Luminescent Binuclear Gold(I) Ring Complexes

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Cyclic digold(I) complexes, containing bridging diphosphine and diacetylide ligands and with 15- to 22-membered rings, are reported. Oligomeric complexes $[C_6H_4(OCH_2C\equiv CAu)_2]_n$ were prepared from AuCl(SMe₂) and *o*-, *m*-, or *p*-bis(propargyloxy)benzene and then reacted with the diphosphines Ph₂P(CH₂)_nPPh₂ (n = 1-6) to give the corresponding ring complexes $[C_6H_4(OCH_2C\equiv CAu)_2\{\mu$ -Ph₂P(CH₂)_nPPh₂]. Alternatively, a two-step procedure in which the soluble isocyanide complex $[p-C_6H_4(OCH_2C\equiv CAuCNtBu)_2]$ was prepared, followed by displacement of the isocyanide ligands by the diphosphine, could be used. The complexes $[m-C_6H_4(OCH_2C\equiv CAu)_2(\mu$ -Ph₂PCH₂PPh₂)], $[m-C_6H_4(OCH_2C\equiv CAu)_2\{\mu$ -Ph₂P(CH₂)₅PPh₂]], and $[p-C_6H_4(OCH_2C\equiv CAu)_2\{\mu$ -Ph₂P(CH₂)₅PPh₂]], and $[p-C_6H_4(OCH_2C\equiv CAu)_2\{\mu$ -Ph₂P(CH₂)₅-PPh₂]] have been characterized by X-ray structure determinations. The ring complexes are emissive at room temperature and may exhibit either red or blue shifts between solution and the solid state.

Introduction

Many gold(I) complexes display interesting photochemistry, often giving room-temperature emission in the visible region.¹ In particular, alkynylgold(I) complexes with tertiary phosphine ligands have been studied intensely for their room-temperature emission and nonlinear optical (NLO) properties and their rich photochemistry.² Organometallic macrocycles based on metal acetylides have properties suggesting potential applications in electronic devices.³ Alkynylgold(I) complexes with tertiary phosphine donors of formula [Au-

(3) (a) Comprehensive Supramolecular Chemistry, Atwood, J. L., Davies, J. E. D., MacNicol, D. D., Vögtle, F., Suslick, K. S., Eds.; Pergamon Press: Oxford, 1996. (b) Onitsuka, K.; Yamamoto, S.; Takahashi, S. Angew. Chem., Int. Ed. **1999**, *38*, 174. $(C \equiv CR)(L)]^4$ and diphosphines $[Au_2(C \equiv CR)_2(\mu - L - L)]^5$ are among the most stable organogold complexes, and so it is possible to design more complex structures based on alkynylgold(I) chemistry. Since propargyl derivatives of bisphenols form linear polymers that were among the first photoconducting polymers,⁶ and gold-substituted propargyl groups have been used to form stable metal-rimmed calixarenes,⁷ propargylgold(I) units have considerable promise.

The preference for gold(I) complexes to adopt a twocoordinate linear geometry makes it an ideal metal for the formation of either linear chains or large macrocycles.⁸ Several polymeric alkynylgold(I) complexes have been synthesized using rigid linear bis(ethynyl)arene ligands.⁹ Kinked linear polymers were formed with bridging diphosphines, whereas rigid-rod polymers were formed with linear diisocyanoarene ligands.⁹ With 1,3,5tris(ethynyl)benzene, cross-linked polymers are formed.^{9c} The linear bis(ethynyl)arene ligands can also yield macrocyclic gold rings on reaction with short bite diphosphines such as bis(diphenylphosphino)methane,

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and it is thought that aurophilic attractions (typical distances and bond energies of 2.75-3.40 Å and 7-11 $kcal/mol, respectively)^{10}$ control conformations and, hence, the preference for rings over chains, in such cases.^{11,12} There are many smaller 8- to 10-membered cyclic dinuclear gold(I) complexes with bidentate phosphines, thiols, ylides, or dialkyldithiocarbamates, ¹³ and complexes with 14-membered rings are known with dithiol and diphosphine ligands,¹⁴ but attempts to prepare larger rings using butanedithiol resulted in the formation of polymers.^{14c} Large alkynylgold(I) ring complexes can interpenetrate by self-assembly to give catenane structures.¹⁵

From the above discussion, it is clear that the combination of two gold(I) centers and two bidentate ligands can give a range of ring or polymeric structures, but that more work is required before confident predictions of the resultant structures can be made. This paper reports gold(I) complexes with flexible angular diacetylide and diphosphine ligands. It was anticipated that assembly of these angular components might yield either unusual ring structures or zigzag one-dimensional polymers with interesting properties. The reactions gave 15- to 22-membered macrocyclic digold(I) complexes with bridging diacetylide and diphosphine ligands, $Ph_2P(CH_2)_nPPh_2$ (n = 1-6), whose structures and photophysical properties are described.

Results and Discussion

Synthesis of New Complexes. Following the established route to oligomeric alkynylgold(I) complexes of the form $[Au(C \equiv CR)]_m^{4,9}$ the reaction of 2 equiv of [AuCl(SMe₂)] and base with the flexible diethynyl arene bifunctional ligands Ar(OCH₂C=CH)₂ gave the oligomeric digold(I) diacetylide complexes [(AuC=CCH₂- $OArOCH_2C \equiv CAu_n$, **1**, $Ar = o - C_6H_4$; **9**, $Ar = m - C_6H_4$; **17**, Ar = p-C₆H₄), as shown in Schemes 1–3. The complexes were obtained as air-stable, light-sensitive, insoluble deep yellow powders, which were characterized by IR and elemental analysis and by conversion to more soluble derivatives. Oligomeric gold acetylides are potentially shock sensitive and should be handled with

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care. The alkyne ν (CC) vibrations appear at 2000, 2009, and 2006 cm^{-1} in **1**, **9**, and **17**, shifted to lower frequency by approximately 100 cm^{-1} from the free ligands (2105, 2122, and 2122 cm^{-1} , respectively). This large decrease

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in $\nu(C\equiv C)$ provides evidence for donation of electron density through π -bonding to an adjacent gold(I) center. Therefore, the complexes are presumed to be coordination polymers involving η^1 and η^2 alkyne coordination to gold(I), analogous to structures proposed for (phenylethynyl)gold(I)¹⁶ and established for the gold(I) catenane [{Au(C=C*t*Bu)}₆]₂.^{15a}

The soft donor ligand triphenylphosphine or *tert*-butyl isocyanide readily replaced the weak gold–alkyne π -bonds in **1**, **9**, or **17** to form complexes that are soluble in dichloromethane (Schemes 1–3).¹⁶ Since the products of reaction of **1**, **9**, and **17** with diphosphine ligands were also soluble, they are likely to exist as rings rather than polymers in all cases (Schemes 1–3). Since complex **20** (Scheme 3) was sparingly soluble, it was more readily prepared by displacement of the *tert*-butyl isocyanide ligands from complex **19** with the diphosphine ligand (Scheme 3).^{9e} This was also the preferred route to complex **22**, since the direct reaction of **17** with Ph₂P(CH₂)₃PPh₂ occurred with partial decomposition to metallic gold.

The products with phosphine or isocyanide ligands shown in Schemes 1–3 were isolated as colorless to pale yellow air-stable solids. They dissolve most readily in chlorinated solvents, but react slowly with replacement of the alkynylgold groups by chlorogold groups.¹⁷ Thus, the diphosphine complexes slowly decompose in dichloromethane solution, and more rapidly in chloroform, to give [(AuCl)₂(μ -Ph₂P(CH₂)_nPPh₂)], and this can be a problem in growing single crystals of the alkynyl-gold(I) complexes.

Structural Characterization. The soluble complexes were characterized by elemental analysis, by their ¹H and ³¹P NMR and IR spectra, and, in some cases, by X-ray structure determinations. The complexes display a weak IR absorption band at ca. 2120-2140 cm⁻¹ corresponding to the ν (C=C) stretch. The isocyanide complex 19 gave $\nu(C \equiv C) = 2138$ and $\nu(C \equiv N) =$ 2226 cm⁻¹, and the isocyanide stretch is shifted approximately 100 cm⁻¹ to higher wavenumber from the free ligand, indicating only weak π -back-bonding from gold(I).¹⁸ In the ¹H NMR spectra, the methylene protons of the propargyl groups appear as singlets in the region δ 4.7–4.9 ppm. The room-temperature ³¹P NMR spectrum of the complexes with diphosphine ligands display sharp singlets in the region 33-40 ppm, indicating a symmetrical arrangement of P-Au-C≡C groups in solution: two gold(I) centers are bridged by a diphosphine and a diacetylide ligand in each case. The related triphenylphosphine complexes 2, 10, and 18 have open structures, and in the ³¹P NMR spectra, they give singlet resonances in the range δ 42–43 ppm. Lowtemperature ³¹P NMR spectra were recorded for complexes 12 and 13 to test for fluxionality, but no changes were observed in the spectra at -80 °C.

X-ray structure determinations were carried out for four of the digold(I) ring complexes, two based on the *meta* complexes of Scheme 2 and two on the *para* complexes of Scheme 3. No suitable single crystals of the *ortho* complexes of Scheme 1 could be obtained.



Figure 1. Molecular structure of $[m-C_6H_4(OCH_2C\equiv CAu)_2-(\mu-Ph_2PCH_2PPh_2)]$, **11**.

 Table 1. Selected Bond Lengths (Å) and Angles

 (deg) for Complex 11^a

	-		
Au(1)-C(1)	1.98(2)	Au(1)-P(1)	2.270(6)
Au(2)-C(14)	1.93(3)	Au(2)-P(2)	2.298(7)
C(1) - C(2)	1.19(3)	C(13)-C(14)	1.28(4)
C(2) - C(3)	1.55(3)	C(12)-C(13)	1.47(4)
C(3)-O(4)	1.43(3)	C(12)-O(11)	1.50(2)
O(4) - C(5)	1.34(3)	O(11) - C(10)	1.37(3)
Au(1)-Au(2)	3.049(1)		
C(1)-Au(1)-P(1)	172.1(7)	C(1)-Au(1)-Au(2)	101.5(7)
P(1)-Au(1)-Au(2)	82.5(2)	C(14) - Au(2) - P(2)	175.0(7)
C(14) - Au(2) - Au(1)	96.4(7)	P(2)-Au(2)-Au(1)	88.5(2)
C(2) - C(1) - Au(1)	177(2)	C(1)-C(2)-C(3)	172(2)
O(4) - C(3) - C(2)	112(1)	C(5) - O(4) - C(3)	120(2)
O(4) - C(5) - C(6)	113(2)	C(8)-C(10)-O(11)	112(2)
C(10) - O(11) - C(12)	119(2)	C(13)-C(12)-O(11)	115(2)
C(14) - C(13) - C(12)	174(2)	C(13)-C(14)-Au(2)	169(2)
C(15) - P(1) - Au(1)	108.8(8)	P(2)-C(15)-P(1)	109(1)
C(15) - P(2) - Au(2)	116.8(8)		

^{*a*} Symmetry transformations used to generate equivalent atoms: -x, -y + 1, -z.

The molecular structure of $[m-C_6H_4(OCH_2C=C-Au)_2 (\mu$ -dppm)], **11**, is shown in Figure 1, and selected bond lengths and angles are presented in Table 1. There are two independent molecules in the unit cell, but their structural parameters are very similar, so only one will be described. The 16-membered ring occurs in a highly twisted, extended chair conformation, with torsion angles $C-Au-Au-C = 41.6^{\circ}$ and $P-Au-Au-P = 34.0^{\circ}$. The ring must be very flexible, with rapid ring inversion, since equivalence of both the CH₂O and CH₂P₂ protons is observed in the ¹H NMR spectrum of **11**. The two gold atoms in 11 are held in close proximity by the bridging bis(diphenylphosphino)methane ligand, with the intramolecular $d(Au \cdot \cdot \cdot Au) = 3.049(1)$ Å, only slightly longer than the P···P bite distance of 3.003 Å. The Au-P bonds are normal for $C \equiv C - Au - P$ coordination, Au(1) - C = C - Au - PP(1) = 2.270(6) Å and Au(2) - P(2) = 2.298(7) Å, but longer than in many gold(I) phosphine complexes as a consequence of the strong *trans* influence of the alkynyl group.^{2,4} The gold-carbon distances are consistent with other reported gold(I) acetylide complexes, with Au(1)-C(1) = 1.98(2) Å and Au(2)-C(14) = 1.93(3) Å.^{2,4,9} The

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Figure 2. Molecular structure of $[m-C_6H_4(OCH_2C\equiv CAu)_2-(\mu-Ph_2P(CH_2)_5PPh_2)]$, **15**.

Table 2. Selected Bond Lengths (Å) and Angles(deg) for Complex 15^a

Au(1)-C(1)	1.99(1)	Au(1)-P(1)	2.273(3)
Au(2)-C(14)	1.98(1)	Au(2)-P(2)	2.270(3)
C(1) - C(2)	1.21(1)	C(13)-C(14)	1.14(1)
C(12)-C(13)	1.59(3)	C(2) - C(3)	1.51(2)
C(12)-O(11)	1.37(2)	C(3)-O(4)	1.30(1)
O(11) - C(9)	1.41(2)	O(4)-C(5)	1.40(2)
C(12)-O(11)#2	1.36(2)	C(3)-O(4)#2	1.37(2)
O(11)-C(9)#2	1.43(2)	O(4)-C(5)#2	1.42(2)
C(1)-Au(1)-P(1)	179.2(4)	C(14)-Au(2)-P(2)	169.6(4)
C(2) - C(1) - Au(1)	175(1)	C(1)-C(2)-C(3)	177(1)
C(14) - C(13) - C(12)	167(2)	C(13)-C(14)-Au(2)	170(1)
C(2) - C(3) - O(4)	111(1)	C(13)-C(12)-O(11)	108(2)
C(3) - O(4) - C(5)	115(2)	C(12)-O(11)-C(9)	125(2)
O(4) - C(5) - C(6)	103(2)	O(11) - C(9) - C(8)	113(2)
C(2)-C(3)-O(4)#2	113(2)	C(13)-C(12)-O(11)#2	113(2)
C(3)-O(4)-C(5)#2	137(2)	C(12)-O(11)-C(9)#2	119(3)
O(4) - C(5) - C(6) #2	118(3)	O(11)-C(9)-C(8)#2	124(3)
Au(1) - P(1) - C(15)	114.4(3)	Au(2)-P(2)-C(19)	108.6(4)

^{*a*} Symmetry transformations used to generate equivalent atoms: #1 - x + 1, *y*, -z + 3/2; #2 - x + 5/2, -y + 1/2, -z + 1.

C-Au-P angles are slightly distorted from linearity $(\angle P-Au-C = 172.1(7)^{\circ} \text{ and } 175.0(7)^{\circ}).$

The molecular structure of $[m-C_6H_4(OCH_2C \equiv C-Au)_2 \{\mu$ -Ph₂P(CH₂)₅PPh₂ $\}$], **15**, is shown in Figure 2, and selected bond lengths and angles given in Table 2. There is disorder of the $C_6H_4(OCH_2)_2$ units, not shown in Figure 2, in which the dioxyaryl group may fold to either side of the diphosphine ligand; these disordered atoms are shown joined by open bonds in Figure 2. Complex 15 has a distorted 20-membered ring structure. The conformation of the diacetylide ligand is very different from that observed in 11 (Figure 1), and this is clearly to allow bridging by the bis(diphenylphosphino)pentane ligand with its much greater bite distance compared to bis(diphenylphosphino)methane. The intramolecular nonbonding distances Au…Au and P…P are 7.73 and 8.07 Å, respectively. The torsion angle C-Au-Au-C =23.5° (the angle between nonbonded CCAuP vectors) indicates a lower degree of twist than in **11**. The angle Au(1)–C(1)=C(2) = $175(1)^{\circ}$ is approximately linear, but Au(2)–C(14) \equiv C(13) = 170(1)° deviates from linearity. Similarly, the angle $C(1)-Au(1)-P(1) = 179.2(4)^{\circ}$ is linear, but $C(14) - Au(2) - P(2) = 169.6(4)^{\circ}$ is distorted from linearity. Overall then, there is significant bowing of the P(2)Au(2)C(14)C(13) unit, perhaps indicating some ring strain is present. The closest intermolecular



Figure 3. Molecular structure of $[p-C_6H_4(OCH_2C\equiv CAu)_2-(\mu-Ph_2P(CH_2)_3PPh_2)]$, **22**.

 Table 3. Selected Bond Lengths (Å) and Angles

 (deg) for Complex 22^a

	-		
Au(1)-C(1)	2.03(2)	Au(1)-P(1)	2.261(7)
Au(3)-C(14)	2.05(3)	Au(3)-P(3)	2.278(7)
C(1)-C(2)	1.13(3)	C(13)-C(14)	1.21(3)
C(12)-C(13)	1.40(3)	C(2) - C(3)	1.51(3)
C(12)-O(11)	1.57(5)	C(3)-O(4)	1.44(2)
C(1)-Au(1)-P(1)	177.6(6)	C(14)-Au(3)-P(3)	176.3(7)
Au(1) - P(1) - C(15)	116 8(8)	Au(3) - P(3) - C(17)	110 4(8)
C(2)-C(1)-Au(1)	174(2)	C(1)-C(2)-C(3)	166(2)
C(14) - C(13) - C(12)	170(3)	C(13)-C(14)-Au(3)	177(2)
C(2) - C(3) - O(4)	114(2)	C(13)-C(12)-O(11)	103(2)
C(3) - O(4) - C(5)	114(2)	C(12)-O(11)-C(10)	107(2)
O(4) - C(5) - C(6)	99(2)	O(11) - C(10) - C(9)	156(3)

^{*a*} There are two independent molecules in the unit cell, only one is described, since they are similar. Symmetry transformations used to generate equivalent atoms: #1 - x + 4, -y, -z, #2 - x + 3, -y, -z + 1.

contact between gold atoms is 3.806 Å, so there are neither intra- nor intermolecular Au···Au attractions in the structure of complex **15**.

The molecular structure of $[p-C_6H_4(\text{OCH}_2\text{C}\equiv\text{C}-\text{Au})_2-{\{\mu-\text{Ph}_2\text{P}(\text{CH}_2)_3\text{PPh}_2\}}]$, **22**, is shown in Figure 3, and selected bond distances and angles are summarized in Table 3. There are two independent but very similar molecules in the unit cell. The 19-membered ring in **22** is more symmetrical than in **15**, with a significantly smaller dihedral angle C-Au-Au-C = 8.5°. The coordination about the gold(I) centers is close to linear, with angles C=Au-P = 177.6(6)° and 176.3(7)°, and the angles C≡C-Au = 174(2)° and 177(2)° are also close to linear. The intramolecular nonbonded distance Au···Au is 6.23 Å and P···P is 5.65 Å.

The molecular structure of $[p-C_6H_4(OCH_2C\equiv C-Au)_2-\{\mu-Ph_2P(CH_2)_5PPh_2\}]$, **24**, is shown in Figure 4, and selected bond lengths and angles are presented in Table 4. Figure 4 shows that the 21-membered ring is skewed but otherwise symmetrical; the dihedral angle C-Au-Au-C = 4.6° is much less than in **15** (23.5°). The intramolecular nonbonding distances are Au···Au = 7.68 Å and P···P = 7.99 Å. The angles C-Au-P = 177.0(3) and 178.4(3) Å and C≡C-Au = 175(1)° and 177(1)° are all close to linear.

Overall, the four structures show that the transannular Au…Au distance is largely controlled by the



Figure 4. Molecular structure of $[p-C_6H_4(OCH_2C\equiv CAu)_2-(\mu-Ph_2P(CH_2)_5PPh_2)]$, **24**.

 Table 4. Selected Bond Lengths (Å) and Angles

 (deg) for Complex 24^a

	0	-	
Au(1)-C(1)	2.03(1)	Au(1)-P(1)	2.282(3)
Au(2)-C(14)	2.02(1)	Au(2)-P(2)	2.273(3)
C(1) - C(2)	1.15(1)	C(13)-C(14)	1.15(1)
C(2)-C(3)	1.48(1)	C(12)-C(13)	1.48(1)
C(3)-O(4)	1.44(1)	C(12)-O(11)	1.45(1)
O(4)-C(5)	1.37(1)	O(11)-C(10)	1.38(1)
C(1) - Au(1) - P(1)	177.0(3)	C(14) - Au(2) - P(2)	178.4(3)
C(2) - C(1) - Au(1)	175(1)	C(1) - C(2) - C(3)	177(1)
C(14) - C(13) - C(12)	175(1)	C(13) - C(14) - Au(2)	177(1)
C(2) - C(3) - O(4)	113.2(9)	C(13) - C(12) - O(11)	111.4(9)
C(3) - O(4) - C(5)	118.7(8)	C(12) - O(11) - C(10)	116.6(8)
O(4) - C(5) - C(6)	124(1)	O(11) - C(10) - C(8)	125(1)
Au(1) - P(1) - C(15)	112.6(3)	Au(2) - P(2) - C(19)	110.2(3)

^{*d*} Symmetry transformations used to generate equivalent atoms: #1 - x + 2, y, -z + 3/2; #2 - x + 1, y, -z + 3/2.

number of methylene spacers in the diphosphine ligand, though the distance Au···Au can be greater or less than the P···P separation, and that the diacetylide ligands are sufficiently flexible to accommodate a wide range of Au···Au distances without creating excessive ring strain. Only with the short-bite distance of the ligand $Ph_2PCH_2PPh_2$ is a transannular gold···gold bonding interaction invoked in the structure of complex **11**, since the analogous distances in **15**, **22**, and **24** are clearly much too long for any bonding to be present.¹³ There are no very close intermolecular Au···Au contacts in any of the structurally characterized complexes.

Luminescence Properties of the Dinuclear Gold-(I) Complexes. The photophysical properties of the gold–acetylide macrocycles were studied and are summarized in Table 5. All the dinuclear gold(I) complexes synthesized exhibit luminescence at room temperature. The luminescence spectra for the cyclic complexes as solids in KBr and as solutions in CH_2Cl_2 display intense emissions, whereas the open-ring triphenylphosphine derivatives display only broad featureless emission peaks of low intensity as solids. The emission spectra for $[m-C_6H_4(OCH_2C=CAu)(\mu-dppm)]$, **11**, as a solid and in solution are shown in Figure 5.

Upon excitation at 340–400 nm, the gold(I)–acetylide complexes in most cases display single broad emission bands in the range 426–460 nm in solution and in the region 414–540 nm in the solid state. In solution the emission can be assigned as a triplet π – π * (C=C) or triplet σ (AuC)– π * transition from AuC=C groups, or a combination of both.^{1,2,20} The π *-orbital may be localized on the alkynyl or an aryl group.^{1,2} The formation of

Table 5. Luminescence Data for the Complexes

Table 5	. Lumine	escence Data for	the Complexes
complex	medium	excitation max, nm	emission max, nm
2	solid	350	535
	CH ₂ Cl ₂	350	440
3	solid	350	535
	CH ₂ Cl ₂	350	455
4	solid	350	485
	CH ₂ Cl ₂	350	530
5	solid	350	485/540
	CH_2Cl_2	350	455
6	solid	350	540
	CH_2Cl_2	350	450/575
7	solid	350	540
	CH_2Cl_2	350	460
8	solid	350	535
	CH_2Cl_2	350	460
10	solid	391	426
	CH_2Cl_2	349	426
11	solid	357	477
	CH_2Cl_2	367	446
12	solid	343	443
	CH_2Cl_2	366	439
13	solid	337	437
	CH_2Cl_2	365	442
14	solid	347	424
	CH_2Cl_2	363	439
15	solid	345	414
	CH_2Cl_2	362	440
16	solid	345	423
	CH ₂ Cl ₂	362	442
18	solid	354	437
	CH_2CI_2	350	433
20	solid	372	488
0.1	CH_2CI_2	350	454
21	Solid	357	463
00	CH ₂ Cl ₂	370	451
22		343	400
99		250	431
20		200	420
94	cl12Cl2	309	449
64 6	CHICL	264	415
95	solid	304	430
20	CHoClo	396	459
	0112012	390	452
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Figure 5. Emission spectra for $[m-C_6H_4(OCH_2C\equiv CAu)_2-(\mu-dppm)]$, **11**, in solid (solid line) and CH_2Cl_2 solution (dashed line).

Au···Au interactions in the solid state has been reported to lead to observation of a red shift in the emission band when compared to the solution phase, and this is thought to arise from greater involvement of the gold

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d- and p-orbitals in the ground and excited state, respectively.^{1,2} For the present complexes, the transannular Au…Au distance will be shortest in the complexes with Ph₂PCH₂PPh₂, and the red shifts from solution to solid are 80 nm in 3 (ortho), 31 nm in 11 (meta), and 34 nm in 20 (para), suggesting a stronger interaction in the ortho derivative 3, as would be expected. As the ring size increases, no such intramolecular interactions are possible and the solid state and solution spectra become similar with the intraligand phosphorescence dominant. In addition, the largest rings have emission maxima similar to [Au(PPh₃)(C≡CPh)],^{2g} with emission at 419 nm, supporting the view that the two AuC≡C units are essentially independent. In some cases, there is a blue shift on going from solution to the solid state (complexes 4, 14, 15, 23–25), and complex 6 gives two emission bands separated by 4830 cm⁻¹. These data are consistent with emission from exciplexes with solvent.²¹

Conclusions

Previously, it was shown that polymeric gold(I) complexes are formed by using rigid linear diacetylide and diisocyanide ligands, but that the combination of linear diacetylide and angular diphosphine ligands could give either polymers or rings depending on the degree of flexibility of the diphosphine used.^{2,9,11,19} It is clear from the present work that binuclear gold complexes have a strong preference for ring formation when both the diacetylide and diphosphine ligands are flexible, as in the compounds reported here. These new ring complexes are luminescent at room temperature in solution and as solid samples.

Experimental Section

[AuCl(SMe₂)] and the bis(propynyloxy)benzene derivatives were prepared by the literature methods.^{22,23} NMR spectra were recorded using a Varian Gemini 300 MHz spectrometer, with ¹H NMR chemical shifts reported relative to TMS and ³¹P chemical shifts relative to an 85% H₃PO₄ external standard. IR spectra were recorded as Nujol mulls using a Perkin-Elmer 2000 FTIR. Emission spectra were recorded at room temperature, using a PTI LS 100 luminescence spectrometer or a Fluorolog-3 spectrofluorimeter. For recording the emission and excitation spectra, solutions were placed in quartz cuvettes, while solid samples were ground finely, in some cases with added KBr. A 1 nm slit width was used for the solid samples and a 3 nm slit width for the solutions. Several of the complexes crystallized with solvent of crystallization that could not be removed under vacuum at room temperature (see X-ray data for example). The formulations given are consistent with composition from NMR data as well as with analytical data. CAUTION: some gold acetylides are shock sensitive: they must be handled in small quantities using protective equipment.

[o-C₆H₄(OCH₂C≡CAu)₂], 1. A solution of o-C₆H₄(OCH₂C≡ CH)₂ (0.332 g, 1.78 mmol) and NaO₂CMe (0.29 g, 1.78 mmol) in THF (25 mL)/MeOH (15 mL) was added to a suspension of [AuCl(SMe₂)] (1.05 g, 3.56 mmol) in THF (100 mL), and the resulting mixture was stirred for 3 h, yielding a bright yellow precipitate. The mixture was filtered, and the yellow solid was washed with THF, MeOH, and pentane and dried in vacuo. Yield: 0.80 g, 78%. The solid is insoluble in common organic solvents: it crystallized with NaCl. IR(Nujol): $\nu(C{\equiv}C)$ 2000 cm $^{-1}$ (w). Anal. Calcd for $C_{12}H_8Au_2O_2{\cdot}NaCl:$ C, 22.6; H, 1.3. Found: C, 22.7; H, 1.4.

[$o \cdot C_6 H_4(OCH_2 C \equiv CAuPPh_3)_2$], 2. A mixture of 1 (0.34 g, 0.59 mmol) and PPh₃ (0.31 g, 1.18 mmol) in dichloromethane (40 mL) was stirred for 30 min at room temperature. The mixture was filtered, and to the resultant solution was added pentane (100 mL). A pale yellow solid precipitated immediately. The solid was collected by filtration and washed with ether and pentane. Yield: 0.40 g, 62%. NMR (CD₂Cl₂): δ (¹H) 7.49 [m, 30H, Ph]; 7.10 [m, 2H, Ar]; 6.88 [m, 2H, Ar]; 4.82 [s, 4H, OCH₂]; δ (³¹P) 42.86 [s]. IR (Nujol): ν (C=C) 2131 cm⁻¹. Anal. Calcd for C₄₈H₃₈Au₂O₂P₂·CH₂Cl₂: C, 49.6; H, 3.4.

[*o*-C₆H₄(OCH₂C≡C−Au)₂(μ -dppm)], **3.** A mixture of **1** (0.41 g, 0.71 mmol) and dppm (0.27 g, 0.71 mmol) in dichloromethane (40 mL) was stirred for 30 min to give a cloudy solution. The mixture was filtered, and pentane (100 mL) was added to the resultant solution to precipitate a white solid. The solid was collected by filtration and washed with ether and pentane. The compound was recrystallized from CH₂Cl₂/pentane. Yield: 0.52 g, 75%. NMR (CD₂Cl₂): δ (¹H) 7.4–7.6 [m, 20H, Ph]; 7.11 [m, 2H, Ar]; 6.98 [m, 2H, Ar]; 4.73 [s, 4H, OCH₂]; 3.69 [sbr, 2H, dppm]; δ (³¹P) 40.17 [s]. IR (Nujol): ν -(C≡C) 2124 cm⁻¹. Anal. Calcd for C₃₇H₃₀Au₂O₂P₂: C, 46.2; H, 3.1. Found: C, 46.1; H, 3.1.

[o-C₆H₄(OCH₂C=CAu)₂(μ -dppe)], 4. Prepared similarly to 3. Yield: 66%. NMR (CD₂Cl₂): δ ⁽¹H) 7.5–7.7 [m, 20H, Ph]; 7.09 [m, 2H, Ar]; 6.88 [m, 2H, Ar]; 4.81 [s, 4H, OCH₂]; 2.66 [sbr, 4H, dppe]; δ ⁽³¹P) 40.09 [s]. IR (Nujol): ν (C=C) 2134 cm⁻¹. Anal. Calcd for C₃₈H₃₂Au₂O₂P₂·CH₂Cl₂: C, 44.1; H, 3.2. Found: C, 44.4; H, 3.2.

[*o*-C₆H₄(OCH₂C≡CAu)₂(*μ*-dppp)], 5. 5 was prepared similarly to 3. Yield: 82%. NMR (CD₂Cl₂): δ (¹H) 7.5−7.8 [m, 20H, Ph]; 6.95 [sbr, 4H, Ar]; 4.82 [s, 4H, OCH₂]; 2.79 [sbr, 4H, dppp]; 1.87 [sbr, 2H, dppp]; δ (³¹P) 37.49 [s]. IR (Nujol): ν (C≡C) 2135 cm⁻¹. Anal. Calcd for C₃₉H₃₄Au₂O₂P₂: C, 47.3; H, 3.5. Found: C, 46.8; H, 3.3.

[*o*-C₆H₄(OCH₂C≡C−Au)₂(μ-dppb)], 6. 6 was prepared similarly to 3. Yield: 81%. NMR (CD₂Cl₂): δ (¹H) 7.4−7.6 [m, 20H, Ph]; 6.91 [sbr, 4H, Ar]; 4.78 [s, 4H, OCH₂]; 2.43 [sbr, 4H, dppb]; 1.70 [sbr, 4H, dppb]; δ (³¹P) 37.25 [s]. IR (Nujol): ν (C≡ C) 2135 cm⁻¹. Anal. Calcd for C₄₀H₃₆Au₂O₂P₂·CH₂Cl₂: C, 45.2; H, 3.5. Found: C, 45.3; H, 3.8.

[*o*-C₆H₄(OCH₂C≡C-Au)₂(μ -dpppe)], 7. 7 was prepared similarly to 3. Yield: 68%. NMR (CD₂Cl₂): δ (¹H) 7.5–7.7 [m, 20H, Ph]; 6.87 [sbr, 4H, Ar]; 4.74 [s, 4H, OCH₂]; 2.33 [sbr, 4H, (dpppe)]; 1.61 [sbr, 6H, dpppe]; δ (³¹P) 39.65 [s]. IR (Nujol): ν -(C≡C) 2130 cm⁻¹. Anal. Calcd for C₄₁H₃₈Au₂O₂P₂·0.5CH₂Cl₂: C, 47.0; H, 3.7. Found: C, 47.6; H, 3.8.

[*o*-C₆H₄(OCH₂C≡C−Au)₂(μ-dpph)], 8. 8 was prepared similarly to 3. Yield: 84%. NMR (CD₂Cl₂): δ (¹H) 7.4−7.6 [m, 20H, Ph]; 6.84 [sbr, 4H, Ar]; 4.75 [s, 4H, CH₂]; 2.23 [sbr, 4H, dpph]; 1.28 [sbr, 8H, dpph]; δ (³¹P) 35.16 [s]. IR (Nujol): ν (C≡ C) 2134 cm⁻¹. Anal. Calcd for C₄₂H₄₀Au₂O₂P₂: C, 48.8; H, 3.9. Found: C, 48.4; H, 3.8.

[*m*-C₆H₄(OCH₂C≡CAu)₂]_{*m*} 9. To a solution of [AuCl(SMe₂)] (0.495 g, 1.70 mmol) in THF (20 mL)/MeOH (10 mL) was added a solution of *m*-C₆H₄(OCH₂C≡CH)₂ (0.160 g, 0.85 mmol) and sodium acetate (0.211 g, 2.55 mmol) in THF (10 mL)/MeOH (10 mL). The reaction mixture was stirred for 3 h to form a yellow precipitate. The solid was collected by filtration, washed with THF, MeOH, ether, and pentane, and dried. Yield: 0.456 g, 94%. The solid is insoluble in common organic solvents. IR (Nujol): *v*(C≡C) 2009 (w) cm⁻¹. Anal. Calcd for C₁₂H₈Au₂O₂: C, 24.9; H, 1.4. Found: C, 25.5; H, 1.3.

[*m*-C₆H₄(OCH₂C=CAuPPh₃)₂], **10.** PPh₃ (0.320 g, 1.22 mmol) was added to a mixture of **8** (0.351 g, 0.61 mmol) in CH₂Cl₂ (20 mL). The mixture was stirred for 3 h. Decolorizing charcoal (100 mg) was added, the mixture was stirred for 15 min and filtered, and the product was precipitated as an off-white solid by addition of pentane (100 mL). The solid was collected by filtration, washed with ether and pentane, and

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dried. Yield: 0.556 g, 82%. NMR (CD₂Cl₂): δ (¹H) 7.4–7.6 [m, 30H, Ph]; 7.20 [t, 1H, ³J = 7.8 Hz, H₅]; 6.60 [m, 3H, H₂, H₄, H₆]; 4.76 [s, 4H, OCH₂]; δ (³¹P) 42.96 [s]. IR (Nujol): ν (C=C) 2136 cm⁻¹. Anal. Calcd for C₄₈H₃₈Au₂O₂P₂: C, 52.3; H, 3.5. Found: C, 52.4; H, 3.4.

[*m*-C₆H₄(OCH₂C=CAu)₂(μ -dppm)], 11. A solution of dppm (0.107 g, 0.27 mmol) in CH₂Cl₂ (10 mL) was added to a suspension of **8** (0.157 g, 0.27 mmol) in CH₂Cl₂ (10 mL). The mixture was stirred for 3 h, and the product was isolated as above. Yield: 0.219 g, 85%. NMR (CD₂Cl₂): δ (¹H) 7.4–7.8 [m, 20H, Ph]; 7.10 [t, 1H, ³*J* = 7.8 Hz, H₅]; 6.50 [m, 3H, H₂, H₄, H₆], 4.85 [s, 4H, OCH₂]; 3.57 [t, 2H, ²*J*(HP) = 11.4 Hz, dppm]; δ (³¹P) 33.63 [s]. IR (Nujol): ν (C=C) 2132 cm⁻¹. Anal. Calcd for C₃₇H₃₀Au₂O₂P₂: C, 46.2; H, 3.1. Found: C, 45.8; H, 2.9.

[*m*-C₆H₄(OCH₂C=CAu)₂(μ -dppe)], 12. 12 was prepared similarly to 11. Yield: 77%. NMR (CD₂Cl₂): δ (¹H) 7.1–7.7 [m, 21H, Ph and H₅ of Ar]; 6.50 [m, 2H, H₂, H₅]; 4.83 [s, 4H, OCH₂]; 2.50 [sbr, dppe]; δ (³¹P) 34.43 [s). IR (Nujol): ν (C=C) 2131 cm⁻¹. Anal. Calcd for C₃₈H₃₂Au₂O₂P₂: C, 46.7; H, 3.3. Found: C, 47.5; H, 3.4.

[*m*-C₆H₄(OCH₂C≡CAu)₂(μ -dppp)], 13. 13 was prepared similarly to 11. Yield: 86%. NMR (CD₂Cl₂): δ (¹H) 7.4–7.7 [m, 20H, Ph]; 7.15 [t, 1H, ³J = 7.8 Hz, H₅]; 6.55 [m, 3H, H₂, H₄, H₆]; 4.85 [s, 4H, OCH₂]; 1.8 [sbr, 2H, dppp]; 2.7 [sbr, 4H, dppp]; δ (³¹P) 36.00[s]. IR (Nujol): ν (C≡C) 2133 cm⁻¹. Anal. Calcd for C₃₉H₃₄O₂P₂Au₂·0.25C₅H₁₂: C, 48.0; H, 3.8. Found: C, 48.2; H, 3.3.

[*m*-C₆H₄(OCH₂C=CAu)₂(μ -dppb)], 14. 14 was prepared similarly to 11. Yield: 79%. NMR (CD₂Cl₂): δ (¹H) 7.4–7.7 [m, 20H, Ph]; 7.15 [t, 1H, ³*J* = 8.2 Hz, H₅]; 6.57 [dd, 2H, ³*J* = 8.2 Hz, ⁴*J* = 2.4 Hz, H₄, H₆]; 4.78 [s, 4H, OCH₂]; 2.3 [sbr, 4H, dppb]; 1.7 [sbr, 4H, dppb]; δ (³¹P) 37.05 [s]. IR(Nujol): ν (C=C) 2133 cm⁻¹. Anal. Calcd for C₄₀H₃₆Au₂O₂P₂·0.25CH₂Cl₂: C, 46.5; H, 3.6. Found: C, 46.7; H, 3.4.

[*m*-C₆H₄(**OCH**₂**C**=**C**-**Au**)₂(μ -**dpppe**)], **15. 15** was prepared similarly to **11**. Yield: 72%. NMR (CD₂Cl₂): δ (¹H) 7.4–7.7 [m, 20H, Ph]; 7.19 [t, 1H, ³*J* = 8.2 Hz, H₅]; 6.65 [d, 1H, ⁴*J* = 2.2 Hz, H₂]; 6.59 [dd, 2H, ³*J* = 8.1 Hz, ⁴*J* = 2.3 Hz, H₄, H₆]; 4.79 [s, 4H, OCH₂]; 2.3 [sbr, 6H, dpppe]; 1.5 [sbr, 4H, dpppe]; δ -(³¹P) 38.10 [s]. IR(Nujol): ν (C=C) 2133 cm⁻¹. Anal. Calcd for C₄₁H₃₈Au₂O₂P₂: C, 48.3; H, 3.8. Found: C, 47.9; H, 3.8.

[*m*-C₆H₄(OCH₂C=CAu)₂(μ -dpph)], 16. 16 was prepared similarly to 11. Yield: 72%. NMR (CD₂Cl₂): δ (¹H) 7.4–7.7 [m, 20H, Ph]; 7.17 [t, 1H, ³*J* = 8.2 Hz, H₅]; 6.67 [d, 1H, ⁴*J* = 2.2 Hz, H₂]; 6.58 [dd, 2H, ³*J* = 8.2 Hz, ⁴*J* = 2.0 Hz, H₄, H₆]; 4.76 [s, 4H, OCH₂]; 2.3 [sbr, 8H, dpph]; 1.5 [sbr, 4H, dpph]; δ (³¹P) 36.17 [s]. IR(Nujol): ν (C=C) 2133 cm⁻¹. Anal. Calcd for C₄₂H₄₀-Au₂O₂P₂: C, 48.8; H, 3.9. Found: C, 48.7; H, 3.8.

[p-C₆H₄(OCH₂C≡C−Au)₂]_n, **17.** To a solution of [AuCl-(SMe₂)] (0.495 g, 1.70 mmol) in THF (20 mL)/MeOH (10 mL) was added a solution of *p*-C₆H₄(OCH₂C≡CH)₂ (0.160 g, 0.85 mmol) and sodium acetate (0.211 g, 2.55 mmol) in THF (10 mL)/MeOH (10 mL). The reaction mixture was stirred for 3 h, forming a yellow precipitate. The solid was collected by filtration, washed with THF, MeOH, ether, and pentane, and dried. Yield: 0.413 g, 84%. IR(Nujol): 2006 (w) cm⁻¹. Anal. Calcd for C₁₂H₈Au₂O₂: C, 24.9; H, 1.4. Found: C, 24.6; H, 1.2.

[*p*-C₆H₄(OCH₂C≡CAuPPh₃)₂], **18.** PPh₃ (0.090 g, 0.345 mmol) was added to a mixture of **17** (0.100 g, 0.172 mmol) in CH₂Cl₂ (20 mL). The mixture was stirred for 3 h. Decolorizing charcoal (100 mg) was added, the mixture was stirred for 15 min and filtered, and the product was precipitated by addition of pentane (100 mL), collected by filtration, washed with ether and pentane, and dried. Yield: 0.146 g, 77%. NMR (CD₂Cl₂): δ(¹H) 7.4–7.6 [m, 30H, Ph]; 6.92 [s, 4H, Ar]; 4.72 [s, 4H, OCH₂]; δ(³¹P) 42.23 [s]. IR (Nujol): ν(C≡C) 2134 cm⁻¹. Anal. Calcd for C₄₈H₃₈O₂P₂Au₂·0.25CH₂Cl₂: C, 51.6; H, 3.4. Found: C, 51.5; H, 3.2.

[*p*-C₆H₄**(OCH₂C≡CAuC≡N^tBu)₂], 19.** *tert*-Butyl isocyanide (0.080 mL, 0.689 mmol) was slowly added to a suspension of complex **17** (0.200 g, 0.345 mmol) in CH₂Cl₂ (10 mL) under nitrogen. The mixture was stirred for 1 h, then decolorizing charcoal (100 mg) was added. The mixture was stirred for 10 min and filtered, and the solvent removed under vacuum. The residue was washed with pentane. A crystalline white powder was obtained. Yield: 0.229 g, 89%. NMR(CD₂Cl₂): δ ⁽¹H) 6.88 [s, Ar]; 4.69 [s, OCH₂]; 1.53 [s, 18H, t-Bu]. IR (Nujol): ν (C=N) 2226 cm⁻¹, ν (C=C) 2138 cm⁻¹. Anal. Calcd for C₂₂H₂₆-Au₂N₂O₂: C, 35.5; H, 3.5; N, 3.8. Found: C, 34.9; H, 3.5; N, 3.7.

[*p*-C₆H₄(OCH₂C≡CAu)₂(*µ*-dppm)], **20.** To a solution of complex **19** (0.257 g, 0.345 mmol) in CH₂Cl₂ (10 mL) was added a solution of dppm (0.133 g, 0.345 mmol) in CH₂Cl₂ (5 mL). The mixture was stirred for 3 h, treated with decolorizing charcoal (100 mg), and filtered, and the product was precipitated with pentane (100 mL), collected by filtration, and washed with acetone, ether, and pentane. Yield: 0.195 g, 59%. NMR (nitrobenzene-*d*₅/CD₂Cl₂): δ (¹H) 7.0−7.7 [m, 20H, Ph]; 4.82 [s, 4H, OCH₂]; 3.81 [sbr, 2H, dppm]; δ (³¹P) 32.86 [s]. IR-(Nujol): ν (C≡C) 2123 cm⁻¹. Anal. Calcd for C₃₇H₃₀Au₂O₂P₂· 0.25CH₂Cl₂: C, 45.5; H, 3.1. Found: C, 45.5; H, 3.1.

[*p*-C₆H₄(OCH₂C≡C−Au)₂(*µ*-dppe)], 21. A solution of dppe (0.107 g, 0.27 mmol) in CH₂Cl₂ (10 mL) was added to a suspension of 17 (0.157 g, 0.27 mmol) in CH₂Cl₂ (10 mL). The mixture was stirred for 3 h. The product was isolated as above. Yield: 0.286 g, 85%. NMR (CD₂Cl₂): δ (¹H) 7.4−7.6 [m, 20H, Ph]; 6.95 [s, 4H, Ar]; 4.73 [s, 4H, OCH₂]; 2.6 [sbr, 4H, dppe]; δ (³¹P) 39.96 [s]. IR(Nujol): *v*(C≡C) 2131 cm⁻¹. Anal. Calcd for C₃₈H₃₂Au₂O₂P₂: C,45.0; H,3.6. Found: C, 44.8; H, 3.3.

[*p*-C₆H₄(OCH₂C≡C−Au)₂(*μ*-dppp)], 22. 22 was prepared similarly to 20. Yield: 72%. NMR (nitrobenzene-*d*₅/CD₂Cl₂): δ (¹H) 7.3−7.6 [m, 20H, Ph]; 5.32 [s, 4H, OCH₂]; 2.5 [sbr, 4H, dppp]; 2.1 [sbr, 2H, dppp]; δ (³¹P) 33.75 [s]. IR(Nujol): *ν*(C≡C) 2136 cm⁻¹. Anal. Calcd for C₃₉H₃₄Au₂O₂P₂: C, 47.3; H, 3.5. Found: C, 47.0; H, 3.5.

[*p*-C₆H₄(OCH₂C≡C−Au)₂(*μ*-dppb)], 23. 23 was prepared similarly to 21. Yield: 74%. NMR (CD₂Cl₂): δ (¹H) 7.4−7.7 [m, 20H, Ph]; 6.96 [s, 4H, Ar]; 4.76 [s, 4H, OCH₂]; 2.4 [sbr, 4H, dppb]; 1.6 [sbr, 4H, dppb]; δ (³¹P) 37.76 [s]. IR(Nujol): ν (C≡C) 2131 cm⁻¹. Anal. Calcd for C₄₀H₃₆Au₂O₂P₂: C, 47.8; H, 3.6. Found: C, 47.9; H, 3.5.

[*p*-C₆H₄(OCH₂C≡C-Au)₂(*µ*-dpppe)], 24. 24 was prepared similarly to 21. Yield: 76%. NMR (CD₂Cl₂): δ (¹H) 7.4–7.7 [m, 20H, Ph]; 7.00 [s, 4H, Ar]; 4.78 [s, 4H, OCH₂]; 2.3 [sbr, 8H, dpppe], 1.6 [sbr, 2H, dpppe]; δ (³¹P) 38.70 [s]. IR(Nujol): ν (C≡ C) 2133 cm⁻¹. Anal. Calcd for C₄₁H₃₈Au₂O₂P₂: C, 48.3; H, 3.8. Found: C, 48.1; H, 3.8.

[*p*-C₆H₄(OCH₂C≡C−Au)₂(*μ*-dpph)], 25. 25 was prepared similarly to 21. Yield: 76%. NMR (CD₂Cl₂): δ (¹H) 7.4−7.7 [m, 20H, Ph]; 6.98 [s, 4H, Ar]; 4.78 [s, 4H, OCH₂]; 2.4 [sbr, 8H, dpph]; 1.5 [sbr, 4H, dpph]; δ (³¹P) 36.68 [s]. IR(Nujol): ν (C≡C) 2131 cm⁻¹. Anal. Calcd for C₄₂H₄₀Au₂O₂P₂: C, 48.8; H, 3.9. Found: C, 48.3; H, 3.8.

X-ray Structure Determination of 11. Crystals of [(m- $C_6H_4(OCH_2CCAu)_2(\mu-Ph_2P(CH_2)PPh_2)]\cdot 1/4$ ether; $1/2CH_2Cl_2$ were grown by slow diffusion of diethyl ether into a solution in dichloromethane. A colorless needle was mounted on a glass fiber. Data were collected at low temperature (-73 °C) using a Nonius Kappa-CCD diffractometer using COLLECT (Nonius, 1998) software. The unit cell parameters were calculated and refined from the full data set. Crystal cell refinement and data reduction were carried out using the Nonius DENZO package. The data were scaled using SCALEPACK (Nonius, 1998), and no other absorption corrections were applied; Friedel pairs were kept separate. The crystal data and refinement parameters are listed in Table 6. The reflection data were consistent with a triclinic space group $P\overline{1}$, with two molecules in the asymmetric unit. The SHELXTL 5.1 (Sheldrick, G. M., Madison, WI) program package was used to solve the structure by direct methods, followed by successive difference Fouriers. The diphenylphosphino groups were modeled isotropically with phenyl groups as regular hexagons (AFIX 66). However, the diacetylide ligand was less well behaved and the atoms C1, C9, and C21 were kept isotropic. All remaining non-hydrogen atoms in the molecule were refined with anisotropic thermal parameters. The hydrogen atoms were calculated geometri-

Table 6. Crystal Data for Complexes 11, 15, 22, and 24

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	11	15	22	24
empirical formula	$C_{38,50}H_{33,50}Au_2ClO_2 \cdot {}_{25}P_2$	$C_{41.63}H_{31.25}Au_2O_2P_2$	C40.38H34Au2Cl10.25O2P2	$C_{43}H_{40}Au_2Cl_4O_2P_2$
fw	1023.48	1019.29	1015.91	1186.42
temp	200(2) K	295(2) K	296(2) K	200(2) K
wavelength	0.71073 Å	0.71073 Å	0.71073 Å	0.71073 Å
cryst syst	triclinic	monoclinic	triclinic	monoclinic
space group	PĪ	C2/c	$P\overline{1}$	C2/c
unit cell dimens	a = 13.5631(11)Å	a = 14.3314(5) Å	a = 12.8486(7) Å	a = 30.0723(10) Å
	b = 16.2617(9) Å	b = 27.2257(10)Å	b = 13.7164(5) Å	b = 11.8721(4) Å
	c = 18.7032(17) Å	c = 21.8460(8) Å	c = 20.9796(11) Å	c = 26.4185(9) Å
	$\alpha = 74.015(4)^{\circ}$	$\beta = 94.136(2)^{\circ}$	$\alpha = 86.079(3)^{\circ}$	$\beta = 110.706(2)^{\circ}$
	$\beta = 69.063(4)^{\circ}$		$\beta = 89.858(3)^{\circ}$	
	$\gamma = 66.952(4)^{\circ}$	9 -	$\gamma = 89.958(3)^{\circ}$	8 m
volume	3500.9(5) A ³	8501.7(5) A ³	3688.7(3) A ³	8822.7(5) A ³
Ζ	4	8	4	8
density (calcd)	1.942 Mg/m^3	1.593 Mg/m^3	1.829 Mg/m^3	1.786 Mg/m^3
abs coeff	8.573 mm^{-1}	6.999 mm^{-1}	8.083 mm^{-1}	6.993 mm^{-1}
F(000)	1950	3880	1938	4560
crystal size	$0.50 \times 0.22 \times 0.20 \text{ mm}^3$	$0.22 \times 0.20 \times 0.18 \text{ mm}^3$	$0.12 \times 0.10 \times 0.09 \text{ mm}^3$	$0.15 \times 0.08 \times 0.02 \text{ mm}^3$
θ range for data	2.58 to 25.00°	1.76 to 28.29°	2.17 to 24.41°	2.55 to 25.04°
collection				
index ranges	$-15 \le h \le 15$,	$-19 \leq h \leq 19$,	$-14 \leq h \leq 14$,	$0 \leq h \leq 35$,
	$-19 \leq k \leq 19$,	$-35 \le k \le 36,$	$-15 \leq k \leq 15$,	$0 \leq k \leq 14$,
	$-21 \le l \le 22$	$-29 \le l \le 29$	$0 \le l \le 24$	$-31 \leq l \leq 29$
no. of reflns collected	16 599	47 214	34 698	39 761
no. of ind refins	7607 [R(int) = 0.098]	$10\ 528\ [R(int) = 0.1440]$	$11\ 850\ [R(int) = 0.0620]$	7789 [R(int) = 0.0960]
completeness to $\theta =$	25.00° 61.7%	28.29° 99.6%	24.41° 97.7%	25.04° 99.7%
abs corr	SCALEPACK	SCALEPACK	INTEGRATION	SCALEPACK
max. and min. transmn	0.2789 and 0.0995	0.3656 and 0.3081	0.5266 and 0.4363	0.8557 and 0.4202
refinement method	full-matrix	full-matrix	full-matrix	full-matrix
	least-squares on F^{z}	least-squares on F^{2}	least-squares on F^{z}	least-squares on F^{z}
no. of data/restraints/	7607/4/468	10528/43/424	11850/7/343	7789/0/479
params				
goodness-of-fit on F^{2}	1.001	0.996	0.846	1.048
final R indices $[I > 2\sigma(I)]$	R1 = 0.0828,	R1 = 0.0691,	R1 = 0.0382,	R1 = 0.0512,
	wR2 = 0.2123	wR2 = 0.1302	wR2 = 0.0884	wR2 = 0.1027
<i>R</i> indices (all data)	RI = 0.1308,	RI = 0.2141,	RI = 0.1424,	RI = 0.0911,
	wR2 = 0.2347	wR2 = 0.1662	wR2 = 0.1171	wR2 = 0.1138
largest diff peak and hole	2.258 and -2.533 e A^{-3}	1.039 and -0.984 e A^{-3}	0.881 and -1.194 e A ⁻³	1.724 and -1.422 e A ⁻³

cally and were riding on their respective carbon atoms. The ether was sitting on a special position and was modeled as two isotropic halves with fixed bond lengths (C-O 1.35 Å; C-C 1.54 Å). The dichloromethane was modeled anisotropically. The largest residual electron density peak (2.258 e/Å³) was associated with one of the gold atoms.

X-ray Structure Determination of 15. Crystals of [m-C₆H₄-(OCH₂C≡CAu)₂(µ-dpppe)]·1/4pentane were grown by slow diffusion of pentane into a solution in dichloromethane. A colorless needle was cut, and the resulting block was mounted on a glass fiber. Data were collected at room temperature (22 °C) and data treated as above. The atoms O4 through C12 were disordered and were modeled as two separate entities (60/40) with isotropic thermal parameters and no hydrogens. The moiety O4-O11 was constrained to be flat, and chemically equivalent bonds were constrained to be equal. All remaining non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were calculated geometrically and were riding on their respective carbon atoms. The pentane of solvation was sitting with one carbon on a center of symmetry, and so only half of the molecule was located in the difference map. The C-C bond distances were fixed. The largest residual electron density peak (1.039 e/Å³) was associated with one of the gold atoms.

X-ray Structure Determination of 22. Crystals of $[p-C_6H_4(OCH_2CCAu)_2(\mu-Ph_2P(CH_2)_3PPh_2)]\cdot 1/4CH_2Cl_2\cdot 1/2THF were grown by slow diffusion of a solution of Ph_2P(CH_2)_3PPh_2 intetrahydrofuran into a solution of <math>[p-C_6H_4(OCH_2-CCAuCNtBu)_2]$ in dichloromethane. A colorless prism was mounted on a glass fiber. Data were collected at 23 °C and treated as above. The reflection data and systematic absences were consistent with a triclinic space group $P\bar{1}$ with two distinct molecules in the asymmetric unit. Only the gold and phosphorus atoms were refined anisotropically. The remaining atoms were refined as rigid hexagons. O11 and C12 were slightly disor-

dered, and therefore two parts were refined in a 60/40 mixture. The hydrogen atoms were calculated geometrically and were riding on their respective carbon atoms. In addition to the two dimers in the asymmetric unit, two solvent molecules were found. The methylene chloride was found on a center of symmetry and was modeled as isotropic atoms (1/4 occupancy) with the C–Cl distance fixed at 1.65 Å. The THF was also found on a center of symmetry and was modeled as isotropic carbon atoms (1/2 occupancy) with the C–C distance fixed at 1.57 Å. No hydrogens were incorporated into the solvent models. The largest residual electron density peak (0.881 e/Å³) was associated with one of the solvent molecules.

X-ray Structure Determination of 24. Crystals of $[p-C_6H_4-(OCH_2C=CAu)_2(\mu-dpppe)]\cdot 3CH_2Cl_2$ were grown from slow diffusion of pentane into a methylene chloride solution. A tiny, colorless plate was mounted on a glass fiber. Data were collected at low temperature (200 K) and treated as above. The reflection data and systematic absences were consistent with a monoclinic space group C2/c. One of the methylene chlorides of solvation was modeled as a complete CH_2Cl_2 molecule; the other two both had the carbon atoms on special positions. The solvent hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were calculated geometrically and were riding on their respective carbon atoms. The largest residual electron density peak (1.724 e/Å^3) was associated with one of the gold atoms.

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

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