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Group 11 Metal Chemistry of a Tetradentate Ligand, Phenylene-1,4-diaminotetra(phosphonite), *p*-$C_6H_4[N\{P(OC_6H_4OMe\text{-}o)_2\}_2]_2$[†]

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The Cu^I, Ag^I, and Au^I chemistry of a tetradentate ligand (phenylene-1,4-diaminotetra(phosphonite), *p*-$C_6H_4[N\{P(OC_6H_4OMe\text{-}o)_2\}_2]_2$ ($P_2N\Phi NP_2$) (**1**)) is described. The flexional conformations in **1** leads to interesting structural variations in transition-metal complexes. The reaction of **1** with 4 equiv of CuX (where X = Br and I) produce the tetranuclear complexes, $[\{Cu_2(\mu\text{-}X)_2(NCCH_3)_2\}_2(\mu\text{-}P_2N\Phi NP_2)]$ (where X = Br (**2**) or X = I (**3**)) in quantitative yield. Treatment of **3** with an excess of pyridine, 2-(piperazin-1-yl)pyrimidine, and pyrazole yielded the tetra-substituted derivatives, $[\{Cu_2(\mu\text{-}I)_2(L)_2\}_2(\mu\text{-}P_2N\Phi NP_2)]$ (where L = pyridine (**4**), 2-(piperazin-1-yl)pyrimidine (**5**), or pyrazole (**6**)). Similar reactions of **3** with 1,10-phenanthroline (phen) and 2,2′-bipyridine in a 1:2 molar ratio afford the disubstituted derivatives, $[(Cu_2(\mu\text{-}I))_2I_2(phen)_2(\mu\text{-}P_2N\Phi NP_2)]$ (**7**) and $[(Cu_2(\mu\text{-}I))_2I_2(bipy)_2(\mu\text{-}P_2N\Phi NP_2)]$ (**8**). The *o*-methoxyphenoxy substituents on phosphorus in complexes **5** and **7** adopt approximately parallel planar conformations and contain lattice solvents. The reaction of **3** with 1,4-diazabicyclo[2.2.2]octane (DABCO) in a 1:2 molar ratio in a dichloromethane−acetonitrile mixture leads to the formation of an ionic complex $[N(CH_2CH_2)_3N^+CH_2Cl]_2[(Cu_2(Cl)(I)_2)_2(NCCH_3)_2(\mu\text{-}P_2N\Phi NP_2)]^{2-}$ (**9**), as a result of the chloromethylation of DABCO. Treatment of **1** with 4 equiv of $AgClO_4$ produces $[\{Ag_2(\mu\text{-}ClO_4)_2\}_2(C_4H_8O)_2\}_2(\mu\text{-}P_2N\Phi NP_2)]$ (**10**). Displacement of perchlorate ions in **10** by $PhN\{P(OC_6H_4OMe\text{-}o)_2\}_2$ (PNP) or 2,2′-bipyridine yielded $[(\mu\text{-}PNP)_2Ag_2(\mu\text{-}P_2N\Phi NP_2)Ag_2(\mu\text{-}PNP)_2](ClO_4)_4$ (**11**) and $[\{Ag_2(bipy)_2\}_2(\mu\text{-}P_2N\Phi NP_2)](ClO_4)_4$ (**12**), respectively. The similar reaction of **1** with 2 equiv of AgOTf, in the presence of 4,4′-bipyridine, gave a three-dimensional Ag^I coordination polymer, $[\{Ag_2(C_{10}H_8N_2)_2(CH_3CN)_2\}_2(P_2N\Phi NP_2)]_n(OTf)_{4n}$ (**13**). The reactions of **1** with $[AuCl(SMe_2)]$, in appropriate ratios, afford the tetranuclear and dinuclear complexes, $[(Au_2Cl_2)_2(\mu\text{-}P_2N\Phi NP_2)]$ (**14**) and $[(AuCl)_2(P_2N\Phi NP_2)]$ (**15**). Complex **14** undergoes moisture-assisted P−N bond cleavage in the presence of $PhN\{P(OC_6H_4OMe\text{-}o)_2\}_2$ to give $[p\text{-}NH_2C_6H_4N\{P(OC_6H_4OMe\text{-}o)_2\}_2Au_2Cl_2]$ (**17**) and $[PhN\{P(OC_6H_4OMe\text{-}o)_2\}_2Au_2Cl_2]$. The structures of the complexes **5**, **7**−**10**, **12**−**15**, and **17** are confirmed by single-crystal X-ray diffraction studies.

Introduction

Recently, the synthesis and structural characterization of Group 11 metal complexes in a +1 oxidation state have attracted much attention, because of their potential application in catalysis,[1] biosystems,[2] and photochemical areas.[3] In addition, Group 11 metals serve as versatile connecting nodes for the synthesis of supramolecular architectures through the use of dynamic coordination chemistry[4] and weak $d^{10}-d^{10}$

[†] Dedicated to Prof. S. S. Krishnamurthy on the occasion of his 69th birthday.

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(1) (a) Gorin, D. J.; Toste, F. D. *Nature* **2007**, *446*, 395–403. (b) Jimenez-Nunez, E.; Echavarren, A. M. *Chem. Commun.* **2007**, 333–346. (c) Hashmi, A. S. K.; Hutchings, G. J. *Angew. Chem., Int. Ed.* **2006**, *45*, 7896–7936. (d) Corti, C. W.; Holliday, R. J. *Gold Bull.* **2004**, *37*, 20–26. (e) Bernardi, L.; Gothelf, A. S.; Hazell, R. G.; Jørgensen, K. A. *J. Org. Chem.* **2003**, *68*, 2583–2591. (f) Shi, W.-J.; Wang, L.-X.; Fu, Y.; Zhu, S.-F.; Zhou, Q.-L. *Tetrahedron: Asymmetry* **2003**, *14*, 3867–3872. (g) Koradin, C.; Polborn, K.; Knochel, P. *Angew. Chem., Int. Ed.* **2002**, *41*, 2535–2538. (h) Martorell, A.; Naasz, R.; Feringa, B. L.; Pringle, P. G. *Tetrahedron: Asymmetry* **2001**, *12*, 2497–2499. (I) Chen, J.-X.; Daeuble, J. F.; Brestensky, D. M.; Stryker, J. M. *Tetrahedron* **2000**, *56*, 2153–2166.

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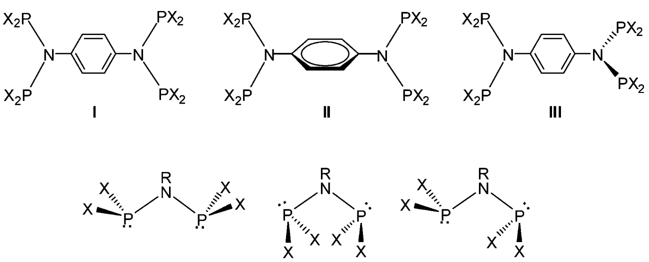
metallophilic interactions.[5] Several rigid *N*-donor ligands, such as 4,4′-bipyridine, 4,4′-dibenzonitrile, pyrazine, and their various derivatives have been extensively used to bridge these metal ions to generate multidimensional, metal-organic materials with diverse properties.[6] Among these ligands, 4,4′-bipyridine has served as an effective bridging group and hundreds of interesting supramolecular architectures have been reported.[7] Instances of the use of rigid linear phosphines, analogous to 4,4′-bipyridine, in the synthesis of polynuclear complexes are less extensive.[8] Several phosphine systems, including a variety of monophosphines (PR_3) and chelating bisphosphines (dppm, dcpm, dppa, etc.), have been used extensively to investigate the coordinating ability of Cu^I, Ag^I, and Au^I centers.[5d,9] In particular, bis(diphenylphosphino)methane (dppm) played a vital role as a bridging ligand and its coordination chemistry has been thoroughly studied.[10] Similar types of bis(phosphines) with an "RN<" spacer in place of the methylene group (known as aminobis(phosphines) with a P−N−P framework) have been studied and found to be thermally more stable, compared to dppm, and sterically less rigid in comparison with P−O−P systems.[11] Furthermore, the binding properties of these ligands can be readily altered by changing the substituents on both the P and N centers, and previous work has shown that such changes can alter the P−N−P angle over the range of 110°−123°, thereby providing ligands capable of spanning a considerable range of intermetallic distances.[12]

Chart 1



Recently, we have extended scope of this chemistry by preparing the novel linear tetraphosphonite ligands $\{(X_2P)_2NC_6H_4N(PX_2)_2\}$ (where X = Cl, F, OMe, OC_6H_4OMe-*o*) (**I**).[13] Interestingly, the compounds of type **I** can adopt several conformations, depending on the orientation of the P−N−P skeleton, with respect to the phenylene ring, as shown in Chart 1. Furthermore, the lone pairs on P atoms can orient in various directions, with respect to the R−N< bridge to afford several geometrical conformations in metal complexes that cannot be achieved with *N*-donor ligands. The

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(2) (a) Marzano, C.; Pellei, M.; Alidori, S.; Brossa, A.; Lobbia, G. G.; Tisato, F.; Santini, C. *J. Inorg. Biochem.* **2006**, *100*, 299–304. (b) Pellei, M.; Lobbia, G. G.; Santini, C.; Spagna, R.; Camalli, M.; Fedeli, D.; Falcioni, G. *Dalton Trans.* **2004**, 2822–2828. (c) McKeage, M. J.; Papathanasiou, P.; Salem, G.; Sjaarda, A.; Swiegers, G. F.; Waring, P.; Wild, S. B. *Met.-Based Drugs* **1998**, *5*, 217–223. (d) Fricker, S. P. *Gold Bull.* **1996**, *29*, 53–60.

(3) (a) Harkins, S. B.; Peters, J. C. *J. Am. Chem. Soc.* **2005**, *127*, 2030–2031. (b) Araki, H.; Tsuge, K.; Sasaki, Y.; Ishizaka, S.; Kitamura, N. *Inorg. Chem.* **2005**, *44*, 9667–9675. (c) Cuttell, D. G.; Kuang, S.-M.; Fanwick, P. E.; McMillin, D. R.; Walton, R. A. *J. Am. Chem. Soc.* **2002**, *124*, 6–7. (d) Song, H.-B.; Wang, Q.-M.; Zhang, Z.-Z.; Mak, T. C. W. *Chem. Commun.* **2001**, 1658–1659. (e) Vogler, A.; Kunkely, H. *Coord. Chem. Rev.* **2001**, *219−221*, 489–507. (f) Yam, V. W.-W.; Chan, C.-L.; Li, C.-K.; Wong, K. M.-C. *Coord. Chem. Rev.* **2001**, *216−217*, 173–194. (g) Yam, V. W.-W.; Lo, K. K.-W. *Chem. Soc. Rev.* **1999**, *28*, 323–334. (h) Ford, P. C.; Cariati, E.; Bourassa, J. *Chem. Rev.* **1999**, *99*, 3625–3647.

(4) (a) Puddephatt, R. J. *Chem. Soc. Rev.* **2008**, *37*, 2012–2027. (b) Bai, J.; Virovets, A. V.; Scheer, M. *Angew. Chem., Int. Ed.* **2002**, *41*, 1737–1740.

(5) (a) Hunks, W. J.; Jennings, M. C.; Puddephatt, R. J. *Inorg. Chem.* **2002**, *41*, 4590–4598. (b) Schmidbaur, H. *Nature* **2001**, *413*, 31–32. (c) Puddephatt, R. J. *Coord. Chem. Rev.* **2001**, *216−217*, 313–332. (d) Gimeno, M. C.; Laguna, A. *Chem. Rev.* **1997**, *97*, 511–522. (e) Schmidbaur, H. *Chem. Soc. Rev.* **1995**, *24*, 391–400. (f) Tzeng, B.-C.; Cheung, K.-K.; Che, C.-M. *Chem. Commun.* **1996**, 1681–1682.

(6) (a) Manzano, B. R.; Jalon, F. A.; Soriano, M. L.; Carrion, M. C.; Carranza, M. P.; Mereiter, K.; Rodriguez, A. M.; de la Hoz, A.; Sanchez-Migallon, A. *Inorg. Chem.* **2008**, *47*, 8957–8971. (b) Dong, Y.-B.; Xu, H.-X.; Ma, J.-P.; Huang, R.-Q. *Inorg. Chem.* **2006**, *45*, 3325–3343. (c) Matsumoto, K.; Harada, Y.; Yamada, N.; Kurata, H.; Kawase, T.; Oda, M. *Cryst. Growth Des.* **2006**, *6*, 1083–1085. (d) Reger, D. L.; Watson, R. P.; Smith, M. D. *Inorg. Chem.* **2006**, *45*, 10077–10087. (e) Oh, M.; Stern, C. L.; Mirkin, C. A. *Inorg. Chem.* **2005**, *44*, 2647–2653. (f) Kitagawa, S.; Kitaura, R.; Noro, S.-I. *Angew. Chem., Int. Ed.* **2004**, *43*, 2334–2375. (g) Dong, Y.-B.; Ma, J.-P.; Huang, R.-Q.; Smith, M. D.; zur Loye, H.-C. *Inorg. Chem.* **2003**, *42*, 294–300. (h) Patra, G. K.; Goldberg, I. *J. Chem. Soc., Dalton Trans.* **2002**, 1051–1057. (i) Blake, A. J.; Champness, N. R.; Hubberstey, P.; Li, W.-S.; Withersby, M. A.; Schroder, M. *Coord. Chem. Rev.* **1999**, *183*, 117–138.

(7) See for example: (a) Sha, J.; Peng, J.; Lan, Y.; Su, Z.; Pang, H.; Tian, A.; Zhang, P.; Zhu, M. *Inorg. Chem.* **2008**, *47*, 5145–5153. (b) Zhao, C.-Q.; Jennings, M. C.; Puddephatt, R. J. *Dalton Trans.* **2008**, 1243–1250. (c) Wu, H.; Dong, X.-W.; Liu, H.-Y.; Ma, J.-F.; Li, S.-L.; Yang, J.; Liu, Y.-Y.; Su, Z.-M. *Dalton Trans.* **2008**, 5331–5341. (d) Deak, A.; Tunyogi, T.; Tarkanyi, G.; Kiraly, P.; Palinkas, G. *CrystEngComm* **2007**, *9*, 640–643. (e) Wheaton, C. A.; Puddephatt, R. J. *Angew. Chem., Int. Ed.* **2007**, *46*, 4461–4463. (f) Cunha-Silva, L.; Ahmad, R.; Carr, M. J.; Franken, A.; Kennedy, J. D.; Hardie, M. J. *Cryst. Growth Des.* **2007**, *7*, 658–667. (g) Zhang, S.; Wang, Z.; Zhang, H.; Cao, Y.; Sun, Y.; Chen, Y.; Huang, C.; Yu, X. *Inorg. Chim. Acta* **2007**, *360*, 2704–2710. (h) Sun, D.; Cao, R.; Sun, Y.; Bi, W.; Li, X.; Wang, Y.; Shi, Q.; Li, X. *Inorg. Chem.* **2003**, *42*, 7512–7518. (i) Abrahams, B. F.; Batten, S. R.; Hoskins, B. F.; Robson, R. *Inorg. Chem.* **2003**, *42*, 2654–2664. (j) Batten, S. R.; Robson, R. *Angew. Chem., Int. Ed.* **1998**, *37*, 1460–1494.

(8) (a) Lin, R.; Yip, J. H. K.; Zhang, K.; Koh, L. L.; Wong, K.-Y.; Ho, K. P. *J. Am. Chem. Soc.* **2004**, *126*, 15852–15869. (b) Catalano, V. J.; Malwitz, M. A.; Horner, S. J.; Vasquez, J. *Inorg. Chem.* **2003**, *42*, 2141–2148. (c) Irwin, M. J.; Vittal, J. J.; Puddephatt, R. J. *Organometallics* **1997**, *16*, 3541–3547. (d) Jia, G.; Puddephatt, R. J.; Scott, J. D.; Vittal, J. J. *Organometallics* **1993**, *12*, 3565–3574.

(9) (a) Lin, Y.; Lai, S.; Che, C.; Fu, W.; Zhou, Z.; Zhu, N. *Inorg. Chem.* **2005**, *44*, 1511–1524. (b) Fournier, E.; Lebrun, F.; Drouin, M.; Decken, A.; Harvey, P. D. *Inorg. Chem.* **2004**, *43*, 3127–3135.

(10) See, for example: (a) Anson, C. E.; Ponikiewski, L.; Rothenberger, A. *Inorg. Chim. Acta* **2006**, *359*, 2263–2267. (b) Yu, S.-Y.; Zhang, Z.-X.; Cheng, E. C.-C.; Li, Y.-Z.; Yam, V. W.-W.; Huang, H.-P.; Zhang, R. *J. Am. Chem. Soc.* **2005**, *127*, 17994–17995. (c) Chen, J.; Mohamed, A. A.; Abdou, H. E.; Bauer, J. A. K.; Fackler Jr, J. P.; Bruce, A. E.; Bruce, M. R. M. *Chem. Commun.* **2005**, 1575–1577. (d) Liaw, B.-J.; Lobana, T. S.; Lin, Y.-W.; Wang, J.-C.; Liu, C. W. *Inorg. Chem.* **2005**, *44*, 9921–9929. (e) Wei, Q.-H.; Yin, G.-Q.; Zhang, L.-Y.; Shi, L.-X.; Mao, Z.-W.; Chen, Z.-N. *Inorg. Chem.* **2004**, *43*, 3484–3491. (f) Yam, V. W.-W.; Lo, W.-Y.; Lam, C.-H.; Fung, W. K.-M.; Wong, K. M.-C.; Lau, V. C.-Y.; Zhu, N. *Coord. Chem. Rev.* **2003**, *245*, 39–47. (g) Fenske, D.; Langetepe, T.; Kappes, M. M.; Hampe, O.; Weis, P. *Angew. Chem., Int. Ed.* **2000**, *39*, 1857–1860.

(11) (a) Alvarez, C. M.; Galan, B.; Garcia, M. E.; Riera, V.; Ruiz, M. A.; Bois, C. *Organometallics* **2003**, *22*, 3039–3048. (b) Perez, J.; Morales, D.; Riera, V.; Rodriguez, A.; Garcia-Granda, S. *Dalton Trans.* **2003**, 1641–1644. (c) Alvarez, M. A.; Alvarez, C.; Garcia, M. E.; Riera, V.; Ruiz, M. A.; Bois, C. *Organometallics* **1997**, *16*, 2581–2589. (d) Liu, X.; Riera, V.; Ruiz, M. A.; Lanfranchi, M.; Tiripicchio, A.; Tiripicchio-Camellini, M. *Organometallics* **1994**, *13*, 1940–1949. (e) Haines, R. J.; Pidcock, A.; Safari, M. *J. Chem. Soc., Dalton Trans.* **1977**, 830–832. (f) Du Preez, A. L.; Marais, I. L.; Haines, R. J.; Pidcock, A.; Safari, M. *J. Organomet. Chem.* **1977**, *141*, C10−C12.

(12) Balakrishna, M. S.; Reddy, S. V.; Krishnamurthy, S. S.; Nixon, J. F.; St. Laurent, J. C. T. R. B. *Coord. Chem. Rev.* **1994**, *129*, 1–90.

(13) Ganesamoorthy, C.; Balakrishna, M. S.; Mague, J. T.; Tuononen, H. M. *Inorg. Chem.* **2008**, *47*, 7035–7047.

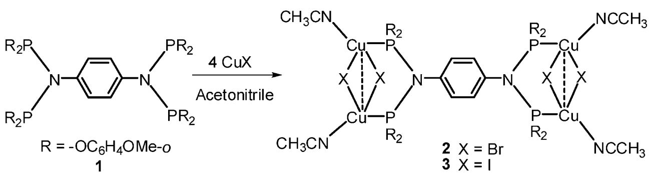
C_{2v} conformation in **I**−**III** (see Chart 1) can bring the metals in close proximity and, therefore, favor metal−metal bonding. Barring C2v′ owing to steric crowding, there is a total of 12 possible conformations (see Chart 1),[14] which could lead to the formation of different types of oligomers and polymeric sheets with metals, the nature of which will be dependent on the coordination geometry of the transition metals and the possible conformations of the ligand.

As a part of our interest in phosphorus-based ligands[15] and their applications in the synthesis of metalla-macromolecules and polymers,[16] we describe herein the synthesis and structural characterization of several dinuclear and tetranuclear Group 11 metal complexes of the phenylene-1,4-diaminotetra(phosphonite), $p\text{-}C_6H_4[N\{P(OC_6H_4OMe\text{-}o)_2\}_2]_2$ ($P_2N\Phi NP_2$) (**1**). This includes the formation of a three-dimensional (3D) Ag^I coordination polymer.

Results and Discussion

Copper(I) Complexes. Tetranuclear copper(I) halide complexes, $[\{Cu_2(\mu\text{-}X)_2(NCCH_3)_2\}_2(\mu\text{-}P_2N\Phi NP_2)]$ (where X = Br (**2**) and I (**3**)), have been prepared by reacting phenylene-1,4-diaminotetra(phosphonite) $p\text{-}C_6H_4[N\{P(OC_6H_4OMe\text{-}o)_2\}_2]_2$ ($P_2N\Phi NP_2$) (**1**) with 4 equiv of CuX (where X = Br and I) in acetonitrile, as shown in Scheme 1.[13] Compounds **2** and **3** are colorless, air-stable, white crystalline solids that are moderately soluble in organic solvents.

Scheme 1. Synthesis of Copper(I) Halide Complexes



Complexes **2** and **3** contain weakly coordinating solvent molecules that can be easily replaced by strong Lewis bases such as pyridine, pyrazole, 2,2′-bipyridine, 1,10-phenanthroline, and 2-(piperazin-1-yl)pyrimidine. These reactions would lead to the formation of several mixed-ligand complexes with additional hard donor sites on the periphery of the ligands that can participate in ligation with hard metals to give heteropoly metallic complexes. In this regard, the tetranuclear iodo derivative **3** was used for reactions with strong Lewis bases to give several mixed-ligand complexes, as shown in Scheme 2. The substitution of the coordinated solvent molecules in complex **3** with pyridine in acetonitrile or dichloromethane did not take place, so that the desired complex, $[\{Cu_2(\mu\text{-}I)_2(C_5H_5N)_2\}_2(\mu\text{-}P_2N\Phi NP_2)]$ (**4**) was prepared as a white crystalline solid by stirring **3** in an excess of pyridine. Similarly, the treatment of complex **3** with an excess of 2-(piperazin-1-yl)pyrimidine or pyrazole (1:6 mol ratio) in dichloromethane/acetonitrile mixtures (1:1) afforded $[\{Cu_2(\mu\text{-}I)_2(L)_2\}_2(\mu\text{-}P_2N\Phi NP_2)]$ (where L = 2-(piperazin-1-yl)pyrimidine (**5**) or pyrazole (**6**)), as white crystalline solids. The ^{31}P NMR spectra of complexes **4**, **5**, and **6** show single resonances at 104.2, 103.9, and 105.1 ppm, respectively. The ^1H NMR spectrum of **4** shows single peaks at 7.11, 7.56, and 8.33 ppm, corresponding to the pyridyl protons. In **5**, the pyrimidyl protons appear as triplet and doublet resonances, centered at 6.76 and 8.27 ppm, respectively, with a $^3J_{HH}$ coupling of 4.8 Hz, whereas the piperazine protons show a broad single resonance at 2.49 ppm. The ^1H NMR spectrum of **6** shows broad single resonances at 6.15 and 7.14, corresponding to the pyrazole protons with a very broad singlet at 10.35 ppm that corresponds to the "NH" protons. The ^1H NMR and analytical data are consistent with the proposed structures of compounds **4**−**6** and the structure of complex **5** was confirmed via an X-ray structure determination.

Treatment of complex **3** with 1,10-phenanthroline or 2,2′-bipyridine in 1:2 molar ratios afforded the complexes $[(Cu_2(\mu\text{-}I))_2I_2(phen)_2(\mu\text{-}P_2N\Phi NP_2)]$ (**7**) and $[(Cu_2(\mu\text{-}I))_2I_2(bipy)_2(\mu\text{-}P_2N\Phi NP_2)]$ (**8**), as bright yellow crystalline solids in good yield. In the formation of complexes **7** and **8**, two acetonitrile groups were replaced and one of the Cu−I−Cu bridges was broken at each end of the molecule by the added chelating ligand (bipy or *o*-phen) to give both tri- and tetra-coordinated copper centers. Complexes **7** and **8** are moderately stable toward air and partially dissolve in acetonitrile and dimethyl sulfoxide. Although the two phosphorus environments are entirely different in **7** and **8**, the ^{31}P NMR spectra of complexes **7** and **8** show single broad peaks at 104.1 and 105.0 ppm, respectively, suggesting interconversion of the terminal and bridging iodides. The compositions of **7** and **8** as 1:2 complexes of **3** and the bidentate *N*-donor ligands were verified by elemental analysis, and the structures were confirmed using single-crystal X-ray structure determinations.

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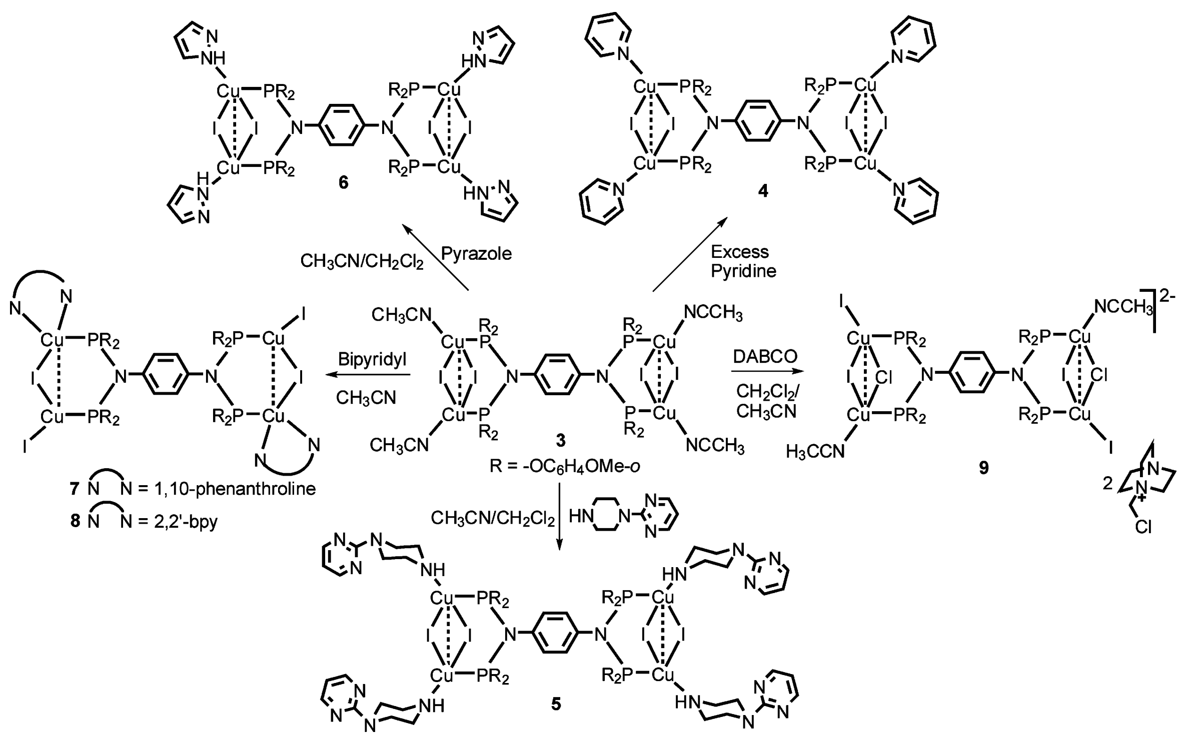
(14) (a) Prout, T. R.; Imiolczyk, T. W.; Barthelemy, F.; Young, S. M.; Haltiwanger, R. C.; Norman, A. D. *Inorg. Chem.* **1994**, *33*, 1783–1790. (b) Schmidbaur, H.; Milewski-Mahrla, B.; Muller, G.; Kruger, C. *Organometallics* **1984**, *3*, 38–43. (c) Schmidbaur, H.; Schier, A.; Lauteschlager, S.; Riede, J.; Muller, G. *Organometallics* **1984**, *3*, 1906–1909. (d) Keat, R.; Manojlovic-Muir, L.; Muir, K. W.; Rycroft, D. S. *J. Chem. Soc., Dalton Trans.* **1981**, 2192–2198. (e) Cross, R. J.; Green, T. H.; Keat, R. *J. Chem. Soc., Dalton Trans.* **1976**, 1424–1428. (f) Colquhoun, I. J.; McFarlane, W. *J. Chem. Soc., Dalton Trans.* **1977**, 1674–1679.

(15) (a) Ganesamoorthy, C.; Mague, J. T.; Balakrishna, M. S. *Eur. J. Inorg. Chem.* **2008**, 596–604. (b) Suresh, D.; Balakrishna, M. S.; Mague, J. T. *Dalton Trans.* **2008**, 2285–2292. (c) Suresh, D.; Balakrishna, M. S.; Mague, J. T. *Dalton Trans.* **2008**, 2812–2814. (d) Ganesamoorthy, C.; Mague, J. T.; Balakrishna, M. S. *J. Organomet. Chem.* **2007**, *692*, 3400–3408. (e) Suresh, D.; Balakrishna, M. S.; Mague, J. T. *Tetrahedron Lett.* **2007**, *48*, 2283–2285. (f) Balakrishna, M. S.; Mague, J. T. *Organometallics* **2007**, *26*, 4677–4679. (g) Chandrasekaran, P.; Mague, J. T.; Balakrishna, M. S. *Inorg. Chem.* **2006**, *45*, 5893–5897. (h) Priya, S.; Balakrishna, M. S.; Mague, J. T. *Inorg. Chem. Commun.* **2001**, *4*, 437–440. (i) Balakrishna, M. S.; Panda, R.; Smith, D. C., Jr.; Klaman, A.; Nolan, S. P. *J. Organomet. Chem.* **2000**, *599*, 159–165. (j) Punji, B.; Mague, J. T.; Balakrishna, M. S. *J. Organomet. Chem.* **2006**, *691*, 4265–4272.

(16) (a) Suresh, D.; Balakrishna, M. S.; Mague, J. T. *Dalton Trans.* **2008**, 3272–3274. (b) Ganesamoorthy, C.; Balakrishna, M. S.; Mague, J. T.; Tuononen, H. M. *Inorg. Chem.* **2008**, *47*, 2764–2776. (c) Ganesamoorthy, C.; Balakrishna, M. S.; George, P. P.; Mague, J. T. *Inorg. Chem.* **2007**, *46*, 848–858. (d) Chandrasekaran, P.; Mague, J. T.; Balakrishna, M. S. *Dalton Trans.* **2007**, 2957–2962. (e) Chandrasekaran, P.; Mague, J. T.; Balakrishna, M. S. *Eur. J. Inorg. Chem.* **2007**, 4988–4997. (f) Venkateswaran, R.; Balakrishna, M. S.; Mobin, S. M.; Tuononen, H. M. *Inorg. Chem.* **2007**, *46*, 6535–6541. (g) Chandrasekaran, P.; Mague, J. T.; Balakrishna, M. S. *Inorg. Chem.* **2006**, *45*, 6678–6683. (h) Chandrasekaran, P.; Mague, J. T.; Balakrishna, M. S. *Organometallics* **2005**, *24*, 3780–3783. (i) Chandrasekaran, P.; Mague, J. T.; Balakrishna, M. S. *Inorg. Chem.* **2005**, *44*, 7925–7932.

Scheme 2. Synthesis of Mixed-Ligand Copper(I) Complexes



The reaction of **3** with the potential intermolecular bridging ligand 1,4-diazabicyclo[2.2.2]octane (DABCO) afforded a product in moderate yield that proved to be $[N(CH_2CH_2)_3\text{-}N^+CH_2Cl]_2[(Cu_2(Cl)(I)_2)_2(NCCH_3)_2(\mu\text{-}P_2N\Phi NP)]^{2-}$ (**9**).

We rationalize this result by noting that 1,4-diazabicyclo[2.2.2]octane is known to undergo a nucleophilic addition reaction with dichloromethane to give the α-chloro quaternary ammonium salt $[N(CH_2CH_2)_3N^+CH_2Cl]Cl$.[17] This monoquaternization reduces the basicity of the remaining nitrogen lone pair by a factor of 10^6, and, because of this lower basicity of the α-chloro quaternary ammonium salt, the substitution of coordinated solvent molecules in **3** by $[N(CH_2CH_2)_3N^+CH_2Cl]$ does not seem to have occurred, despite the existence of considerable studies of the donor properties of the *N*-chloromethyl-dabconium ligand with Mn(II), Co(II), Zn(II), Fe(II), Cu(II), and Ni(II) salts.[18] Because of the poor solubility of complex **9** in most suitable solvents, NMR spectroscopic studies could not be performed; however, the molecular composition was confirmed from elemental analysis data and the primary structural features of complex **9** were established through a single-crystal X-ray diffraction (XRD) study.

Silver(I) Complexes. The reaction of **1** with $AgClO_4$ in a 1:4 molar ratio in tetrahydrofuran (THF) leads to the formation of a tetranuclear complex, $[\{Ag_2(\mu\text{-}ClO_4)_2(C_4H_8O)_2\}_2(\mu\text{-}P_2N\Phi NP_2)]$ (**10**) in good yield. In complex **10**, the Ag^I atoms are bridged by a pair of perchlorate ions and a $P_2N\Phi NP_2$ ligand. The displacement of perchlorate ligands in **10** by 4 equiv of $PhN(P(OC_6H_4OMe\text{-}o)_2)_2$ (PNP) afforded a "manxane"-like triply bridged tetranuclear complex, $[(\mu\text{-}PNP)_2Ag_2(\mu\text{-}P_2N\Phi NP_2)Ag_2(\mu\text{-}PNP)_2](ClO_4)_4$ (**11**), as shown in Scheme 3. Treatment of **10** with 4 equiv of 2,2′-bipyridine produces a tetranuclear complex, $[\{Ag_2(bipy)_2\}_2(\mu\text{-}P_2N\Phi NP_2)](ClO_4)_4$ (**12**), whereas the similar reaction of **1** with 2 equiv AgOTf in the presence of 4,4′-bipyridine affords a three-dimensional Ag^I coordination polymer, $[\{Ag_2(bipy)_2(CH_3CN)_2\}_2(P_2N\Phi NP_2)]_n(OTf)_{4n}$ (**13**) in quantitative yield. Complexes **10**−**12** are white crystalline solids that are only soluble in DMSO; however, complex **13** is an insoluble white solid. The ^{31}P NMR spectra of complexes **10**, **11**, and **12** show broad single resonances at 120.8, 120.1, and 125.7 ppm, respectively. The spectral and analytical data are consistent with the proposed structures of compounds **10**−**13**, and the structures of complexes **10** and **13** were confirmed by X-ray structure determination.

Gold(I) Complexes. The reaction of **1** with $[AuCl(SMe_2)]$ in a 1:4 molar ratio produces a tetranuclear complex, $[(Au_2Cl_2)_2(\mu\text{-}P_2N\Phi NP_2)]$ (**14**), with the ligand exhibiting the bridging mode of coordination. A similar reaction of **1** with $[AuCl(SMe_2)]$ in a 1:2 molar ratio furnishes a dinuclear complex, $[(AuCl)_2(P_2N\Phi NP_2)]$ (**15**) along with a small quantity of **14** (see Scheme 4). Treatment of complex **14** with $PhN(P(OC_6H_4OMe\text{-}o)_2)_2$ (PNP) in a 1:2 molar ratio did not give the desired bridged tetranuclear complex $[(\mu\text{-}PNP)Au_2Cl_2(\mu\text{-}P_2N\Phi NP_2)Au_2Cl_2(\mu\text{-}PNP)]$, even under refluxing conditions. Instead, the reaction leads to the formation of **15** and $[PhN(P(OC_6H_4OMe\text{-}o)_2)_2AuCl]$ (**16**) in high yields,

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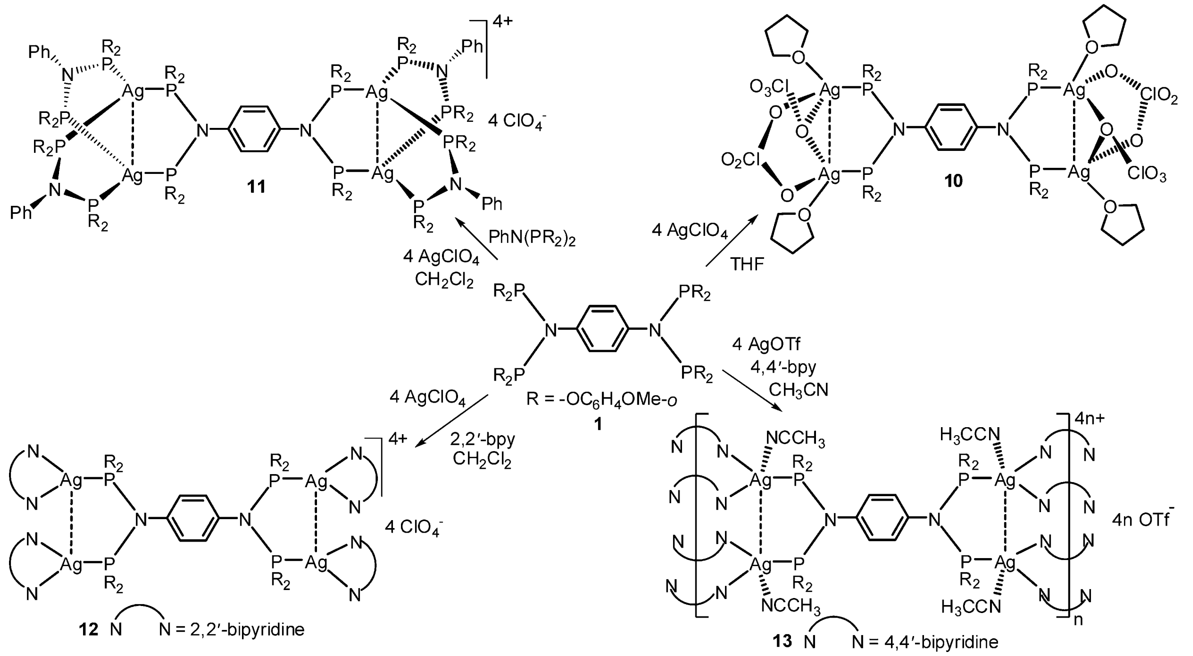
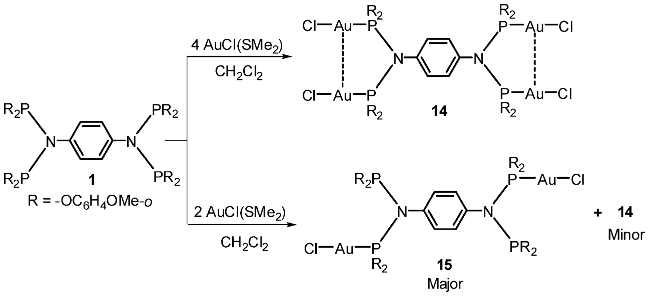
(17) (a) Gustafsson, B.; Hakansson, M.; Jagner, S. *Inorg. Chim. Acta* **2005**, *358*, 1309–1312. (b) Banks, R. E.; Besheesh, M. K.; Mohialdin-Khaffaf, S. N.; Sharif, I. *J. Chem. Soc., Perkin Trans. I* **1996**, 2069–2076. (c) Abdul-Ghani, M.; Banks, R. E.; Besheesh, M. K.; Sharif, I.; Syvret, R. G. *J. Fluorine Chem.* **1995**, *73*, 255–257. (d) Almarzoqi, B.; George, A. V.; Isaacs, N. S. *Tetrahedron* **1986**, *42*, 601–607. (e) Vallarino, L. M.; Goedken, V. L.; Quagliano, J. V. *Inorg. Chem.* **1973**, *12*, 102–107.

(18) (a) Vallarino, L. M.; Goedken, V. L.; Quagliano, J. V. *Inorg. Chem.* **1972**, *11*, 1466–1469. (b) Quagliano, J. V.; Banerjee, A. K.; Goedken, V. L.; Vallarino, L. M. *J. Am. Chem. Soc.* **1970**, *92*, 482–488. (c) Garrett, B. B.; Goedken, V. L.; Quagliano, J. V. *J. Am. Chem. Soc.* **1970**, *92*, 489–493. (d) Goedken, V. L.; Quagliano, J. V.; Vallarino, L. M. *Inorg. Chem.* **1969**, *8*, 2331–2337.

Scheme 3. Synthesis of Silver(I) Complexes



Scheme 4. Synthesis of Gold(I) Complexes: Reaction of **1** To Produce **14** and **15**



with a small quantity of **14** remaining, as shown in Scheme 5. Complexes **15** and **16** were separated by fractional crystallization in a dichloromethane/*n*-hexane (2:1) mixture. Several attempts were made to prepare the bridged tetranuclear complex [(μ-PNP)Au$_2$Cl$_2$(μ-P$_2$NΦNP$_2$)Au$_2$Cl$_2$(μ-PNP)], and, in one instance, the entry of trace amount of moisture to the reaction mixture prompted the P−N bond cleavage in **14**, which leads to the transfer of two Au−Cl units to PhN(P(OC$_6$H$_4$OMe-*o*)$_2$)$_2$ to give the stoichiometric mixture of [H$_2$NC$_6$H$_4${N{P(OC$_6$H$_4$OMe-*o*)$_2$}$_2$}$_2$Au$_2$Cl$_2$] (**17**) and [Ph{N{P(OC$_6$H$_4$OMe-*o*)$_2$}$_2$}$_2$Au$_2$Cl$_2$], as indicated by the ^{31}P NMR data and the XRD studies.

The ^{31}P NMR spectrum of **14** consists of a single peak at 114.3 ppm, whereas **15** shows two doublets, centered at 110.5 and 132.2 ppm, with a large $^2J_{PP}$ coupling of 348 Hz.[14d−f,19] The ^{1}H NMR spectrum of **14** shows single resonance corresponding to the *ortho*-methoxy groups at 3.81, whereas **15** shows two resonances at 3.60 and 3.63 ppm for *ortho*-methoxy groups present on uncoordinated and coordinated P atoms, respectively. The structures of complexes **14**, **15**, and **17** were confirmed using X-ray structure determinations.

Crystal and Molecular Structures of 5, 7−10, 12−15, and 17. Perspective views of the molecular structures of compounds **5**, **7–10**, **12–15**, and **17**, with atom numbering schemes, are shown in Figures 1–10, respectively. Crystal data and the details of the structure determinations are given in Tables 1 and 2, while selected bond lengths and bond angles are given in Tables 3−6. The molecular structure of compound **5** consists of two discrete Cu$_2$I$_2$ cores with the copper(I) centers tetrahedrally coordinated by a P atom, two bridging iodides, and a solvent molecule. As observed in complexes **2** and **3**, the Cu$_2$I$_2$ core adopts a butterfly shape with the I atoms at the wingtips.[13] The eight Cu−I bond lengths differ significantly from each other but can be seen (Table 3) to fall roughly into a “longer” pair and a “shorter” pair, with each Cu atom forming a “long” and a “short” Cu−I bond. The distances between the two copper centers Cu1···Cu2 and Cu3···Cu4 are 2.715 and 2.762 Å, respectively, which indicate the presence of ligand-supported Cu···Cu interactions.[16c] The Cu(I) centers exhibit distorted tetrahedral coordination geometries, as indicated by the interligand angles, which range from 134.3(2)° to 87.8(2)°. The average Cu−P distance and Cu−I−Cu angle are 2.168 Å and 61.46°, respectively. As is evident from Figure 1, the conformations of the 2-(piperazin-1-yl)pyrimidine ligands and the relatively short backbone of the phosphonite ligand constrain the *o*-methoxyphenoxy substituents on phosphorus to adopt approximately parallel planar conformations which generates a “pocket” on either side of the ligand backbone. These are occupied by the solvent acetonitrile molecules, which participate in weak C−H···O hydrogen bonding with some of the phenoxy O atoms.

In complex **7**, the Cu1 is tetra-coordinated [one P, one I, and two N (from the *o*-phen moiety) atoms], whereas the Cu2 center is tricoordinated being bound to one phosphorus

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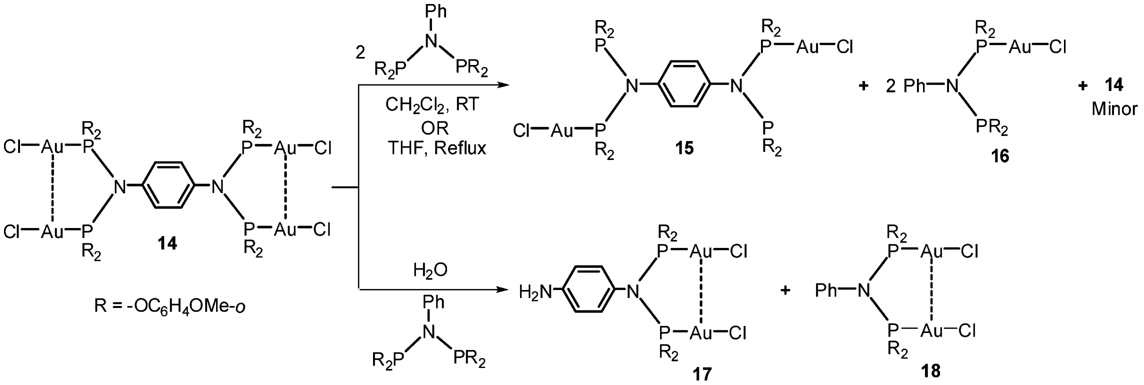
(19) (a) Keat, R. *J. Chem. Soc., Dalton Trans.* **1972**, 2189–2192. (b) Rudolph, R. W.; Newmark, R. A. *J. Am. Chem. Soc.* **1970**, *92*, 1195–1199. (c) Nixon, J. F. *J. Chem. Soc. A* **1969**, 1087–1089.

Scheme 5. Synthesis of Gold(I) Complexes: Reaction of **14** To Produce **15**−**18**



and two iodine centers. The molecule has crystallographically imposed centrosymmetry so that the two Cu atoms chelated by 1,10-phenanthroline are required to adopt a *trans* disposition. The two Cu−P distances differ significantly (Cu1−P1 = 2.1630(6) Å, Cu2−P2 = 2.1875(6) Å), as do the Cu−I distances to the bridging I atom (Cu2−I1 = 2.5702(3) Å and Cu1−I1 = 2.5943(3) Å) with the shorter Cu−P distance to the 4-coordinated Cu atom. The Cu−N bond lengths (Cu1−N2 = 2.0749(2) Å and Cu1−N3 = 2.065(2) Å) are approximately equal, whereas the terminal Cu2−I1 bond distance is 2.5178(4) Å. The distance between two copper centers is 2.957 Å. The I1−Cu2−I2 angle is 119.48(1)°, whereas the Cu1−I1−Cu2 angle is 69.87(1)°. These angles obviously indicate a distortion of the copper coordination sphere, which is occasioned primarily by the small bite angle of the 1,10-phenanthroline (N2−Cu1−N3 = 81.39(8)°). As with **5**, the *o*-methoxyphenoxy substituents on phosphorus adopt approximately parallel planar conformations (Figure 2) and the lattice solvent acetonitrile resides in the "pockets" thus created.

Complexes **7** and **8** have several similar structural features. In both complexes, the structures, the chelating moiety, and the terminal I atom are displaced to the same side of the Cu_2P_2 plane while the Cu(μ-I)Cu bridge is folded away from the terminal I atom. Furthermore, the Cu(μ-I)Cu bridge and terminal I atoms are pointed away from each other. However, in **8**, which has no crystallographically imposed symmetry, the two 2,2′-bipy moieties are on the same side in contrast to the *trans* orientation of **7**. Furthermore, in **8**, the oxygen atom O4 (or O26) of the methoxy group of one of the

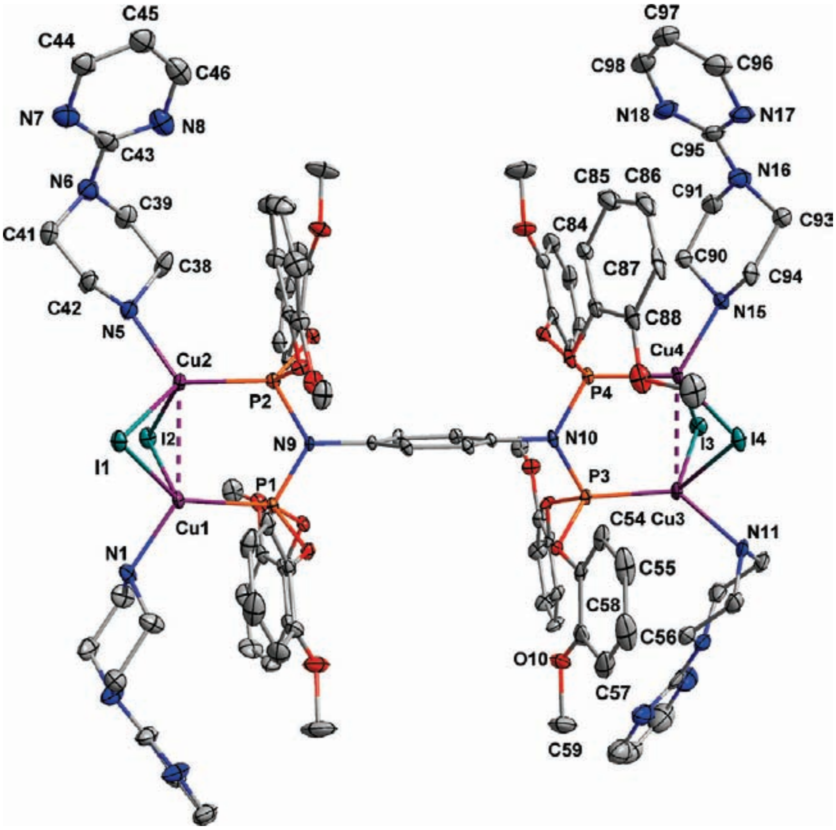


Figure 1. Molecular structure of **5**. All H atoms and lattice solvents have been omitted for clarity. Displacement ellipsoids are drawn at the 30% probability level.

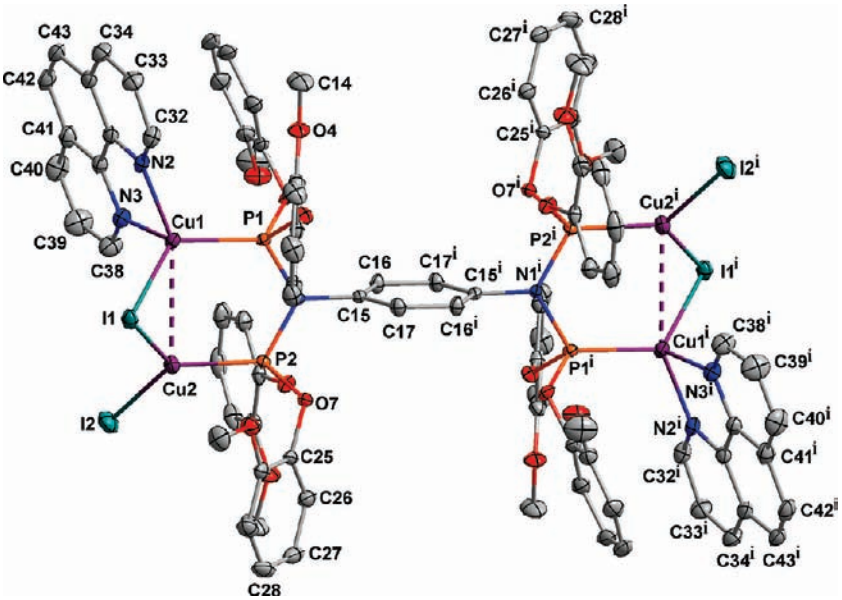


Figure 2. Molecular structure of **7**. All H atoms and lattice solvent have been omitted for clarity. Displacement ellipsoids are drawn at the 50% probability level.

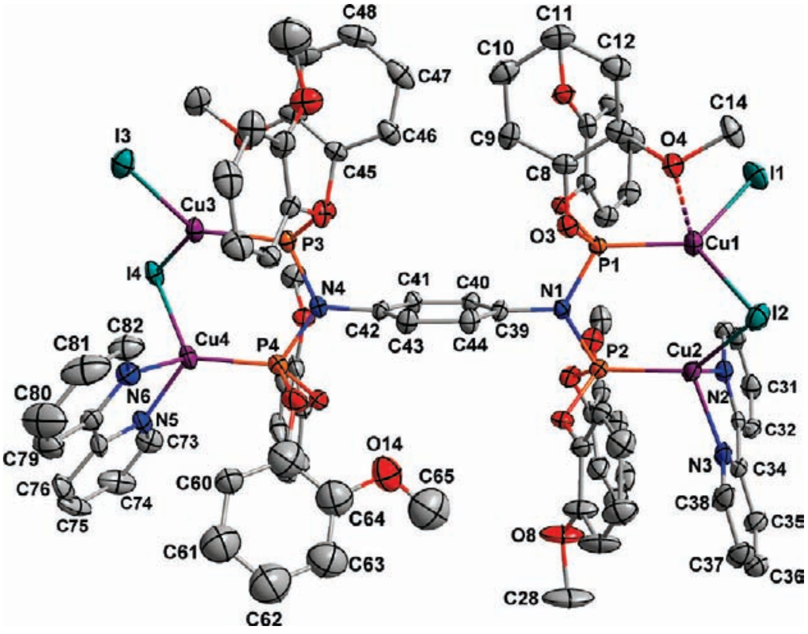


Figure 3. Molecular structure of **8**. All H atoms and lattice solvents have been omitted for clarity. Displacement ellipsoids are drawn at the 50% probability level. Only one orientation is shown for each of the disordered moieties.

phenoxy substituents makes a close approach to Cu1 (or Cu7) (Cu1···O4 = 2.818 Å; Cu7···O26 = 2.790 Å). Because Cu1 is formally 3-coordinated and, at this distance, is less than the sum of the van der Waals radii of O and Cu (2.90 Å), it is likely that this represents a weak bonding interaction with the copper center.[20] The patterns of bond lengths and bond angles in **8** are similar to those in **7**; however, unlike that in the former, not all of the *o*-methoxyphenoxy substituents on phosphorus adopt the parallel plane arrangement.

The molecular structure of **9** consists of an anionic $[Cu_4(\mu\text{-}I)_2(\mu\text{-}X)_2X_2(NCCH_3)_2(\mu\text{-}P_2N\Phi NP_2)]^{2-}$ (where X = Cl, I) core with two chloromethylated units (1,4-diazabicyclo[2.2.2]-octane, $[N(CH_2CH_2)_3N^+CH_2Cl]$) as countercations. During the course of the refinement, it became clear that a partial incorporation of chloride into sites shown as I1 (bridging, ca. 70%) and I3 (terminal, ca. 30%) had occurred in the crystal that was used for the data collection. As a result, metrical parameters that involve these atoms have noticeably higher errors than for the remainder of the structure.[21] The anion has crystallographically imposed centrosymmetry and the Cu_2X_2 core adopts a butterfly-shaped structure with the

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(20) Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441–451.

(21) Although the elemental analyses data taken for the crystalline sample clearly show the partial replacement of iodide by chloride, it is not entirely clear how the exchange takes place. Attempts to react DABCO with **3** in acetonitrile resulted in the formation of an insoluble precipitate that could not be further analyzed or crystallized to obtain X-ray quality crystals. X-ray quality crystals were obtained only when a dichloromethane solution of DABCO was added to **3** in acetonitrile.

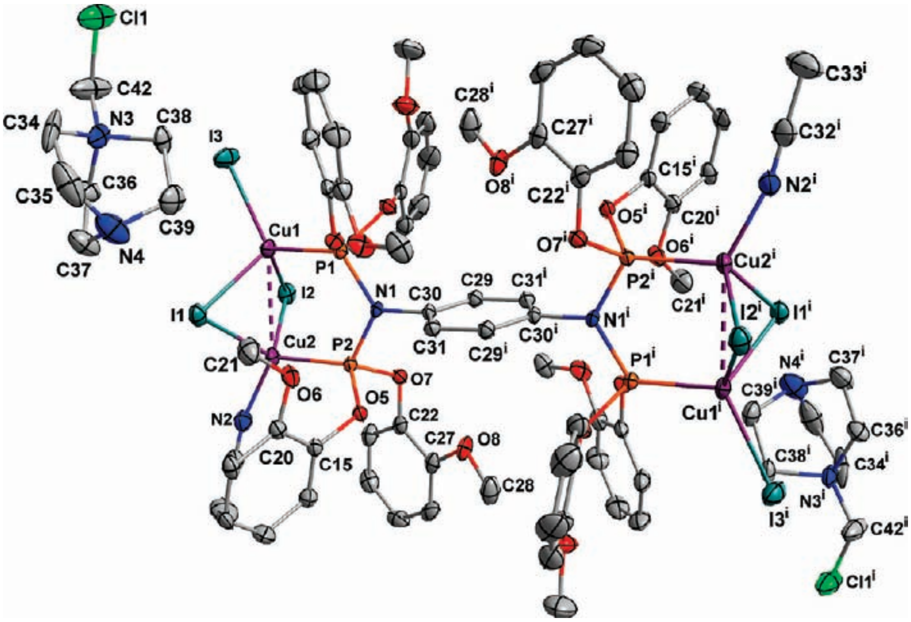

Figure 4. Molecular structure of **9**. All H atoms and the lattice solvent have been omitted for clarity. Displacement ellipsoids are drawn at the 50% probability level. Only one orientation is shown for the disordered portion of the cation, and only the iodine positions are shown for I1 and I3, where partial replacement by chloride occurred.

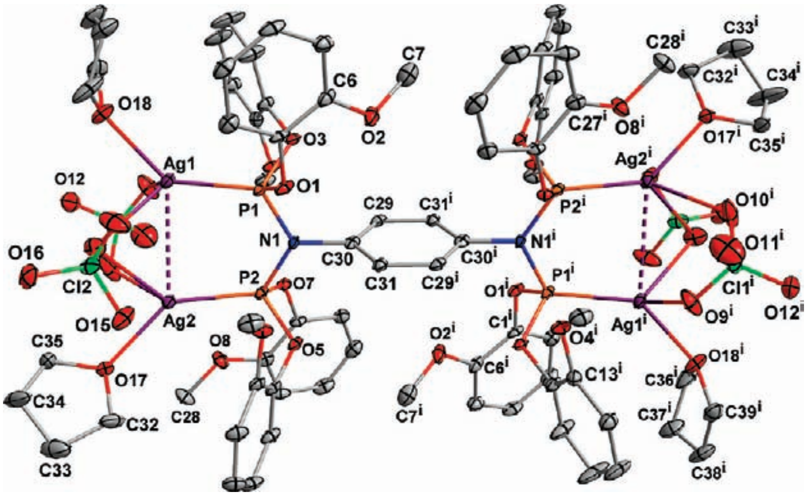

Figure 5. Molecular structure of **10**. All H atoms and lattice solvents have been omitted for clarity. Displacement ellipsoids are drawn at the 30% probability level.

halogen atoms at the wingtips. Both of the copper(I) centers are tetrahedrally coordinated by a P atom, two bridging halogen atoms, and a terminal halogen atom on Cu1 and a solvent molecule on Cu2. The four bridging Cu−I bond lengths vary from 2.52(2) Å to 2.764(1) Å. The terminal Cu−I bond distance is 2.568(1) Å. The distance between the two copper centers is Cu1···Cu2 = 2.789 Å, which is slightly longer that that observed in **2**, **3**, and **5**. In **9**, the two independent Cu−P distances are virtually the same [P1−Cu1 = 2.190(1) Å and P2−Cu2 = 2.184(1) Å], whereas the I−Cu−I angles [I1−Cu1−I2 = 101.7(4)° and I1−Cu2−I2 = 105.9(4)°] show distortion in the tetrahedral environment around copper.

The crystals of **10** suitable for XRD analysis were grown by keeping the saturated THF solution of **10** at room temperature for several days (in darkness). The molecule has crystallographically imposed centrosymmetry and the Ag(I) atoms exhibit distorted tetrahedral geometry with an Ag1···Ag2 distance of 3.090 Å. One of the perchlorate ions coordinates in a bridged bidentate fashion to both of the Ag atoms while the other forms an almost-symmetrical μ-oxo bridge between the two metals. The complex has two slightly different Ag−P bonds (2.3378(1) and 2.3431(1) Å) and the P1−N−P2 bond angle (121.47(2)°) is smaller than that observed in complexes **2** and **3**.

In complex **12**, the Ag(I) atoms have a trigonal planar geometry and are surrounded by two N atoms and a P atom. The sums of the angles around the Ag1, Ag2, Ag3, and Ag4 centers are 359.6°, 359.7°, 357.2°, and 359.9°, respectively. The Ag−P bond distances vary from 2.3109(1) Å to 2.3326(1) Å and are shorter than those observed in **10**. The Ag−N bond distances vary from 2.241(3) Å to 2.292(3) Å and the bite angles created by the 2,2′-bipyridines at the Ag1, Ag2, Ag3, and Ag4 centers are 73.10(1)°, 72.57(1)°,

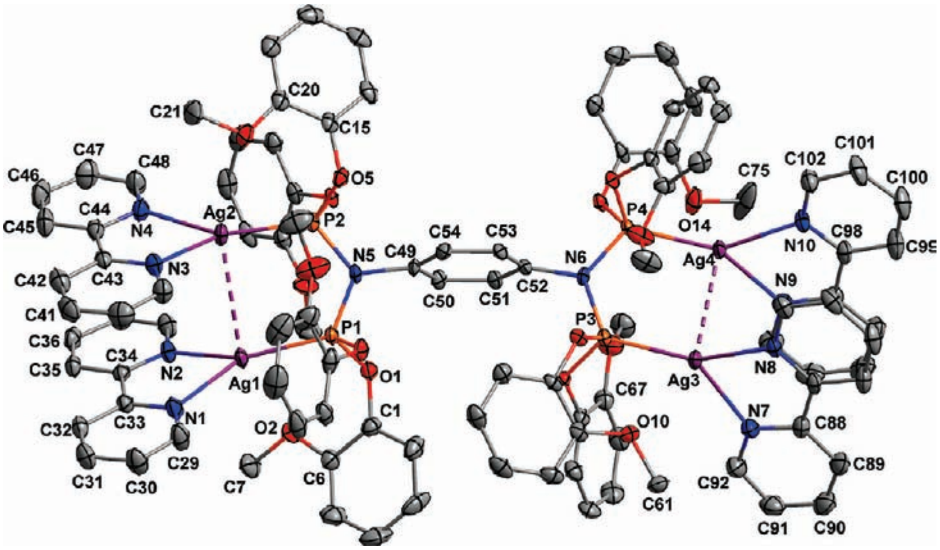

Figure 6. Molecular structure of **12**. All H atoms, perchlorate ions, and lattice solvents have been omitted for clarity. Displacement ellipsoids are drawn at the 50% probability level.

73.50(1)°, and 72.17(1)°, respectively. The four bipyridyl rings are parallel to each other and show offset or slipped stacking $\pi-\pi$ alignment with the minimum distance between the bipyridyl rings being 3.506 Å.[22]

The colorless crystals of **13** were obtained from a dichloromethane−acetonitrile mixture at room temperature. The molecular structure of compound **13** consists of repeating $[(P_2N\Phi NP_2)Ag_4]$ and 4,4′-bipyridine units with Ag atoms disposed approximately in a plane. The 4,4′-bipyridine units are distributed above and below the P−N−P skeleton to form a bowl-shaped molecule. Each bowl is joined to neighboring bowls by four Ag atoms to form a 54-membered macrocyclic cage that encapsulates two CH_2Cl_2 molecules and a triflate ion. The observed minimum and maximum distances between the Ag atoms are 6.078(1) Å and 23.318(3) Å, respectively (see Figure 7c). The coordination geometry around the Ag(I) atom is tetrahedral and consists of two N atoms of two 4,4′-bipyridine ligands, one P atom of **1**, and one N atom of an acetonitrile molecule. The molecule has two different Ag−P bonds, with bond distances of 2.338(2) and 2.397(2) Å. The molecule did not show any metal−metal interactions, because of the twisted conformations of the Ag−P vectors, which make an angle of ~103° with each other. The Ag−N bond distances to the bipyridyl moieties vary from 2.292(7) Å to 2.361(8) Å and are shorter than those observed for the coordinated acetonitrile molecules (2.395(8) Å and 2.407(9) Å). The P1−N4−P2 angle is 125.2(3)°.

The molecular structure of **14** consists of a discrete $[(AuCl)_2(\mu\text{-}P_2N\Phi NP_2)(AuCl)_2]$ species having crystallographically imposed centrosymmetry. The two independent Au(I) centers adopt approximately linear geometries with P−Au−Cl angles of 169.97(3)° and 168.37(3)°. The P−Au−Cl units are *cis*-oriented with an intramolecular Au···Au distance of 3.102 Å. This is well within the Au···Au distances that are considered to represent aurophilic interactions.[23] The Au−P and Au−Cl bond distances are ~2.20 and ~2.28 Å, respectively. The P1−N−P2 bond angle is 124.84(14)°. In the crystal identified as **17**, there are two independent molecules of $[RC_6H_4\{N\{P(OC_6H_4OMe\text{-}o)_2\}_2\}_2Au_2Cl_2]$ (where R = H, NH_2) in the asymmetric unit that differ only slightly in geometry and conformation. In the unit that contains Au1 and Au2, ~30% of the R group is NH_2 and ~70% of the R group is H, whereas in the unit that contains Au3 and Au4, 70% of the R group is NH_2 and 30% of the R group is H. The P−Au−Cl units are *cis*-oriented with an average intramolecular Au···Au distance of 3.1119(4) Å.

As observed from the nuclear magnetic resonance (NMR) spectroscopic data, the molecular structure of **15** has alternating coordinated and uncoordinated P atoms with a discrete $[(AuCl)(P_2N\Phi NP_2)(AuCl)]$ core. The complex has crystallographically imposed centrosymmetry and the unique Au(I) center adopts an approximately linear geometry with a P−Au−Cl angle of 176.62(4)°. The structure did not show any intermolecular or intramolecular Au···Au interactions. The Au−P and Au−Cl bond distances are 2.205(1) Å and 2.282(1) Å, respectively, whereas the P1−N−P2 bond angle is 118.8(2)°. In all of the structures of complexes of **1**, the bridging phenylene ring is almost perpendicular to the P−N−P planes, with the torsion angles varying from 74.8(4)° to 103.5(4)°.

Conclusion

Although several polydentate phosphorus ligands are known in the literature, many of them have restricted coordination behavior, often forming either chelating or polycyclic cagelike complexes. In this context, the tetraphosphonite **1** is unique and can be compared to two 4,4′-bipyridine units fused sideways containing both electronically

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[22] (a) Roesky, H. W.; Andruh, M. *Coord. Chem. Rev.* **2003**, *236*, 91–119. (b) Janiak, C. *J. Chem. Soc., Dalton Trans.* **2000**, 3885–3896.

[23] (a) Schmidbaur, H.; Schier, A. *Chem. Soc. Rev.* **2008**, *37*, 1931–1951. (b) Schmidbaur, H. *Gold Bull.* **2000**, *33*, 3–10. (c) Pyykkö, P.; Mendizabal, F. *Inorg. Chem.* **1998**, *37*, 3018–3025. (d) Pyykkö, P. *Chem. Rev.* **1997**, *97*, 597–636.

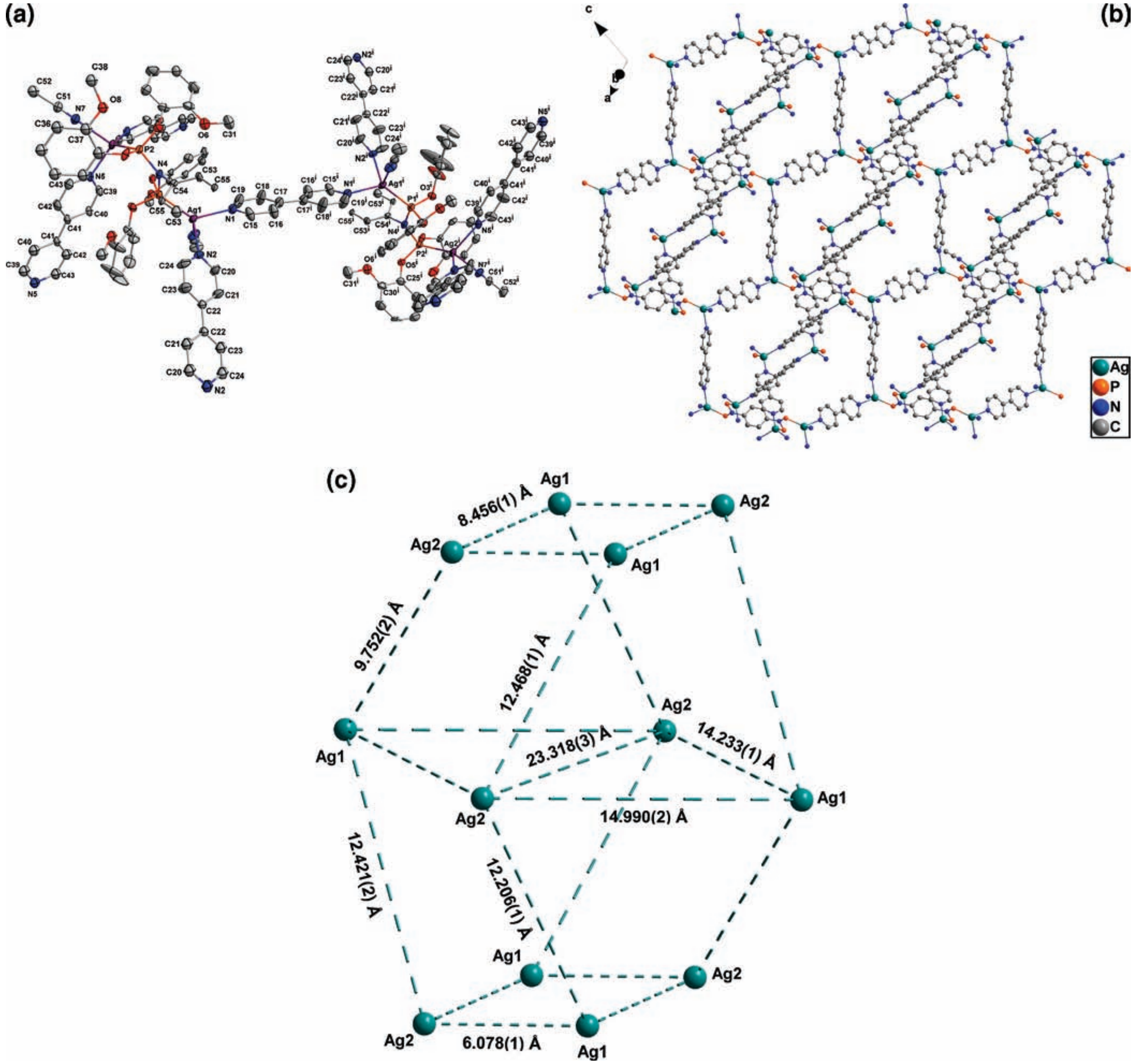

Figure 7. (a) The repeating unit of **13**. All H atoms, triflate ions, and lattice solvents have been omitted for clarity. Displacement ellipsoids are drawn at the 30% probability level. Only one orientation of the disordered phenoxy group is shown. (b) Portion of three-dimensional view of **13**. All H atoms, triflate ions, and lattice solvents have been omitted for clarity. (Symmetry operations: (i) $1 - x$, $1 - y$, $1 - z$; (ii) $2 - x$, $2 - y$, $1 - z$; (iii) $1 - x$, $2 - y$, $-z$; (iv) $-x$, $1 - y$, $-z$; (v) $1 - x$, $2 - y$, $1 - z$.) (c) Distribution of Ag atoms in macrocyclic cage.

and sterically tunable phosphorus donor centers. The tetraphosphonite **1** has the advantage of being rigid and, at the same time, is able to offer various conformations as shown in Chart 1. Such conformational fluxionality in **1** can lead to interesting structural variations in transition-metal complexes. For instance, the formation of a three-dimensional (3-D) polymer **13** is associated with the rotation of phosphorus lone pairs, with respect to phosphorus substituents, to give twisted Ag^I complex and that must have occurred through the pre-formation of $[(OTf)_2Ag_2(\mu\text{-}P_2N\Phi NP_2)Ag_2(OTf)_2]$, followed by the reaction with 4,4′-bipyridine. The different orientations of phosphorus substitutions can induce unique behavior to the complexes as observed in **5** and **7**. *o*-Methoxyphenoxy substituents on phosphorus in **5** and **7** adopt approximately parallel planar conformations and generate a "pocket" on either side of the ligand backbone to give sufficient space to house lattice solvents. Simple substitution reactions of **2**, **3**, and **10** with several bipyridyls clearly indicate that these complexes could serve as efficient tectons for the construction of several "conglomerates" with the assistance of bipyridyls and linear phosphorus ligands. Furthermore, complex **14** is a potential precursor for the preparation of several polynuclear gold(I) complexes, because of the presence of highly polar Au−Cl bonds. We have actively focused on these two latter aspects to create several "conglomerates" with different properties.

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(24) Armarego, W. L. F.; Perrin, D. D. *Purification of Laboratory Chemicals*, 4th ed.; Butterworth−Heinemann: Oxford, U.K., 1996.

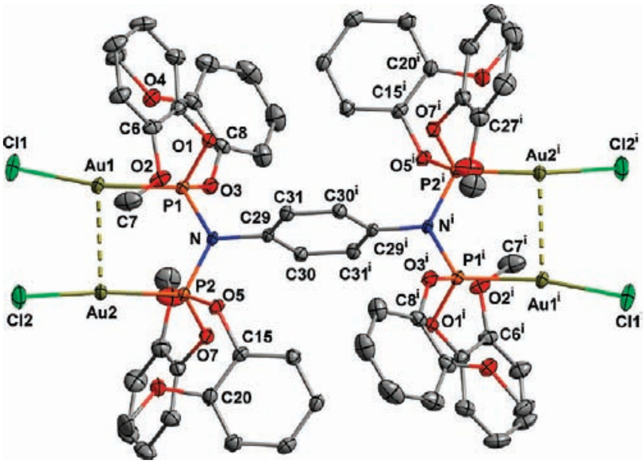

Figure 8. Molecular structure of **14**. All H atoms have been omitted for clarity. Displacement ellipsoids are drawn at the 50% probability level.

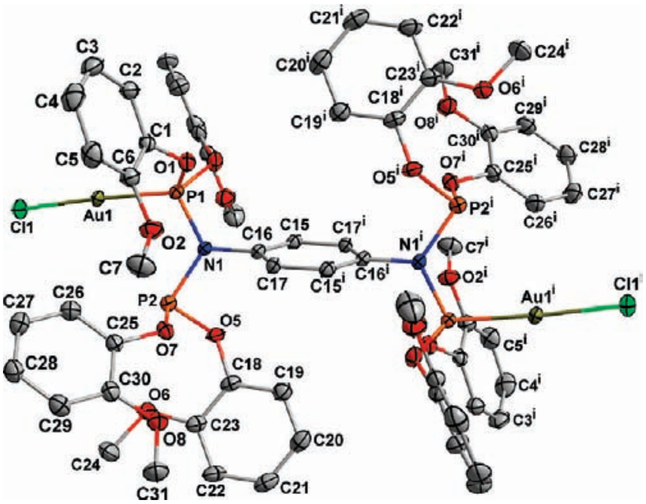

Figure 9. Molecular structure of **15**. All H atoms have been omitted for clarity. Displacement ellipsoids are drawn at the 50% probability level.

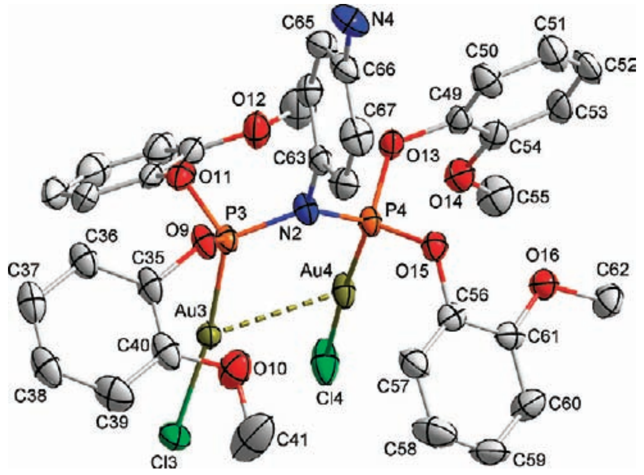

Figure 10. Molecular structure of **17**. All H atoms have been omitted for clarity. Displacement ellipsoids are drawn at the 50% probability level.

Experimental Section

General Procedures. All manipulations were performed under rigorously anaerobic conditions using Schlenk techniques. The gold(I) and silver(I) complexes were prepared with minimum exposure to light by wrapping the reaction vessel with aluminum foil. All the solvents were purified by conventional procedures and distilled prior to use.[24] The compounds p-$C_6H_4[N\{P(OC_6H_4OMe\text{-}o)_2\}_2]_2$,[13] $PhN\{P(OC_6H_4OMe\text{-}o)_2\}_2$,[25] CuBr,[26] and $AuCl(SMe_2)$[27] were prepared according to the published procedures. AgX (where X = OTf and ClO_4), 1,10-phenanthroline, 2-(piperazin-1-yl)pyrimidine, pyrazole, 2,2′-bipyridine, and 4,4′-bipyridine were purchased from Aldrich Chemical Company and used as such without further purification. [*Caution! Perchlorate salts of metal complexes with organic ligands are potentially explosive. A small amount was used in all the reactions and handled with great caution.* Except for **10**, all perchlorate compounds were determined to be resistant to shock.] Other chemicals were obtained from commercial sources and purified prior to use.

Instrumentation. The ^1H and $^{31}P\{^1H\}$ NMR (δ in ppm) spectra were recorded using a Varian VXR 300 or VXR 400 spectrometer operating at the appropriate frequencies using tetramethylsilane (TMS) and 85% H_3PO_4, as internal and external references, respectively. The microanalyses were performed using a Carlo Erba Model 1112 elemental analyzer. The melting points were observed in capillary tubes and are uncorrected.

Synthesis of $[\{Cu_2(\mu\text{-}I)_2(py)_2\}_2(\mu\text{-}P_2N\Phi NP_2)]$ (4). To 5 mL of pyridine, compound **3** (0.050 g, 0.023 mmol) was added and the mixture stirred at room temperature for 3 h. The resulting yellow solution was taken to dryness under vacuum, and the residue was dissolved in dichloromethane, layered with petroleum ether, and stored at −30 °C to give white crystals of **4**. Yield: 91% (0.049 g). Anal. Calcd. for $C_{82}H_{80}N_6O_{16}P_4Cu_4I_4$: C 42.98, H 3.52, N 3.67. Found: C 42.87, H 3.43, N, 3.60. mp >250 °C. ^1H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 8.33-6.58$ (m, 56H; Ph, Py), 3.50 (s, 24H; OCH_3). $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$, 25 °C, H_3PO_4): $\delta = 104.2$ (br s).

Synthesis of $[\{Cu_2(\mu\text{-}I)_2(C_8H_{12}N_4)_2\}_2(\mu\text{-}P_2N\Phi NP_2)]$ (5). A solution of 1-(2-pyrimidyl)piperazine (0.008 g, 0.050 mmol) in dichloromethane (5 mL) was added dropwise to a solution of **3** (0.018 g, 0.008 mmol) in acetonitrile (5 mL), and the reaction mixture was stirred at room temperature for 4 h. The resulting clear solution was concentrated and kept at room temperature for 1 day to give analytically pure white crystals of **5**. Yield: 72% (0.016 g); mp 194−196 °C (dec). Anal. Calcd. for $C_{94}H_{108}N_{18}O_{16}P_4Cu_4I_4$: C 42.90, H 4.13, N 9.58. Found: C 42.87, H 4.08, N 9.72. ^1H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 8.27$ (d, 8H; $C_4H_3N_2$), 6.76 (t, ^3J(H, H) = 4.8 Hz, 4H; $C_4H_3N_2$), 7.65−6.46 (m, 36H; C_6H_4), 3.67 (s, 24H; OCH_3), 2.49 (br s, 32H; $C_4H_8N_2$). $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$, 25 °C, H_3PO_4): $\delta = 103.9$ (br s).

Synthesis of $[\{Cu_2(\mu\text{-}I)_2(C_3H_4N_2)_2\}_2(\mu\text{-}P_2N\Phi NP_2)]$ (6). This compound was synthesized using a procedure similar to that of **5**, using **3** (0.070 g, 0.033 mmol) and pyrazole (0.013 g, 0.198 mmol). Yield: 81% (0.060 g). mp 196−198 °C (dec). Anal. Calcd. for $C_{74}H_{76}N_{10}O_{16}P_4Cu_4I_4$: C 39.55, H 3.41, N 6.23. Found: C 39.50, H 3.36, N 6.16. ^1H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 10.35$ (br s, 4H; NH), 7.99−6.15 (m, 48H; Ar, $C_3H_3N_2$), 3.55 (s, 24H; OCH_3). $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$, 25 °C, H_3PO_4): $\delta = 105.1$ (br s).

Synthesis of $[(Cu_2(\mu\text{-}I))_2I_2(C_{12}H_8N_2)_2(\mu\text{-}P_2N\Phi NP_2)]$ (7). A solution of 1,10-phenanthroline (0.012 g, 0.058 mmol) in the same solvent (5 mL) was added dropwise to a solution of **3** (0.062 g, 0.029 mmol) in acetonitrile (10 mL), and the reaction mixture was

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(25) Balakrishna, M. S.; George, P. P.; Mague, J. T. *J. Organomet. Chem.* **2004**, *689*, 3388–3394.

(26) Furniss, B. S.; Hannaford, A. J.; Smith, P. W. G.; Tatchell, A. R. *Vogel's Textbook of Practical Organic Chemistry*, 5th ed.; Longman Scientific and Technical: Harlow, England, 1989; pp 428−429.

(27) Brandys, M.-C.; Jennings, M. C.; Puddephatt, R. J. *J. Chem. Soc., Dalton Trans.* **2000**, 4601–4606.

Table 1. Crystallographic Information for Compounds **5** and **7**−**10**

	complex **5**	complex **7**	complex **8**	complex **9**	complex **10**
empirical formula	$C_{98}H_{114}Cu_4I_4N_{20}O_{16}P_4$	$C_{90}H_{82}Cu_4I_4N_8O_{16}P_4$	$C_{86}H_{81.50}Cu_4I_4N_8O_{16}P_4$	$C_{84}H_{100}Cl_4Cu_4I_4N_{10}O_{16}P_4$	$C_{104}H_{132}Ag_4Cl_4N_2O_{43}P_4$
formula weight, Fw	2713.73	2417.28	2368.73	2533.18	2795.28
cryst. system	monoclinic	monoclinic	triclinic	triclinic	triclinic
space group	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)	$P\bar{1}$(No. 2)
a	33.029(2) Å	11.5637(6) Å	17.484 (1) Å	11.8672(9) Å	13.743(2) Å
b	10.4259(6) Å	24.811(1) Å	24.135(2) Å	11.9366(9) Å	15.530(2) Å
c	36.587(2) Å	17.2689(8) Å	25.987(2) Å	18.003(1) Å	16.198(2) Å
α	90°	90°	112.878(1)°	96.277(1)°	109.135(2)°
β	112.337(1)°	108.182 (1)°	100.200(1)°	103.143(1)°	110.464(2)°
γ	90°	90°	105.222(1)°	95.784(1)°	90.280(2)°
V	11653.6(12) Å^3	4707.2(4) Å^3	9255.7(12) Å^3	2447.6(3) Å^3	3032.0(7) Å^3
Z	4	2	2	1	1
ρ_{calc}	1.547 g/cm^3	1.706 g/cm^3	1.700 g/cm^3	1.719 g/cm^3	1.531 g/cm^3
μ (Mo Kα)	1.901 mm^{-1}	2.339 mm^{-1}	2.377 mm^{-1}	2.359 mm^{-1}	0.861 mm^{-1}
F (000)	5432	2388	4678	1258	1430
T	100 K	100 K	100 K	100 K	100 K
2θ range	2.1°−27.5°	2.0°−29.2°	2.3°−25.6°	2.2°−28.0°	2.3°−26.6°
total number of reflns	190140	84294	133988	42641	81438
number of indep reflns	26841 [R_{int} = 0.080]	12414 [R_{int} = 0.045]	34555 [R_{int} = 0.054]	11706 [R_{int} = 0.062]	23267 [R_{int} = 0.083]
GOF (F^2)	1.07	1.02	1.04	1.03	0.93
$R_1{}^a$	0.0675	0.0276	0.0488	0.0450	0.0579
$wR_2{}^b$	0.1538	0.0641	0.1440	0.1059	0.1686

[a] $R_1 = \sum||F_0|-|F_c||/\sum|F_0|$. [b] $R_2 = \{[\sum w(F_0^2 - F_c^2)/\sum w(F_0^2)^2]\}^{1/2}$ and $w = 1/[\sigma^2(F_0^2) + (xP)^2]$ (where $P = (F_0^2 + 2F_c^2)/3$).

Table 2. Crystallographic Information for Compounds **12**−**15**, and **17**

	complex **12**	complex **13**	complex **14**	complex **15**	complex **17**
empirical formula	$C_{105}H_{98}Ag_4Cl_6N_{10}O_{32.50}P_4$	$C_{113.5}H_{102}Ag_4ClF_{12}N_{14}O_{29}P_4S_4$	$C_{62}H_{60}Au_4Cl_4N_2O_{16}P_4$	$C_{62}H_{60}Au_2Cl_2N_2O_{16}P_4$	$C_{34}H_{32.75}Au_2Cl_2N_{1.50}O_8P_2$
Fw	2787.99	3073.19	2142.67	1677.84	1117.10
cryst. system	triclinic	triclinic	monoclinic	monoclinic	monoclinic
space group	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)	$P2_1/n$ (No. 14)	$P2_1/c$ (No. 14)	$P2_1/n$ (No. 14)
a	19.399(1) Å	13.465(2) Å	10.7400(8) Å	11.933(5) Å	19.815(2) Å
b	16.586(1) Å	15.172(2) Å	12.1116(8) Å	15.241(6) Å	18.739(2) Å
c	19.374(1) Å	18.297(2) Å	25.674(2) Å	17.673(7) Å	20.610(2) Å
α	96.091(1)°	103.965(2)°	90°	90°	90°
β	99.812(1)°	103.251(2)°	92.880(1)°	107.117(7)°	106.594(1)°
γ	88.538(1)°	104.149(2)°	90°	90°	90°
V	6107.6(6) Å^3	3348.4(8) Å^3	3335.4(4) Å^3	3072(2) Å^3	7334.1(13) Å^3
Z	1	1	2	2	4
ρ_{calc}	1.516 g/cm^3	1.524 g/cm^3	2.134 g/cm^3	1.814 g/cm^3	2.023 g/cm^3
μ (Mo Kα)	0.893 mm^{-1}	0.797 mm^{-1}	9.094 mm^{-1}	5.033 mm^{-1}	8.277 mm^{-1}
F (000)	2816	1550	2036	1652	4266
T	100 K	100 K	100 K	100 K	100 K
2θ range	2.1°−28.4°	1.2°−24.8°	2.3°−28.3°	2.2°−29.6°	2.0°−26.0°
total number of reflns	108634	39668	57943	54500	107386
number of indep reflns	30072 [R_{int} = 0.047]	11319 [R_{int} = 0.048]	8256 [R_{int} = 0.033]	8208 [R_{int} = 0.038]	14416 [R_{int} = 0.069]
GOF (F^2)	1.06	1.06	1.06	1.04	1.04
$R_1{}^a$	0.0516	0.0669	0.0219	0.0313	0.0343
$wR_2{}^b$	0.1508	0.2023	0.0564	0.0845	0.0818

[a] $R_1 = \sum||F_0| - |F_c||/\sum|F_0|$. [b] $R_2 = \{[\sum w(F_o^2 - F_c^2)/\sum w(F_0^2)^2]\}^{1/2}$ and $w = 1/[\sigma^2(F_0^2) + (xP)^2]$ (where $P = (F_0^2 + 2F_c^2)/3$).

stirred at room temperature for 4 h. The resulting yellow solution was concentrated and kept at room temperature for 1 day to give analytically pure bright yellow crystals of **7**. Yield: 83% (0.056 g). mp 194−196 °C (dec). Anal. Calcd. for $C_{86}H_{76}N_6O_{16}P_4Cu_4I_4$: C 44.23, H 3.28, N 3.60. Found: C 44.14, H 3.21, N 3.68. ^{1}H NMR (400 MHz, [d$_6$] DMSO, 25 °C, TMS): δ = 8.06−6.70 (m, 52H; Ph, $C_{12}H_8N_2$). ^{31}P{^{1}H} NMR (162 MHz, [d$_6$] DMSO, 25 °C, H_3PO_4): δ = 104.1 (br s).

Synthesis of [(Cu$_2$(*μ*-I))$_2$I$_2$(C$_{10}$H$_8$N$_2$)$_2$(*μ*-P$_2$NΦNP$_2$)] (8). This compound was synthesized using a procedure similar to that of **7**, using **3** (0.071 g, 0.033 mmol) and 2,2′-bipyridine (0.005 g, 0.066 mmol). Yield: 89% (0.068 g). mp 230−232 °C (dec). Anal. Calcd. for $C_{82}H_{76}N_6O_{16}P_4Cu_4I_4$: C 43.06, H 3.35, N 3.67. Found: C 43.14, H 3.41, N 3.74. ^{1}H NMR (400 MHz, [d$_6$] DMSO, 25 °C, TMS): δ = 8.22−6.66 (m, 52H; Ph, $C_{10}H_8N_2$). ^{31}P{^{1}H} NMR (162 MHz, [d$_6$] DMSO, 25 °C, H_3PO_4): δ = 105.0 (br s).

Synthesis of (C$_6$H$_{12}$N$_2$CH$_2$Cl)$_2$[(Cu(Cl)(I$_2$))$_2$(NCCH$_3$)$_2$(*μ*-P$_2$NΦNP$_2$)] (9). A solution of **3** (0.030 g, 0.014 mmol) in acetonitrile (3 mL) was added dropwise to a solution of 1,4-diazabicyclo[2.2.2]octane (0.0032 g, 0.028 mmol) in dichloromethane (3 mL). The resulting solution was kept undisturbed at room temperature for 3−4 days, to give analytically pure white crystals of **9**. Yield: 60% (0.022 g). mp 174−176 °C (dec). Anal. Calcd. for $C_{84}H_{100}N_{10}Cl_4O_{16}P_4Cu_4I_4$: C 39.87, H 3.98, N 5.53. Found: C 39.40, H 4.06, N 5.44.

Synthesis of [{Ag$_2$(*μ*-ClO$_4$)$_2$(C$_4$H$_8$O)$_2$}$_2$(*μ*-P$_2$NΦNP$_2$)] (10). A solution of **1** (0.073 g, 0.060 mmol) in THF (10 mL) was added dropwise to a suspension of $AgClO_4$ (0.054 g, 0.240 mmol) also in THF (5 mL) with constant stirring. The reaction mixture was subjected to stirring at room temperature for 4 h. The resulting solution was concentrated to 4 mL under vacuum and kept at room temperature overnight to give analytically pure product **10** as white crystals. Yield: 90% (0.126 g). mp: 154−156 °C

Table 3. Selected Bond Distances and Bond Angles for Complexes **5**, **7**, and **8**

Complex **5**				Complex **7**				Complex **8**			
bond	bond distance (Å)	bond	bond angle (°)	bond	bond distance (Å)	bond	bond angle (°)	bond	bond distance (Å)	bond	bond angle (°)
P1−N9	1.680(5)	P1−N9−P2	119.8(3)	P1−N1	1.681(2)	P1−N1−P2	120.35(10)	P1−N1	1.681(5)	P1−N1−P2	120.1(3)
P2−N9	1.695(5)	P3−N10−P4	121.2(3)	P2−N1	1.690(2)	N2−Cu1−N3	81.39(8)	P2−N1	1.685(5)	P3−N4−P4	121.1(3)
P3−N10	1.685(5)	Cu1−I1−Cu2	61.11(2)	Cu1−P1	2.1630(6)	Cu1−I1−Cu2	69.87(1)	P3−N4	1.687(5)	N2−Cu2−N3	80.9(2)
P4−N10	1.690(5)	Cu1−I2−Cu2	60.78(2)	Cu2−P2	2.1875(6)	I1−Cu2−I2	119.48(1)	P4−N4	1.672(5)	N5−Cu4−N6	80.4(3)
Cu1−P1	2.173(2)	Cu3−I3−Cu4	63.12(2)	Cu1−N2	2.075(2)	P1−Cu1−N2	112.82(6)	Cu1−P1	2.181(2)	Cu1−I2−Cu2	69.93(3)
Cu2−P2	2.159(2)	Cu3−I4−Cu4	60.81(2)	Cu1−N3	2.065(2)	P1−Cu1−N3	116.72(6)	Cu2−P2	2.145(2)	Cu3−I4−Cu4	71.41(3)
Cu3−P3	2.166(2)	I1−Cu1−I2	100.47(3)	I1−Cu1	2.5943(3)	I1−Cu1−P1	118.66(2)	Cu3−P3	2.165(2)	I1−Cu1−I2	112.26(4)
Cu4−P4	2.174(2)	I1−Cu2−I2	101.71(3)	I1−Cu2	2.5702(3)	I1−Cu1−N2	105.90(6)	Cu4−P4	2.159(2)	I3−Cu3−I4	115.75(4)
Cu1−N1	2.039(6)	I3−Cu3−I4	102.23(3)	I2−Cu2	2.5178(4)	I1−Cu1−N3	114.54(6)	Cu2−N2	2.047(7)	P2−Cu2−N2	112.27(17)
Cu2−N5	2.077(6)	I3−Cu4−I4	102.69(3)			I1−Cu2−P2	121.18(2)	Cu2−N3	2.054(5)	P2−Cu2−N3	111.44(17)
Cu3−N11	2.066(6)	I1−Cu1−P1	118.27(5)			I2−Cu2−P2	119.08(2)	Cu4−N5	2.066(5)	P4−Cu4−N5	122.81(19)
Cu4−N15	2.051(6)	I2−Cu1−P1	109.40(5)					Cu4−N6	2.071(7)	P4−Cu4−N6	114.2(2)
I1−Cu1	2.7207(8)	I1−Cu2−P2	111.61(5)					Cu1−I1	2.516(1)	P2−Cu2−I2	122.93(7)
I1−Cu2	2.6178(9)	I2−Cu2−P2	115.84(5)					Cu1−I2	2.593(1)	P4−Cu4−I4	120.50(6)
I2−Cu1	2.6557(9)	I3−Cu3−P3	110.97(5)					Cu2−I2	2.586(1)	P1−Cu1−I1	130.21(6)
I2−Cu2	2.7109(9)	I4−Cu4−P4	106.22(5)					Cu3−I3	2.497(1)	P1−Cu1−I2	117.17(6)
I3−Cu3	2.5886(9)	P1−Cu1−N1	120.31(18)					Cu3−I4	2.564(1)	P3−Cu3−I3	125.84(7)
I3−Cu4	2.6847(9)	P2−Cu2−N5	124.47(19)					Cu4−I4	2.637(1)	P3−Cu3−I4	118.04(7)
I4−Cu3	2.7821(9)	P3−Cu3−N11	134.36(18)								
I4−Cu4	2.6711(9)	P4−Cu4−N15	121.64(18)								

Table 4. Selected Bond Distances and Bond Angles for Complexes **9**, **10**, and **12**

Complex **9**				Complex **10**				Complex **12**			
bond	bond distance (Å)	bond	bond angle (°)	bond	bond distance (Å)	bond	bond angle (°)	bond	bond distance (Å)	bond	bond angle (°)
P1−N1	1.693(3)	P1−N1−P2	119.8(2)	P1−N1	1.665(4)	P1−N1−P2	121.47(18)	P1−N5	1.684(3)	P1−N5−P2	120.65(18)
P2−N1	1.675(4)	I1−Cu1−I2	101.7(4)	P2−N1	1.679(4)	P1−Ag1−O9	116.27(11)	P2−N5	1.661(3)	P3−N6−P4	120.51(18)
P1−Cu1	2.190(1)	I1−Cu2−I2	105.9(4)	Ag1−P1	2.338(1)	P1−Ag1−O13	123.12(10)	P3−N6	1.680(3)	P1−Ag1−N1	142.88(9)
P2−Cu2	2.184(1)	I1−Cu1−I3	111.35(1)	Ag2−P2	2.343(1)	P1−Ag1−O18	135.22(10)	P4−N6	1.668(3)	P1−Ag1−N2	143.67(9)
Cu1−I1	2.60(2)	I2−Cu1−I3	108.74(3)	P1−O1	1.615(3)	P2−Ag2−O10	125.07(11)	Ag1−P1	2.311(1)	P2−Ag2−N3	147.80(9)
Cu1−I2	2.764(1)	I1−Cu2−N2	106.7(5)	P1−O3	1.618(3)	P2−Ag2−O13	129.74(9)	Ag2−P2	2.322(1)	P2−Ag2−N4	139.30(9)
Cu1−I3	2.568(1)	I2−Cu2−N2	107.05(10)	P2−O5	1.612(3)	P2−Ag2−O17	138.65(8)	Ag3−P3	2.304(1)	P3−Ag3−N7	139.66(9)
Cu2−I1	2.524(19)	P1−Cu1−I1	105.1(4)	P2−O7	1.609(3)	Ag1−P1−N1	119.07(13)	Ag4−P4	2.333(1)	P3−Ag3−N8	144.06(8)
Cu2−I2	2.6928(6)	P1−Cu1−I2	112.07(4)	Ag1−O9	2.434(4)	Ag2−P2−N1	120.14(12)	Ag1−N1	2.261(4)	P4−Ag4−N9	147.24(9)
Cu2−N2	1.993(4)	P2−Cu2−I1	114.1(4)	Ag1−O13	2.468(4)	O9−Ag1−O13	95.65(15)	Ag1−N2	2.258(3)	P4−Ag4−N10	140.52(9)
N3−C42	1.486(7)	P2−Cu2−I2	106.36(3)	Ag1−O18	2.259(4)	O9−Ag1−O18	87.43(14)	Ag2−N3	2.281(3)	Ag1−P1−N5	122.19(11)
C42−Cl1	1.778(7)	P1−Cu1−I3	116.80(4)	Ag2−O10	2.400(5)	O13−Ag1−O18	88.51(13)	Ag2−N4	2.262(4)	Ag2−P2−N5	119.55(11)
		P2−Cu2−N2	116.08(11)	Ag2−O13	2.589(4)	O10−Ag2−O13	75.17(16)	Ag3−N7	2.267(3)	Ag3−P3−N6	120.95(11)
		Cu1−I1−Cu2	65.9(5)	Ag2−O17	2.285(3)	O10−Ag2−O17	79.87(15)	Ag3−N8	2.241(3)	Ag4−P4−N6	119.39(12)
		Cu1−I2−Cu2	61.45(2)	Ag1−Ag2	3.0900(8)	O13−Ag2−O17	85.31(11)	Ag4−N9	2.292(3)	N1−Ag1−N2	73.10(12)
								Ag4−N10	2.265(3)	N3−Ag2−N4	72.57(12)
								Ag1−Ag2	3.0907(5)	N7−Ag3−N8	73.50(12)
								Ag3−Ag4	2.9954(4)	N9−Ag4−N10	72.17(12)

Table 5. Selected Bond Distances and Bond Angles for Complexes **13** and **14**

Complex **13**				Complex **14**			
bond	bond distance (Å)	bond	bond angle (°)	bond	bond distance (Å)	bond	bond angle (°)
P1−N4	1.687(7)	P1−N4−P2	125.2(3)	P1−N1	1.674(2)	P1−N1−P2	124.84(1)
P2−N4	1.686(7)	N1−Ag1−N2	97.9(3)	P2−N1	1.676(2)	P1−Au1−Cl1	169.97(3)
P1−O1	1.616(6)	N1−Ag1−N3	87.7(3)	P1−O1	1.603(2)	P2−Au2−Cl2	168.37(3)
P1−O3	1.613(6)	N2−Ag1−N3	95.1(3)	P1−O3	1.589(2)	Au1−P1−O1	113.39(9)
P2−O5	1.602(7)	N5−Ag2−N6	96.8(2)	P2−O5	1.600(2)	Au1−P1−O3	118.83(9)
P2−O7	1.613(6)	N5−Ag2−N7	93.5(3)	P2−O7	1.589(2)	Au1−P1−N1	118.44(9)
Ag1−P1	2.338(2)	N6−Ag2−N7	101.9(3)	P1−Au1	2.1981(8)	Au2−P2−O5	112.26(9)
Ag2−P2	2.397(2)	P1−Ag1−N1	131.0(2)	P2−Au2	2.2003(8)	Au2−P2−O7	119.82(8)
Ag1−N1	2.312(8)	P1−Ag1−N2	122.7(2)	Au1−Cl1	2.2657(8)	Au2−P2−N1	117.33(9)
Ag1−N2	2.292(7)	P1−Ag1−N3	112.2(2)	Au2−Cl2	2.2852(9)		
Ag1−N3	2.407(9)	P2−Ag2−N5	120.7(2)	Au1−Au2	3.1019(8)		
Ag2−N5	2.361(8)	P2−Ag2−N6	122.2(2)				
Ag2−N6	2.336(7)	P2−Ag2−N7	116.4(2)				
Ag2−N7	2.395(8)						

(dec). [*Caution! Compound **10** explodes violently at 170 °C*. In all cases, 1−2 mg of perchlorate complexes have been used to note the melting point.] Anal. Calcd. for $C_{78}H_{92}Cl_4N_2O_{36}P_4Ag_4$: C 40.19, H 3.98, N 1.20. Found: C 40.25, H 3.92, N 1.21. ^1H NMR (400 MHz, [d_6] DMSO, 25 °C, TMS): $\delta = 7.73-6.69$ (m, 36H; Ph), 3.74 (s, 24H; OCH_3), 3.62 (t, 16H; OCH_2), 1.77 (t, 16H; CH_2). $^{31}P\{^1H\}$ NMR (162 MHz, [d_6] DMSO, 25 °C, H_3PO_4): $\delta = 120.8$ (br s).

Synthesis of [{(*μ*-PNP)$_2$Ag$_2$}$_2$(*μ*-P$_2$NΦNP$_2$)](ClO$_4$)$_4$ (11). A solution of PhN(P(OC$_6$H$_4$OMe-*o*)$_2$)$_2$ (PNP) (0.104 g, 0.162 mmol) in THF (10 mL) was added dropwise to a solution of **10** (0.094 g, 0.040 mmol) also in THF (10 mL) with constant stirring. The

Table 6. Selected Bond Distances and Bond Angles for Complexes **15** and **17**

Complex **15**				Complex **17**			
bond	bond distance (Å)	bond	bond angle (°)	bond	bond distance (Å)	bond	bond angle (°)
P1−N1	1.656(4)	P1−N1−P2	118.75(19)	P3−N2	1.664(6)	P3−N2−P4	122.7(4)
P2−N1	1.741(3)	P1−Au1−Cl1	176.62(4)	P4−N2	1.681(6)	P3−Au3−Cl3	170.16(8)
P1−O1	1.596(3)	Au1−P1−O1	118.50(11)	P3−O9	1.595(5)	P4−Au4−Cl4	175.57(7)
P1−O3	1.594(3)	Au1−P1−O3	117.44(11)	P3−O11	1.608(6)	Au3−P3−O9	115.3(2)
P2−O5	1.624(3)	Au1−P1−N1	112.37(12)	P4−O13	1.585(6)	Au3−P3−O11	113.33(19)
P2−O7	1.633(3)	N1−P1−O1	104.88(16)	P4−O15	1.599(5)	Au3−P3−N2	120.8(2)
P1−Au1	2.205(1)	N1−P1−O3	103.37(16)	P3−Au3	2.198(2)	Au4−P4−O13	120.3(2)
Au1−Cl1	2.282(1)	O1−P1−O3	98.18(15)	P4−Au4	2.198(2)	Au4−P4−O15	114.6(2)
N1−C16	1.446(5)	N1−P2−O5	94.25(15)	Au3−Cl3	2.264(2)	Au4−P4−N2	114.8(2)
		N1−P2−O7	100.79(16)	Au4−Cl4	2.272(2)		
		O5−P2−O7	98.69(14)	Au3−Au4	3.0975(4)		

reaction mixture was subjected to stirring at room temperature for 2 h. The resulting solution was concentrated to 4 mL, layered with 3 mL of *n*-hexane, and kept at room temperature for one day to give analytically pure white microcrystals of **11**. Yield: 65% (0.121 g). mp 132−134 °C (dec). Anal. Calcd. for $C_{198}H_{192}N_6O_{64}P_{12}Ag_4Cl_4$: C 51.42, H 4.18, N 1.82. Found: C 51.40, H 4.15, N 1.84. ^{1}H NMR (400 MHz, [d$_6$] DMSO, 25 °C, TMS): $\delta = 7.31-6.52$ (m, 120H; Ph), 3.77 (br s, 72H; OCH_3). $^{31}P\{^1H\}$ NMR (162 MHz, [d$_6$] DMSO, 25 °C, H_3PO_4): $\delta = 120.1$ (br s).

Synthesis of $[\{Ag_2(C_{10}H_8N_2)_2\}_2(\mu\text{-}P_2N\Phi NP_2)](ClO_4)_4$ (12). A solution of **1** (0.051 g, 0.042 mmol) in CH_2Cl_2 (6 mL) was added dropwise to a suspension of $AgClO_4$ (0.038 g, 0.167 mmol) also in CH_2Cl_2 (8 mL) with constant stirring. The reaction mixture was stirred for 2 h and then a solution of 2,2′-bipyridine (0.026 g, 0.167 mmol) in CH_2Cl_2 (3 mL) was added dropwise. The resulting solution was concentrated to 4 mL, layered with 2 mL of *n*-hexane, and stored at −30 °C for 3 days to give white crystals of **12**. Yield: 70% (0.078 g). mp 176−178 °C (dec). Anal. Calcd. for $C_{102}H_{92}N_{10}O_{32}P_4Ag_4Cl_4$: C 45.93, H 3.48, N 5.25. Found: C 46.01, H, 3.40, N 5.28. ^{1}H NMR (400 MHz, [d$_6$] DMSO, 25 °C, TMS): $\delta = 8.22-6.92$ (m, 68H; Ph, $C_{10}H_8N_2$), 3.68 (s, 24H; OCH_3). $^{31}P\{^1H\}$ NMR (162 MHz, [d$_6$] DMSO, 25 °C, H_3PO_4): $\delta = 125.7$ (br s).

Synthesis of $[\{Ag_2(C_{10}H_8N_2)_2(CH_3CN)_2\}_2(\mu\text{-}P_2N\Phi NP_2)]_n(OTf)_{4n}$ (13). A solution of **1** (0.035 g, 0.029 mmol) in CH_2Cl_2 (6 mL) was added dropwise to a suspension of AgOTf (0.030 g, 0.117 mmol) also in CH_2Cl_2 (8 mL) with constant stirring. The reaction mixture was allowed to stir at room temperature for 2 h and then was layered with an acetonitrile (3 mL) solution of 4,4′-bipyridine (0.018 g, 0.117 mmol). Analytically pure white crystals of **13** formed after the mixture was allowed to stand at room temperature for several days. Yield: 54% (0.048 g). mp 160−162 °C (dec). Anal. Calcd. for $C_{114}H_{104}F_{12}N_{14}O_{28}P_4S_4Ag_4$: C 45.19, H 3.46, N 6.47, S 4.23. Found: C 45.25, H 3.40, N 6.52, S 4.20.

Synthesis of $[(Au_2Cl_2)_2(\mu\text{-}P_2N\Phi NP_2)]$ (14). A solution of **1** (0.031 g, 0.026 mmol) in CH_2Cl_2 (5 mL) was added dropwise to a solution of $AuCl(SMe_2)$ (0.030 g, 0.102 mmol) also in CH_2Cl_2 (5 mL). The reaction mixture was subjected to stirring at room temperature for 4 h. The resulting solution was concentrated to 3 mL, followed by the addition of *n*-hexane, to give a white precipitate of **14**. White crystals were obtained upon recrystallization from a 1:1 dichloromethane/*n*-hexane mixture at −30 °C. Yield: 87% (0.048 g). mp 204−206 °C (dec). Anal. Calcd. for $C_{62}H_{60}N_2O_{16}P_4Au_4Cl_4$: C 34.75, H 2.82, N 1.31. Found: C 34.64, H 2.75, N 1.29. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 7.97-6.72$ (m, 36H; Ph), 3.81 (s, 24H; OCH_3). $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$, 25 °C, H_3PO_4): $\delta = 114.3$ (s).

Synthesis of $[(AuCl)_2(P_2N\Phi NP_2)]$ (15). Method 1. A solution of $PhN(P(OC_6H_4OMe\text{-}o)_2)_2$ (0.044 g, 0.068 mmol) in CH_2Cl_2 (5 mL) was added dropwise to a stirred solution of **14** (0.073 g, 0.034 mmol) that also was in CH_2Cl_2 (7 mL). The reaction mixture was subjected to stirring at room temperature for 8 h. The resulting solution was concentrated to 5 mL, layered with 3 mL of *n*-hexane, and kept at −30 °C for one day to give analytically pure white crystals of **15** in the first crop. Yield: 76% (0.043 g).

Method 2. A solution of $AuCl(SMe_2)$ (0.039 g, 0.132 mmol) in THF (5 mL) was added dropwise to a solution of **1** (0.080 g, 0.066 mmol) that also was in THF (8 mL). The reaction mixture was refluxed for 6 h and then cooled to room temperature. The solution was concentrated to 5 mL, layered with 3 mL of *n*-hexane, and kept at −30 °C for one day to give analytically pure white crystals of **15**. Yield: 88% (0.098 g). mp 188−190 °C (dec). Anal. Calcd. for $C_{62}H_{60}N_2O_{16}P_4Au_2Cl_2$: C 44.38, H 3.60, N 1.67. Found: C 44.42, H 3.50, N 1.61.^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 7.64-6.63$ (m, 36H; Ph), 3.60 (br s, 12H; OCH_3), 3.63 (br s, 12H; OCH_3). $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$, 25 °C, H_3PO_4): $\delta = 132.2$ (d, $^2J(P,P) = 348$ Hz), 110.5 (d).

X-ray Crystallography. A crystal of each of the compounds **5**, **7**−**10**, **12**−**14**, **15**, and **17** suitable for X-ray crystal analysis was mounted in a Cryoloop with a drop of Paratone oil and placed in the cold nitrogen stream of the Kryoflex attachment of a Bruker APEX CCD diffractometer. Full spheres of data were collected using 606 scans in ω (0.3° per scan) at $\phi = 0°$, 120°, and 240° (**13**) or a combination of three sets of 400 scans in ω (0.5° per scan) at $\varphi = 0°$, 90°, and 180° plus two sets of 800 scans in φ (0.45° per scan) at $\omega = -30°$ and 210° (**5**, **7**−**10**, **12**, **14**, **15**, and **17**) under the control of the SMART software package[28a] (**10**, **12**, and **14**) or the APEX2 program suite[28b] (**5**, **7**−**9**, **13**, **15**, and **17**). The raw data were reduced to F^2 values using the SAINT+ software[29] and global refinements of unit-cell parameters using 1448−9967 reflections chosen from the full data sets were performed. Multiple measurements of equivalent reflections provided the basis for empirical absorption corrections, as well as corrections for any crystal deterioration during the data collection (SADABS,[30] for all but **10** and **13**). In the cases of **10** and **13**, initial attempts to obtain a unit cell were unsuccessful and further analysis of 1280 and 2110 reflections, respectively, with $I/\sigma(I) \geq 15$ with CELL_NOW,[31] suggested that the crystal of **10** had a triclinic cell twinned by a 180° rotation about the reciprocal direction 1,0,$^1/_2$, whereas for **13**, the large majority of the crystal consisted of a triclinic cell twinned by a 180° rotation about the real axis 1,1,0. Processing of the raw intensity data for these structures was accomplished with the multicomponent version of SAINT,[28] under the control of the two-component input file

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(28) (a) *SMART, Version 5.625*; Bruker-AXS: Madison, WI, 2000. (b) *APEX2, Version 2.1-0*; Bruker-AXS: Madison, WI, 2006.

(29) *SAINT+, Versions 6.35A and 7.34A*; Bruker-AXS: Madison, WI, 2002, 2006.

(30) Sheldrick, G. M. *SADABS, Versions 2.05 and 2007/2*; University of Göttingen: Göttingen, Germany, 2002, 2007.

(31) Sheldrick, G. M. *CELL_NOW*; University of Göttingen: Göttingen, Germany, 2005.

generated by CELL_NOW. The empirical absorption correction was performed with TWINABS,[32] which also provided a one-component reflection set that was used to solve the structures and perform the initial refinement. The structures were solved by direct methods (for **5**, **7**−**10**, **12**, **13**, and **17**) or the positions of the heavy atoms were obtained from a sharpened Patterson function (for **14** and **15**). All structures were refined by full-matrix least-squares procedures using the SHELXTL program package.[33] H atoms were placed in calculated positions and included as riding contributions with isotropic displacement parameters tied to those of the attached non-H atoms. For **8**, the *o*-methoxyphenoxy substituents built on C52 and C59 were each disordered over two resolvable sites, as was the THF molecule coordinated to silver; in **13**, the *o*-methoxyphenoxy substituent built on C32 is disordered over two sites; and in **12**, the perchlorate ion containing Cl4 is disordered over two sites with two O atoms in common. All of these were refined subject to the restraints that both orientations of each group have equivalent geometry and that these approximate ideal geometry. In the case of **9**, inspection of difference maps in the vicinity of atoms initially assigned as I1 and I3, as well as the equivalent isotropic displacement parameters for these two atoms, suggested partial occupancy of these ligating sites by chloride. The evidence consisted of the appearance of partially resolved peaks in the difference map slightly closer to the metal atoms and equivalent isotropic displacement parameters for I1 and I3 significantly larger than that for I2, which appeared well-behaved. Assignment of the partially resolved peaks as Cl and refinement of the occupancy factors of Cl and I in both bridging and terminal sites subject to their sum at each location being 1.0 led to the values presented in the Results and Discussion section. In addition, the entire cation seems to be disordered to some extent, but because the only well-resolved part of the disorder involved the Cl atom, this was the only part of this disorder that was modeled. In **17**, there are two independent $R-C_6H_4N(P(OR')_2AuCl)_2$ (where R = H, NH_2 and $R' = o\text{-}C_6H_4OMe$) moieties in the asymmetric unit, each of which is a mixture of the R = H and $R = NH_2$ complexes. Based on inspection of difference maps and trial refinements of occupancy parameters for the nitrogen of the $R = NH_2$ substituent, there seemed to be a 70:30 mixture in the first site and a 30:70 mixture in the other.

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Supporting Information Available: X-ray crystallographic files in CIF format for the structure determinations of **5**, **7**−**10**, **12**−**14**, **15**, and **17**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(32) Sheldrick, G. M. *TWINABS, Version 2007/5*; University of Göttingen: Göttingen, Germany, 2007.

(33) (a) *SHELXTL, Version 6.10*; Bruker-AXS: Madison, WI, 2000. (b) Sheldrick, G. M. *SHELXS97 and SHELXL97*; University of Göttingen: Göttingen, Germany, 1997.