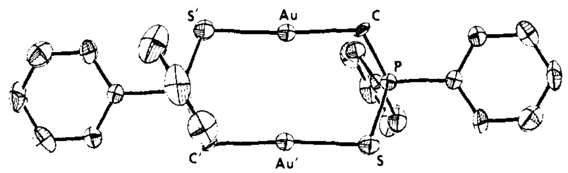

Figure 1. Molecular structure of $[Au^{I}CH_2P(S)(C_6H_5)_2]_2$, $[Au^{I}(mtp)]_2$ (50% probability thermal ellipsoids); see table I for bond distances.

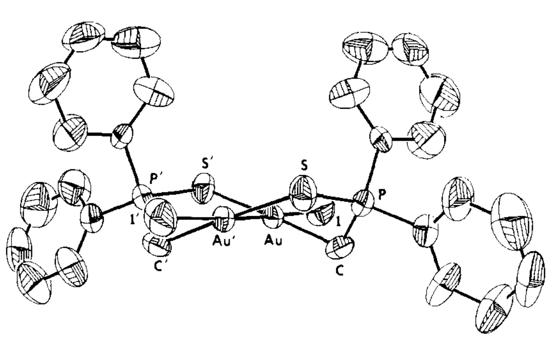

Figure 2. Molecular structure of $[Au^{II}(mtp)I]_2$ (50% probability thermal ellipsoids).

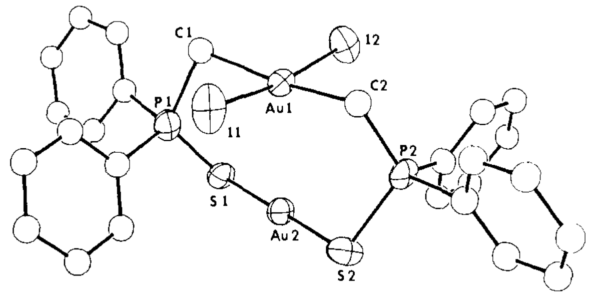

Figure 3. Molecular structure of $[Au^{I}(mtp)_2Au^{III}I_2]$ (50% probability thermal ellipsoids for non-carbon atoms).

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.

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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.

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[23] **Experimental data.** $C_{26}H_{28}P_2S_2Au_2$: monoclinic, space group $C2/c$ (No. 15), a = 23.874 (4) Å, b = 9.030 (1) Å, c = 12.172 (2) Å, β = 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, β = 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, β = 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

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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

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[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.

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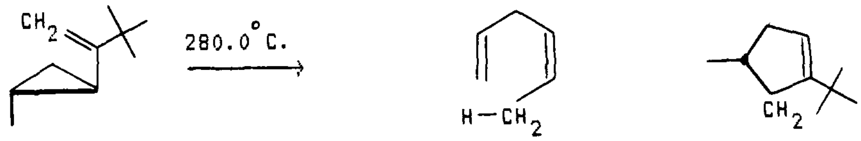
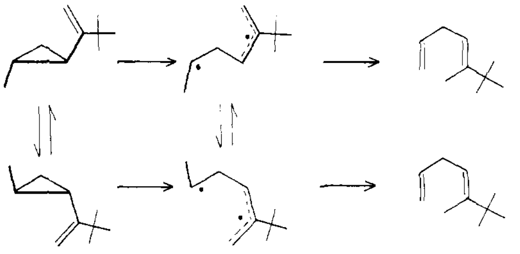
Scheme I[a]



	k(enant)	k(rear)	k(1.5-H)	k(1.3-C)
	2.50 ± 0.15	1,30 ± 0.03	0.915 ± 0.02	0.385 ± 0.01 (7.1 ± 1% net ret)
$CH_2 \rightarrow CD_2$	2.50 ± 0.09	1.35 ± 0.02	1,00 ± 0.03	0,35 ± 0.01 (4.1 ± 1,5% net ret)
k^H/k^{D_2}	1.00 ± 0.07	1/1,045 ± 0,04	1/1.11 ± 0.04	1.1250 ± 0.04 (1.88 ± 0,68 on ret)

[a] k's in units of 10^{-5}/s at 280.0 °C from at least four points, KIEs corrected to 100% D_2,[5] optical purities from ref 2 and 6.

Scheme II



separate concerted 1,3 shifts or formation of a biradical that closes competively with bond rotation. There are two geometric isomers of the allyl portion of the biradical: the transoid one, which cannot give a cyclopentene but only recombine to cyclopropane, and the cisoid one, which can undergo both reactions. This complicates mechanistic analyses.

In an effort to resove the mechanistic question in the 1,3–shift, concerted or not, (−)-(*R*,*R*)-*trans*-2-methyl-1-(1-*tert*-butylvinyl)cyclopropane and its 1-(2,2-dideuterio-1-*tert*-butylvinyl) derivative (80% deuterated) were prepared and heated in the gas phase in a static well-conditioned reactor at 280.0 °C (Scheme I). These materials were chosen in order to force the cisoid conformation on the possible diradical so that the 1,3 shift is competitive with geometric isomerization to allow application of the Dolbier isotope effect criterion for intervention of an intermediate.[4]

The *tert*-butyl group appears to promote the formation of the cisoid biradical since the ratio of diene to cyclopentene in every other *trans*-2-methyl-1-vinylcycloproapne rearrangement is ~16.[3] However, the rate constant for 1,3 shift in the *tert*-butyl derivative is very similar to that from every other of these rearrangements at 280 °C indicating relatively little perturbation of this pathway.

The difference in stereochemistry between this experiment and Baldwin's is that there is no steric bias in the formation of the 1,3-shift product above whereas the previously observed preference for inversion may have resulted from the favored formation of the more stable, trans isomer of 3,4-dimethylcyclopentene.

The observed normal isotope effect on the 1,3 shift is in the opposite direction from that usually associated with secondary α deuterium isotope effects resulting from changes in bonding,[7] but it is in the direction previously attributed to a rotational isotope effect.[8] Of significance is the inverse isotope effect on the 1,5-H shift. Such an effect is unexpected since this product must arise by either rate-determining geometric isomerization to the cis-2-methyl material, a reaction that should not be affected by remote deuterium, or the product may arise by hydrogen shift in a biradical, which, by virtue of its enormous exergonicity, should have but a small isotope effect.[9] It would therefore appear that this inverse isotope effect arises by induction from the rotational effect on the 1,3-shift; that is, rate-determining formation of a biradical followed by fast closure will result in more 1,5-shift product if the 1,3-shift process is retarded regardless of whether the biradical undergoes the hydrogen shift or closes to the cis isomer. Supporting this interpretation is the fact that the cyclopentene product is more highly racemized when formed from the D_2 material. Thus, the intermediate can undergo more bond rotation due to retardation of the closure of the biradical to the cyclopentene (Scheme II).

This mechanistic hypothesis, however, is not consistent with the relatively large rate constant for enantiomerization *unless* the enantiomerization is a separate process. It may be that there is a separate concerted double-rotation process as in phenylcyclopropane or cyclopropane itself[10] or that the two processes, double rotation and biradical reaction, occur out of different noninterconverting conformations of the biradical. In any event, this vinylcyclopropane 1,3 shift does not appear to be concerted; therefore it is unlikely that the stereochemistry is due to orbital symmetry control. A face-to-face 1,3-biradical resulting from stretching the C-1,C-2 bond will rationalize the stereochemistry if the biradical closes with least motion control. Formation of a face-to-face 1,3-biradical can also rationalize the stereochemistry of the spiropentane to methylenecyclobutane rearrangment[11] and of the norcaradiene circumambulation[12] suggesting that this species may be a minimum on the cyclopropane energy surface despite sophisticated calculations to the contrary.[13]

Acknowledgment. We thank the National Science Foundation for generous financial support.

Registry No. (−)-(*R*,*R*)-*trans*-2-Methyl-1-(1-*tert*-butylvinyl)cyclopropane, 88158-46-7; (−)-(*R*,*R*)-*trans*-2-methyl-1-(2,2-dideuterio-1-*tert*-butylvinyl)cyclopropane, 88179-96-8.

Supplementary Material Available: A listing of the kinetic data and the data analysis (2 pages). Ordering information is given on any current masthead page.

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(4) Dolbier, W. R., Jr.; Dai, S.-H. *J. Am. Chem. Soc.* **1970**, *92*, 1774; **1972**, *94*, 3946.

(5) Gajewski, J. J.; Benner, C. W.; Stahly, B. N.; Hall, R. F.; Sato, R. I. *Tetrahedron* **1982**, *38*, 853.

(6) (a) (R,R)-*trans*-2-Phenylcyclopropanecarboxylic acid $[\alpha]_D$ −302° (EtOH), 97% optically pure[6b] was converted to (−)-(*R*,*R*)-*trans*-2-methyl-1-(1-*tert*-butylvinyl)cyclopropane with $[\alpha]_{365}$ −84.3° (cyclohexane). NMR: δ 0.29 (m, 1 H), 0.61 (m, 1 H), 0.93 (m, 2 H), 1.07 (br s, 12 H), 4.32 (s, 1 H), 4.57 (s, 1 H). The 80% deuterated olefin had $[\alpha]_{365}$–84.4°. (b) Inouye, Y.; Sugita, T.; Walborsky, H. W. *Tetrahedron* **1964**, *20*, 1695. (c) Optically pure[6d] (*R*)-3-methylcyclopentanone $[\alpha]_D$ +154° was treated with *tert*-butyl lithium then dehydrated with dilute sulfuric acid to (*R*)-4-methyl-1-*tert*-butylcyclopentene $[\alpha]_{365}$ +150.4° (cyclohexane). NMR: δ 1.0 (s superimposed on a doublet, 12 H), 1.62–2.6, (m 5 H), .19 (m, 1 H). (d) Kokke, W. C. M. C.; Varkevisser, F. A. *J. Org. Chem.* **1974**, *39*, 1535. (e) The homo-1,5-shift diene, (*E*)-5-*tert*-butyl-1,4-hexadiene, was identified by NMR: δ 1.04 (s, 9 H), 1.61 (s, 3 H), 2.72 (t, *J* = 7 Hz, 2 H), 4.82 (m, 2 H), 5.27 (t, *J* = 7 Hz, 1 H), 5.70 (m, 1 H).

(7) Hartshorn, S. R.; Shiner, V. J., Jr. *J. Am. Chem. Soc.* **1972**, *94*, 9002.

(8) Crawford, R. J.; Cameron, D. M. *J. Am. Chem. Soc.* **1966**, *88*, 2589. And ref 4.

(9) The calculated KIE for complete change in bonding at the methyl center at 280 °C is only 1/1.05.[7]

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(11) Gajewski, J. J.; Burka, L. T. *J. Am. Chem. Soc.* **1972**, *94*, 8865.

(12) Klärner, F.-G.; Brassel, B. *J. Am. Chem. Soc.* **1980**, *102*, 2469.

(13) See footnotes 34 and 35 of ref 10 for references to calculations with appropriate comments.