Organometallics **2000,** *19,* 5063−5070

Luminescent Binuclear Gold(I) Ring Complexes

William J. Hunks, Mary-Anne MacDonald, Michael C. Jennings, and Richard J. Puddephatt*

Department of Chemistry, University of Western Ontario, London, Canada N6A 5B7

Received June 21, 2000

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 $AuCl(SMe_2)$ and *o*-, *m*-, or *p*-bis(propargyloxy)benzene and then reacted with the diphosphines $Ph_2P(CH_2)_nPPh_2$ ($n = 1-6$) to give the corresponding ring complexes $[C_6H_4(OCH_2C{\equiv}CAu)_2\{\mu\text{-}Ph_2P(CH_2)_nPPh_2\}]$. Alternatively, a two-step procedure in which the soluble isocyanide complex $[p\text{-}C_6H_4(OCH_2C{\equiv}CAuCN\mathit{t}Bu)_2]$ was prepared, followed by displacement of the isocyanide ligands by the diphosphine, could be used. The complexes $[m\text{-}C_6H_4(OCH_2C{\equiv}CAu)_2(\mu\text{-}Ph_2PCH_2PPh_2)]$, $[m\text{-}C_6H_4(OCH_2C{\equiv}CAu)_2\{\mu\text{-}Ph_2P(CH_2)_5PPh_2\}]$, $[p\text{-}C_6H_4(OCH_2C{\equiv}CAu)_2\{\mu\text{-}Ph_2P(CH_2)_3PPh_2\}]$, and $[p\text{-}C_6H_4(OCH_2C{\equiv}CAu)_2\{\mu\text{-}Ph_2P(CH_2)_5\text{-}PPh_2\}]$ 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 $[Au(C{\equiv}CR)(L)]$[4] and diphosphines $[Au_2(C{\equiv}CR)_2(\mu\text{-}L{-}L)]$[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 two-coordinate 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 1,3,5-tris(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,

---

(1) (a) Forward, J. M.; Fackler, J. P., Jr.; Assefa, Z. In *Optoelectronic Properties of Inorganic Compounds*; Roundhill, D. M., Fackler, J. P., Jr., Eds.; Plenum Press: New York, 1999; pp 195−239. (b) Yam, V. W. W.; Lo, K. K. W. *Chem. Soc. Rev.* **1999**, *28*, 323.

(2) (a) Yam, V. W. W.; Lo, K. K. W.; Wong, K. M. C. *J. Organomet. Chem.* **1999**, *578*, 3. (b) Yam, V. W. W.; Choi, S. W. K. *J. Chem. Soc., Dalton Trans.* **1996**, 4227. (c) Hong, X.; Cheung, K. K.; Che, C. M. *J. Chem. Soc., Dalton Trans.* **1996**, 3699. (d) Yam, V. W. W.; Choi, S. W. K.; Cheung, K. K. *J. Chem. Soc., Dalton Trans.* **1996**, 3411. (e) Shieh, S. J.; Xiao, H.; Peng, S. M.; Che, C. M. *J. Chem. Soc., Dalton Trans.* **1994**, 3067. (f) Che, C. M.; Yip, H. K.; Lo, W. C.; Peng, S. M. *Polyhedron* **1994**, 887. (g) Li, D.; Xiao, H.; Che, C. M.; Lo, W. C.; Peng, S. M. J. *Chem. Soc., Dalton Trans.* **1993**, 2929. (h) Xiao, H.; Cheung, K. K.; Guo, C. X.; Che, C. M. *J. Chem. Soc., Dalton Trans.* **1994**, 1867. (i) Müller, T. E.; Choi, S. W. K.; Mingos, D. M. P.; Murphy, D.; Williams, D. J.; Yam, V. W. W. *J. Organomet. Chem.* **1994**, *484*, 209. (j) Xiao, H.; Weng, S. M.; Che, C. M. *J. Chem. Soc., Dalton Trans.* **1996**, 3155. (k) Tzeng, B. C.; Lo, W. C.; Che, C. M.; Peng, S. M. *J. Chem. Soc., Chem. Commun.* **1996**, 181. (l) Yam, V. W. W.; Choi, S. W. K.; Cheung, K. K. *Organometallics* **1996**, *15*, 1734. (m) Irwin, M. J.; Vittal, J. J.; Puddephatt, R. J. *Organometallics* **1997**, *16*, 3541. (n) Jones, W. B.; Yuan, J.; Narayanaswamy, R.; Young, M. A.; Elder, R. C.; Bruce, A. E.; Bruce, M. R. M. *Inorg. Chem.* **1995**, *34*, 1996. (o) Whittall, I. R.; Humphrey, M. G.; Samoc, M.; Luther-Davies, B.; Hockless, D. C. R. *J. Organomet. Chem.* **1997**, *544*, 189. (p) Whittall, I. R.; Humphrey, M. G.; Houbrechts, S.; Maes, J.; Persoons, A.; Schmid, S.; Hockless, D. C. R. *J. Organomet. Chem.* **1997**, *544*, 277. (q) Whittall, I. R.; Humphrey, M. G.; Houbrechts, S.; Persoons, A. *Organometallics* **1996**, *15*, 5738. (r) Naulty, R. H.; Cifuentes, M. P.; Humphrey, M. G.; Houbrechts, S.; Boutton, C.; Persoons, A.; Heath, G. A.; Hockless, D. C. R.; Luther-Davies, B.; Samoc, M. *J. Chem. Soc., Dalton Trans.* **1997**, 4167.

(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.

(4) (a) Corfield, P. W. R.; Shearer, H. M. M. *Acta Crystallogr.* **1967**, *23*, 156. (b) Bruce, M. I.; Horn, E.; Matisons, J. G.; Snow, M. R. *Aust. J. Chem.* **1984**, *37*, 1163. (c) Carriedo, G. A.; Riera, V.; Solans, X.; Solans, J. *Acta Crystallogr.* **1988**, *C44*, 978. (d) Vicente, J.; Chicote, M. T.; Abrisqueta, M. D. *Organometallics* **1997**, *16*, 5628. (e) Müller, T. E.; Mingos, D. M. P.; Williams, D. J. *J. Chem. Soc., Chem. Commun.* **1994**, 1787. (f) Cross, R. J.; Davidson, M. F. *J. Chem. Soc., Dalton Trans.* **1986**, 411. (g) Cross, R. J.; Davidson, M. F.; McLennan, A. J. *J. Organomet. Chem.* **1984**, *265*, C37.

(5) (a) Payne, N. C.; Ramachandran, R.; Puddephatt, R. J. *Can. J. Chem.* **1995**, *73*, 6. (b) Payne, N. C.; Ramachandran, R.; Treurnicht, I.; Puddephatt, R. J. *Organometallics* **1990**, *9*, 880.

(6) Mylnikov, V. S. *Adv. Polym. Sci.* **1994**, *115*, 1.

(7) Xu, W.; Vittal, J. J.; Puddephatt, R. J. *Can. J. Chem.* **1996**, *74*, 766.

(8) (a) Grohmann, A.; Schmidbaur, H. In *Comprehensive Organometallics II*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Elsevier: Oxford, 1995; Vol. 3, pp 1−56. (b) Puddephatt, R. J. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, U.K., 1982; Vol. 2, p 756 ff. (c) Anderson, G. K. *Adv. Organomet. Chem.* **1982**, *20*, 39. (d) Puddephatt, R. J. In *The Chemistry of Gold*; Elsevier: Amsterdam, 1978.

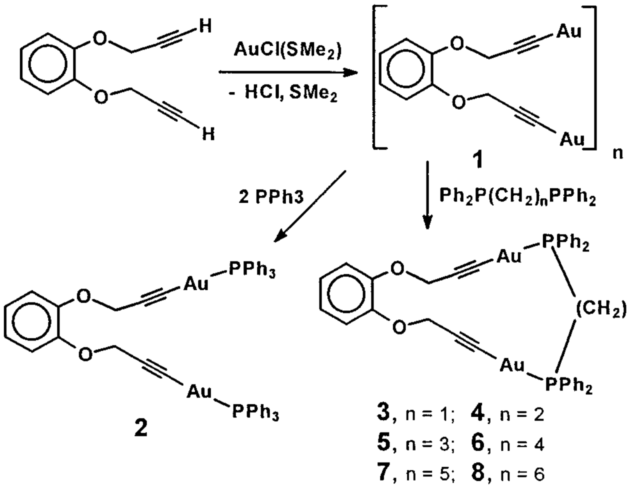
10.1021/om000528c CCC: \$19.00
Publication on Web 10/21/2000

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]

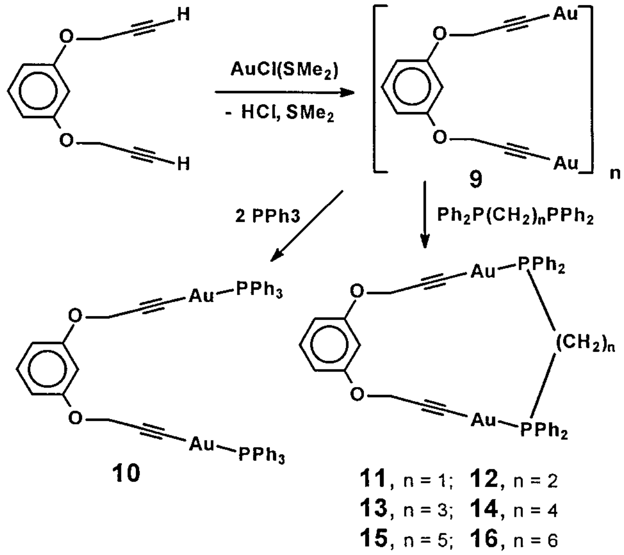
From the above discussion, it is clear that the combination of two gold(I) centers and two bidentate ligands can give a range of ring or polymeric structures, but that more work is required before confident predictions of the resultant structures can be made. This paper reports gold(I) complexes with 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

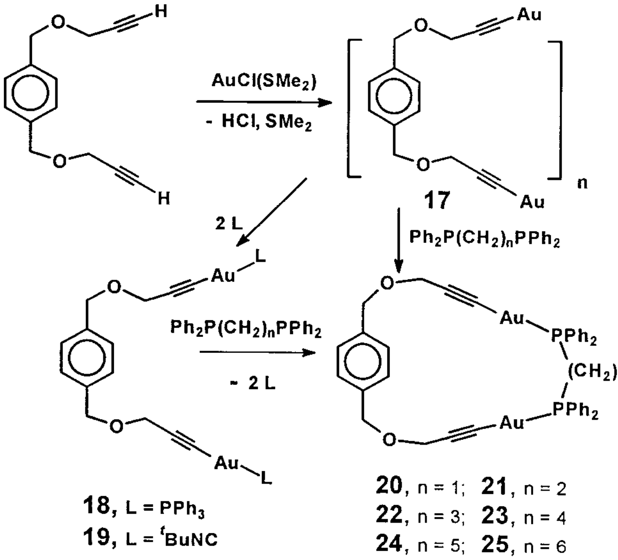
Scheme 1



Scheme 2



Scheme 3



Synthesis of New Complexes. Following the established route to oligomeric alkynylgold(I) complexes of the form $[Au(C\equiv CR)]_n$,[4,9] the reaction of 2 equiv of $[AuCl(SMe_2)]$ and base with the flexible diethynyl arene bifunctional ligands $Ar(OCH_2C\equiv CH)_2$ gave the oligomeric digold(I) diacetylide complexes $[(AuC\equiv CCH_2OArOCH_2C\equiv CAu)_n]$, **1**,Ar = *o*-$C_6H_4$; **9**, Ar = *m*-$C_6H_4$; **17**, Ar = *p*-$C_6H_4$), 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 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

---

(9) (a) Puddephatt, R. J. *J. Chem. Soc., Chem. Commun.* **1998**, 1055. (b) Jia, G.; Puddephatt, R. J.; Scott, J. D.; Vittal, J. J. *Organometallics* **1993**, *12*, 3565. (c) Irwin, M. J.; Manojlović-Muir, L.; Muir, K. W.; Puddephatt, R. J. *J. Chem. Soc., Chem. Commun.* **1997**, 219. (d) Irwin, M. J.; Jia, G.; Payne, N. C.; Puddephatt, R. J. *Organometallics* **1996**, *15*, 51. (e) Jia, G.; Payne, N. C.; Vittal, J. J.; Puddephatt, R. J. *Organometallics* **1993**, *12*, 4771. (f) Jia, G.; Puddephatt, R. J.; Vittal, J. J. *J. Organomet. Chem.* **1993**, *449*, 211. (g). MacDonald, M.-A.; Puddephatt, R. J.; Yap, G. P. A. *Organometallics* **2000**, *19*, 2194.

(10) (a) Kaltsoyannis, N. *J. Chem. Soc., Dalton Trans.* **1997**, 1. (b) Pyykkö, P.; Li, J.; Runeberg, N. *Chem. Phys. Lett.* **1994**, *218*, 133. (c) Schmidbaur, H. *Gold Bull.* **1990**, *23*, 11. (d) Mingos, D. M. P. *J. Chem. Soc., Dalton Trans.* **1996**, 561.

(11) Irwin, M. J.; Rendina, L. M.; Vittal, J. J.; Puddephatt, R. J. *J. Chem. Soc., Chem. Commun.* **1996**, 1281.

(12) Schmidbaur, H.; Wohlleben, A.; Wagner, F.; Orama, O.; Huttner, G. *Chem. Ber.* **1977**, *110*, 1748.

(13) Schmidbaur, H., Ed. *Gold: Progress in Chemistry, Biochemistry and Technology*; Wiley: Chichester, 1999.

(14) (a) Khan, Md. N. I.; Wang, S.; Fackler, J. P., Jr. *Inorg. Chem.* **1989**, *28*, 3579. (b) Dávila, R. M.; Elduque, A.; Grant, T.; Staples, R. J.; Fackler, J. P., Jr. *Inorg. Chem.* **1993**, *32*, 1749. (c) Narayanaswamy, R.; Young, M. A.; Parkhurst, E.; Ouellette, M.; Kerr, M. E.; Ho, D. M.; Elder, R. C.; Bruce, A. E.; Bruce, M. R. M. *Inorg. Chem.* **1993**, *32*, 2506.

(15) (a) Mingos, D. M. P.; Yau, J.; Menzer, S.; Williams, D. J. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1894. (b) McArdle, C. P.; Irwin, M. J.; Jennings, M. C.; Puddephatt, R. J., *Angew. Chem., Int. Ed.* **1999**, *38*, 3376.

in ν(C≡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 $[\{Au(C{\equiv}CtBu)\}_6]_2$.[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 $Ph_2P(CH_2)_3PPh_2$ 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 $[(AuCl)_2(\mu\text{-}Ph_2P(CH_2)_nPPh_2)]$, and this can be a problem in growing single crystals of the alkynylgold(I) complexes.

Structural Characterization. The soluble complexes were characterized by elemental analysis, by their ^{1}H and ^{31}P 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 ν(C≡C) = 2138 and ν(C≡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 ^{1}H NMR spectra, the methylene protons of the propargyl groups appear as singlets in the region δ 4.7−4.9 ppm. The room-temperature ^{31}P 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 ^{31}P NMR spectra, they give singlet resonances in the range δ 42−43 ppm. Low-temperature ^{31}P 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.

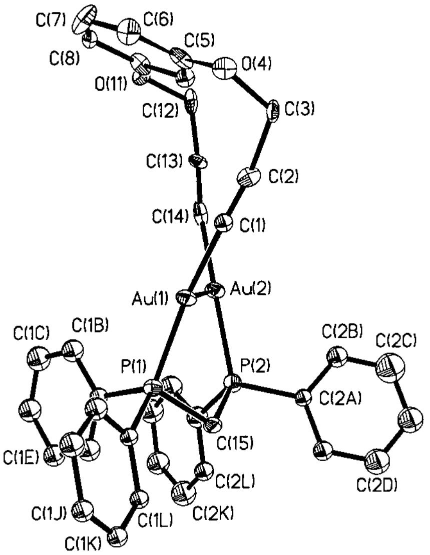


Figure 1. Molecular structure of $[m\text{-}C_6H_4(OCH_2C{\equiv}CAu)_2\text{-}(\mu\text{-}Ph_2PCH_2PPh_2)]$, **11**.

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 $[m\text{-}C_6H_4(OCH_2C{\equiv}C{-}Au)_2\text{-}(\mu\text{-dppm})]$, **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° and P−Au−Au−P = 34.0°. The ring must be very flexible, with rapid ring inversion, since equivalence of both the CH_2O and CH_2P_2 protons is observed in the ^{1}H 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···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≡C−Au−P coordination, Au(1)−P(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

---

[16] Coates, G. E.; Parkin, C. *J. Chem. Soc.* **1962**, 3220.

[17] Payne, N. C.; Puddephatt, R. J.; Ravindranath, R.; Treurnicht, I. *Can. J. Chem.* **1988**, *66*, 3176.

[18] Sarapu, A. C.; Fenske, R. F. *Inorg. Chem.* **1975**, *14*, 247.

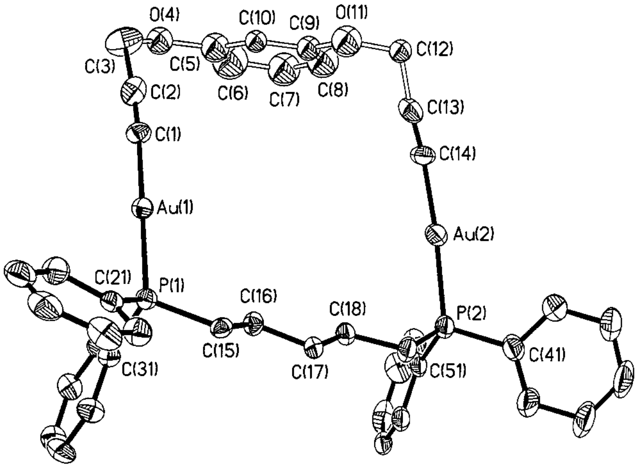


Figure 2. Molecular structure of [m-$C_6H_4(OCH_2C{\equiv}CAu)_2$-($\mu$-$Ph_2P(CH_2)_5PPh_2$)], **15**.

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 (∠P−Au−C = 172.1(7)° and 175.0(7)°).

The molecular structure of [m-$C_6H_4(OCH_2C{\equiv}C{-}Au)_2$-{$\mu$-$Ph_2P(CH_2)_5PPh_2$}], **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)° is approximately linear, but Au(2)−C(14)≡C(13) = 170(1)° deviates from linearity. Similarly, the angle C(1)−Au(1)−P(1) = 179.2(4)° is linear, but C(14)−Au(2)−P(2) = 169.6(4)° 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 contact between gold atoms is 3.806 Å, so there are neither intra- nor intermolecular Au···Au attractions in the structure of complex **15**.

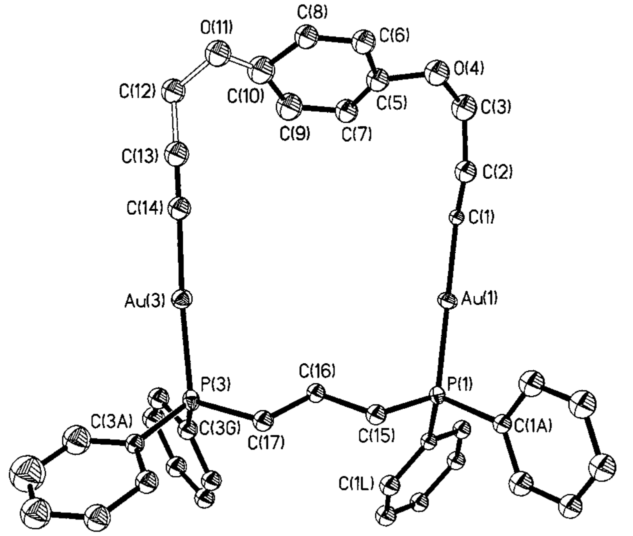


Figure 3. Molecular structure of [p-$C_6H_4(OCH_2C{\equiv}CAu)_2$-($\mu$-$Ph_2P(CH_2)_3PPh_2$)], **22**.

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 $-x + 3, -y, -z + 1$.

The molecular structure of [p-$C_6H_4(OCH_2C{\equiv}C{-}Au)_2$-{$\mu$-$Ph_2P(CH_2)_3PPh_2$}], **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

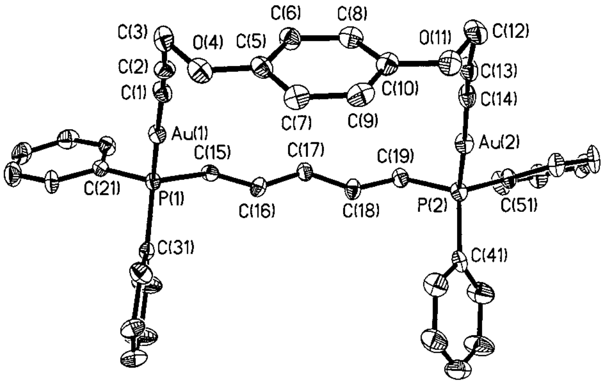


Figure 4. Molecular structure of [*p*-$C_6H_4(OCH_2C{\equiv}CAu)_2$-($\mu$-$Ph_2P(CH_2)_5PPh_2$)], **24**.

Table 4. Selected Bond Lengths (Å) and Angles (deg) for Complex 24[a]

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*-$C_6H_4(OCH_2C{\equiv}CAu)$($\mu$-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 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

Table 5. Luminescence Data for the Complexes

complex	medium	excitation max, nm	emission max, nm
2	solid	350	535
	CH_2Cl_2	350	440
3	solid	350	535
	CH_2Cl_2	350	455
4	solid	350	485
	CH_2Cl_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_2Cl_2	362	442
18	solid	354	437
	CH_2Cl_2	350	433
20	solid	372	488
	CH_2Cl_2	350	454
21	solid	357	463
	CH_2Cl_2	370	451
22	solid	345	466
	CH_2Cl_2	338	451
23	solid	350	426
	CH_2Cl_2	369	449
24	solid	346	415
	CH_2Cl_2	364	450
25	solid	347	424
	CH_2Cl_2	396	452

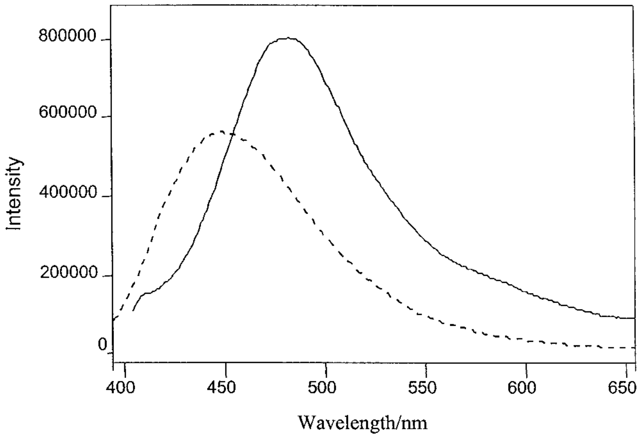


Figure 5. Emission spectra for [*m*-$C_6H_4(OCH_2C{\equiv}CAu)_2$-($\mu$-dppm)], **11**, in solid (solid line) and CH_2Cl_2 solution (dashed line).

---

(19) Irwin, M. J.; Vittal, J. J.; Yap, G. P. A.; Puddephatt, R. J. *J. Am. Chem. Soc.* **1996**, *118*, 13101.

(20) Bancroft, G. M.; Chan, T.; Puddephatt, R. J.; Tse, J. S. *Inorg. Chem.* **1982**, *21*, 2946.

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 $Ph_2PCH_2PPh_2$, 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(PPh$_3$)(C$\equiv$CPh)],[2g] with emission at 419 nm, supporting the view that the two AuC$\equiv$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(SMe$_2$)] 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 ^{1}H NMR chemical shifts reported relative to TMS and ^{31}P chemical shifts relative to an 85% H_3PO_4 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*-C$_6$H$_4$(OCH$_2$C$\equiv$CAu)$_2$], 1. A solution of *o*-C$_6$H$_4$(OCH$_2$C$\equiv$CH)$_2$ (0.332 g, 1.78 mmol) and NaO$_2$CMe (0.29 g, 1.78 mmol) in THF (25 mL)/MeOH (15 mL) was added to a suspension of [AuCl(SMe$_2$)] (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): ν(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*-C$_6$H$_4$(OCH$_2$C$\equiv$CAuPPh$_3$)$_2$], 2. A mixture of **1** (0.34 g, 0.59 mmol) and PPh$_3$ (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 (CD$_2$Cl$_2$): δ(^{1}H) 7.49 [m, 30H, Ph]; 7.10 [m, 2H, Ar]; 6.88 [m, 2H, Ar]; 4.82 [s, 4H, OCH$_2$]; δ(^{31}P) 42.86 [s]. IR (Nujol): ν(C$\equiv$C) 2131 cm^{-1}. Anal. Calcd for $C_{48}H_{38}Au_2O_2P_2{\cdot}CH_2Cl_2$: C, 49.6; H, 3.4. Found: C, 49.9; H, 3.4.

[*o*-C$_6$H$_4$(OCH$_2$C$\equiv$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 CH$_2$Cl$_2$/pentane. Yield: 0.52 g, 75%. NMR (CD$_2$Cl$_2$): δ(^{1}H) 7.4−7.6 [m, 20H, Ph]; 7.11 [m, 2H, Ar]; 6.98 [m, 2H, Ar]; 4.73 [s, 4H, OCH$_2$]; 3.69 [sbr, 2H, dppm]; δ(^{31}P) 40.17 [s]. IR (Nujol): ν(C$\equiv$C) 2124 cm^{-1}. Anal. Calcd for $C_{37}H_{30}Au_2O_2P_2$: C, 46.2; H, 3.1. Found: C, 46.1; H, 3.1.

[*o*-C$_6$H$_4$(OCH$_2$C$\equiv$CAu)$_2$(μ-dppe)], 4. Prepared similarly to **3**. Yield: 66%. NMR (CD$_2$Cl$_2$): δ(^{1}H) 7.5−7.7 [m, 20H, Ph]; 7.09 [m, 2H, Ar]; 6.88 [m, 2H, Ar]; 4.81 [s, 4H, OCH$_2$]; 2.66 [sbr, 4H, dppe]; δ(^{31}P) 40.09 [s]. IR (Nujol): ν(C$\equiv$C) 2134 cm^{-1}. Anal. Calcd for $C_{38}H_{32}Au_2O_2P_2{\cdot}CH_2Cl_2$: C, 44.1; H, 3.2. Found: C, 44.4; H, 3.2.

[*o*-C$_6$H$_4$(OCH$_2$C$\equiv$CAu)$_2$(μ-dppp)], 5. 5 was prepared similarly to **3**. Yield: 82%. NMR (CD$_2$Cl$_2$): δ(^{1}H) 7.5−7.8 [m, 20H, Ph]; 6.95 [sbr, 4H, Ar]; 4.82 [s, 4H, OCH$_2$]; 2.79 [sbr, 4H, dppp]; 1.87 [sbr, 2H, dppp]; δ(^{31}P) 37.49 [s]. IR (Nujol): ν(C$\equiv$C) 2135 cm^{-1}. Anal. Calcd for $C_{39}H_{34}Au_2O_2P_2$: C, 47.3; H, 3.5. Found: C, 46.8; H, 3.3.

[*o*-C$_6$H$_4$(OCH$_2$C$\equiv$C−Au)$_2$(μ-dppb)], 6. 6 was prepared similarly to **3**. Yield: 81%. NMR (CD$_2$Cl$_2$): δ (^{1}H) 7.4−7.6 [m, 20H, Ph]; 6.91 [sbr, 4H, Ar]; 4.78 [s, 4H, OCH$_2$]; 2.43 [sbr, 4H, dppb]; 1.70 [sbr, 4H, dppb]; δ(^{31}P) 37.25 [s]. IR (Nujol): ν(C$\equiv$C) 2135 cm^{-1}. Anal. Calcd for $C_{40}H_{36}Au_2O_2P_2{\cdot}CH_2Cl_2$: C, 45.2; H, 3.5. Found: C, 45.3; H, 3.8.

[*o*-C$_6$H$_4$(OCH$_2$C$\equiv$C−Au)$_2$(μ-dpppe)], 7. 7 was prepared similarly to **3**. Yield: 68%. NMR (CD$_2$Cl$_2$): δ(^{1}H) 7.5−7.7 [m, 20H, Ph]; 6.87 [sbr, 4H, Ar]; 4.74 [s, 4H, OCH$_2$]; 2.33 [sbr, 4H, (dpppe)]; 1.61 [sbr, 6H, dpppe]; δ(^{31}P) 39.65 [s]. IR (Nujol): ν(C$\equiv$C) 2130 cm^{-1}. Anal. Calcd for $C_{41}H_{38}Au_2O_2P_2{\cdot}0.5CH_2Cl_2$: C, 47.0; H, 3.7. Found: C, 47.6; H, 3.8.

[*o*-C$_6$H$_4$(OCH$_2$C$\equiv$C−Au)$_2$(μ-dpph)], 8. 8 was prepared similarly to **3**. Yield: 84%. NMR (CD$_2$Cl$_2$): δ(^{1}H) 7.4−7.6 [m, 20H, Ph]; 6.84 [sbr, 4H, Ar]; 4.75 [s, 4H, CH$_2$]; 2.23 [sbr, 4H, dpph]; 1.28 [sbr, 8H, dpph]; δ(^{31}P) 35.16 [s]. IR (Nujol): ν(C$\equiv$C) 2134 cm^{-1}. Anal. Calcd for $C_{42}H_{40}Au_2O_2P_2$: C, 48.8; H, 3.9. Found: C, 48.4; H, 3.8.

[*m*-C$_6$H$_4$(OCH$_2$C$\equiv$CAu)$_2$]$_n$, 9. To a solution of [AuCl(SMe$_2$)] (0.495 g, 1.70 mmol) in THF (20 mL)/MeOH (10 mL) was added a solution of *m*-C$_6$H$_4$(OCH$_2$C$\equiv$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): ν(C$\equiv$C) 2009 (w) cm^{-1}. Anal. Calcd for $C_{12}H_8Au_2O_2$: C, 24.9; H, 1.4. Found: C, 25.5; H, 1.3.

[*m*-C$_6$H$_4$(OCH$_2$C$\equiv$CAuPPh$_3$)$_2$], 10. PPh$_3$ (0.320 g, 1.22 mmol) was added to a mixture of **8** (0.351 g, 0.61 mmol) in CH$_2$Cl$_2$ (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

---

(21) Fu, W. F.; Chan, K. C.; Miskowski, V. M.; Che, C. M. *Angew. Chem., Int. Ed.* **1999**, *38*, 2783.

(22) Tamaki, A.; Kochi, J. K. *J. Organomet. Chem.* **1974**, *64*, 411.

(23) Simon, D. Z.; Brookman, S.; Beliveau, J.; Salvador, R. L. *J. Pharm. Sci.* **1977**, *66*, 431.

dried. Yield: 0.556 g, 82%. NMR (CD_2Cl_2): $\delta(^1H)$ 7.4−7.6 [m, 30H, Ph]; 7.20 [t, 1H, ^3J = 7.8 Hz, H_5]; 6.60 [m, 3H, H_2, H_4, H_6]; 4.76 [s, 4H, OCH_2]; $\delta(^{31}P)$ 42.96 [s]. IR (Nujol): $\nu(C\equiv C)$ 2136 cm^{-1}. Anal. Calcd for $C_{48}H_{38}Au_2O_2P_2$: C, 52.3; H, 3.5. Found: C, 52.4; H, 3.4.

[*m*-$C_6H_4(OCH_2C\equiv CAu)_2(\mu$-dppm)], 11. A solution of dppm (0.107 g, 0.27 mmol) in CH_2Cl_2 (10 mL) was added to a suspension of **8** (0.157 g, 0.27 mmol) in CH_2Cl_2 (10 mL). The mixture was stirred for 3 h, and the product was isolated as above. Yield: 0.219 g, 85%. NMR (CD_2Cl_2): $\delta(^1H)$ 7.4−7.8 [m, 20H, Ph]; 7.10 [t, 1H, ^3J = 7.8 Hz, H_5]; 6.50 [m, 3H, H_2, H_4, H_6], 4.85 [s, 4H, OCH_2]; 3.57 [t, 2H, $^2J(HP)$ = 11.4 Hz, dppm]; $\delta(^{31}P)$ 33.63 [s]. IR (Nujol): $\nu(C\equiv C)$ 2132 cm^{-1}. Anal. Calcd for $C_{37}H_{30}Au_2O_2P_2$: C, 46.2; H, 3.1. Found: C, 45.8; H, 2.9.

[*m*-$C_6H_4(OCH_2C\equiv CAu)_2(\mu$-dppe)], 12. 12 was prepared similarly to **11**. Yield: 77%. NMR (CD_2Cl_2): $\delta(^1H)$ 7.1−7.7 [m, 21H, Ph and H_5 of Ar]; 6.50 [m, 2H, H_2, H_5]; 4.83 [s, 4H, OCH_2]; 2.50 [sbr, dppe]; $\delta(^{31}P)$ 34.43 (s). IR (Nujol): $\nu(C\equiv C)$ 2131 cm^{-1}. Anal. Calcd for $C_{38}H_{32}Au_2O_2P_2$: C, 46.7; H, 3.3. Found: C, 47.5; H, 3.4.

[*m*-$C_6H_4(OCH_2C\equiv CAu)_2(\mu$-dppp)], 13. 13 was prepared similarly to **11**. Yield: 86%. NMR (CD_2Cl_2): $\delta(^1H)$ 7.4−7.7 [m, 20H, Ph]; 7.15 [t, 1H, ^3J = 7.8 Hz, H_5]; 6.55 [m, 3H, H_2, H_4, H_6]; 4.85 [s, 4H, OCH_2]; 1.8 [sbr, 2H, dppp]; 2.7 [sbr, 4H, dppp]; $\delta(^{31}P)$ 36.00[s]. IR (Nujol): $\nu(C\equiv C)$ 2133 cm^{-1}. Anal. Calcd for $C_{39}H_{34}O_2P_2Au_2\cdot 0.25C_5H_{12}$: C, 48.0; H, 3.8. Found: C, 48.2; H, 3.3.

[*m*-$C_6H_4(OCH_2C\equiv CAu)_2(\mu$-dppb)], 14. 14 was prepared similarly to **11**. Yield: 79%. NMR (CD_2Cl_2): $\delta(^1H)$ 7.4−7.7 [m, 20H, Ph]; 7.15 [t, 1H, ^3J = 8.2 Hz, H_5]; 6.57 [dd, 2H, ^3J = 8.2 Hz, ^4J = 2.4 Hz, H_4, H_6]; 4.78 [s, 4H, OCH_2]; 2.3 [sbr, 4H, dppb]; 1.7 [sbr, 4H, dppb]; $\delta(^{31}P)$ 37.05 [s]. IR(Nujol): $\nu(C\equiv C)$ 2133 cm^{-1}. Anal. Calcd for $C_{40}H_{36}Au_2O_2P_2\cdot 0.25CH_2Cl_2$: C, 46.5; H, 3.6. Found: C, 46.7; H, 3.4.

[*m*-$C_6H_4(OCH_2C\equiv C{-}Au)_2(\mu$-dpppe)], 15. 15 was prepared similarly to **11**. Yield: 72%. NMR (CD_2Cl_2): $\delta(^1H)$ 7.4−7.7 [m, 20H, Ph]; 7.19 [t, 1H, ^3J = 8.2 Hz, H_5]; 6.65 [d, 1H, ^4J = 2.2 Hz, H_2]; 6.59 [dd, 2H, ^3J = 8.1 Hz, ^4J = 2.3 Hz, H_4, H_6]; 4.79 [s, 4H, OCH_2]; 2.3 [sbr, 6H, dpppe]; 1.5 [sbr, 4H, dpppe]; $\delta(^{31}P)$ 38.10 [s]. IR(Nujol): $\nu(C\equiv C)$ 2133 cm^{-1}. Anal. Calcd for $C_{41}H_{38}Au_2O_2P_2$: C, 48.3; H, 3.8. Found: C, 47.9; H, 3.8.

[*m*-$C_6H_4(OCH_2C\equiv CAu)_2(\mu$-dpph)], 16. 16 was prepared similarly to **11**. Yield: 72%. NMR (CD_2Cl_2): $\delta(^1H)$ 7.4−7.7 [m, 20H, Ph]; 7.17 [t, 1H, ^3J = 8.2 Hz, H_5]; 6.67 [d, 1H, ^4J = 2.2 Hz, H_2]; 6.58 [dd, 2H, ^3J = 8.2 Hz, ^4J = 2.0 Hz, H_4, H_6]; 4.76 [s, 4H, OCH_2]; 2.3 [sbr, 8H, dpph]; 1.5 [sbr, 4H, dpph]; $\delta(^{31}P)$ 36.17 [s]. IR(Nujol): $\nu(C\equiv C)$ 2133 cm^{-1}. Anal. Calcd for $C_{42}H_{40}Au_2O_2P_2$: C, 48.8; H, 3.9. Found: C, 48.7; H, 3.8.

[*p*-$C_6H_4(OCH_2C\equiv C{-}Au)_2]_n$, 17. To a solution of [AuCl(SMe_2)] (0.495 g, 1.70 mmol) in THF (20 mL)/MeOH (10 mL) was added a solution of *p*-$C_6H_4(OCH_2C\equiv CH)_2$ (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 $C_{12}H_8Au_2O_2$: C, 24.9; H, 1.4. Found: C, 24.6; H, 1.2.

[*p*-$C_6H_4(OCH_2C\equiv CAuPPh_3)_2$], 18. PPh_3 (0.090 g, 0.345 mmol) was added to a mixture of **17** (0.100 g, 0.172 mmol) in CH_2Cl_2 (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 (CD_2Cl_2): $\delta(^1H)$ 7.4−7.6 [m, 30H, Ph]; 6.92 [s, 4H, Ar]; 4.72 [s, 4H, OCH_2]; $\delta(^{31}P)$ 42.23 [s]. IR (Nujol): $\nu(C\equiv C)$ 2134 cm^{-1}. Anal. Calcd for $C_{48}H_{38}O_2P_2Au_2\cdot 0.25CH_2Cl_2$: C, 51.6; H, 3.4. Found: C, 51.5; H, 3.2.

[*p*-$C_6H_4(OCH_2C\equiv CAuC\equiv N^tBu)_2$], 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 CH_2Cl_2 (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(CD_2Cl_2): $\delta(^1H)$ 6.88 [s, Ar]; 4.69 [s, OCH_2]; 1.53 [s, 18H, t-Bu]. IR (Nujol): $\nu(C\equiv N)$ 2226 cm^{-1}, $\nu(C\equiv C)$ 2138 cm^{-1}. Anal. Calcd for $C_{22}H_{26}Au_2N_2O_2$: C, 35.5; H, 3.5; N, 3.8. Found: C, 34.9; H, 3.5; N, 3.7.

[*p*-$C_6H_4(OCH_2C\equiv CAu)_2(\mu$-dppm)], 20. To a solution of complex **19** (0.257 g, 0.345 mmol) in CH_2Cl_2 (10 mL) was added a solution of dppm (0.133 g, 0.345 mmol) in CH_2Cl_2 (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/CD_2Cl_2): $\delta(^1H)$ 7.0−7.7 [m, 20H, Ph]; 4.82 [s, 4H, OCH_2]; 3.81 [sbr, 2H, dppm]; $\delta(^{31}P)$ 32.86 [s]. IR(Nujol): $\nu(C\equiv C)$ 2123 cm^{-1}. Anal. Calcd for $C_{37}H_{30}Au_2O_2P_2\cdot 0.25CH_2Cl_2$: C, 45.5; H, 3.1. Found: C, 45.5; H, 3.1.

[*p*-$C_6H_4(OCH_2C\equiv C{-}Au)_2(\mu$-dppe)], 21. A solution of dppe (0.107 g, 0.27 mmol) in CH_2Cl_2 (10 mL) was added to a suspension of **17** (0.157 g, 0.27 mmol) in CH_2Cl_2 (10 mL). The mixture was stirred for 3 h. The product was isolated as above. Yield: 0.286 g, 85%. NMR (CD_2Cl_2): $\delta(^1H)$ 7.4−7.6 [m, 20H, Ph]; 6.95 [s, 4H, Ar]; 4.73 [s, 4H, OCH_2]; 2.6 [sbr, 4H, dppe]; $\delta(^{31}P)$ 39.96 [s]. IR(Nujol): $\nu(C\equiv C)$ 2131 cm^{-1}. Anal. Calcd for $C_{38}H_{32}Au_2O_2P_2$: C,45.0; H,3.6. Found: C, 44.8; H, 3.3.

[*p*-$C_6H_4(OCH_2C\equiv C{-}Au)_2(\mu$-dppp)], 22. 22 was prepared similarly to **20**. Yield: 72%. NMR (nitrobenzene-d_5/CD_2Cl_2): $\delta(^1H)$ 7.3−7.6 [m, 20H, Ph]; 5.32 [s, 4H, OCH_2]; 2.5 [sbr, 4H, dppp]; 2.1 [sbr, 2H, dppp]; $\delta(^{31}P)$ 33.75 [s]. IR(Nujol): $\nu(C\equiv C)$ 2136 cm^{-1}. Anal. Calcd for $C_{39}H_{34}Au_2O_2P_2$: C, 47.3; H, 3.5. Found: C, 47.0; H, 3.5.

[*p*-$C_6H_4(OCH_2C\equiv C{-}Au)_2(\mu$-dppb)], 23. 23 was prepared similarly to **21**. Yield: 74%. NMR (CD_2Cl_2): $\delta(^1H)$ 7.4−7.7 [m, 20H, Ph]; 6.96 [s, 4H, Ar]; 4.76 [s, 4H, OCH_2]; 2.4 [sbr, 4H, dppb]; 1.6 [sbr, 4H, dppb]; $\delta(^{31}P)$ 37.76 [s]. IR(Nujol): $\nu(C\equiv C)$ 2131 cm^{-1}. Anal. Calcd for $C_{40}H_{36}Au_2O_2P_2$: C, 47.8; H, 3.6. Found: C, 47.9; H, 3.5.

[*p*-$C_6H_4(OCH_2C\equiv C{-}Au)_2(\mu$-dpppe)], 24. 24 was prepared similarly to **21**. Yield: 76%. NMR (CD_2Cl_2): $\delta(^1H)$ 7.4−7.7 [m, 20H, Ph]; 7.00 [s, 4H, Ar]; 4.78 [s, 4H, OCH_2]; 2.3 [sbr, 8H, dpppe], 1.6 [sbr, 2H, dpppe]; $\delta(^{31}P)$ 38.70 [s]. IR(Nujol): $\nu(C\equiv C)$ 2133 cm^{-1}. Anal. Calcd for $C_{41}H_{38}Au_2O_2P_2$: C, 48.3; H, 3.8. Found: C, 48.1; H, 3.8.

[*p*-$C_6H_4(OCH_2C\equiv C{-}Au)_2(\mu$-dpph)], 25. 25 was prepared similarly to **21**. Yield: 76%. NMR (CD_2Cl_2): $\delta(^1H)$ 7.4−7.7 [m, 20H, Ph]; 6.98 [s, 4H, Ar]; 4.78 [s, 4H, OCH_2]; 2.4 [sbr, 8H, dpph]; 1.5 [sbr, 4H, dpph]; $\delta(^{31}P)$ 36.68 [s]. IR(Nujol): $\nu(C\equiv C)$ 2131 cm^{-1}. Anal. Calcd for $C_{42}H_{40}Au_2O_2P_2$: 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$1/4ether; 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 $P\bar{1}$, 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

	11	**15**	**22**	**24**
empirical formula	$C_{38.50}H_{33.50}Au_2ClO_2{\cdot}_{25}P_2$	$C_{41.63}H_{31.25}Au_2O_2P_2$	$C_{40.38}H_{34}Au_2Cl_{10.25}O_2P_2$	$C_{43}H_{40}Au_2Cl_4O_2P_2$
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	$P\bar{1}$	$C2/c$	$P\bar{1}$	$C2/c$
unit cell dimens	$a = 13.5631(11)$ Å $b = 16.2617(9)$ Å $c = 18.7032(17)$ Å $\alpha = 74.015(4)°$ $\beta = 69.063(4)°$ $\gamma = 66.952(4)°$	$a = 14.3314(5)$ Å $b = 27.2257(10)$ Å $c = 21.8460(8)$ Å $\beta = 94.136(2)°$	$a = 12.8486(7)$ Å $b = 13.7164(5)$ Å $c = 20.9796(11)$ Å $\alpha = 86.079(3)°$ $\beta = 89.858(3)°$ $\gamma = 89.958(3)°$	$a = 30.0723(10)$ Å $b = 11.8721(4)$ Å $c = 26.4185(9)$ Å $\beta = 110.706(2)°$
volume	3500.9(5) Å^3	8501.7(5) Å^3	3688.7(3) Å^3	8822.7(5) Å^3
Z	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 × 0.22 × 0.20 mm^3	0.22 × 0.20 × 0.18 mm^3	0.12 × 0.10 × 0.09 mm^3	0.15 × 0.08 × 0.02 mm^3
θ range for data collection	2.58 to 25.00°	1.76 to 28.29°	2.17 to 24.41°	2.55 to 25.04°
index ranges	$-15 \le h \le 15$, $-19 \le k \le 19$, $-21 \le l \le 22$	$-19 \le h \le 19$, $-35 \le k \le 36$, $-29 \le l \le 29$	$-14 \le h \le 14$, $-15 \le k \le 15$, $0 \le l \le 24$	$0 \le h \le 35$, $0 \le k \le 14$, $-31 \le l \le 29$
no. of reflns collected	16 599	47 214	34 698	39 761
no. of ind reflns	7607 [R(int) = 0.098]	10 528 [R(int) = 0.1440]	11 850 [R(int) = 0.0620]	7789 [R(int) = 0.0960]
completeness to θ =	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 least-squares on F^2	full-matrix least-squares on F^2	full-matrix least-squares on F^2	full-matrix least-squares on F^2
no. of data/restraints/params	7607/4/468	10528/43/424	11850/7/343	7789/0/479
goodness-of-fit on F^2	1.001	0.996	0.846	1.048
final R indices [$I > 2\sigma(I)$]	R1 = 0.0828, wR2 = 0.2123	R1 = 0.0691, wR2 = 0.1302	R1 = 0.0382, wR2 = 0.0884	R1 = 0.0512, wR2 = 0.1027
R indices (all data)	R1 = 0.1308, wR2 = 0.2347	R1 = 0.2141, wR2 = 0.1662	R1 = 0.1424, wR2 = 0.1171	R1 = 0.0911, wR2 = 0.1138
largest diff peak and hole	2.258 and −2.533 e Å^{-3}	1.039 and −0.984 e Å^{-3}	0.881 and −1.194 e Å^{-3}	1.724 and −1.422 e Å^{-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/Å^3) was associated with one of the gold atoms.

X-ray Structure Determination of 15. Crystals of [m-C_6H_4-($OCH_2C{\equiv}CAu$)$_2$(μ-dppe)]·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/Å^3) was associated with one of the gold atoms.

X-ray Structure Determination of 22. Crystals of [p-C_6H_4(OCH_2CCAu)$_2$(μ-$Ph_2P(CH_2)_3PPh_2$)]·1/4CH_2Cl_2·1/2THF were grown by slow diffusion of a solution of $Ph_2P(CH_2)_3PPh_2$ in tetrahydrofuran into a solution of [p-C_6H_4(OCH_2-$CCAuCN$*t*Bu)$_2$] 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 isotropically, and the phenyl rings were refined as rigid hexagons. O11 and C12 were slightly disordered, 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 five isotropic carbon atoms (1/2 occupancy) with the C−C distance fixed and allowed to refine to a value of 1.587 Å. No hydrogens were incorporated into the solvent models. The largest residual electron density peak (0.881 e/Å^3) was associated with one of the solvent molecules.

X-ray Structure Determination of 24. Crystals of [p-C_6H_4-($OCH_2C{\equiv}CAu$)$_2$(μ-dpppe)]·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 not incorporated into the model. All non-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.

Acknowledgment. We thank the NSERC (Canada) for financial support and for a scholarship to W.H.

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.

OM000528C