as shown in Table II. Virtually infinitely large slope was estimated for *t*-BuOH. The intercept falls always near 0, while it depends on the slope.

On the basis of these results, we propose a more elaborate mechanism for the addition of alcohol to a silaethene as shown in Scheme I. Thus, after the first formation of an alcohol–silene complex **5** as suggested by Wiberg,[5] the intramolecular proton migration in **5** (the first-order rate constant, $k_1$) competes with the intermolecular proton transfer from an extra alcohol to **5** (the second-order rate constant, $k_2$). These two processes give the cis and trans isomers, **3** and **4**, respectively.[10] The mechanism is fully compatible with the observed linear relationship between the product ratio **3**/**4** and 1/[ROH], since the initial product ratio should be represented by eq 2.

$$d[3]/d[4] = (k_1/k_2)/[ROH] \quad (2)$$

The slope, which means the relative rate constant ($k_1/k_2$), would thus reflect the relative ease between the intra- and intermolecular proton transfer. According to the Brønsted catalysis law, $k_2$ and $k_1$ are expected to increase with increasing acidity of ROH and the protonated alcohol, respectively. As shown in Table II, the $pK_a$ values of alcohols decrease in the following order: MeOH > *n*-PrOH > *i*-PrOH > *t*-BuOH. The inverse order is known for the protonated alcohols, $RO^+H_2$: *t*-$BuO^+H_2$ > *i*-$PrO^+H_2$ > *n*-$PrO^+H_2$ > $MeO^+H_2$. The more acidic the alcohol is, the less acidic the corresponding protonated alcohol. Thus $k_1/k_2$ should increase in the following order: MeOH < *n*-PrOH < *i*-PrOH < *t*-BuOH. The observed dependence of the slope on the kind of alcohol is in good agreement with the above prediction.

**Supplementary Material Available:** Experimental and spectroscopic details, NOESY spectra of **3a** and a related compound, and plot of [**3a**]/[**4a**] vs $[MeOH]^{-1}$ (9 pages). Ordering information is given on any current masthead page.

(10) If the intermolecular proton transfer occurs at the same side of the complexed alcohol with the rate constant of $k_2'$, the intercept will correspond to $k_2'/k_2$. Apparently meaninglessly small values of the intercept suggest that the intermolecular syn addition can be neglected.
(11) Bordwell, F. G. *Acc. Chem. Res.* **1988**, *21*, 456.
(12) Arnett, E. M. *Prog. Phys. Org. Chem.* **1963**, *1*, 223.
(13) Olmsted, W. N.; Margolin, Z.; Bordwell, F. G. *J. Org. Chem.* **1980**, *45*, 3295.

## Intramolecular Bis-Silylation of Carbon–Carbon Double Bonds Leading to Stereoselective Synthesis of 1,2,4-Triols

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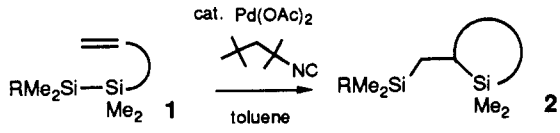
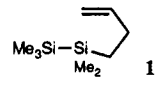
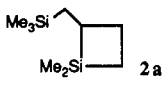
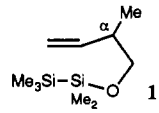
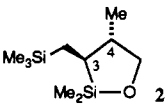
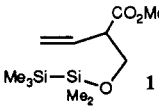
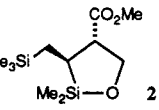
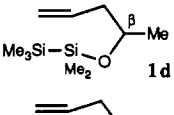
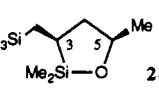
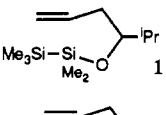
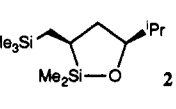
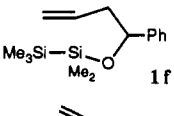
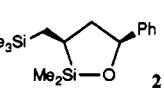
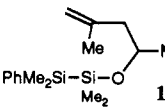
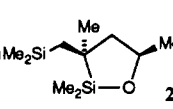
Reactions using organosilicon reagents have become a major tool in organic synthesis,[1] and a variety of pathways to such organosilicon reagents have been developed. Bis-silylation of functional groups such as carbon–carbon multiple bonds with Si–Si is potentially useful since two Si–C bonds are created at once. However, bis-silylation has attracted less attention than hydrosilylation[2] mainly because of the paucity of effective catalysts. Bis-silylation of ethene was achieved with a platinum catalyst, though satisfactory yields were limited to disilanes having electron-withdrawing groups.[3] We reported palladium-catalyzed bis-silylation of isocyanides[4] and very recently found that a new catalyst system, palladium acetate–*tert*-alkyl isocyanide, is extremely efficient for bis-silylation of alkynes with otherwise unreactive disilanes such as hexamethyldisilane.[5] Now we report *intra*molecular bis-silylation of C=C bonds catalyzed by palladium acetate–*tert*-alkyl isocyanide, which leads to stereoselective synthesis of 1,2,4-triols.

**Table I.** Intramolecular Bis-Silylation of Carbon–Carbon Double Bonds




| entry | 1 | conditions | product (2) | yield, % (cis : trans) |
|---|---|---|---|---|
| 1 |  **1a** | reflux 1 h |  **2a** | 83 (-) |
| 2 |  **1b** | 25 °C 6 h |  **2b** | 90 (7 : 93) |
| 3 |  **1c** | 25 °C 8 h |  **2c** | 85 (0 : 100) |
| 4 |  **1d** | 25 °C 6 h |  **2d** | 85 (96 : 4) |
| 5 |  **1e** | 35 °C 10 h |  **2e** | 97 (93 : 7) |
| 6 |  **1f** | 75 °C 6 h |  **2f** | 95 (97 : 3) |
| 7 |  **1g** | 100 °C 1 h |  **2g** | 96 (95 : 5) |

A solution of a terminal alkene **1** incorporating a disilyl group, palladium acetate (1–5 mol %), and 1,1,3,3-tetramethylbutyl isocyanide[6] in toluene[7] was stirred under the conditions specified in Table I. Subsequent Kugelrohr distillation furnished a cyclic bis-silylation product **2** in good yield. Intramolecular stereo- and regioselective addition of the Si—Si linkage to a C=C bond readily took place with **1a–g**; **1a**, having two methylene groups between the C=C bond and the disilyl group, afforded a four-membered exo ring closure product **2a**. Exo ring closure also occurred with **1b–g** to give five-membered products **2b–g**. With disilanes tethered to a C=C bond by chains of more than four atoms, the intramolecular bis-silylation did not proceed. It is not surprising, therefore, that *inter*molecular bis-silylation of olefins with disilanes did not occur at all under similar conditions. Thus, C=C bonds appropriately juxtaposed with disilanes are endowed

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(1) Colvin, E. W. *Silicon Reagents in Organic Synthesis*; Academic Press: London, 1988.
(2) Tamao, K.; Nakajima, T.; Sumiya, R.; Arai, H.; Higuchi, N.; Ito, Y. *J. Am. Chem. Soc.* **1986**, *108*, 6090. Ojima, I. In *The chemistry of organic silicon compounds*; Patai, S., Rappoport, Z., Eds.; Wiley-Interscience: Chichester, 1989; Chapter 25.
(3) Hayashi, T.; Kobayashi, T.; Kawamoto, A. M.; Yamashita, H.; Tanaka, M. *Organometallics* **1990**, *9*, 280.
(4) Ito, Y.; Matsuura, T.; Murakami, M. *J. Am. Chem. Soc.* **1988**, *110*, 3692.
(5) Ito, Y.; Suginome, M.; Murakami, M. *J. Org. Chem.* **1991**, *56*, 1948.
(6) An excess of the isocyanide [1,1,3,3-tetramethylbutyl isocyanide/Pd(OAc)$_2$ = 6–15] was added. Use of less than 6 equiv of isocyanide with respect to Pd(OAc)$_2$ seriously retarded the reaction. Detailed reaction conditions for each experiment are reported in the supplementary material.
(7) Use of THF as solvent gives similar chemical yields and diastereoselectivities.

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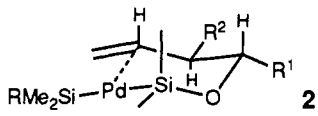
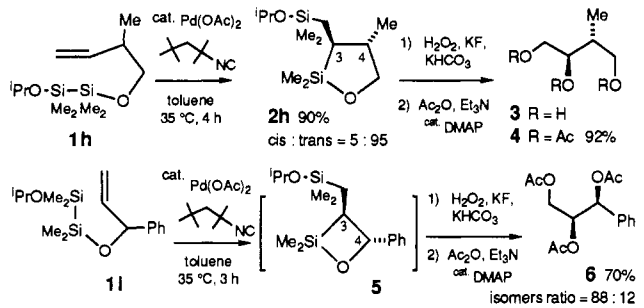
with an enhanced reactivity toward bis-silylation. The present bis-silylation did not require an electron-withdrawing group on the silicon atom (entry 1). Furthermore, a tertiary alkyl-silicon bond was readily formed by the bis-silylation of a geminally disubstituted olefin (entry 7). However, vicinally disubstituted olefins were found not to undergo bis-silylation.

It is noteworthy that bis-silylation of alkenes having an asymmetric center in the tether proceeded with high diastereoselection.[8] Alkenes having allylic substituents, i.e., $\alpha$ to the C=C bond, gave *trans*-**2** (entries 2 and 3), whereas substituents $\beta$ to the C=C bond favored *cis*-**2** (entries 4-7). The stereoselectivity of the reaction is formulated as arising through a preference for a six-membered cyclic transition state **2t**, in which the substituents $R^1$ or $R^2$ are equatorial.




**2t**

The stereoselective intramolecular bis-silylation of olefinic disilanyl ethers, readily prepared from allylic and homoallylic alcohols, is synthetically useful. Thus, oxidation of the two carbon-silicon bonds of the bis-silylation products introduces two hydroxyl groups leading to the stereo- and regio-defined synthesis of triols as demonstrated in the **1h** to **4** and **1i** to **6** conversions. The use of isopropoxydisilyl ether derivatives of olefinic alcohols facilitates the ultimate oxidation of the silicon-carbon bond. The olefinic disilanyl ether **1h** underwent stereoselective bis-silylation to furnish **2h**, which was oxidized with retention of stereochemistry at carbon[9] to *threo*-3-methylbutane-1,2,4-triol (**3**), a versatile intermediate for the syntheses of $\delta$-multistriatin[10] and ionophore antibiotic X-14547A.[11] Similarly, the olefinic disilanyl ether **1i** was converted to 1,2,3-triol triacetate **6** with moderate stereoselection (88:12) by intramolecular bis-silylation and subsequent oxidation. The stereochemistry of **6** suggests formation of the trans-disubstituted four-membered bis-silylation product **5** analogous to **2a**, although the four-membered silyl ether **5** was too unstable to be isolated and characterized.[12] Thus, intramolecular bis-silylation followed by oxidation offers a new entry to stereoselective dihydroxylation of olefins.

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**Supplementary Material Available:** Experimental details for the synthesis and identification of **2a-h**, **4**, and **6** (6 pages). Ordering information is given on any current masthead page.

(8) Details of the assignment of stereochemistry are described in the supplementary material.

(9) Tamao, K.; Ishida, N.; Tanaka, T.; Kumada, M. *Organometallics* **1983**, *2*, 1694.

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(12) The mixture was oxidized directly to triol after removal of catalyst by filtration through a short column of Florisil.

## Models for Non-Heme Iron Oxygenases: A High-Valent Iron-Oxo Intermediate

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The ferryl (Fe=O) species has been demonstrated to be an intermediate in heme peroxidase chemistry[1] and implicated in cytochrome P-450 catalyzed oxygenations.[2] By analogy to these heme enzymes, ferryl species are increasingly being proposed in the mechanisms of dioxygen activation by non-heme iron enzymes[3-6] and invoked in the chemistry of several non-heme alkane functionalization catalysts.[7] Although transient non-heme iron-oxo species have been reported, they have not been fully characterized,[8,9] and the actual viability of an iron(oxo) intermediate in the absence of a porphyrin ligand has yet to be firmly established. During the course of our alkane functionalization studies,[10] we have identified a reactive intermediate derived from the reaction of a ($\mu$-oxo)diferric complex with hydrogen peroxide and report here the spectroscopic characterization of this novel high-valent non-heme iron species.

The reaction of $Fe(ClO_4)_3$ with TPA[11] in the absence of other coordinating anions affords $Fe_2TPA_2O(ClO_4)_4$ (**1**),[12] which has

(1) (a) Schulz, C. E.; Devaney, P. W.; Winkler, H.; Debrunner, P. G.; Doan, N.; Chiang, R.; Rutter, R.; Hager, L. P. *FEBS Lett.* **1979**, *103*, 102-105. (b) Roberts, J. E.; Hoffman, B. M.; Rutter, R.; Hager, L. P. *J. Biol. Chem.* **1981**, *256*, 2118-2121. (c) LaMar, G. N.; deRopp, J. S.; Smith, K. M.; Langry, K. C. *J. Biol. Chem.* **1981**, *256*, 237-243. (d) Hashimoto, S.; Teraoka, J.; Inubushi, T.; Yonetani, T.; Kitagawa, T. *J. Biol. Chem.* **1986**, *261*, 11110-11118. (e) Penner-Hahn, J. E.; Eble, K. S.; McMurry, T. J.; Renner, M.; Balch, A. L.; Groves, J. T.; Dawson, J. H.; Hodgson, K. O. *J. Am. Chem. Soc.* **1986**, *108*, 7819-7825.

(2) McMurry, T. J.; Groves, J. T. *Cytochrome P-450: Structure, Mechanism, and Biochemistry*; Ortiz de Montellano, P. R., Ed.; Plenum: New York, 1986; p 3 and references therein.

(3) Methane monooxygenase: (a) Fox, B. G.; Borneman, J. G.; Wackett, L. P.; Lipscomb, J. D. *Biochemistry* **1990**, *29*, 6419-6427. (b) Fox, B. G.; Froland, W. A.; Dege, J. E.; Lipscomb, J. D. *J. Biol. Chem.* **1989**, *264*, 10023-10033. (c) Green, J.; Dalton, H. *J. Biol. Chem.* **1989**, *264*, 17698-17703.

(4) Ribonucleotide reductase: (a) Sahlin, M.; Sjöberg, B.-M.; Backes, G.; Loehr, T.; Sanders-Loehr, J. *Biochem. Biophys. Res. Commun.* **1990**, *167*, 813-818. (b) Fontecave, M.; Gerez, C.; Atta, M.; Jeunet, A. *Biochem. Biophys. Res. Commun.* **1990**, *168*, 659-664.

(5) Phenylalanine hydroxylase: Dix, T. A.; Benkovic, S. J. *Acc. Chem. Res.* **1988**, *21*, 101-107.

(6) Isopenicillin N synthase: Baldwin, J. E.; Abraham, E. *Nat. Prod. Rep.* **1988**, *5*, 129-145.

(7) (a) Groves, J. T.; Van Der Puy, M. *J. Am. Chem. Soc.* **1976**, *98*, 5290-5297. (b) Sugimoto, H.; Sawyer, D. T. *J. Am. Chem. Soc.* **1976**, *98*, 4283-4285. (c) Vincent, J. B.; Huffman, J. C.; Christou, G.; Li, Q.; Nanny, M. A.; Hendrickson, D. N.; Fong, R. H.; Fish, R. H. *J. Am. Chem. Soc.* **1988**, *110*, 6898-6900. (d) Barton, D. H. R.; Halley, F.; Ozbalik, N.; Young, E.; Balavoine, G.; Gref, A.; Boivin, J. *New J. Chem.* **1989**, *13*, 177-182. (e) Herron, N. *New J. Chem.* **1989**, *13*, 761-766.

(8) Proniewicz, L. M.; Bajdor, K.; Nakamoto, K. *J. Phys. Chem.* **1986**, *90*, 1760-1766.

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(10) Leising, R. A.; Norman, R. E.; Que, L., Jr. *Inorg. Chem.* **1990**, *29*, 2553-2555.

(11) Abbreviations used: TPA = tris(2-pyridylmethyl)amine; OAc = acetate; Por = porphyrin.

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