Gravel for their very helpful discussions.

Registry No. 2a, 17698-48-5; **2b**, 85185-50-8; **2c**, 85185-49-5; **2d**, 88179-92-4; **3a**, 6990-64-3; **3b**, 3005-32-1; **3c**, 3005-32-1; **3d**, 72454-26-3; $CH_2{=}C(CH_3)C(CH_3){=}CH_2$, 513-81-5; $CH_2{=}C(Ph)C(Ph){=}CH_2$, 2548-47-2; $CH_3C(CH_3){=}CHCH_2CH_2C({=}CH_2)CH{=}CH_2$, 123-35-3; Ph_3PBr_2, 1034-39-5; $Ph_3P{=}S$, 3878-45-3; S_2, 23550-45-0; 1,1′-dicyclohexenyl, 1128-65-0; 3,6-dihydro-4,5-dimethyl-1,2-dithiin, 18655-88-4; 3,6-dihydro-4,5-dimethyl-1,2-dithiin, 34804-73-4; 3,6-dihydro-4-(4-methylpenta-3-enyl)-1,2-dithiin, 73188-23-5; 1,2,3,4,4a,6a,7,8,9,10-decahydrodibenzo[*c*,*e*][1,2]dithiin, 88157-92-0.

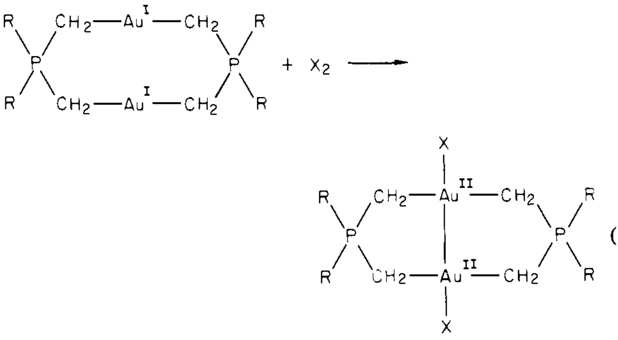
Isomeric Species of $[AuCH_2P(S)(C_6H_5)_2I]_2$. Mixed-Valent Au(I)/Au(III) and Isovalent Au(II)–Au(II) Complexes with the Same Methylenethiophosphinate Ligand

Anthony M. Mazany and John P. Fackler, Jr.*

Department of Chemistry, Texas A&M University
College Station, Texas 77843

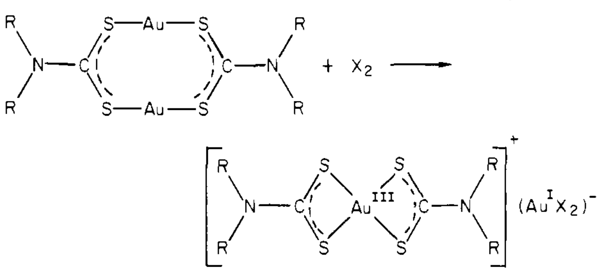
Received September 23, 1983

While continuing our studies with methylenethiophosphinate complexes[1] and organogold ylide complexes,[2,3] we have synthesized a new dinuclear gold ylide species $[AuCH_2P(S)(C_6H_5)_2]_2$, $[Au(mtp)]_2$ (I). The oxidative-addition properties of this species have proved to be especially interesting since both two-center and single-center, two-electron oxidative-addition products have been obtained incorporating I_2. The oxidative addition of halogens and pseudohalogens to dimeric Au(I) phosphorus ylide complexes to yield Au(II)–Au(II) species is now well established[3-5] (reaction A). Analogous dinuclear dithiocarbamate gold(I) compounds are oxidized at room temperature to monomeric Au(I)/Au(III) complexes under similar conditions[6-9] (reaction B).



(A)

X = Cl, Br, I, S_2CNR_2



(B)

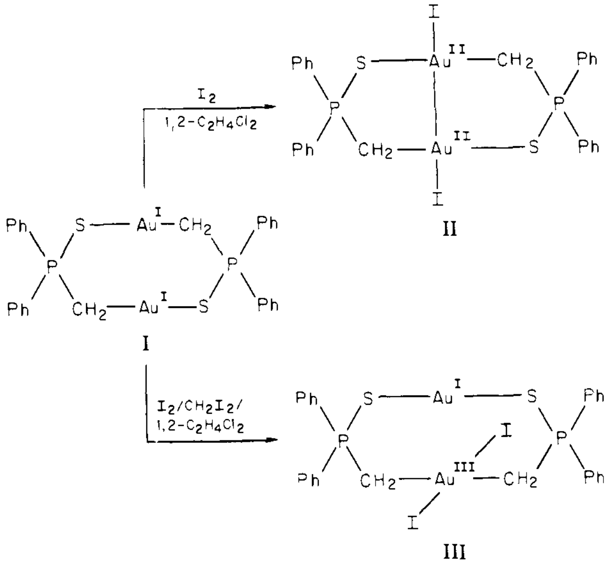
X = Cl, Br, I, CN

Table I. Selected Bond Distances (Å)

	I	II	III[a]
Au···Au	3.040 (1)	2.607 (1) 2.611 (1)	3.050 (3)
Au–C	2.115 (9)	2.092 (15) 2.101 (15)	2.12 (4) 2.13 (5)
Au–S	2.323 (3)	2.370 (5) 2.369 (4)	2.308 (13) 2.316 (12)
Au–I		2.693 (2) 2.681 (1)	2.615 (4) 2.611 (4)
P–C	1.750 (8)	1.798 (15) 1.762 (15)	1.77 (5) 1.87 (5)
P–S	2.018 (3)	2.014 (6) 2.030 (5)	2.02 (2) 2.01 (2)

[a] Preliminary refinement to 10%.

Methylenethiophosphinate complexes are expected to exhibit properties characteristic of both phosphorus ylide and dithioate complexes. This is indeed the case with the chemistry of $[Au(mtp)]_2$. In separate reactions, the oxidative addition of iodine to I has yielded both an isovalent Au(II)–Au(II) complex, II, as observed with gold(I) phosphorus ylide dimers, and a unique mixed-valent Au(I)/Au(III) isomer, III, (C).



(C)

All three compounds, I–III, have been characterized structurally by X-ray diffraction methods.[23] The Au(I)–Au(I) dimer, I, has

---

(1) Mazany, A. M.; Fackler, J. P., Jr. *Organometallics* **1982**, *1*, 752.

(2) Stein, J.; Fackler, J. P., Jr.; Pararizos, C.; Chen, H.-W. *J. Am. Chem. Soc.* **1981**, *103*, 2192–2198.

(3) (a) Fackler, J. P., Jr.; Basil, J. D. *ACS Symp. Ser.* **1983**, *211*, 201–208. (b) Fackler, J. P., Jr.; Basil, J. D. *Organometallics* **1983**, *1*, 871.

(4) (a) Anderson, G. K. *Adv. Organomet. Chem.* **1982**, *20*, 39–114. (b) Puddephatt, R. J., In "Topics in Inorganic and General Chemistry"; Clark, R. J. H., Ed.; Elsevier: Amsterdam, 1978; Vol. 16, "The Chemistry of Gold".

(5) (a) Schmidbaur, H. "Gmelin Handbuch der Anorganischen Chemie-Au, Organogold Compounds"; Springer-Verlag: Berlin, Heidelberg, 1980. (b) Kaska, C. *Coord. Chem. Rev.* **1983**, *48*, 1–58.

(6) Beurskens, P. T.; Blaauw, H. J. A.; Cras, J. A.; Steggerda, J. J. *Inorg. Chem.* **1968**, *7*, 805.

(7) Beurskens, P. T.; Cras, J. A.; Steggerda, J. J. *Inorg. Chem.* **1968**, *7*, 810.

(8) Blaauw, H. J. A.; Nivard, R. J. F.; van der Kerk, G. J. M. *J. Organomet. Chem.* **1964**, *2*, 236.

(9) Calabro, D. C.; Harrison, B. A.; Palmer, G. T.; Moguel, M. K.; Rebbert, R. L.; Burmeister, J. L. *Inorg. Chem.* **1981**, *20*, 4311–4316.

(10) Neira, R. Ph.D. Dissertation, Case Western Reserve University, Cleveland, OH, 1983.

(11) Akerstrom, S. *Ark. Kemi* **1959**, *14*, 387.

(12) Hesse, R.; Jennische, P. *Acta Chem. Scand.* **1972**, *26*, 3855.

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

(14) Crane, W. S.; Becall, H. *Inorg. Chim. Acta* **1978**, *31*, L469.

(15) Hofmann, K. A.; Hochtlein, F. *Ber. Dtsch. Chem. Ges.* **1903**, *36*, 3090.

(16) Kuchen, W.; Mayatepek, H. *Chem. Ber.* **1968**, *101*, 3454.

(17) Schmidbaur, H.; Franke, R.; Eberlein, J. *Chem.-Ztg.* **1975**, *99*, 91.

(18) Ford-Smith, M. H.; Habeed, J. J.; Rawsthorne, J. H. *J. Chem. Soc., Dalton Trans.* **1972**, 2116.

(19) Isci, H.; Mason, W. R. *Inorg. Chem.* **1982**, *22*, 2266–2272.

(20) Westland, A. D. *Can. J. Chem.* **1969**, *47*, 4135.

(21) Schmidbaur, H.; Dash, K. C. *Adv. Inorg. Chem. Radiochem.* **1982**, *25*, 239–266.

(22) Manojlovic-Muir, L. *J. Organomet. Chem.* **1974**, *73*, C45.

0002-7863/84/1506-0801$01.50/0

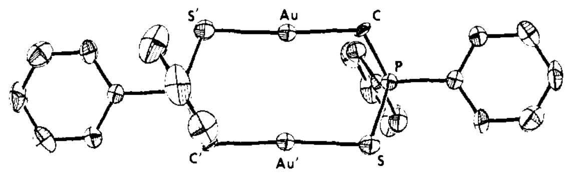


Figure 1. Molecular structure of $[Au^{I}CH_2P(S)(C_6H_5)_2]_2$, $[Au^{I}(mtp)]_2$ (50% probability thermal ellipsoids); see table I for bond distances.

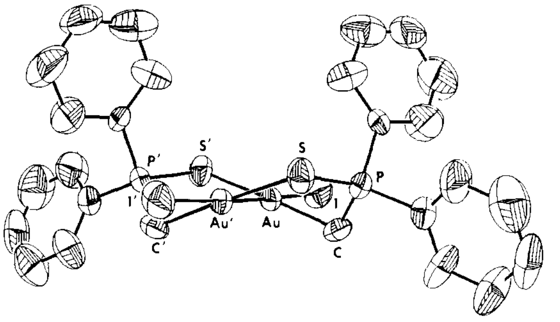


Figure 2. Molecular structure of $[Au^{II}(mtp)I]_2$ (50% probability thermal ellipsoids).

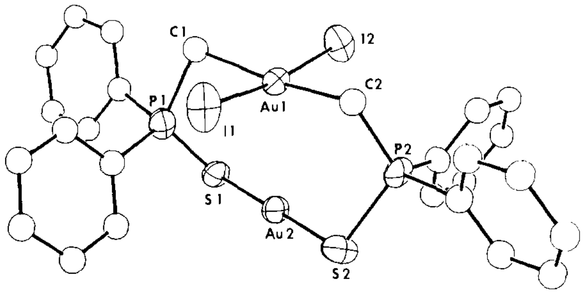


Figure 3. Molecular structure of $[Au^{I}(mtp)_2Au^{III}I_2]$ (50% probability thermal ellipsoids for non-carbon atoms).

a trans ligand geometry (Figure 1), which is retained upon oxidation to the isovalent Au(II) iodide dimer (Figure 2). The intramolecular Au···Au distance in I is 3.040 (1) Å while the intermolecular Au···Au distance is 3.223 (1) Å. The Au–Au bond length in II averages 2.609 (1) Å, without any intermolecular Au–Au interactions. The Au–Au bond length is substantially reduced in length in comparison to that observed in $[Au(CH_2)_2PR_2I]_2$ (2.69 Å), while the Au–I distances (2.69 Å) are similar.[5,10] The Au–Au distance in the mixed-valent Au(I)/Au(III) dimer (III) is 3.05 Å. The Au(I)/Au(III) dimers stack along the *y* axis with an intermolecular spacing of ~3.4 Å (Table I).

The Au(I)/Au(III) dimer, however, exhibits a cis chelate ligand configuration with both a linear S–Au(I)–S geometry and a *trans*-$Au^{III}I_2C_2$ planar arrangement (Figure 3). Although numerous examples of Au(I) dimers incorporating sulfur are known,[11-17] there are few examples with higher oxidation states of gold, and none previously have been conclusively verified to be Au(II)–Au(II) or mixed valent.

The nature of the $Ph_2P(S)CH_2^-$ ion permits the isolation of a complex that contains two well-established bonding configurations, a linear S–Au(I)–S as found in the dithioate gold(I) dimers and *trans*-$Au^{III}C_2I_2$ as observed with $[Au^{III}(CN)_2I_2]^-$[18,19] or $[([4\text{-}CH_3C_6H_4NH]_2C)_2AuI_2]ClO_4$.[22] The nature of the ligand rearrangement that yields the novel Au(I)/Au(III) dimer is not yet known. However, the electronic spectrum of the reaction mixture that produces the mixed-valence species, III, indicates the presence also of the Au(II)···Au(II) diiodide dimer, II. Further details of the chemistry of $[AuCH_2P(S)Ph_2]_2$ and the isovalent and mixed-valent diiodide species will be reported later.

Synthesis of $[AuCH_2P(S)Ph_2]_2$. The dimer I was synthesized by adding 1 equiv of Li(mtp) dropwise to an diethyl ether suspension of $Ph_3AsAuCl$[20] under nitrogen at −30 °C. As the reaction mixture is allowed to warm to ambient temperature, the arsine complex gradually disappears, and a colorless solution results. After approximately 30 min, the solution becomes yellow, and I is isolated as a yellow precipitate. The yield is 80%. Recrystallization from hot toluene yields light yellow crystals, mp 250 °C dec, FDMS *m/e* 856. Anal. Calcd for $Au_2C_{26}H_{24}P_2S_2$: C, 36.46; H, 2.82. Found: C, 36.67; H, 2.91.

Acknowledgment. Support for this work at Texas A&M has been received from the Robert A. Welch Foundation in the form of a fellowship for A.M.M. We thank Dr. C. Campana for some preliminary crystallographic work, the National Science Foundation, CHE 8305046, and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for supplies. We are grateful to the BFGoodrich Co. for obtaining the mass spectral results.

Registry No. I, 88272-19-9; II, 88272-20-2; III, 88287-59-6; I_2, 7553-56-2; Li(mtp), 52101-86-7; $Ph_3AsAuCl$, 25749-29-5.

Supplementary Material Available: Positional and thermal parameters for I, II, and III (7 pages). Ordering information is given on any current masthead page.

---

[23] **Experimental data.** $C_{26}H_{28}P_2S_2Au_2$: monoclinic, space group $C_{2/c}$ (No. 15), $a = 23.874$ (4) Å, $b = 9.030$ (1) Å, $c = 12.172$ (2) Å, $\beta = 105.61$ (1)°, $Z = 4$, 2161 independent reflections with $I > 2.5\sigma(I)$. $R = 0.047$, $R_w = 0.059$. $C_{26}H_{28}P_2S_2I_2Au^{II}_2$**[Au(II)–Au(II)]**: monoclinic, space group $P2/n$, $a = 12.615$ (4) Å, $b = 12.804$ (2) Å, $c = 19.303$ (3) Å, $\beta = 94.30$ (1)°, $Z = 4$, 3473 independent reflections with $I > 2.5\sigma(I)$. Two independent molecules were found; $R = 0.052$, $R_w = 0.053$. Red crystals of $[Au^{II}(mtp)I]_2$ were obtained by evaporation of a 1,2-$C_2H_4Cl_2$ solution of $[Au(mtp)]_2$ and I_2 (1.0:0.9 molar ratio of $[Au(mtp)]_2$:I_2). No molecular ion observed in FDMS. The ^1H NMR spectrum in $CDCl_3$ exhibits resonances at δ 3.88 ($-CH_2$, $^2J_{PCH} = 12$ Hz) and 7.4–8.0 (C_6H_5). $C_{26}H_{28}P_2S_2I_2Au_2$**[Au(III)/Au(I)]**: monoclinic, space group $C2/c$ (No. 15), $a = 25.187$ (4) Å, $b = 6.4465$ (8) Å, $c = 42.5443$ (11) Å, $\beta = 92.14$ (2)°, $Z = 8$, 3747 independent reflections with $I > 2.5\sigma(I)$ preliminary refinement to 10% R factor. Red crystals of $[Au^{I}(mtp)_2Au^{III}I_2]$ were obtained by the evaporation of a (v:v) solution of CH_2I_2 and 1,2-$C_2H_4Cl_2$ containing $[Au(mtp)]_2$ and iodine. No molecular ion observed in FDMS. Both diiodide species exhibit a peak at *m/e* 659 corresponding to $[Au(mtp)_2]^+$. All calculations were performed using both Enraf-Nonius SDP and Nicolet SHELXTL crystallographic programs. All data was collected on Nicolet P3f four-circle diffractometer at ambient temperature with graphite-monochromated Mo Kα radiation. All data corrected for Lorentz, decay, polarization, and absorption effects.

Stereochemistry and Kinetic Deuterium Isotope Effects in the Thermal 1,3-Sigmatropic Rearrangement of (−)-(*R*,*R*)-*trans*-2-Methyl-1-(1-*tert*-butylvinyl)cyclopropane: Evidence for a Biradical Intermediate

Joseph J. Gajewski* and James Michael Warner

Department of Chemistry, Indiana University
Bloomington, Indiana 47405

Received June 10, 1983
Revised Manuscript Received November 14, 1983

The thermally induced, first-order 1,3-sigmatropic shift in vinylcyclopropane to cyclopentene proceeds concurrently with geometric isomerization of the cyclopropane. Willcott showed that a freely rotating biradical is involved in the geometric isomerization,[1] and Baldwin found that the 1,3 shift in *trans*-2-methyl-1-(*trans*-propenyl)cyclopropane occurs with 65% *si*, 22% *sr*, 8% *ar*, and 5% *ai* stereochemistry.[2] In the latter case appropriate corrections were made for the loss of optical activity of starting material. Also formed was the 1,4-diene resulting from the well-known homo-1,5-hydrogen shift of *cis*-2-(methylvinyl)cyclopropanes.[3] This data may be interpreted as indicating four

---

[1] Willcott, M. R., III; Cargle, V. H. *J. Am. Chem. Soc.* **1969**, *91*, 4310.

[2] Andrews, G. D.; Baldwin, J. E. *J. Am. Chem. Soc.* **1976**, *98*, 6705.

[3] Gajewski, J. J. "Hydrocarbon Thermal Isomerizations"; Academic Press: New York, 1981.

0002-7863/84/1506-0802$01.50/0 © 1984 American Chemical Society