to significant crystal decay during data collection provided metrical parameters of limited accuracy.[12] However, a number of key structural features are readily apparent. Compound **4** may be described as a dimeric, base-stabilized silylene complex, as indicated by distinct Si–N distances for each silicon center (1.82 (2) and 1.93 (2) Å; 1.81 (2) and 1.91 (2) Å), corresponding to covalent and dative bonds. The length of the new C–C bond that links the two halves of the dimer is 1.57 (3) Å, which is most consistent with sp^3 character at the two carbon centers. Figure 2 illustrates how the monomer units are positioned in the dication of **4** and reveals the presence of tolyl group–phenanthroline π-stacking.

Note that this carbon–carbon coupling reaction of two phenanthroline rings is made possible by the conversion of one of the Si $\leftarrow$ N dative bonds in **3** to a Si–N normal covalent bond. Related processes, such as the reduction of alkylpyridinium salts by sodium amalgam to afford 4,4′-tetrahydrobipyridyl, have been reported.[13]

Acknowledgment is made to the National Science Foundation for their generous support. We thank Johnson Matthey Inc. for a loan of ruthenium, and T.D.T. thanks the Alfred P. Sloan Foundation for a research fellowship (1988–1992).

Supplementary Material Available: Experimental procedures and characterization data for **2–4**, a packing diagram for **4**, and tables of crystal, data collection, and refinement parameters, bond distances and angles, anisotropic displacement parameters, and hydrogen atom coordinates for **3** and **4** (25 pages); listings of observed and calculated structure factors for **3** and **4** (59 pages). Ordering information is given on any current masthead page.

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(12) X-ray structure analysis of **4**: M_r = 1738; purple crystal (0.30 × 0.30 × 0.33 mm); monoclinic; space group $P2_1/c$; a = 19.516 (7), b = 21.893 (7), c = 20.639 (7) Å, β = 112.36 (3)° at 23 °C; V = 8155 (5) Å^3; Z = 4; D_x = 1.416 g cm^{-3}; λ(Mo Kα) = 0.71073 Å; $F(000)$ = 3592. A total of 10726 independent reflections ($2\theta_{max}$ = 45°). The decay of monitored reflections was ca. 50% during 146 h of X-ray exposure, and an appropriate scale factor was applied to account for the decay. A total of 4280 reflections with $F > 4\sigma(F)$ were observed and used for structure solution (Patterson method) and refinement (full-matrix least squares); R = 9.51, R_w = 10.34. The Ru, P, and Si atoms were refined anisotropically. The hydrogen atoms were calculated and fixed in idealized positions (d(C–H) = 0.96 Å, $U = 1.2U_{iso}$ for the carbon to which it was attached). One of the triflates was disordered and the S–C bond was fixed at 1.80 Å.

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Room Temperature Isomerization of Siloxycyclopropanes to Silyl Ethers of 2-Methylenealkanols Catalyzed by Zeise's Dimer

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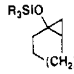
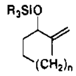
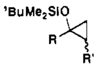
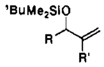
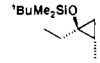
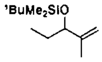
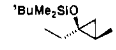
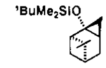
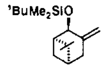
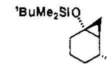
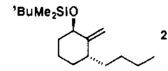
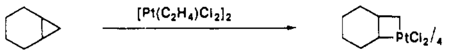
Table I. Pt(II)-Catalyzed Isomerization of Siloxycyclopropanes **1** to Allyl Silyl Ethers **2**[a]

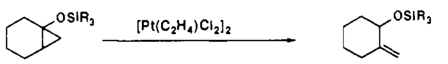
entry	substrate	No.	product	No.	yield (%)[b]
					
1	n = 1, R$_3$Si = ^{t}BuMe$_2$Si	1a	n = 1, R$_3$Si = ^{t}BuMe$_2$Si	2a	96
2	n = 2, R$_3$Si = ^{t}BuMe$_2$Si	1b	n = 2, R$_3$Si = ^{t}BuMe$_2$Si	2b	96
3	n = 2, R$_3$Si = Me$_3$Si	1c	n = 2, R$_3$Si = Me$_3$Si	2c	74
4	n = 3, R$_3$Si = ^{t}BuMe$_2$Si	1d	n = 3, R$_3$Si = ^{t}BuMe$_2$Si	2d	73
					
5	R = Pr, R′ = Et	1e[c]	R = Pr, R′ = Et	2e	88
6	R = H, R′ = ^{i}Pr	1f[d]	R = H, R′ = ^{i}Pr	2f	71
7		1g		2g	83
8		1h		2g	89
9[e]		1i		2i	72
10		1j		2j	89

[a] Reactions were conducted in CHCl$_3$ using 2–5 mol % of [Pt(C$_2$H$_4$)Cl$_2$]$_2$ at 20 °C for 0.5–10 h. [b] Isolated yields after chromatographic purification. [c] E/Z = 50/50. [d] E/Z = 82/18. [e] Using 10 mol % of [Pt(C$_2$H$_4$)Cl$_2$]$_2$.

The transition-metal-promoted isomerization of cyclopropanes has attracted much attention for the past two decades.[1] Investigations using rhodium[2] and iridium[3] catalysts have been successful, but the utility of these catalysts often suffered from drastic conditions and poor stereo- and regioselectivity. On the other hand, very few publications have appeared which deal with the catalytic isomerization of cyclopropanes by platinum complexes.[4] The main reason for this may be the formation of well-known *stable* platinacyclobutane complexes (eq 1).[5] In this communication, we report an efficient catalytic isomerization achieved by the introduction of a siloxy group onto a cyclopropane ring (eq 2). This reaction proceeds smoothly *at ambient temperature* and is quite general for 2-alkyl-substituted siloxycyclopropanes **1**.[6] Furthermore, the isomerization exhibits complete regio- and stereoselectivity to give allyl silyl ethers **2**.



(1)



(2)

In a preliminary experiment, we attempted the stoichiometric reaction of bicyclic siloxycyclopropane **1b** with Zeise's dimer in CHCl$_3$ at room temperature. Isomerization of **1b** took place immediately to give an *exo*-methylene-type allyl silyl ether **2b**, quantitatively. This result stands in sharp contrast to our earlier study[7] on the reaction of 1-aryl-1-siloxycyclopropanes with Zeise's dimer, wherein β-platinum ketone complexes were formed with liberation of chlorosilane. Thus, we tested the catalytic isomer-

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(4) Doyle, M. P.; van Leusen, D. *J. Org. Chem.* **1982**, *47*, 5326.

(5) (a) Puddephatt, R. J. *Coord. Chem. Rev.* **1980**, *33*, 149. (b) Hartley, F. R. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, 1982; Vol. 6, p 573.

(6) ZnI$_2$-promoted isomerization of siloxycyclopropanes was restricted to strained bicyclo[n.1.0] (n = 3, 4, 5) and spiro[4.2] systems. See: (a) Murai, S.; Aya, T.; Renge, T.; Ryu, I.; Sonoda, N. *J. Org. Chem.* **1974**, *39*, 858. (b) Ryu, I.; Murai, S.; Otani, S.; Sonoda, N. *Tetrahedron Lett.* **1977**, 1995. (c) Ryu, I.; Murai, S.; Sonoda, N. *Tetrahedron Lett.* **1977**, 4611; **1978**, 856. (d) Ryu, I.; Aya, T.; Otani, S.; Murai, S.; Sonoda, N. *J. Organomet. Chem.* **1987**, *321*, 279.

(7) Ikura, K.; Ryu, I.; Ogawa, A.; Sonoda, N.; Harada, S.; Kasai, N. *Organometallics* **1991**, *10*, 528.

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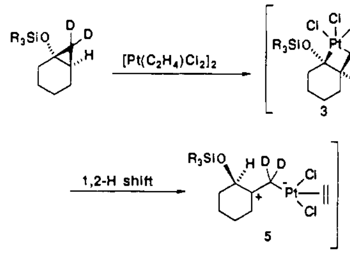
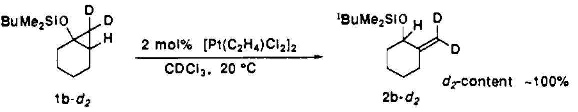
Scheme I



ization of a variety of 2-alkyl-substituted siloxycyclopropanes **1** and found the reaction to be quite general. Reaction of a chloroform solution of **1** with 2–10 mol % of Zeise's dimer at room temperature for 0.5–10 h afforded allyl silyl ethers **2** in good to excellent yields (Table I). Olefin formation was regioselective, and no other isomeric enol silyl ethers were detected.[8] Bicyclic siloxycyclopropanes **1a** and **1b** having 5- and 6-membered rings underwent a particularly rapid isomerization to **2a** and **2b**, respectively (entries 1 and 2). 2-Alkyl-substituted **1f**, prepared from 3-methylbutanal in two steps, was similarly converted to **2f** (entry 6). In all cases studied, the ring opening of **1** took place only between the methylene and the siloxy carbons. Other solvents (CH_2Cl_2, CH_3CO_2Et, THF, Et_2O, and PhH) can also be used to affect the isomerization.

To gain some insight into this reaction, an experiment using a deuterium-labeled substrate was carried out. The reaction of **1b**-d_2, possessing two deuteriums at a peripheral carbon in the cyclopropane ring, with 2 mol % of Zeise's dimer in $CDCl_3$ afforded **2b**-d_2 with ~100% d_2 content (eq 3). The two deuteriums were located exclusively on the exocyclic methylene carbon.[9]



(3)

The reaction of chiral siloxycyclopropane **1i** is noteworthy in terms of its stereochemistry and mechanism. The isomerization of **1i** afforded an optically active allyl silyl ether **2i** in which the observed stereochemistry of the siloxy carbon corresponded to ~100% inversion of configuration (entry 9).[10] Diastereoselective isomerization of **1j** also proceeded with inversion at the siloxy carbon (entry 10).[11] It is known that β-hydrogen abstraction causes the decomposition of platinacyclobutanes into olefins.[12] However, this mechanism seems less likely in our case, since β-hydride elimination and subsequent reductive elimination at the siloxy carbon should cause retention of configuration. Thus, we propose the reaction pathway involving a zwitterion (Scheme I) to explain the above stereochemical outcome. First, the insertion of platinum between the methylene and siloxy carbons takes place to form platinacycle **3**. Heterolytic cleavage of the platinum–siloxy carbon bond to give a zwitterion **4**, followed by a 1,2-hydrogen shift at the β-carbon to platinum, gives the allyl silyl ether. The key factor in this reaction would be stabilization of **4** by the siloxy group which permits the catalytic process.

We anticipate that the mildness and efficiency of the Pt(II)-promoted isomerization of siloxycyclopropanes to allyl silyl ethers will find considerable use in organic chemistry.[13]

Acknowledgment. We thank Professor S. Murai at Osaka University and Professors A. Tai and T. Sugimura at Himeji Institute of Technology for helpful discussions. We also thank Professor H. Alper at the University of Ottawa for his valuable comments. This work was supported by a Grant-in-Aid from the Ministry of Education, Science and Culture of Japan.

Supplementary Material Available: Typical experimental procedure and spectral data for all compounds prepared (4 pages). Ordering information is given on any current masthead page.

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[8] Cf. Ikura, K.; Ryu, I.; Ogawa, A.; Kambe, N.; Sonoda, N. *Tetrahedron Lett.* **1989**, *30*, 6887.

[9] After termination of the reaction, ^1H NMR data suggested no change in the integration of the ethylene protons coordinated to platinum, while the ethylene resonance gave a broad singlet. This may suggest that key species of the catalyst have ethylene ligands.

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[11] For determination of the stereochemistry of **2j**, see the supplementary material.

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Chemistry of Isoprenylated Cysteinyl Containing Peptides. [2,3] Sigmatropic Rearrangement of *S*-Farnesylcysteinyl Sulfoxides. Studies toward a Mild Method of Deprenylating Lipopeptides

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The recent identification of posttranslational modifications which involve the S-isoprenylation of cysteinyl residues to form thioether-containing lipoproteins has received a great deal of attention, most notably due to the role of farnesylated proteins in cancer mediated by *ras* oncogenes.[1] The chemical literature of isoprenylated cysteine systems is sparse,[2,3] and present methods for deprenylation of proteins/peptides, and hence structural identification, are limited and involve fairly harsh conditions (Raney nickel desulfurization, sulfonium ion formation).[4] Though these procedures may suffice for simple isoprenoids, they may ultimately be inadequate should lipid components be isolated which contain more delicate functionalities[5] (such as allylic alcohols as

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[1] Goldstein, J. L.; Brown, M. S. Regulation of the Mevalonate Pathway. *Nature* **1990**, *343*, 425–430. Barbacid, M. Ras Genes. *Annu. Rev. Biochem.* **1987**, *56*, 779–827. Schafer, W. R.; Trueblood, C. E.; Yang, C. C.; Mayer, M.; Rosenberg, S.; Poulter, C. D.; Kim, S. H.; Rine, J. Enzymatic Coupling of Cholesterol Intermediates to a Mating Pheromone Precursor and to the Ras Protein. *Science* **1990**, *249*, 1133–1134. Hancock, J. F.; Magee, A. I.; Childs, J. E.; Marshall, C. J. All Ras Proteins are Polyisoprenylated but Only Some are Palmitoylated. *Cell* **1989**, *57*, 1167–1177. Maltese, W. A. Post-Translational Modification of Proteins by Isoprenoids in Mammalian Cells. *FASEB J.* **1990**, *4*, 3319–3328. Gibbs, J. B. Ras C-terminal Processing Enzymes – New Drug Targets? *Cell* **1991**, *65*, 1–4. Glomset, J. A.; Gelb, M. H.; Farnsworth, C. C. The Prenylation of Proteins. *Curr. Opin. Lipid* **1991**, *2*, 188–124.

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