca. 531, 575, and 543 nm, respectively. We attribute the bathochromic shift to an increased delocalization of  $\pi$  electrons into the aromatic segment by virtue of the metal to ligand  $\pi$  back-bonding interaction in the presence of filled metal d orbitals, leading to a stabilization of the first  $\pi^*$  orbital of the acetylide groups.<sup>2c,3a,c</sup> The more marked effect for Au(I) is consistent with the lower oxidation state of +1 in **4**, which would enhance the back-donation to  $\pi^*$ . The same trend is observed for other complexes. The emis-

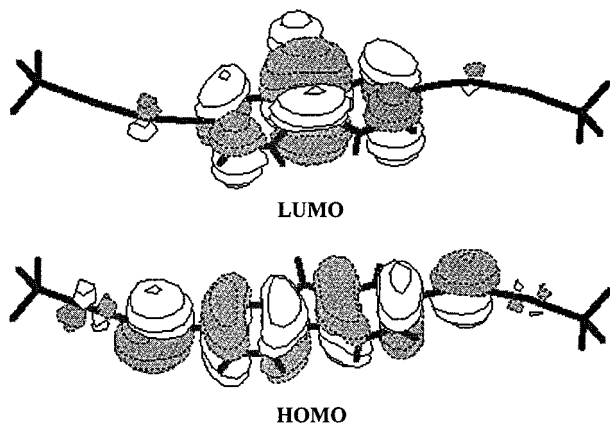
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**Table 4. Electronic Absorption and Emission Data for Compounds 1–12 and Their Free Alkynes**

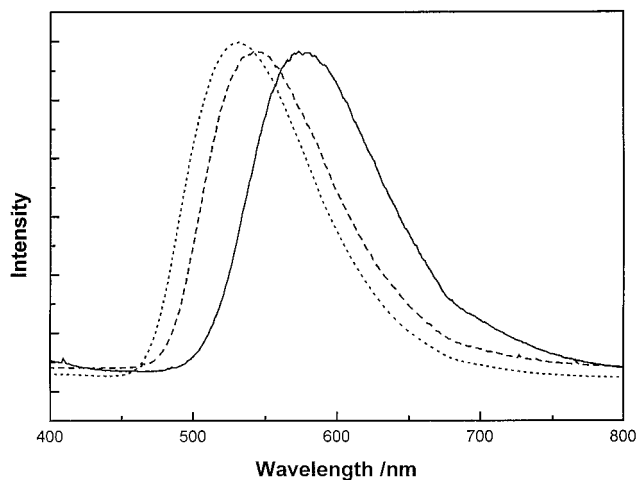
complex	absorption <sup>a</sup> $\lambda_{\text{max}}/\text{nm}$ ( $\epsilon/10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ )	energy gap <sup>b/</sup> eV	emission <sup>c</sup>	
			medium( <i>T</i> /K)	$\lambda_{\text{max}}/\text{nm}$
<b>1</b>	242 (4.4), 325 (4.4), 360 (2.6)	3.35	solid (290)	583
<b>2</b>	275 (1.2), 307 sh (2.3), 319 (4.4), 343 (9.7), 359 (9.0)	3.28	solid (11)	551, 592
			solid (290)	567
<b>3</b>	236 (4.8), 276 (2.4), 339 (3.5), 355 (4.7), 422 sh (0.5)	2.82	solid (11)	549, 597
			solid (290)	vw
<b>4</b>	239 (4.3), 291 (4.3), 337 (3.8), 355 (2.3), 458 (0.3)	2.34	solid (11)	vw
			CH <sub>2</sub> Cl <sub>2</sub> (290)	575
<b>5</b>	295 (5.8), 336 (4.0), 351 (4.1), 461 (0.4)	2.35	solid (290)	589
			solid (11)	590
<b>6</b>	268 (1.2), 301 (1.3), 338 (0.7), 354 (1.0), 389 (0.3), 409 (0.2), 465 (0.1)	2.36	CH <sub>2</sub> Cl <sub>2</sub> (290)	583
			solid (290)	628
<b>7</b>	236 (11.9), 268 (2.7), 276 (2.8), 323 (17.9), 351 sh (9.9), 579 (0.2)	1.84	solid (11)	633
			solid (290)	577
<b>8</b>	231 (1.5), 258 sh (0.5), 311 (3.0), 344sh (2.3)	3.52	solid (290)	596
			solid (11)	604
<b>9</b>	296 sh (2.0), 311 (4.0), 330 (6.4), 346 (8.2)	3.45	solid (290)	736
			solid (11)	737
<b>10</b>	238 (3.0), 286 (3.3), 326 (3.3), 460 sh (0.3)	2.82	solid (290)	567
			solid (11)	564
<b>11</b>	292 (3.4), 315 (1.3), 329 (2.0), 336 (1.4), 343 (2.1), 439 (0.2)	2.50	solid (290)	444, 457, 548 sh
			solid (11)	444, 457, 555
<b>12</b>	231 (2.2), 286 (3.9), 315 (1.9), 329 (2.6), 337 (2.1), 343 (2.4), 437 (0.4)	2.48	CH <sub>2</sub> Cl <sub>2</sub> (290)	vw
			solid (11)	vw
<b>I</b>	314 (1.2), 319 (1.1), 324 (1.1), 327 (1.2)	3.54	CH <sub>2</sub> Cl <sub>2</sub> (290)	555
			solid (290)	597
<b>II</b>	291 (3.3), 302 (4.7), 316 (4.0), 323 sh (3.8), 330 (7.1)	3.67	solid (290)	599
			solid (290) <sup>d</sup>	429 sh, 505
<b>III</b>	236 (4.3), 276 (4.5), 316 (3.6), 328 (4.2), 357 (1.8)	2.88	solid (290)	492
			solid (290)	vw
<b>IV</b>	283 (4.4), 308 (1.7), 321 (2.3), 334 (1.6), 421 (0.2)	2.59	CH <sub>2</sub> Cl <sub>2</sub> (290)	531
			solid (290)	555
<b>V</b>	296 (2.5), 325 (1.8), 347 (1.5), 364 (1.2), 505 (0.1)	2.10	solid (290)	562
			solid (290)	562

<sup>a</sup> All absorption spectra were recorded in CH<sub>2</sub>Cl<sub>2</sub> at 290 K. Abbreviations: sh = shoulder. vw = very weak. <sup>b</sup> Estimated from the onset of absorption. <sup>c</sup> Excitation wavelength is 325 nm. <sup>d</sup> Sample as a thin film was used.



**Figure 4.** Spatial plots of the highest occupied (HOMO) and the lowest unoccupied molecular orbitals (LUMO) for H<sub>3</sub>PAuC≡CRC≡CAuPH<sub>3</sub> (R = fluoren-9-one-2,7-diyl).

sion wavelengths of fluorenone-linked complexes are longer than those of their fluorene analogues because of the higher degree of  $\pi$ -conjugation of the fluorenone unit. The emission of **5** is also red-shifted relative to **4**. This can be rationalized by the fact that the PMe<sub>3</sub> ligand is electron-donating in nature, which renders the Au(I) center more electron-rich. We observe that the order of emission energies is **4** > **6** > **5**, which is in line with the  $\sigma$ -donating ability of the phosphines: i.e., PMe<sub>3</sub> > PAnPh<sub>2</sub> > PPh<sub>3</sub>. Similarly, the order of emission energies **12** > **11** is expected on the basis of the different



**Figure 5.** Emission spectra for **IV** (dotted line), **4** (solid line), and **12** (dashed line) in CH<sub>2</sub>Cl<sub>2</sub> solutions.

$\sigma$ -donating capacities of the hydrocarbonyl groups, i.e., Me > Ph.

**Electrochemistry.** The redox data for electroactive complexes in CH<sub>2</sub>Cl<sub>2</sub> are summarized in Table 5. Each of the cyclic voltammograms of **3** and **10** displays one quasi-reversible ferrocenyl oxidation couple with the half-wave potential in the order **10** > **3** > **III**. This is in accord with the unsaturation of the organometallic end-capped ethynyl bridges, which would render the ferrocenyl center less electron-rich. The  $E_{1/2}$  value is substantially more anodic in **10** than in **3** because of the

**Table 5. Redox Data for Electroactive Compounds and Their Ligand Precursors**

compd	$E_{1/2}/V$ ( $\Delta E/mV$ )	$E_{red}/V$	compd	$E_{1/2}/V$ ( $\Delta E/mV$ )	$E_{red}/V$
<b>3</b>	0.03 (160)		<b>11</b>		-1.64
<b>4</b>		-1.70	<b>12</b>		-1.61
<b>5</b>		-1.68	<b>III</b>	0.02 (115)	
<b>6</b>		-1.57 <sup>a</sup>	<b>IV</b>		-1.55
<b>7</b>		-1.12, -1.75	<b>V</b>		-1.02, -1.65
<b>10</b>	0.10 (108)				

<sup>a</sup> Irreversible wave.

higher formal oxidation state of mercury(II) than that of gold(I). For **4**, **5**, **11**, and **12**, a quasi-reversible reduction wave is observed in each case (-1.61 to -1.70 V), which is assigned as the fluorenone-centered reduction. The observation of a less cathodic potential in the free alkyne **IV** is a manifestation of a more  $\pi$  delocalized system in the Au(I) and Hg(II) complexes, and the reduction potentials are more negative for Au(I) species than for the Hg(II) counterparts. Variation of the PR<sub>3</sub> ligands in the Au(I) compounds or changing the alkyl by an aryl group in the Hg(II) complexes incurs a slight shift in the reduction potentials, in agreement with the absorption and emission data. The good  $\sigma$ -donating PMe<sub>3</sub> groups enhance the  $\sigma$ (P-Au) back-donation to  $\pi^*$  in **5**, which leads to a slight positive shift of 0.02 V as compared to the relatively  $\pi$ -accepting PPh<sub>3</sub> ligands. Likewise, the purely  $\sigma$ -donating Me group in **11** makes the reduction potential of **11** appear at a more negative value. Complex **6**, however, only underwent an irreversible ligand-based reduction event at -1.57 V. Two reversible reduction waves, attributable to the central 9-(dicyanomethylene)fluorene unit,<sup>20</sup> are noted for **7**, and they occur at potentials more cathodic than those of the diethynyl ligand **V**.

### Concluding Remarks

Our present work has demonstrated the versatility of preparing a new family of luminescent binuclear gold(I) and mercury(II) bis(alkynyl) complexes showing adjustable electronic and optical properties by insertion of different peripheral substituents on the central fluorene spacer units. The results have shown that electronic absorption and emission spectral features of these compounds extend over a wide range and can be varied by modifying the 9-substituent of the fluorenyl ring system and the metal center as well as their auxiliary ligands. The empirical trends observed indicate that delocalization of  $\pi$  electrons prevails over the molecule and metal to ligand  $\pi$  back-donation is more significant for the Au(I) complexes than the Hg(II) congeners. Work is in progress to investigate oligomeric and polymeric alkynylmercury(II) materials and subsequently compare them with the gold(I) systems.

### Experimental Section

**General Comments.** All reactions were carried out under a nitrogen atmosphere with the use of standard Schlenk techniques, but no special precautions were taken to exclude oxygen during workup. Solvents were predried and distilled from appropriate drying agents. All chemicals, unless other-

wise stated, were obtained from commercial sources and used as received. Preparative TLC was performed on 0.7 mm silica plates (Merck Kieselgel 60 GF<sub>254</sub>) prepared in our laboratory. The starting materials 4-ferrocenylbenzaldehyde,<sup>14</sup> 2,7-bis((trimethylsilyl)ethynyl)fluorene,<sup>12a</sup> 2,7-diethynylfluorene (**I**),<sup>12a</sup> 2,7-bis(trimethylethynyl)fluorene-9-one,<sup>12a</sup> 2,7-diethynylfluorene-9-one (**IV**),<sup>12a</sup> and AuCl(PANPh<sub>2</sub>)<sup>17c</sup> were prepared by literature methods. Infrared spectra were recorded as KBr pellets using a Perkin-Elmer Paragon 1000 PC or Nicolet Magna 550 Series II FTIR spectrometer. NMR spectra were measured in appropriate solvents on a JEOL EX270 or a Varian INOVA 400 MHz FT-NMR spectrometer, with <sup>1</sup>H NMR chemical shifts quoted relative to TMS and <sup>31</sup>P chemical shifts relative to an 85% H<sub>3</sub>PO<sub>4</sub> external standard. Electron impact (EI) and fast atom bombardment (FAB) mass spectra were recorded on a Finnigan MAT SSQ710 mass spectrometer. Electronic absorption spectra were obtained with a Hewlett-Packard 8453 UV-vis spectrometer. For emission spectra measurement, the 325 nm line of a He-Cd laser was used as an excitation source. The luminescence spectra were analyzed by a 0.25 m focal length double monochromator with a Peltier cooled photomultiplier tube and processed with a lock-in amplifier. For low-temperature measurements, samples were mounted in a closed-cycle cryostat (Oxford CC1104) in which the temperature can be adjusted from 10 to 330 K. Cyclic voltammetry experiments were done with a Princeton Applied Research (PAR) Model 273A potentiostat. A conventional three-electrode configuration consisting of a glassy-carbon working electrode and a Pt wire as the counter and reference electrodes was used. The solvent in all measurements was deoxygenated CH<sub>2</sub>Cl<sub>2</sub>, and the supporting electrolyte was 0.1 M [Bu<sub>4</sub>N]PF<sub>6</sub>. Ferrocene was added as a calibrant after each set of measurements, and all potentials reported were quoted with reference to the ferrocene-ferrocenium couple. Density functional calculations at the B3LYP level<sup>21</sup> were performed on **2**, **4**, and **11** on the basis of their experimentally determined geometries obtained from crystallographic data. The basis set used for C, O, and H atoms was 6-31G,<sup>22</sup> while effective core potentials with a LanL2DZ basis set<sup>23</sup> were employed for P, Au, and Hg atoms. The Gaussian 98 program was used for the calculations.<sup>24</sup> Polarization functions were added for P ( $\xi_d(P) = 0.34$ ). For theoretical simplicity, PH<sub>3</sub> was used to replace PPh<sub>3</sub> in the calculations. The hexyl groups were also replaced by H atoms. *Caution!* Organomercurials are extremely toxic, and all experimentation involving these reagents should be carried out in a well-vented hood.

**[Ph<sub>3</sub>PAuC≡CRC≡CAuPPh<sub>3</sub>] (R = Fluorene-2,7-diyl; **1**).** AuCl(PPh<sub>3</sub>) (19.8 mg, 0.04 mmol) in MeOH (15 mL) was mixed with 2,7-diethynylfluorene (**I**; 4.3 mg, 0.02 mmol) in THF (5 mL). To this solution mixture was added 2 mL of basic MeOH (0.40 mmol, prepared by dissolving 0.20 g of NaOH in 25 mL of MeOH). Within a few minutes, a light yellow solid precipitated from the homogeneous solution. The solid was then collected by filtration after stirring for 2 h, washed with MeOH, and air-dried to furnish **1** in 95% yield (21.5 mg). IR (KBr):

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$\nu(\text{C}=\text{C})$  2095  $\text{cm}^{-1}$ .  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  7.65–7.45 (m, 36H, aromatic H), 3.81 (s, 2H,  $\text{CH}_2$ ).  $^{31}\text{P NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  43.67. FAB-MS ( $m/z$ ): 1130 [ $\text{M}^+$ ]. Anal. Calcd for  $\text{C}_{53}\text{H}_{38}\text{Au}_2\text{P}_2$ : C, 56.30; H, 3.39. Found: C, 56.15; H, 3.30.

**[Ph<sub>3</sub>PAuC≡CRC≡CAuPPh<sub>3</sub>] (R = 9,9-Dihexylfluorene-2,7-diyl; 2).** Complex **2** was synthesized using the same conditions described above for **1**, but 9,9-dihexyl-2,7-diethynylfluorene (**II**; 7.7 mg, 0.02 mmol) was used instead to produce a light yellow solid in 86% yield (22.3 mg). IR (KBr):  $\nu(\text{C}=\text{C})$  2099  $\text{cm}^{-1}$ .  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  7.59–7.43 (m, 36H, aromatic H), 1.85 (m, 4H,  $\text{CH}_2(\text{CH}_2)_4\text{CH}_3$ ), 1.05–0.88 (m, 12H,  $\text{CH}_2(\text{CH}_2)_3\text{CH}_2\text{CH}_3$ ), 0.75 (t,  $J = 7.2$  Hz, 6H,  $(\text{CH}_2)_5\text{CH}_3$ ), 0.54 (m, 4H,  $\text{CH}_2(\text{CH}_2)_3\text{CH}_2\text{CH}_3$ ).  $^{31}\text{P NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  43.74. FAB-MS ( $m/z$ ): 1299 [ $\text{M}^+$ ]. Anal. Calcd for  $\text{C}_{65}\text{H}_{62}\text{Au}_2\text{P}_2$ : C, 60.10; H, 4.81. Found: C, 60.02; H, 4.64.

**[Ph<sub>3</sub>PAuC≡CRC≡CAuPPh<sub>3</sub>] (R = 9-((Ferrocenylphenylene)methylene)fluorene-2,7-diyl; 3).** According to the same procedure described for the synthesis of **1**, complex **3** was obtained from 9-((ferrocenylphenylene)methylene)-2,7-diethynylfluorene (**III**; 9.7 mg, 0.02 mmol) as a red solid in 85% yield (23.9 mg). IR (KBr):  $\nu(\text{C}=\text{C})$  2095  $\text{cm}^{-1}$ .  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  7.92 (m, 1H,  $\text{H}_1$  or  $\text{H}_8$ ), 7.62–7.39 (m, 40H,  $\text{C}_6\text{H}_4$ , vinyl CH,  $\text{H}_{3,4,5,6}$  and  $\text{H}_1$  or  $\text{H}_8$ ), 4.67 (t,  $J = 1.8$  Hz, 2H,  $\text{H}_{a,a'}$ ), 4.28 (t,  $J = 1.8$  Hz, 2H,  $\text{H}_{b,b'}$ ), 4.02 (s, 5H,  $\text{C}_5\text{H}_5$ ).  $^{31}\text{P NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  43.70, 43.46. FAB-MS ( $m/z$ ): 1402 [ $\text{M}^+$ ]. Anal. Calcd for  $\text{C}_{70}\text{H}_{50}\text{Au}_2\text{FeP}_2$ : C, 59.93; H, 3.59. Found: C, 60.02; H, 3.50.

**[Ph<sub>3</sub>PAuC≡CRC≡CAuPPh<sub>3</sub>] (R = Fluorene-9-one-2,7-diyl; 4).** Compound **4** was prepared similarly from 2,7-diethynylfluorene-9-one (**IV**; 4.6 mg, 0.02 mmol), and it was isolated as a bright yellow solid in 86% yield (19.7 mg). IR (KBr):  $\nu(\text{C}=\text{C})$  2107,  $\nu(\text{C}=\text{O})$  1717  $\text{cm}^{-1}$ .  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  7.73 (s, 2H,  $\text{H}_{1,8}$ ), 7.59–7.41 (m, 32H,  $\text{H}_{3,6}$  and Ph), 7.34 (d,  $J = 7.8$  Hz, 2H,  $\text{H}_{4,5}$ ).  $^{31}\text{P NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  43.55. FAB-MS ( $m/z$ ): 1144 [ $\text{M}^+$ ]. Anal. Calcd for  $\text{C}_{53}\text{H}_{36}\text{Au}_2\text{OP}_2$ : C, 55.61; H, 3.17. Found: C, 55.58; H, 3.20.

**[Me<sub>3</sub>PAuC≡CRC≡CAuPMe<sub>3</sub>] (R = Fluorene-9-one-2,7-diyl; 5).** Addition of an excess of basic MeOH to a mixture of AuCl(PMe<sub>3</sub>) (24.7 mg, 0.08 mmol) in MeOH and **IV** (9.1 mg, 0.04 mmol) in THF leads to the precipitation of **5** as an orange powder in 80% yield (24.7 mg). IR (KBr):  $\nu(\text{C}=\text{C})$  2100,  $\nu(\text{C}=\text{O})$  1713  $\text{cm}^{-1}$ .  $^1\text{H NMR}$  (acetone-*d*<sub>6</sub>):  $\delta$  7.69 (m, 2H,  $\text{H}_{1,8}$ ), 7.55 (m, 2H,  $\text{H}_{3,6}$ ), 7.34 (d,  $J = 7.7$  Hz, 2H,  $\text{H}_{4,5}$ ), 1.56 (s, 9H, Me), 1.52 (s, 9H, Me).  $^{31}\text{P NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  2.53. FAB-MS ( $m/z$ ): 772 [ $\text{M}^+$ ]. Anal. Calcd for  $\text{C}_{23}\text{H}_{24}\text{Au}_2\text{OP}_2$ : C, 35.77; H, 3.13. Found: C, 35.45; H, 3.02.

**[Ph<sub>2</sub>AnPAuC≡CRC≡CAuPAnPh<sub>2</sub>] (R = Fluorene-9-one-2,7-diyl; 6).** AuCl(PAnPh<sub>2</sub>) (23.8 mg, 0.04 mmol) and **IV** (4.6 mg, 0.02 mmol) were dissolved in  $\text{CH}_2\text{Cl}_2$  separately before mixing, and 2 mL of 0.2 M basic MeOH was then added to the mixture. After this mixture was stirred at room temperature for 2 h, the yellow precipitate was collected by filtration and washed with MeOH to give **6** in 71% yield (19.1 mg). IR (KBr):  $\nu(\text{C}=\text{C})$  2099,  $\nu(\text{C}=\text{O})$  1716  $\text{cm}^{-1}$ .  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  8.70 (s, 2H, anthracenyl H), 8.32 (d,  $J = 8.6$  Hz, 4H, anthracenyl H), 8.06 (d,  $J = 8.6$  Hz, 4H, anthracenyl H), 7.68–7.57 (m, 12H,  $\text{H}_{1,3,6,8}$  and anthracenyl H), 7.48–7.35 (m, 22H,  $\text{H}_{4,5}$  and Ph).  $^{31}\text{P NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  28.24. FAB-MS ( $m/z$ ): 1345 [ $\text{M}^+$ ]. Anal. Calcd for  $\text{C}_{69}\text{H}_{44}\text{Au}_2\text{OP}_2$ : C, 61.62; H, 3.30. Found: C, 61.50; H, 3.22.

**[Ph<sub>3</sub>PAuC≡CRC≡CAuPPh<sub>3</sub>] (R = 9-(Dicyanomethylene)fluorene-2,7-diyl; 7).** To a mixture of AuCl(PPh<sub>3</sub>) (29.7 mg, 0.06 mmol) and 9-(dicyanomethylene)-2,7-diethynylfluorene (**V**;  $^{12}\text{C}$ , 8.3 mg, 0.03 mmol) in  $^i\text{Pr}_2\text{NH}/\text{CH}_2\text{Cl}_2$  (20 mL, 1/1 v/v) was added CuI (1.0 mg). A dark blue suspension was obtained within a short time, and the mixture was stirred at room temperature for 15 h. The dark blue precipitate was isolated by filtration and washed with MeOH. The crude solid was then extracted with  $\text{CH}_2\text{Cl}_2$  to afford an analytically pure sample of **7** (20.0 mg, 56%) after solvent removal. IR (KBr):

$\nu(\text{C}=\text{N})$  2224,  $\nu(\text{C}=\text{C})$  2113  $\text{cm}^{-1}$ .  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  8.46 (m, 2H,  $\text{H}_{1,8}$ ), 7.59–7.42 (m, 32H,  $\text{H}_{3,6}$  and Ph), 7.36 (d,  $J = 7.8$  Hz, 2H,  $\text{H}_{4,5}$ ).  $^{31}\text{P NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  43.50. FAB-MS ( $m/z$ ): 1192 [ $\text{M}^+$ ]. Anal. Calcd for  $\text{C}_{56}\text{H}_{36}\text{Au}_2\text{N}_2\text{P}_2$ : C, 56.39; H, 3.04; N, 2.35. Found: C, 56.15; H, 2.96; N, 2.25.

**[MeHgC≡CRC≡CHgMe] (R = Fluorene-2,7-diyl; 8).** The diyne **I** (8.6 mg, 0.04 mmol) in THF (5 mL) was first combined with MeHgCl (20.1 mg, 0.08 mmol) in MeOH (15 mL), and 0.2 M basic MeOH (4 mL) was subsequently added to give a pale yellow suspension. The solvents were then decanted, and the light yellow solid of **8** (20.6 mg, 80%) was air-dried. IR (KBr):  $\nu(\text{C}=\text{C})$  2121  $\text{cm}^{-1}$ .  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  7.67 (d,  $J = 7.8$  Hz, 2H,  $\text{H}_{3,6}$ ), 7.63 (s, 2H,  $\text{H}_{1,8}$ ), 7.49 (d,  $J = 7.8$  Hz, 2H,  $\text{H}_{4,5}$ ), 3.87 (s, 2H,  $\text{CH}_2$ ), 0.72 (s,  $^2J_{\text{HgH}} = 148.5$  Hz, 6H, Me). FAB-MS ( $m/z$ ): 643 [ $\text{M}^+$ ]. Anal. Calcd for  $\text{C}_{19}\text{H}_{14}\text{Hg}_2$ : C, 35.46; H, 2.19. Found: C, 35.35; H, 2.08.

**[MeHgC≡CRC≡CHgMe] (R = 9,9-Dihexylfluorene-2,7-diyl; 9).** A procedure similar to that illustrated for **8** was used to obtain the title compound in 90% yield (29.2 mg) from **II** (15.3 mg, 0.04 mmol). IR (KBr):  $\nu(\text{C}=\text{C})$  2124  $\text{cm}^{-1}$ .  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  7.57 (m, 2H,  $\text{H}_{1,8}$ ), 7.43 (m, 4H,  $\text{H}_{3,4,5,6}$ ), 1.92 (m, 4H,  $\text{CH}_2(\text{CH}_2)_4\text{CH}_3$ ), 1.12–0.96 (m, 12H,  $\text{CH}_2(\text{CH}_2)_3\text{CH}_2\text{CH}_3$ ), 0.76 (t,  $J = 7.2$  Hz, 6H,  $(\text{CH}_2)_5\text{CH}_3$ ), 0.72 (s,  $^2J_{\text{HgH}} = 148.5$  Hz, 6H, Me), 0.54 (m, 4H,  $\text{CH}_2(\text{CH}_2)_3\text{CH}_2\text{CH}_3$ ). FAB-MS ( $m/z$ ): 811 [ $\text{M}^+$ ]. Anal. Calcd for  $\text{C}_{31}\text{H}_{38}\text{Hg}_2$ : C, 45.86; H, 4.72. Found: C, 45.55; H, 4.50.

**[MeHgC≡CRC≡CHgMe] (R = 9-((Ferrocenylphenylene)methylene)fluorene-2,7-diyl; 10).** Similar to **8**, complex **10** was prepared from **III** (19.5 mg, 0.04 mmol) and isolated as a deep orange solid in 95% yield (34.8 mg). IR (KBr):  $\nu(\text{C}=\text{C})$  2129  $\text{cm}^{-1}$ .  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  8.37 (m, 1H,  $\text{H}_1$  or  $\text{H}_8$ ), 7.88 (m, 1H,  $\text{H}_1$  or  $\text{H}_8$ ), 7.66–7.43 (m, 9H,  $\text{C}_6\text{H}_4$ , vinyl CH and  $\text{H}_{3,4,5,6}$ ), 4.74 (t,  $J = 1.8$  Hz, 2H,  $\text{H}_{a,a'}$ ), 4.53 (t,  $J = 1.8$  Hz, 2H,  $\text{H}_{b,b'}$ ), 4.23 (s, 5H,  $\text{C}_5\text{H}_5$ ), 0.73 (s,  $^2J_{\text{HgH}} = 148.5$  Hz, 3H, Me), 0.69 (s,  $^2J_{\text{HgH}} = 148.5$  Hz, 3H, Me). FAB-MS ( $m/z$ ): 916 [ $\text{M}^+$ ]. Anal. Calcd for  $\text{C}_{36}\text{H}_{26}\text{FeHg}_2$ : C, 47.22; H, 2.86. Found: C, 47.02; H, 2.56.

**[MeHgC≡CRC≡CHgMe] (R = Fluorene-9-one-2,7-diyl; 11).** A procedure similar to that for **8** was employed using **IV** (9.1 mg, 0.04 mmol) to produce bright orange **11** in 93% yield (24.5 mg) after filtration and washing. IR (KBr):  $\nu(\text{C}=\text{C})$  2127,  $\nu(\text{C}=\text{O})$  1712  $\text{cm}^{-1}$ .  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  7.71 (d,  $J = 1.2$  Hz, 2H,  $\text{H}_{1,8}$ ), 7.57 (dd,  $J = 1.2, 7.8$  Hz, 2H,  $\text{H}_{3,6}$ ), 7.43 (d,  $J = 7.8$  Hz, 2H,  $\text{H}_{4,5}$ ), 0.73 (s,  $^2J_{\text{HgH}} = 148.5$  Hz, 6H, Me). FAB-MS ( $m/z$ ): 657 [ $\text{M}^+$ ]. Anal. Calcd for  $\text{C}_{19}\text{H}_{12}\text{Hg}_2\text{O}$ : C, 34.71; H, 1.84. Found: C, 34.58; H, 1.90.

**[PhHgC≡CRC≡CHgPh] (R = Fluorene-9-one-2,7-diyl; 12).** Instead of using MeHgCl, the reaction between PhHgCl (25.1 mg, 0.08 mmol) and **IV** (9.1 mg, 0.04 mmol) in basic MeOH solution resulted in the precipitation of the desired product **12** as a pale orange solid (27.5 mg, 88%). IR (KBr):  $\nu(\text{C}=\text{C})$  2130,  $\nu(\text{C}=\text{O})$  1716  $\text{cm}^{-1}$ .  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  7.77 (d,  $J = 1.2$  Hz, 2H,  $\text{H}_{1,8}$ ), 7.63 (dd,  $J = 1.2, 7.9$  Hz, 2H,  $\text{H}_{3,6}$ ), 7.50–7.30 (m, 12H,  $\text{H}_{4,5}$  and Ph). FAB-MS ( $m/z$ ): 781 [ $\text{M}^+$ ]. Anal. Calcd for  $\text{C}_{29}\text{H}_{16}\text{Hg}_2\text{O}$ : C, 44.56; H, 2.06. Found: C, 44.58; H, 1.95.

**Crystallography.** Yellow crystals of **2**, **4**, and **11** suitable for X-ray diffraction studies were grown by slow evaporation of their respective solutions in hexane/ $\text{CH}_2\text{Cl}_2$  at room temperature. Geometric and intensity data were collected using graphite-monochromated Mo  $K\alpha$  radiation ( $\lambda = 0.71073$  Å) on a Bruker AXS SMART 1000 CCD area detector (**2** and **4**) and MAR Research image plate scanner (**11**). The collected frames were processed with the software SAINT,<sup>25a</sup> and an absorption correction was applied (SADABS<sup>25b</sup>) to the collected reflections. For **11** interframe scaling was employed for the absorption correction.

(25) (a) SAINT Reference Manual; Siemens Energy and Automation: Madison, WI, 1994–1996. (b) Sheldrick, G. M. SADABS, Empirical Absorption Correction Program; University of Göttingen, Göttingen, Germany, 1997.



**Table 6. Crystal Data for Complexes 2·0.5C<sub>6</sub>H<sub>14</sub>, 4, and 11**

	2·0.5C <sub>6</sub> H <sub>14</sub>	4	11
empirical formula	C <sub>68</sub> H <sub>69</sub> Au <sub>2</sub> P <sub>2</sub>	C <sub>53</sub> H <sub>36</sub> Au <sub>2</sub> OP <sub>2</sub>	C <sub>19</sub> H <sub>12</sub> Hg <sub>2</sub> O
fw	1342.10	1144.69	657.48
cryst size, mm	0.32 × 0.15 × 0.10	0.30 × 0.16 × 0.14	0.34 × 0.14 × 0.12
cryst syst	triclinic	monoclinic	monoclinic
space group	<i>P</i> $\bar{1}$	<i>Pc</i>	<i>P2</i> <sub>1</sub> / <i>c</i>
<i>a</i> , Å	9.1206(6)	13.729(2)	7.182(1)
<i>b</i> , Å	16.970(1)	11.503(1)	16.414(1)
<i>c</i> , Å	19.639(1)	14.523(2)	13.727(1)
$\alpha$ , deg	96.399(1)		
$\beta$ , deg	90.335(1)	111.803(2)	98.38(1)
$\gamma$ , deg	101.956(1)		
<i>V</i> , Å <sup>3</sup>	2954.0(3)	2129.5(4)	1600.9(2)
<i>Z</i>	2	2	4
<i>D</i> <sub>calcd</sub> , g cm <sup>-3</sup>	1.509	1.785	2.728
$\mu$ , mm <sup>-1</sup>	5.054	6.996	19.204
<i>F</i> (000)	1330	1100	1176
temp, K	293	293	293
$\theta$ range, deg	1.52–27.49	1.77–27.52	1.00–25.59
min/max <i>hkl</i>	–5 to +11, –21 to +21, –25 to +24	–17 to +16, –14 to +13, –12 to +18	0–8, 0–19, –16 to +16
no. of rflns collected	17 347	12 371	10 753
no. of unique rflns ( <i>R</i> (int))	12 606 (0.0260)	6645 (0.0402)	2836 (0.050)
no. of rflns with <i>I</i> > <i>n</i> $\sigma$ ( <i>I</i> )	12 606 ( <i>n</i> = 2.0)	6645 ( <i>n</i> = 2.0)	1955 ( <i>n</i> = 1.5)
no. of params	638	524	199
final <i>R</i> indices ( <i>I</i> > <i>n</i> $\sigma$ ( <i>I</i> )) <sup>a</sup>	<i>R</i> 1 = 0.0362 w <i>R</i> 2 = 0.0839	<i>R</i> 1 = 0.0421 w <i>R</i> 2 = 0.0974	<i>R</i> = 0.047 <i>R</i> <sub>w</sub> = 0.052
goodness of fit	0.923 (on <i>F</i> <sup>2</sup> )	0.941 (on <i>F</i> <sup>2</sup> )	1.240 (on <i>F</i> )
largest diff peak and hole, e Å <sup>-3</sup>	1.287 and –0.640	2.395 and –1.126	1.14 and –2.10

$$^a R = R1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}, R_w = \frac{[\sum w(|F_o| - |F_c|)^2 / \sum w(F_o)^2]^{1/2}}, wR2 = \frac{[\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]^{1/2}}$$

The structures of these molecules were solved by direct methods (SHELXTL<sup>26</sup> for **2** and **4**, SIR92<sup>27</sup> for **11**) in conjunction with standard difference Fourier techniques and subsequently refined by full-matrix least-squares analyses on *F*<sup>2</sup> (for **2** and **4**) and *F* (for **11**). In each case, all non-hydrogen atoms were assigned with anisotropic displacement parameters. The hydrogen atoms were generated in their idealized positions and allowed to ride on the respective carbon atoms. The absolute configuration of **4** cannot be established successfully, because racemic twinning is present. The highest residual electron density peaks are all close to the heavy-atom positions. Crystal data and other experimental details are summarized in Table 6.

(26) Sheldrick, G. M. *SHELXTL Reference Manual*, version 5.1; Siemens Energy and Automation: Madison, WI, 1997.

**Acknowledgment.** We thank the Hong Kong Research Grants Council (Grant No. HKBU 2048/01P) and the Hong Kong Baptist University (Grant No. FRG/99-00/II-58) for financial support.

**Supporting Information Available:** Text giving preparations of diethynylfluorene-based precursors, figures giving emission spectra, and tables of X-ray crystal data for the complexes. This material is available free of charge via the Internet at <http://pubs.acs.org>.

OM0106229

(27) Sheldrick, G. M. In *Crystallographic Computing 3*; Sheldrick, G. M., Kruger, C., Goddard, R. Eds.; Oxford University Press: London, 1985; p 175.