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; CH₂=C(CH₃)C(CH₃)=CH₂, 513-81-5; CH₂=C(Ph)C(Ph)=CH₂, 2548-47-2; CH₃C(CH₃)=CHCH₂CH₂C(=CH₂)CH=CH₂, 123-35-3; Ph₃PBr₂, 1034-39-5; Ph₃P=S, 3878-45-3; S₂, 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-(4methylpenta-3-enyl)-1,2-dithiin, 73188-23-5; 1,2,3,4,4a,6a,7,8,9,10decahydrodibenzo[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 complexes¹ and organogold ylide complexes, 2,3 we have synthesized a new dinuclear gold ylide species [AuCH₂P(S)(C₆H₅)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 I2. The oxidative addition of halogens and pseudohalogens to dimeric Au(I) phosphorus ylide complexes to yield Au(II)-Au(II) species is now well established³⁻⁵ (reaction A). Analogous dinuclear dithiocarbamate gold(I) compounds



 $X = Cl, Br, I, S_2CNR_2$

are oxidized at room temperature to monomeric Au(I)/Au(III) complexes under similar conditions⁶⁻⁹ (reaction B).



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Table I. Selected Bond Distances (Å)

		<u>т</u>	IIIa
Au…Au	3.040 (1)	2.607 (1)	3.050 (3)
		2.611(1)	
Au-C	2.115 (9)	2.092 (15)	2.12 (4)
		2.101 (15)	2.13 (5)
Au-S	2.323 (3)	2.370 (5)	2.308 (13)
		2.369 (4)	2.316 (12)
Au-I		2.693 (2)	2.615 (4)
		2.681(1)	2.611 (4)
P-C	1.750 (8)	1.798 (15)	1.77 (5)
		1.762 (15)	1.87 (5)
P_S	2.018(3)	2 014 (6)	2.02(2)
1.5	2.010 (0)	2.030(5)	2.01(2)
		2.030(3)	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).



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

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Figure 1. Molecular structure of $[Au^ICH_2P(S)(C_6H_5)_2]_2$, $[Au^I(mtp)]_2$ (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-(CH₂)₂PR₂I]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}I₂C₂ planar arrangement (Figure 3). Although nu-

merous 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 Ph₂P(S)CH₂⁻ 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}C₂I₂ as observed with $[Au^{III}(CN)_2I_2]^{-18,19}$ or $[([4-C-H_3C_6H_4NH]_2C)_2AuI_2]ClO_4^{.22}$ 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 Ph₃AsAuCl²⁰ 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 Au₂C₂₆H₂₄P₂S₂: C, 36.46; H, 2.82. Found: C, 36.67; H, 2.91.

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Registry No. I, 88272-19-9; II, 88272-20-2; III, 88287-59-6; I₂, 7553-56-2; Li(mtp), 52101-86-7; Ph₃AsAuCl, 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.

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

⁽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, $R_w = 0.059$. $C_{26}H_{28}P_2S_2I_2Au_1^{II}[Au(II)-Au(II)]$: 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-C₂H₄Cl₂ solution of $[Au(mtp)]_2$ and I₂ (1.0:0.9 molar ratio of $[Au(mtp)]_{2}I_2$). No molecular ion observed in FDMS. The ¹H NMR spectrum in CDCl₃ exhibits resonances at δ 3.88 (-CH₂, ²J_{PCH} = 12 Hz) and 7.4-8.0 (C₆H₃). $C_{26}H_{28}P_3S_2I_4Au_2[Au(III)/Au(I)]$: 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 CH₂I₂ and 1,2-C₂H₄Cl₂ containing $[Au(mtp)]_2$ and iodine. No molecular ion observed in FDMS. Both diiodide species exhibit a peak at m/e 659 corresponding to $[Au(mtp_2)_2^*$. 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-mono-chromated Mo K α radiation. All data corrected for Lorentz, decay, polarization, and absorption effects.

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