Inorg. Chem. **2003**, *42*, 5311–5319

Inorganic Chemistry

Article

Syntheses and Structures of Dinuclear Gold(I) Dithiophosphonate Complexes and the Reaction of the Dithiophosphonate Complexes with Phosphines: Diverse Coordination Types

Angelo Maspero,[†,‡] Ibrahim Kani,[†] Ahmed A. Mohamed,[†] Mohammad A. Omary,[*,§]
Richard J. Staples,[||] and John P. Fackler, Jr.[*,†]

Department of Chemistry and Laboratory for Molecular Structure and Bonding,
Texas A&M University, P.O. Box 30012 College Station, Texas 77842-3012, Dipartimento di
Scienze Chimiche, Fisiche e Matematiche, Universita' dell'Insubria, Via Valleggio 11,
22100 Como, Italy, Department of Chemistry, University of North Texas, P.O. Box 305070,
Denton, Texas 76203, and Department of Chemistry and Chemical Biology, Harvard University,
12 Oxford Street, Cambridge, Massachusetts 02138

Received January 31, 2003

The dinuclear gold(I) dithiophosphonate complex, $[Au_2(dtp)_2]$ (**1**), where dtp = $[S_2P(R)(OR')]^-$ with R = p-C_6H_4-OCH_3; R′= c-C_5H_9, has been synthesized and its reaction studied with the phosphine ligands PPh_3 and $Ph_2P(CH_2)_n$-PPh_2 (n = 1–4). Compound **1** contains two gold atoms homobridged by the anionic dithiophosphonate ligand, forming an eight-membered ring complex in a chair form. After the reaction of **1** with diphosphine ligands, the dinuclear open-ring complexes $Au_2(dppm)(dtp)_2$ (**2**), $Au_2(dppe)(dtp)_2$ (**3**), $Au_2(dppp)(dtp)_2$ (**4**), $Au_2(dppb)(dtp)_2$ (**5**) were formed (dppm = diphenylphosphinomethane; dppe = diphenylphosphinoethane; dppp = diphenylphosphinopropane; dppb = diphenylphosphinobutane). The reaction with dppm is stoichiometry-dependent. Thus, when **1** reacts with 2 equiv of dppm, the ionic complex $[Au_2(dppm)_2(dtp)]$dtp forms. This dtp counterion was exchanged with tetrafluoroborate to yield $[Au_2(dppm)_2(dtp)]BF_4$, the crystallization of which afforded two interconvertible isomers, **6**-yellow and **7**-white. Reaction of **1** with PPh_3 affords the tetracoordinate mononuclear complex $[Au(dtp)(PPh_3)_2]$ (**8**). The molecular structures of **1**–**8** were confirmed by X-ray crystallography and show multiple coordination modes and geometries. The crystal structures of **1** and its reaction products with dppm (**2**, **6**, **7**) show short intramolecular Au···Au aurophilic bonding interactions of 2.95–3.10 Å while no intermolecular interactions were discernible. However, reaction products of **1** with longer-chain $Ph_2P(CH_2)_nPPh_2$ ligands, n = 2–4, exhibit structures that lack both intra- and intermolecular Au···Au interactions.

Introduction

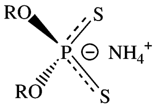
Gold(I) thiolate complexes have been used in a variety of applications in modern technology[1] such as photosensitizers for photographic emulsions[2] and luminescence-based chemical sensors.[3] A variety of gold(I) thiolate and phosphine thiolate complexes of potential application in medicine such as Auranofin, Solganol, and Myochrysine have been used for the treatment of rheumatoid arthritis in humans as well as skin disease in cats and dogs.[4−6] Thiophosphorus ligands represent an important class of S-donor ligands. Members of this class include dithiophosphates, dithiophosphonates, and dithiophosphinates. Generally, organophosphor-l,l-dithiolate ligands can be synthesized as ammonium salts by reacting Lawesson's reagent, $[S_2P(p\text{-}C_6H_4OMe)]_2$, with the

---

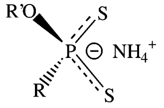
* Corresponding author. E-mail: fackler@mail.chem.tamu.edu.
[†] Texas A&M University.
[‡] Universita' dell'Insubria.
[§] University of North Texas.
[||] Harvard University.

[1] (a) *Gold*: *Progress in Chemistry, Biochemistry and Technology*; Schmidbaur, H., Ed.; John Wiley & Sons: New York, 1999. (b) Murray, R. W. *Acc. Chem. Res.* **1980**, *13*, 135. (c) Roberts, G. G. *Adv. Phys.* **1985**, *34*, 475. (d) Cheng, S.; Peng, G.-Z.; Clearfield, A. *Ind. Eng. Chem. Prod. Res. Dev.* **1984**, *23*, 2. (e) Clearfield, A. In *New Developments in Ion Exchange Materials*; Abe, M., Kataoka, T., Suzuki, T., Eds.; Kodansha, Ltd.: Tokyo, 1991. (f) Wang, J. D.; Clearfield, A.; Peng. G.-Z. *Mater. Chem. Phys.* **1993**, *35*, 208. (g) Alberti, G.; Casciola, M.; Palombari, R. *Solid State Ionics* **1993**, *61*, 241. (h) Vermeulen, L. A.; Thompson, M. E. *Nature* **1992**, *358*, 656. (i) Vermeulen, L. A.; Snover, J. L.; Sapochak, L. S.; Thompson, M. E. *J. Am. Chem. Soc.* **1993**, *115*, 11767. (j) Cao, G.; Hong, H.; Mallouk, T. E. *Acc. Chem. Res.* **1992**, *25*, 420.

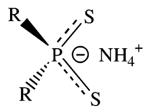
10.1021/ic034114y CCC: $25.00



dithiophosphate



dithiophosphonate (dtp)



dithiophosphinate

appropriate alcohol in benzene by bubbling NH_3(g) through the solution.[7]

Dithiophosphonate complexes are known to possess biologically important properties[8] and may also inhibit hydrocarbon oxidation.[9] *O*-Benzyl and *O*-allyl dithiophosphonates have been used as insecticides[10] and nematocides.[11,12] Dithiophosphonates of the general formula ArO(R)P(S)SH (ArO = hindered phenolic group, R = alkoxy, amino, alkylthio) and their salts are useful as antioxidants in lubricants and plastics.[13] The coordination patterns, molecular structures, and supramolecular associations in dithiophosphates, $[S_2P(OR)_2]^-$, dithiophosphinates, $[S_2PR_2]^-$, and related compounds have been reviewed by Haiduc;[14] however, only few reports are available on the chemistry of dithiophosphonates and their complexes. The synthesis and characterization of dithiphosphonates with some metals such as Cu(I) and Cr(III) have been reported. The structures of new copper bis(4-ethoxyphenyl-*O*-alkyl)dithiophosphonate and chromium tris(4-ethoxyphenyl-*O*-methyl, -ethyl, or -isopropyl)dithiophosphonate complexes were reported by Haiduc et al.[15] Our group has reported the first dinuclear Au(I) dithiophosphonate (dtp) complexes of the type $[AuS_2PR(OR')]_2$ (R = Ph, R′ = Et; R = *p*-$C_6H_4OCH_3$, R′ = $SiPh_3$; R = Ph, R′ = C_5H_9; R = *p*-C_6H_4OMe, R′ = (1S,5S,2S)-(−)-menthyl), and R = Fc, R′ = $(CH_2)_2O(CH_2)_2OMe$).[16]

Organophosphor-1,1-dithiolato ligands, which coordinate to two or more metal atoms, lead to supramolecular associations. In such cases, the ligand participates in primary bond formation while additional interactions (such as metal−metal interactions in d^{10} elements) may lead to dimeric, trimeric, or supramolecular association. The presence of metal−metal interactions was reported in Au(I) complexes[17] through aurophilic metal−metal bonding.[18] Homobridged and heterobridged Au(I) dimers with dithiolate,[19] dithiocarbamate,[3,20] and diphosphine[21] ligands have been reported. The photophysical properties of these complexes are of interest due to the large polarizability of metal−ligand bonds and the observation of visible luminescence properties in many d^{10} closed-shell complexes.[22,23]

Here we report the synthesis of the dinuclear dithiophosphonatogold(I) complex $[AuS_2P(p\text{-}C_6H_4OCH_3)(O\text{-}c\text{-}C_5H_9)]_2$ and its reactions with a series of phosphine ligands that includes bis(diphenylphosphino)methane (dppm), bis(diphenylphosphino)ethane (dppe), bis(diphenylphosphino)propane (dppp), bis(diphenylphosphino)butane (dppb), and triphenylphosphine. All compounds have been characterized by X-ray crystallography, NMR spectroscopy, and chemical

---

(2) (a) Deaton, J. C.; Luss, H. R. *J. Chem. Soc., Dalton Trans.* **1999**, 3163. (b) Lushington, K. J.; Gysling, H. J. Gold Chemical Sensitizers for Silver Halides. Eastman Kodak Co., U.S. Patent 5,759,761, 1998. (c) Lok, R.; White, W. W. Photographic Elements Containing New Gold(I) Compounds. Eastman Kodak Co., U.S. Patent 5,620,841, 1997. (d) Deaton, J. C. Photographic Silver Halide Material Comprising Gold Compound. Eastman Kodak Co. Eur. Pat. Appl. Patent 560209 Al, 1993. (e) Deaton, J. C. Silver halide photographic material containing gold compound. Eastman Kodak Co.. U.S. Patent 5,049,485, 1991.

(3) Mansour, M. A.; Connick, W. B.; Lachicotte, R. J.; Gysling, H. J.; Eisenberg, R. *J. Am. Chem. Soc.* **1997**, *117*, 11329.

(4) (a) Shaw, C. F., III, p 257 in ref la. (b) Sadler, P. S. *Adv. Inorg. Chem.* **1991**, *36*, 1. (c) Parish, R. V.; Cottrill, S. M. *Gold Bull.* **1987**, *20*, 3. (d) Coffer, M. T.; Shaw, C. F., III; Eidsness, M. K.; Watkins, J. W., II; Elder, R. L. *Inorg. Chem.* **1986**, *25*, 333.

(5) Parish, R. V.; Cottrill, S. M. *Gold Bull.* **1987**, *20, 3.*

(6) (a) Mohamed, A. A.; Abdou, H. E.; Chen, J.; Bruce, A. E.; Bruce, M. R. M. *Comments on Inorg. Chem.* **2002**, *23*, 321. (b) Mohamed, A. A.; Chen, J.; Krause Bauer, J. A. Bruce, A. E.; Bruce, M. R. M. *Inorg. Chem.* **2003**, *42*, 2203. (c) Shaw, C. F., III. *Chem. Rev.* **1999**, *99*, 2589.

(7) van Zyl, W. E.; Fackler, J. P., Jr. *Phosphorus, Sulfur and Silicon*, **2000**, *167*, 117.

(8) Livingstone, E.; Mikhelson, A. E. *Inorg. Chem.* **1970**, *9*, 2545.

(9) Shopov, D.; Yordanov, N. D. *Inorg. Chem.* **1970**, *9*, 1943.

(10) Patnaik, P. *A Comprehensive Guide to the Hazardous Properties of Chemical Substances*; Van Nostrand Reinhold: New York, 1992; Chapter 40 and references therein.

(11) Chavdarian, C. G. Preparation of 0-(substituted benzyl) dithiophosphonate intecticides. Stauffer Chemical Co. U.S. Patent 4,683,225, 1987.

(12) Chavdarian, C. G. O-(substituted allylic) dithiophosphonate insecticides. Stauffer Chemical Co. U.S. Patent 4,656,164, 1987,

(13) (a) Klaman, D.; Ed. *Lubricants and Related Products*; Verlag Chemie, Weinheim, Germany, 1984. (b) Colclough, T. *Ind. Eng. Chem. Res.* **1987**, *26*, 1888. (c) Dumdum, J. M.; Mendelson, L. T.; Pilling, *R. L.* U.S. Patent 4,908,142, 1990; *Chem. Abstr.* **1990**, *112*, 201925.

(14) (a) Haiduc, I.; Sowerby, D. B.; Lu, S.-F. *Polyhedron* **1995**, *14*, 3389. (b) Haiduc, I. *J. Organomet. Chem.* **2001**, *623*, 29.

(15) Haiduc, I.; Cozar, O.; Micu-Semeniuc, R.; Mezei, G.; Armenean, M. *J. Mol. Struct.* **1999**, *482*−*483*, 153.

(16) (a) van Zyl, W. E.; Staples, R. J.; Fackler, J. P., Jr. *Inorg. Chem. Commun.* **1998**, *1*, 51. (b) van Zyl, W. E.; López-de-Luzuriaga, J. M.; Fackler, J. P., Jr. *J. Mol. Struct.* **2000**, *516*, 99. (c) van Zyl, W. E.; López-de-Luzuriaga, J. M.; Mohamed, A. A.; Staples, R. J.; Fackler, J. P., Jr. *Inorg. Chem.* **2002**, *41*, 4579.

(17) (a) Jones, P. G. *Gold Bull.* **1981**, *14*, 102. (b) Schmidbaur, H. *Interdiscip. Sci. Rev.* **1992**, *17*, 23. (c) Pathanemi, S. S.; Desiraju, G. R. *J. Chem. Soc., Dalton Trans.* **1993**, 319.

(18) (a) Pyykkö, P.; Li, J.; Runeberg, N. *Chem. Phys. Lett.* **1994**, *218*, 133. (b) Pyykkö, P. *Chem. Rev.* **1997**, *3*, 597.

(19) (a) Preisenberger, M.; Bauer, A.; Schier, A.; Schmidbaur, H. *J. Chem. Soc., Dalton Trans.* **1997**, 4753. (b) Khan, M. N. I.; Wang, S.; Fackler, J. P., Jr. *Inorg. Chem.* **1989**, *28*, 3579. (c) Bishop, P.; Marsh, P.; Brisdon, A. K.; Brisdon, B. J.; Mahon, M. F. *J. Chem. Soc., Dalton Trans.* **1998**, 675.

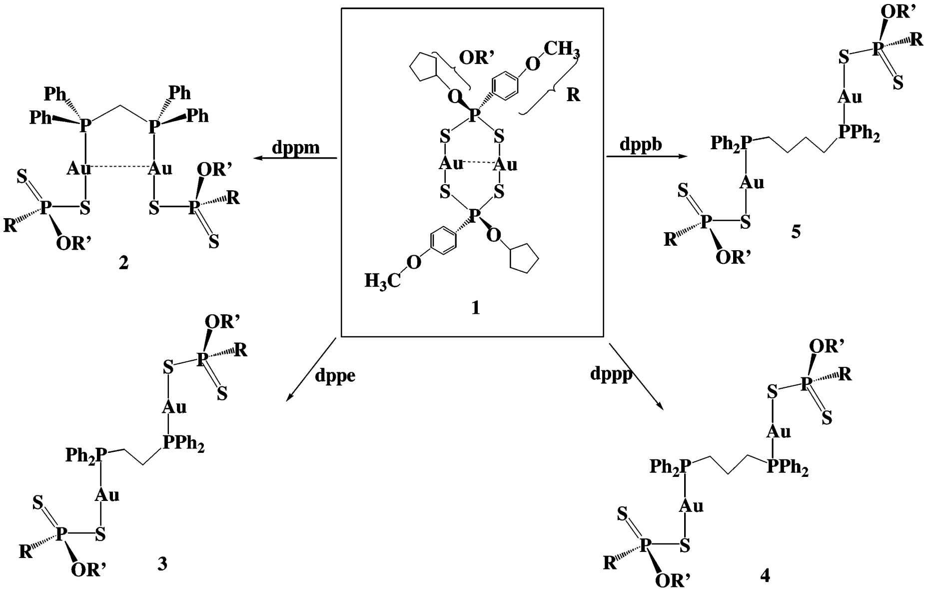
(20) (a) Bardaji, M.; Jones, P. G.; Laguna, A.; Laguna, M. *Organometallics* **1995**, *14*, 1310. (b) Fernandez, E. J.; Lopez-de-Luzuriga, J. M.; Monge, M.; Olmos, E.; Gimeno, M. C.; Laguna, A.; Jones, P. G. *Inorg. Chem.* **1998**, *37*, 5532.

(21) (a) Pyykkö, P.; Zhao, Y. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1894. (b) Schmidbaur, H. *Chem. Soc. Rev.* **1995**, 391. (c) Vickery, J. C.; Balch, A. L. *Inorg. Chem.* **1997**, *36*, 5978. (d) Puddephatt, R. J. *Chem. Commun.* **1998**, 1055. (e) Gimeno, M. C.; Laguna, A. *Chem. Rev.* **1997**, *97*, 511. (f) Jaw, H. R. C.; Savas, M. M.; Rogers, R. O.; Mason, W. R. *Inorg. Chem.* **1989**, *28*, 1028. (g) Kudwig, W.; Meyer, W. W. *Helv. Chim. Acta* **1982**, *65*, 934. (h) Kozelka, J.; Oswald, H. R.; Dubbier, E. *Acta Crystallogr.* **1986**, *C42*, 1007. (i) Schmidbaur, H.; Wohlleben, U. S.; Frank, A.; Huttner, G. *Chem Ber.* **1977**, *110*, 2751. (j) Lin, I. J. B.; Bin, C. W.; Liu, L. K.; Wen, Y. S. *Organometallics* **1992**, *11*, 2227. (k) Khan, M. N. I.; King, C.; Heinrich, D. D.; Fackler, J. P., Jr.; Porter, L. C. *Inorg. Chem.* **1989**, *28*, 2150.

(22) For example, see: (a) Che, C. M.; Kwong, H. K.; Yam, V. W. W.; Cho, K. C. *J. Chem. Soc., Chem. Commun.* **1989**, 885. (b) Che, C. M.; Kwong, H, L.; Yam, V. W. W.; Lai, T. F.; Che, C. M. *J. Chem. Soc., Dalton Trans.* **1990**, 3747. (c) Yam, V. W. W.; Lee, W. K. *J. Chem. Soc. Dalton Trans.* **1993**, 2097. (d) Assefa, Z.; McBurnett, B. G.; Staples, R. J.; Fackler, J. P., Jr.; Assmann, B.; Angermaier, K.; Schmidbaur, H. *Inorg. Chem.* ***1995,*** *34*, 7518. (e) Fu, W. F.; Chan, K. C.; Miskowski, V. M.; Che, C. M. *Angew. Chem., Int. Ed.* **1999**, *38*, 2783. (f) Rawashdeh-Omary, M. A.; Omary, M. A.; Patterson, H. H.; Fackler, J. P., Jr. *J. Am. Chem. Soc.* **2001**, *123*, 11237.

(23) For reviews, see: (a) Forward, J. M.; Fackler. J. P., Jr.; Assefa, Z. In *Optoelectronic Properties of Inorganic Compounds*; Plenum Press: New York, 1998; pp 194−228. (b) Yam, V. W. W.; Lo, K. K. W. *Chem. Soc. Rev.* **1999,** *28*, 323.

Scheme 1. Reaction Products of **1** with dppm (**2**), dppe (**3**), dppp (**4**), and dppb (**5**)



analysis. The multiple coordination modes and geometries in these dinuclear Au(I) complexes and the relationship between Au···Au interactions and the length of the alkyl chain in the bridging diphosphine ligand are discussed.

Results

Synthesis of 1. The reaction of Au(tht)Cl with NH_4(dtp) in dichloromethane at room temperature affords a dull yellow product characterized as $[Au_2(dtp)_2]$ (**1**) (dtp = $S_2P(p\text{-}C_6H_4\text{-}OCH_3)(O\text{-}c\text{-}C_5H_9)$; tht = tetrahydrothiophene). The dithiophosphonates, due to asymmetry at P, allow the formation of syn- and anti-geometric isomers of $[Au_2(dtp)_2]$. NMR spectroscopy was used to elucidate the structure of **1** in solution versus the solid state. The $^{31}P\{^1H\}$ NMR spectrum of the synthesized product in $CDCl_3$ at room temperature shows sharp singlets at 102.8 and 100.9 ppm with a relative intensity of about 1:1.5. These peaks can be associated with a mixture of syn- and anti-isomers of **1**. This observation is consistent with the literature.[16c] In contrast, the solid-state $^{31}P\{^1H\}$ NMR spectrum of **1** at 293 K shows only one signal at 95.4 ppm. On the basis of these spectral data, it has been concluded that only one type of isomer is present in the crystal, which was later shown by X-ray crystallography as the anti-isomer (vide infra). $^{31}P\{^1H\}$ NMR spectra for crystals of **1** in $CDCl_3$ show sharp singlets at 102.8 and 100.9 ppm.

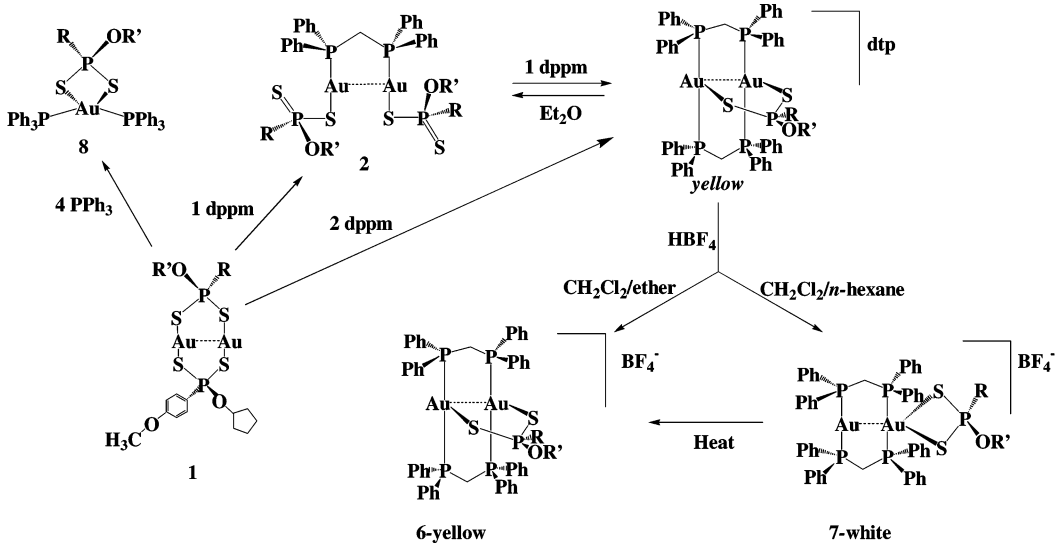
Reaction of 1 with Phosphines. Compound **1** reacts in dichloromethane solution with the diphosphine ligands dppm, dppe, dppp, and dppb to yield the neutral dinuclear complexes $Au_2(dppm)(dtp)_2$ (**2**), $Au_2(dppe)(dtp)_2$ (**3**), $Au_2(dppp)(dtp)_2$ (**4**), and $Au_2(dppb)(dtp)_2$ (**5**), respectively; Scheme 1. The reaction products show that the cyclic eight-membered ring compound **1** forms open-chain dinuclear structures with all of the bridged diphosphine ligands used here. The Au···Au intramolecular interaction was maintained only with the dppm ligand in **2** while the longer methylene chains in dppe, dppp, and dppb precluded such interaction in **3**−**5**.

The reaction between **1** and dppm is dependent on the stoichiometric ratio of the components. Two different products were obtained depending upon the dppm/Au ratio employed (Scheme 2). With a dppm/Au stoichiometric ratio of 1:1, a white product characterized as $[Au_2(dppm)(dtp)_2]$ (**2**) was isolated. If the reaction is carried out with an excess of dppm (dppm/Au > 3:2), a bright yellow solid is obtained characterized as the cationic complex $[Au_2(dppm)_2(dtp)](dtp)$. The cationic complex can be also obtained by reaction of **2** with dppm, suggesting the intermediacy of **2** in the formation of $[Au_2(dppm)_2(dtp)](dtp)$. Suspending the cationic complex in diethyl ether leads to the dissociation of one dppm ligand with the regeneration of **2**.

The $^{31}P\{^1H\}$ NMR spectrum of **2** in $CDCl_3$ at room temperature shows two sharp signals: a singlet at 100 ppm associated with the two magnetically equivalent dtp ligands and a second singlet at 30 ppm associated with two magnetically equivalent dppm ligands. The spectral features do not change appreciably on lowering the temperature to 198 K. The NMR data for **2** are consistent with a dinuclear gold(I) complex with a dppm bridge between two metal centers, consistent with the X-ray data (vide infra). The coordination sphere of each Au(I) is saturated by two monodentate dtp ligands coordinated by only one sulfur atom.

The structure of the cationic complex $[Au_2(dppm)_2(dtp)](dtp)$ in the solid state and solution was confirmed by NMR spectroscopy and X-ray crystallography. The crystal structure of $[Au_2(dppm)_2(dtp)](dtp)$ is similar to that of $[Au_2(dppm)_2(dtp)]BF_4$ but highly disordered particularly at the dtp counteranion. The crystal structure of the latter compound is discussed below. The X-ray structure of $[Au_2(dppm)_2(dtp)](dtp)$ shows that the two gold(I) centers are held together by one dtp ligand and two dppm bridges, giving rise to a three-coordinate environment for each gold(I) center (Scheme 2). The behavior of the complex in solution is more complex. NMR spectra suggest a structure in solution different from that in the solid state. The $^{31}P\{^1H\}$ NMR spectrum of $[Au_2(dppm)_2(dtp)](dtp)$ in $CDCl_3$ at room temperature shows two peaks; a sharp singlet at 102.6 ppm due to the dtp ligand, and a broad band centered at 27.6 ppm due to the dppm

Scheme 2. Reaction Pathways of **1** with PPh_3 and Different Mole Ratios of dppm



ligand. The presence of only one peak for the dtp ligands and unresolved signals for the dppm ligands suggests the presence of a fast ligand-exchange equilibrium in solution. Consistent with this suggestion, the spectral features of the cationic complex change drastically upon lowering the temperature. In fact, the $^{31}P\{^1H\}$ NMR spectrum in CD_2Cl_2 at T = 173 K is in agreement with the solid state structure with sharp singlets at 29.6, 101.3, and 105.4 ppm. The resonance at 29.6 ppm is assigned to the two dppm ligands coordinated to the metal centers. The 101.3 ppm peak is assigned to a bridging dtp ligand coordinated to the two gold(I) atoms while the sharp singlet at 105.4 ppm is assigned to the dtp^- counterion (Scheme 2). Consistent with the three-coordinate arrangement of the cationic complex is its strong green luminescence at room temperature while the linear 2-coordinate complex **2** shows strong luminescence only at 78 K.[23] Details of the luminescence studies for compounds in this paper will be the subject of a future paper.

Because of the ionic nature of the compound $[Au_2(dppm)_2(dtp)](dtp)$, we decided to exchange the dtp counterion with a more conventional counterion such as BF_4^-. Thus, reaction of the bright yellow solid $[Au_2(dppm)_2(dtp)](dtp)$ with tetrafluoroboric acid at room temperature in methanol leads to a white product that is characterized as $[Au_2(dppm)_2(dtp)]BF_4$. The IR spectrum of the white solid shows a broad band (1070 cm^{-1}) typical of the tetrafluroborate anion absorption. The $^{31}P\{^1H\}$ NMR spectrum in CD_3OD at room temperature shows two peaks: a singlet centered at 30.6 ppm assigned to the dppm and another singlet centered at 101.8 ppm assigned to the dtp ligand. The solution behavior of $[Au_2(dppm)_2(dtp)]BF_4$ is rather different from that of $[Au_2(dppm)_2(dtp)](dtp)$ as the NMR spectral features do not change appreciably on lowering the temperature to 178 K. The differences in color and $^{31}P\{^1H\}$ NMR data between $[Au_2(dppm)_2(dtp)](dtp)$ and $[Au_2(dppm)_2(dtp)]BF_4$ suggest different X-ray structures. Interestingly, while trying to crystallize $[Au_2(dppm)_2(dtp)]BF_4$ from different solvent combinations, two isomers have been obtained. Crystals grown from CH_2Cl_2/diethyl ether are bright yellow and have the structure denoted as **6**-yellow while crystals grown from CH_2Cl_2/*n*-hexane are colorless and have the structure denoted as **7**-white in Scheme 2. The X-ray data show that the dtp ligand in the isomer **6**-yellow is coordinated as a bridge with each of the two sulfur atoms bonded to a different gold(I) center. In contrast, the colorless crystals of isomer **7**-white have the dtp ligand coordinated as a chelate with both sulfur atoms bonded to only one gold(I) atom. The structures shown in Scheme 2 are also consistent with the NMR data. Furthermore, we have noticed that heating the white powder of $[Au_2(dppm)_2(dtp)]BF_4$ (**7**-white) converts it to a bright yellow powder, **6**-yellow. While the two isomers **6**-yellow and **7**-white are distinguishable in the solid state (the water content of crystals of **7**-white is higher than for crystals of **6**-yellow**),** solutions of both isomers in $CDCl_3$ give essentially identical $^{31}P\{^1H\}$ NMR spectra. Compound **7**-white rearranges to **6**-yellow in solvents such as acetone, THF, dichloromethane, ethanol, DMSO, acetonitrile, and chloroform.

Also illustrated in Scheme 2 is the reaction of **1** with triphenylphosphine. Thus, addition of 4 equiv of PPh_3 to a solution of **1** in dichloromethane at room temperature leads to the formation of a stable species characterized as $[Au(dtp)(PPh_3)_2]$ (**8**). As confirmed by X-ray crystallography, the gold(I) atom is coordinated by two PPh_3 ligands and by two sulfur atoms of the dtp ligand in a distorted tetrahedral geometry. The $^{31}P\{^1H\}$ NMR solid-state spectrum of **8** at room temperature is in agreement with the X-ray structure as it shows two sharp singlets at 35.5 (due to the PPh_3 ligand) and 106.6 ppm (due to dtp chelating ligand). The solution $^{31}P\{^1H\}$ NMR spectrum of **8** (room temperature, CD_2Cl_2) shows a peak at 99.0 ppm, assigned to the chelated dtp, and another signal at 18.4 ppm. This chemical shift is perturbed by adding PPh_3. The $^{31}P\{^1H\}$ NMR of **8** at room temperature in CD_2Cl_2 after adding PPh_3 shows two peaks, one at 99.8 ppm due to dtp and the other at 7.0 ppm due to free PPh_3. This confirms that there is an equilibrium between **8** and a new species $[Au(PPh_3)(dtp)]$ in solution. These spectral features change upon lowering the temperature. At 183 K, broad bands centered at 102.2 and 37.9 ppm are present.

Structures. Compounds **1**−**8** have been characterized by single-crystal X-ray crystallography. Table 1 shows the crystal data for these compounds. Selected bond lengths and angles are listed in Tables 2−9. Thermal ellipsoid drawings are shown in Figures 1−8.

Compound **1** crystallizes in the monoclinic space group $P2_1/c$ with an inversion center between the two gold atoms. An ORTEP drawing of **1** is shown in Figure 1 and selected bond distances and angles are listed in Table 2. The two linear S−Au−S fragments are parallel; they do not "cross". There are numerous examples of dinuclear Au(I) cyclic complexes where the linear coordination around the gold center is maintained.[19−21,24] Among these, eight-membered ring Au(I) complexes are the best examples available to examine the effect of intramolecular Au···Au interactions. However, intermolecular Au···Au interactions may or may not exist in complexes such as $[Au(dithiolate)]_2^{n-}$ [25] with dithiolate = $S_2P(OR)_2^-$,[26] $S_2C_2(CN)_2^{2-}$,[27] S_2PR_2,[28] S_2CS,[29] and $S_2PR(OR)$,[16b] with R = alkyl, $n = 0$, 2. Many of which are known to form polymeric chains with both intra- and intermolecular Au···Au interactions. Compound **1** shows a typical elongated chair molecular conformation with a short Au···Au interaction, 3.1002(4) Å. This weak Au···Au interaction has been attributed to correlation effects that are enhanced by relativistic effects, to mixing and hybridization, or both, between the 6s and 5d orbitals.[18,30] Contrary to what is observed for $[AuS_2PPh_2]$,[28,31] $\{[Au(i\text{-}C_3H_7)_2PS_2]_2\}_n$,[26] and $[PPN]_2[Au_2(\mu^2\text{-}\eta^2\text{−}S_2CS)_2]$,[29] packing of the dimers in the unit cell of **1** is not associative. There are no close intermolecular contacts between gold atoms (the shortest Au···Au distance is 6.814 Å) or between the gold and sulfur atoms of adjacent molecules.

The two Au(I) atoms in **2** (Figure 2) are bridged by one dppm ligand. The Au− S and Au−P bond lengths and angles are typical of phosphine gold(I) thiolate complexes (Table 2).[22,32] The two gold atoms are at a separation of 3.0353(3) Å, well within the range of aurophilic bonding, somewhat shorter than the distance of 3.351 Å found in $[Au_2(dppm)Cl_2]$,[33] and close to the distances found in [dppm{Au-

Table 1. Summary of Crystal Data for Compounds **1**−**8**

	1	**2**	**3**	**4**	**5**	**6**-yellow	**7**-white	**8**
formula	$C_{24}H_{32}Au_2O_4P_2S_4$	$C_{49}H_{54}Au_2O_4P_4S_4$	$C_{50}H_{56}Au_2O_4P_4S_4$	$C_{51}H_{58}Au_2O_4P_4S_4$	$C_{52}H_{60}Au_2O_4P_{47}S_4$	$C_{62}H_{63.5}Au_2BF_4O_3P_5S_2$	$C_{62}H_{62}Au_2BF_4O_{3.50}P_5S_2$	$C_{48}H_{46}AuO_2P_3S_2$
fw, g	968.61	1352.97	1367	1381.03	1395.05	1556.34	1562.83	1008.18
temp, K	213(2)	293(2)	293(2)	213(2)	213(2)	213(2)	213(2)	293(2)
λ, Å	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
cryst syst	monoclinic	monoclinic	triclinic	triclinic	monoclinic	monoclinic	monoclinic	triclinic
space group	$P2_1/c$	$P2_1/c$	$P\bar{1}$	$P\bar{1}$	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P\bar{1}$
a, Å	8.5087(3)	12.3551(4)	8.3230(10)	12.207(3)	13.106(6)	22.0680(12)	14.3292(7)	10.7834(2)
b, Å	9.7968(3)	22.8195(7)	11.1147(13)	14.501(4)	8.597(4)	24.3554(11)	21.1005(11)	13.4375(3)
c, Å	18.2039(6)	18.2119(6)	14.4695(17)	17.165(4)	23.919(10)	24.7299(13)	21.7215(11)	15.2389(2)
α, deg	90	90	93.370(2)	65.546(4)	90	90	90	79.0130(10)
β, deg	99.889(1)	95.118(1)	97.118(2)	89.092(4)	97.370(10)	110.2490(10)	108.0930(10)	79.3850(10)
γ, deg	90	90	106.682(2)	76.577(4)	90	90	90	88.9130(10)
V, Å^3	1494.90(9)	5114.1(3)	1266.0(3)	2679.3(11)	2673(2)	12470.2(11)	6242.8(5)	2130.28(7)
Z	2	4	1	2	2	8	4	2
D (calcd), Mg/m^3	2.152	1.757	1.793	1.712	1.733	1.658	1.663	1.537
abs coeff., mm^{-1}	10.218	6.061	6.122	5.787	5.802	4.951	4.946	3.701
F(000)	920	2648	670	1356	1372	6124	3072	966
cryst size, mm^3	0.10 × 0.10 × 0.10	0.15 × 0.15 × 0.05	0.10 × 0.10 × 0.04	0.18 × 0.12 × 0.12	0.15 × 0.10 × 0.1	0.15 × 0.10 × 0.10	0.15 × 0.10 × 0.10	0.15 × 0.10 × 0.10
θ range, deg	2.27−27.70	1.43−27.72	1.43−28.30	1.31−25.00	1.57−25.00	1.21−22.50	1.38−22.50	1.38−28.81
reflns collected	9095	31867	9452	14402	14076	57095	26698	13708
GOF	1.000	1.11	1.119	1.096	1.076	1.073	1.065	1.215
R1,[a] wR2[b] [$I > 2\sigma(I)$]	0.0291, 0.0708	0.0410, 0.0681	0.0289 0.0565	0.0549, 0.1317	0.0531, 0.1351	0.0456, 0.0881	0.0665, 0.1403	0.0226, 0.0802

[a] $R1 = \sum||F_o| - |F_c||/|F_o|$. [b] $wR2 = \{[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$.

---

(24) (a) Fernandez, E. J.; López-de-Luzuriga, J. M.; Monge, M.; Rodriguez, M. A.; Crespo, M. O.; Gimeno, M. C.; Laguna, A.; Jones, P. G. *Inorg. Chem.* **1998**, *37*, 6002. (b) Davila, M. R.; Eldugue, A.; Grant, T.; Staples, R. J.; Fackler, J. P., Jr. *Inorg. Chem.* **1993**, *32*, 1749. (c) Tang, S. S.; Chang, C.-P.; Lin, I. J. B.; Liu, L.-S.; Wang, J.-C. *Inorg. Chem.* **1997**, *36*, 2294.

(25) Heinrich, D. D.; Wang, J. C.; Fackler, J. P., Jr. *Acta Crystallogr.* **1990**, *C46*, 1447.

(26) Lawton, S. L.; Rohrbaugh, W. J.; Kokotailo, G. T. *Inorg. Chem.* **1972**, *11*, 2227.

(27) Khan, M. N. I.; Fackler, J. P., Jr.; King, C.; Wang, J. C.; Wang, S. *Inorg. Chem.* **1988**, *27*, 1672.

(28) van Zyl, W. E.; López-de-Luzuriga, J. M.; Fackler, J. P., Jr.; Staples, R. J. *Can. J. Chem.* **2001**, *79*, 896.

(29) Vicente, J.; Chicote, M.-T.; Herrero, P. G.; Jones, P. G. *J. Chem. Soc., Chem. Commun.* **1995**, 745.

(30) Jiang, Y.; Alvarez, S.; Hoffmann, R. *Inorg. Chem.* **1985**, *24*, 749.

(31) Siasios, G.; Tiekink, E. R. T. *Z. Kristallogr.* **1995**, *210*, 698.

(32) (a) Davila, R. M.; Staples, R. J.; Eldugue, A.; Harlass, M.; Kyle, L.; Fackler, J. P., Jr. *Inorg. Chem.* **1994**, *33*, 5940. (b) Gimeno, M. C.; Jones, P. G.; Laguna, A.; Laguna, M.; Terroba, R. *Inorg. Chem.* **1994**, *33*, 3932.

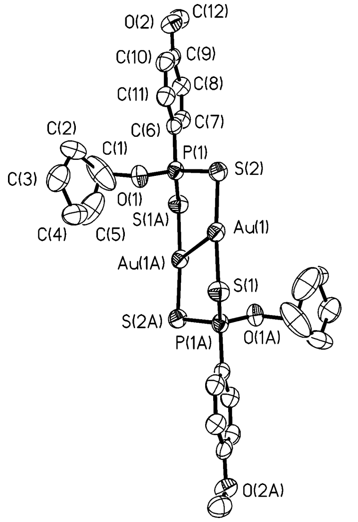


Figure 1. Thermal ellipsoid drawing of **1** with 50% probability. Hydrogen atoms are omitted for clarity.

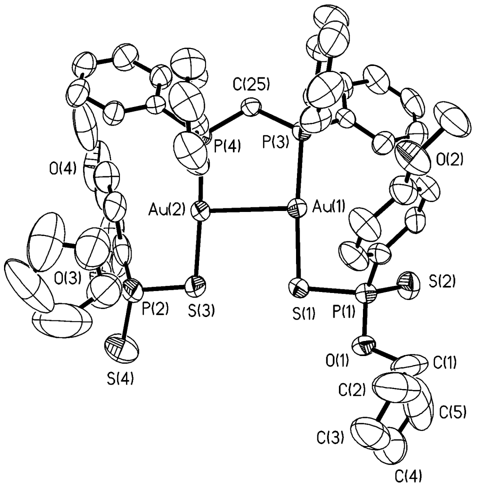


Figure 2. Thermal ellipsoid drawing of **2** with 50% probability. Hydrogen atoms are omitted for clarity.

Table 2. Selected Bond Distances (Å) and Angles (deg) of **1**

Au(1)−S(2)	2.2973(16)	S(2)−P(1)	2.0201(19)
Au(1)−S(1)	2.3020(16)	S(1)−P(1A)	2.020(2)
Au(1)···Au(1A)	3.1002(4)		
S(2)−Au(1)−S(1)	171.49(5)	P(1)−S(2)−Au(1)	102.24(8)
S(2)−Au(1)···Au(1A)	93.75(4)	S(1)−Au(1)···Au(1A)	94.75(4)
P(1A)−S(1)−Au(1)	101.44(8)	S(1A)−P(1)−S(2)	116.83(9)

$(SSNH_2)\}_2]\cdot 2DMF$[34] (3.099 Å) and similar compounds.[3,30,32,33,35] The torsion angle defined by Au(1)−P(1)···P(2)−Au(2) in **2** is −16.2°.

The two P−Au−S fragments in **3**−**5** adopt an anti-geometry (Figures 3−5). The Au−S distance of ~3.5−3.8 Å is normal for a secondary Au···S interaction. Selected bond distances and angles for **3**−**5** are listed in Tables 3−5.

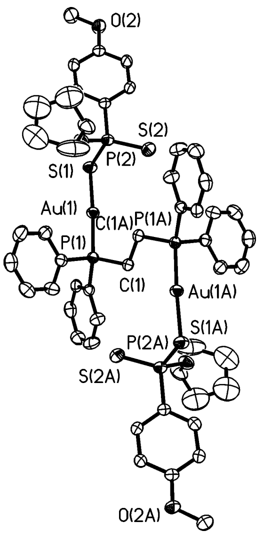


Figure 3. Thermal ellipsoid drawing of **3** with 50% probability. Hydrogen atoms are omitted for clarity.

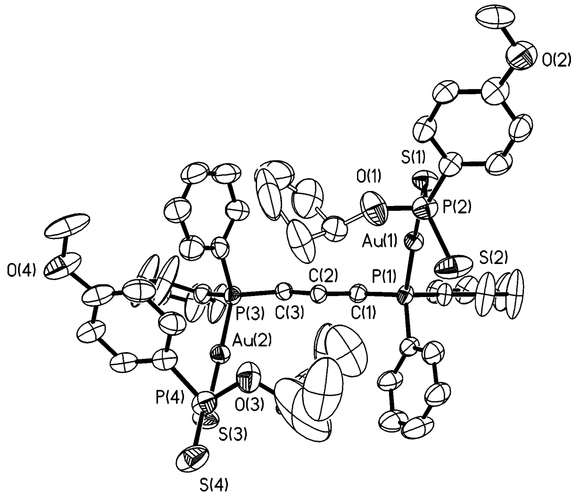


Figure 4. Thermal ellipsoid drawing of **4** with 50% probability. Hydrogen atoms are omitted for clarity.

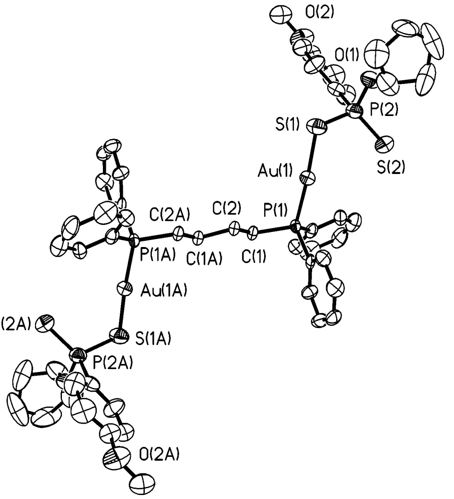


Figure 5. Thermal ellipsoid drawing of **5** with 50% probability. Hydrogen atoms are omitted for clarity.

The asymmetric unit of **6**-yellow has two independent but closely similar formula units, the cation of one of which is shown in Figure 6. Both molecules consist of two gold atoms bridged by two diphosphines and one dtp ligand. They show short intramolecular gold−gold contacts of 2.9556(6) Å

---

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

(34) Tzeng, B.-C.; Schier, A.; Schmidbaur, H. *Inorg. Chem.* **1999**, *38*, 8, 3978.

(35) (a) King, C.; Wang, J.-C.; Khan, M. N. I.; Fackler, J. P., Jr. *Inorg. Chem.* **1989**, *28*, 2145. (b) Hao, L.; Lachicotte, R. J.; Gysling, H. J.; Eisenberg, R. *Inorg. Chem.* **1999,** *38*, 4616.

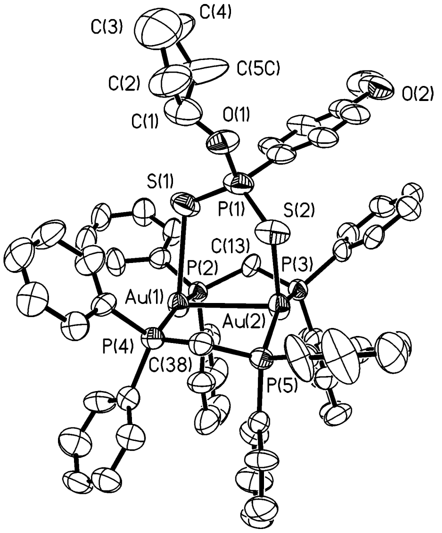


Figure 6. Thermal ellipsoid drawing of the cation of **6**-yellow with 50% probability. Hydrogen atoms are omitted for clarity.

Table 3. Selected Bond Distances (Å) and Angles (deg) of **2**

Au(1)−P(3)	2.2587(14)	Au(2)−P(4)	2.2664(15)
Au(1)−S(1)	2.3138(15)	Au(2)−S(3)	2.3151(17)
Au(1)···Au(2)	3.0353(3)	S(1)−P(1)	2.053(2)
P(3)−Au(1)−S(1)	175.08(6)	P(3)−Au(1)···Au(2)	93.70(4)
S(1)−Au(1)···Au(2)	91.04(4)	P(4)−Au(2)−S(3)	176.76(6)
P(4)−Au(2)···Au(1)	83.53(4)	S(3)−Au(2)···Au(1)	99.37(5)

Table 4. Selected Bond Distances (Å) and Angles (deg) of **3**

Au(1)−P(1)	2.2580(10)	S(1)−P(2)	2.0489(16)
Au(1)−S(1)	2.3207(10)	S(2)−P(2)	1.9450(16)
P(2)−O(1)	1.608(3)	O(1)−C(14)	1.483(5)
P(2)−S(1)−Au(1)	97.50(5)	P(1)−Au(1)−S(1)	176.52(4)
S(1)−P(2)−S(2)	114.36(13)	O(1)−P(2)−C(19)	105.33(16)

Table 5. Selected Bond Distances (Å) and Angles (deg) of **4**

Au(1)−P(1)	2.247(2)	Au(1)−S(1)	2.315(2)
Au(2)−P(3)	2.253(3)	S(1)−P(2)	2.039(4)
Au(2)−S(3)	2.315(3)	P(2)−O(1)	1.589(9)
P(1)−Au(1)-S(1)	176.45(9)	P(3)−Au(2)−S(3)	177.24(10)
P(2)−S(1)−Au(1)	100.22(13)	P(4)−S(3)−Au(2)	102.36(14)

Table 6. Selected Bond Distances (Å) and Angles (deg) of **5**

Au(1)-P(1)	2.233(3)	S(1)−P(2)	2.055(4)
Au(1)−S(1)	2.306(3)	P(2)−O(1)	1.594(8)
P(1)−Au(1)−S(1)	175.61(9)	P(2)−S(1)−Au(1)	98.69(14)
O(1)−P(2)−S(1)	103.3(3)	C(20)−P(2)−S(1)	108.0(4)

Table 7. Selected Bond Distances (Å) and Angles (deg) of **6**

Au(1)−P(4)	2.307(3)	Au(2)−P(3)	2.300(3)
Au(1)−P(2)	2.318(3)	Au(2)−P(5)	2.347(3)
Au(1)−S(1)	2.899(3)	Au(2)−S(2)	2.708(3)
Au(1)···Au(2)	2.9556(6)	S(1)−P(1)	1.992(5)
P(4)−Au(1)−P(2)	165.13(9)	P(4)−Au(1)−S(1)	111.23(9)
P(2)−Au(1)−S(1)	83.29(9)	P(4)−Au(1)···Au(2)	94.14(8)
P(2)−Au(1)···Au(2)	89.87(7)	S(1)−Au(1)···Au(2)	86.24(7)
P(3)−Au(2)−P(5)	154.95(9)	P(3)−Au(2)−S(2)	118.17(9)
P(5)−Au(2)−S(2)	86.81(9)	P(3)−Au(2)···Au(1)	92.86(7)
P(5)−Au(2)···Au(1)	87.47(8)	S(2)−Au(2)···Au(1)	92.79(8)

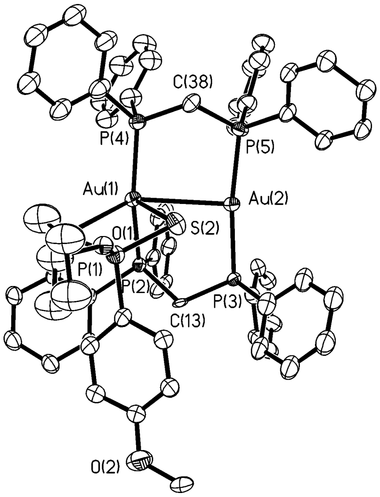


Figure 7. Thermal ellipsoid drawing of the cation of **7**-white with 50% probability. Hydrogen atoms are omitted for clarity.

Table 8. Selected Bond Distances (Å) and Angles (deg) of **7**

Au(1)···Au(1A)	3.0428(8)	P(2)−Au(1)	2.346(4)
Au(1)−S(2)	2.880(4)	S(1)−P(1A)	1.983(5)
Au(1)−S(1)	2.841(4)		
P(4)−Au(1)−P(2)	151.87(14)	P(4)−Au(1)−S(1)	112.84(13)
P(2)−Au(1)−S(1)	91.66(12)	S(1)−Au(1)−S(2)	72.08(11)
P(4)−Au(1)···Au(2)	89.77(10)	S(1)−Au(1)···Au(2)	137.54(8)
P(5)−Au(2)−P(3)	171.97(13)	S(1)−P(1)−S(2)	115.3(2)

(Table 7), which is similar to that found in [$Au_2(S_2CNEt_2)(dppm)_2$][BH_3CN], 2.949(1) Å.[21k] The Au−S bond distances, 2.899(3) and 2.708(3) Å, are longer than those in [$Au_2(S_2CNEt_2)(dppm)_2$][BH_3CN] (2.648(3) and 2.703(3) Å). The coordination of the two dppm ligands to gold constitutes a boat conformation. The angles at P−Au−P are 154.95(9)° and 165.13(9)°. The dihedral angle between P(2)−Au(1)−P(4) and P(3)−Au(2)−P(5) is 16.1°. The Au−P bond distances lie in the range 2.300(3)−2.347(3) Å.

The structure of **7**-white (Figure 7) is similar to that of [$Au_2(PhCS_2)(\mu\text{-dppm})_2$]C1.[36] The dithiophosphonate is chelated to only one center with Au−S = 2.880(4) and 2.841(4) Å. The [$Au_2(dppm)_2$]$^+$ unit adopts a boat conformation, and the P−Au−P angle is shifted from linearity to 151.87(14)° at the gold center that is connected to the dtp ligand; while the angle at the other gold center is 171.97(13)° (Table 8). The coordination around the gold atom coordinated to dtp is nearly tetrahedral. The Au···Au distance is 3.0428(8) Å, similar to the distance in [$Au_2(PhCS_2)(\mu\text{-dppm})_2$]Cl, Au···Au = 3.0176(5) Å.

The gold atom in **8** is pseudotetrahedrally coordinated by the two triphenylphosphines and the chelating dtp ligand (Figure 8). The angles at P−Au−P and S−Au−S are 138.3(2)° and 73.10(19)°, respectively (Table 9). The Au−S bond distances in the chelate ring, 2.810(6) and 2.829(6) Å, are similar to those in **6**-yellow and **7**-white**.**

Discussion

The structural results for the phosphine derivatives of **1** show that each gold atom in **2**−**5** is two-coordinate and linearly bonded to a sulfur of the dtp ligand and one of the P atoms of the bridged diphosphine ligand. Compounds **2**−**5** show neither sulfur chelation to the Au(I) atoms nor any discernible intermolecular gold−sulfur interaction. Com-

---

(36) Wang, J.-C.; Liu, L.-K. *Acta Crystallogr.* **1994**, *C50*, 704.

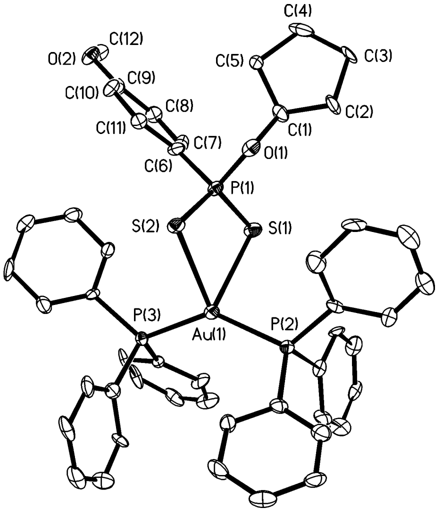


Figure 8. Thermal ellipsoid drawing of **8** with 50% probability. Hydrogen atoms are omitted for clarity.

Table 9. Selected Bond Distances (Å) and Angles (deg) of **8**

Au(1)−P(3)	2.326(4)	Au(1)−S(1)	2.849(5)
Au(1)−S(2)	2.803(4)	Au(1)−P(2)	2.324(5)
P(3)−Au(1)−P(2)	137.70(15)	P(3)−Au(1)−S(2)	102.12(14)
P(2)−Au(1)−S(1)	97.35(15)	S(1)−Au(1)−S(2)	73.17(13)
P(3)−Au(1)−S(1)	112.13(16)		

pounds **6**−**8** show relatively uncommon coordination numbers for gold(I)−sulfur complexes of three, **6**-yellow, and four, **7**-white and **8**, around the gold atoms. The chelation of the dtp to one of the gold atoms in **7**-white is found to generate some steric strain and causes the sulfur atoms of the dtp ligand to be involved in a dynamic process. The structural result is the observation of **6** and **7**.

The packing diagrams of **2**−**8** show no close aurophilic intermolecular interactions with Au(I)···Au(I) distances well beyond the normal range for such interactions. The coordination at each Au(I) center in **2**−**5** is, as expected, almost linear with a P−Au−S angle of 176° (Tables 2−8). The gold−sulfur distances from nonbonded sulfur atoms are found to be 4.093, 3.827, 3.593, and 3.519 Å in structures **2**−**5**, respectively. This is longer than the nonbonded Au(I)···S distances found in Au(I)−dithiocarbamate complexes such as [Au(S_2CNEt_2)(PPh_3)], 3.105 Å.[37] The P−S distances are consistent with a P═S (1.941 Å) double bond for the noncoordinated S atoms and a P−S (2.048 Å) single bond for the Au(I)−S bonded sulfur atom of the dtp. The presence of an intramolecular interaction in **2**, Au···Au = 3.0035 Å, shows that the dppm brings the two Au(I) centers into close proximity. The average of P−Au and S−Au bond lengths in **2**−**8** are ~2.2 and ~2.3 Å, respectively. This corresponds well with the reported values in other phosphine Au(I) thiolate complexes.[38]

Conclusions

This study demonstrates the facile formation of phosphine gold(I) dithiophosphonates from the reaction of mono- and diphosphine ligands with dinuclear gold(I) dithiophosphonate. The characterized gold complexes are diverse in their coordination types about the gold(I) centers such as tetrahedral, distorted trigonal (T-shape) in addition to the known linear coordination. Some of the isolated complexes show strong orange, yellow, and green luminescence at room temperature and at 77 K. Details of the luminescence studies for compounds in this paper will be the subject of a future paper.

Experimental Section

Au(tht)Cl was prepared by literature methods.[39] Solvents were dried and distilled under dry oxygen-free nitrogen prior to use; all other chemicals were obtained from commercial sources and used as received. All reactions were carried out under an inert atmosphere using standard Schlenk techniques.[40] ^1H and $^{31}P\{^1H\}$ NMR spectra were obtained using a Unity Plus 300 spectrometer operating at 300 MHz for proton spectra. The chemical shifts in the $^{31}P\{^1H\}$ NMR spectra are reported relative to 85% H_3PO_4 in D_2O.

Synthesis of $NH_4[S_2P(p\text{-}C_6H_4OMe)(O\text{-}c\text{-}C_5H_9)]$, NH_4(dtp). A 4.46-g (0.011 mmol) sample of Lawesson's reagent [$S_2P(\mu\text{-}C_6H_4\text{-}OMe)$]$_2$ was dissolved in 30 mL of distilled benzene, and 2.2 mL (2.24 × 10^{-2} mmol) of C_5H_9OH was added via a syringe. The suspension was refluxed at 80 °C for 3 h. The solution was then cooled in an ice bath for 20 min. Anhydrous NH_3 (g) was slowly bubbled through the solution with vigorous agitation. The white precipitate was filtered, washed with diethyl ether, and dried under vacuum; yield 5.4 g (90%). Anal. Calcd for $C_{12}H_{20}NO_2PS_2$: C, 47.21; H, 6.56; S, 20.98. Found: C, 46.68; H, 6.26; S, 21.30. $^{31}P\{^1H\}$ NMR (300 MHz, $CDCl_3$): 104.54 ppm (s).

Synthesis of [Au(μ-dtp)]$_2$ (1). A 0.318-g (0.99 mmol) sample of Au(tht)Cl was dissolved in 15 mL of CH_2Cl_2, and 0.302 g (0.99 mmol) of NH_4[dtp] was added in one portion. The resulting mixture was stirred for 20 min in the dark at 0 °C, and then the solution was stirred an additional 2 h under reduced pressure at room temperature. The NH_4Cl salt was filtered, and the volume of the filtrate was reduced to 2 mL. The product was precipitated by adding 50 mL of diethyl ether and filtered. The product was washed with distilled water to remove any NH_4Cl residue and dried under vacuum for 1 h. The dull yellow product was obtained in an 83% yield (0.396 g). Crystals suitable for X-ray analysis were obtained by a slow diffusion of *n*-hexane or diethyl ether into a dichloromethane solution of the product. ^1H NMR (300 MHz, $CDCl_3$): 1.67−1.97 (m, 8H, O-*c*-C_5H_9), 3.89 (3H, OCH_3), 5.42 (s, IH, O-*c*-C_5H_9), 6.99 (d, 2H, *m*-$C_6H_4OCH_3$), 8.1 ppm (t, 2H, *o*-$C_6H_4OCH_3$). $^{31}P\{^1H\}$ NMR (300 MHz, $CDCl_3$): 100.9 (s), 102.8 ppm (s). Anal. Calcd for $C_{24}H_{32}Au_2O_4P_2S_4$: C, 29.75; H, 3.30; S, 13.22. Found: C, 28.93; H, 3.32; S, 12.42.

Synthesis of Au_2(μ-dppm)(dtp)$_2$ (2). To a CH_2C1_2 solution (4 mL) of **1** (107 mg, 0.11 mmol), 43 mg (0.11 mmol) of dppm was added. The clear yellow solution turned colorless while being stirred for 5 h at room temperature, after which the solvent was evaporated under vacuum to 1 mL. The white solid was extracted and washed with diethyl ether and then dried under vacuum; yield 110 mg (74%). Crystals suitable for X-ray analysis were obtained by a slow diffusion of *n*-hexane or diethyl ether into a dichloromethane

---

(37) Lanfredi, A. M.; Ugozzoli, F.; Asaro, F.; Pellizer, G.; Marsich, N.; Camus, A. *Inorg. Chim. Acta* **1992**, *192*, 271.

(38) 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.

(39) Usón, R.; Laguna, A. In *Organometallic Syntheses*; King, R. B., Eisch, J. J., Eds.; Elsevier: Amsterdam, 1986; Vol. 3, p 322.

(40) Shriver, D. F.; Drezdzon, M. A. *The Manipulation of Air-Sensitive Compounds*, 2nd ed.; Wiley: New York, 1986.

solution of the product. ^{1}H NMR (300 MHz, $CDCl_3$): 1.63−1.87 (m, 8H, O-*c*-C_5H_9), 4.713 (t, 2H, CH_2), 3.88 (3H, O-C*H*$_3$), 5.29 (s, 1H, O-*c*-C_5H_9), 6.96 (d, 2H, *m*-$C_6H_4OCH_3$), 7.88 (t, 2H, *o*-C_6H_4-OCH_3), 7.37−7.79 ppm (m, 20H, *Ph*$_2$*CH*$_2$*Ph*$_2$*)*. ^{31}P {^{1}H} NMR (300 MHz, $CDCl_3$): 33.17 (s, dppm), 93.12 ppm (s, dtp). Anal. Calcd for $C_{49}H_{54}Au_2O_4P_4S_4$: C, 43.49; H, 3.99. Found: C, 43.03; H, 4.13.

Synthesis of Au_2(μ-dppe)(dtp)$_2$ (3). To a CH_2Cl_2 solution (10 mL) of **1** (100 mg, 0.103 mmol) was added dppe (81.99 mg, 0.107 mmol). The reaction mixture was stirred for 3 h at room temperature. The solvent was concentrated under vacuum, and hexane was added (30 mL). The white solid was filtered off, washed with hexane, and dried under vacuum; yield 122.7 mg (81%). Crystals suitable for X-ray analysis were obtained by a slow diffusion of *n*-hexane or diethyl ether into a dichloromethane solution of the product. ^{1}H NMR (300 MHz, $CDCl_3$): 1.78−1.92 (m, 8H, *O-c*-C_5H_9), 2.79 (t, 4H, CH_2), 3.83 (3H, O-C*H*$_3$), 5.25 (s, 1H, O-*c*-C_5H_9), 6.87 (d, 2H, *m*-$C_6H_4OCH_3$), 8.14 (t, 2H, *o*0$C_6H_4OCH_3$), 7.23−7.74 ppm (m, 20H, *Ph*$_2$PCH$_2$CH$_2$P*Ph*$_2$). ^{31}P{^{1}H} NMR (300 MHz, $CDCl_3$): 21.95 (s, dppe), 99.50 ppm (s, dtp).

Synthesis of Au_2(μ-dppp)(dtp)$_2$ (4). To a CH_2Cl_2 solution (10 mL) of **1** (100 mg, 0.103 mmol) was added dppp (85.1 mg, 0.107 mmol). After stirring for 3 h at room temperature, the solvent was reduced under vacuum and a white precipitate formed by addition of hexane (30 mL). The solid was filtered off, washed with hexanes, and dried under vacuum; yield 108 mg (76%). Crystals suitable for X-ray analysis were obtained by a slow diffusion of *n*-hexane or diethyl ether into a dichloromethane solution of the product. ^{1}H NMR (300 MHz, $CDCl_3$): 1.75−1.92 (m, 8H, O-*c*-C_5H_9), 2.83 (t, 2H, CH_2), 1.92 (m, 2H, CH_2), 3.83 (3H, O-C*H*$_3$), 5.25 (s, 1H, O-*c*-C_5H_9), 6.89 (d, 2H, *m*-$C_6H_4OCH_3$), 8.08 (t, 2H, *o*-$C_6H_4OCH_3$), 7.46−7.70 ppm (m 20H, *Ph*$_2$CH$_2$*Ph*$_2$*)*. ^{31}P{^{1}H} NMR (300 MHz, $CDCl_3$): 31.24 (s, dppp), 99.25 ppm (s, dtp).

Synthesis of Au_2(μ-dppb)(dtp)$_2$ (5). To a CH_2C1_2 solution (10 mL) of **1** (100 mg, 0.10 mmol) was added dppb (88 mg, 0.21 mmol). The reaction was allowed to stir for 3 h at room temperature. The solvent was concentrated under vacuum, and the product was isolated upon addition of hexane (30 mL). The solid was filtered off, washed with hexane, and dried under vacuum; yield 131 mg (91%). Crystals suitable for X-ray analysis were obtained by a slow diffusion of *n*-hexane or diethyl ether into a dichloromethane solution of the product. ^{1}H NMR (300 MHz, $CDCl_3$): 1.76−1.89 (m 8H, O-*c*-C_5H_9), 2.41 (t, 4H, CH_2), 1.92 (m, 4H, CH_2), 3.82 (3H, O-C*H*$_3$), 5.25 (s, 1H, O-*c*-C_5H_9), 6.89 (d, 2H, *m*-$C_6H_4OCH_3$), 8.10 (t, 2H, *o*-$C_6H_4OCH_3$), 7.44−7.65 ppm (m, 20H, *Ph*$_2$CH$_2$*Ph*$_2$*)*. ^{31}P-{^{1}H} NMR (300 MHz, $CDCl_3$): 32.74 (s, dppb), 99.45 ppm (s, dtp).

Synthesis of [Au_2(μ-dppm)$_2$(μ-dtp)](dtp). Complex **1** (100 mg; 0.10 mmol) was dissolved in 4 mL of dichloromethane, and bis(diphenylphosphino)methane (84 mg, 0.22 mmol) was added and stirred under inert atmosphere. The reaction mixture was stirred for 3 h, after which the solvent was evaporated to dryness. The bright yellow product was treated with diethyl ether, filtered off, and dried under reduced pressure (90% yield). Anal. Calcd for $C_{74}H_{76}Au_2O_4P_6S_4$: C, 51.15; H, 4.38; S. 7.37. Found C, 51.12; H, 4.37; S, 7.22. Crystals suitable for X-ray structural analysis were obtained by a slow evaporation of an acetonitrile solution of **2** at 293 K.

Synthesis of [Au_2(dppm)$_2$(dtp)](BF_4), 6-yellow and 7-white. Complex [Au_2(μ−dppm)$_2$(μ-dtp)](dtp) (0.053 g, 3.5 × 10^{-5} mol) was dissolved in methanol (4 mL), and fluoroboric acid in water (60 μL of a 48 wt % solution) was added under stirring. In few minutes, a white complex formed. The reaction mixture was stirred for 1 h, and at the end of this period, the white complex was filtered off, washed with water and methanol, and dried under vacuum. Anal. Calcd for $C_{62}H_{60}Au_2BF_4O_2P_5S_2$: C, 48.43; H, 3.90. Found: C, 47.90; H, 3.77. Crystals suitable for X-ray analysis were obtained by a slow diffusion of diethyl ether or *n*-hexane into a dichloromethane solution of the product to yield, respectively, the yellow crystals of **6** or the colorless crystals of **7**.

Synthesis of [Au(dtp)(PPh_3)$_2$] (8). To a solution of **1** (100 mg, 0.10 mmol) in dichloromethane (5 mL), triphenylphosphine (111 mg, 0.42 mmol) was added in one portion under inert atmosphere. The yellow reaction mixture was stirred for 2 h. At the end of this period, the colorless solution was dried under vacuum and then the complex was washed with diethyl ether and dried under vacuum (80% yield). Anal. Calcd for $C_{48}H_{46}AuO_2P_3S_2$: C, 57.14; H, 4.56. Found C, 57.25; H, 4.72. Crystals suitable for X-ray structure analysis were obtained by a slow evaporation of dichloromethane solution at 293 K.

X-ray Crystallography. Data were collected using a Bruker SMART charge-coupled device (CCD) diffractometer equipped with an LT-3 low-temperature apparatus operating at 213 K. A suitable crystal was chosen and mounted on a glass fiber using grease. Data were measured using ω scans of 0.3°/frame for 10 s, such that a hemisphere was collected. A total of 1271 frames were collected with a maximum resolution of 0.75 Å. The first 50 frames were recollected at the end of data collection to monitor for decay. Cell parameters were retrieved using SMART[41] software and refined using SAINT on all observed reflections. Data reduction was performed using the SAINT software,[42] which corrects for Lp and decay. Absorption corrections were applied using SADABS.[43] The structures are solved by the direct method using the SHELXS-97[44] program and refined by a least-squares method on F^2, SHELXL-97,[45] incorporated in SHELXTL V5.10.[46]

Structures **1**, **2**, and **5**−**7** and were solved in the monoclinic space group $P2_1/c$ and **3** and **4** were solved in the triclinic space group *P*-1 by analysis of systematic absences. The structure of **8** was solved in the triclinic space group $P\bar{1}$. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were calculated by geometrical methods and refined as a riding model. The crystal used for the diffraction study showed no decomposition during data collection. All thermal ellipsoid drawings are at 50% probability. Cyclopentanes and the counteranions (BF_4^-) were disordered.

Acknowledgment. The Robert A. Welch Foundation of Houston, TX is acknowledged for financial support of this work to J.P.F. and M.A.O. The CCD-based X-ray diffractometer at Harvard University was purchased through the NIH Grant I SlO 1RR1 1937-01.

Supporting Information Available: X-ray crystallographic files, in CIF format, for complexes **1**−**8**. This material is available free of charge via the Internet at http://pubs.acs.org.

IC034114Y

---

(41) SMART V 5.050 (NT) *Software for the CCD Detector System*; Bruker Analytical X-ray Systems, Madison, WI, 1998.

(42) SAINT V 5.01 (NT) *Software for the CCD Detector System;* Bruker Analytical X-ray Systems, Madison, WI, 1998.

(43) Blessing, R. H. *Acta Crystallogr.* **1995**, *A51*, 33.

(44) Sheldrick, G. M. SHELXS-97, *Program for the Solution of Crystal Structure*; University of Göttingen, Germany, 1990.

(45) Sheldrick, G. M. SHELXL-97. *Program for the Refinement of Crystal Structure*; University of Göttingen, Germany, 1997.

(46) SHELXTL 5.10 (PC Version). *Program Library for Structure Solution and Molecular Graphics*; Bruker Analytical X-ray Systems, Madison, WI, 1998.