# Rhodium-Catalyzed Intramolecular Silylformylation of Alkenes

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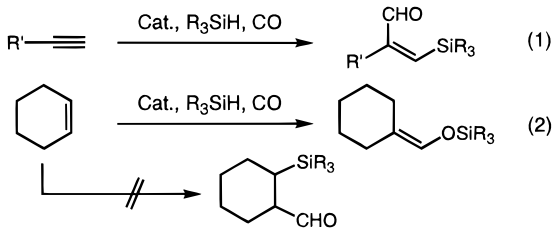
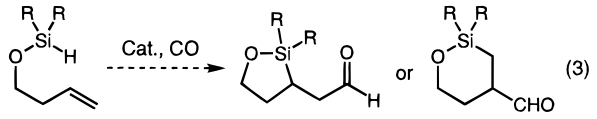
Silylformylation, defined as the addition of $R_3Si-$ and $-CHO$ across various types of bonds with use of a silane $R_3SiH$, CO, and a transition metal catalyst, was discovered by Murai and co-workers, who developed the $Co_2(CO)_8$-catalyzed silylformylation of aldehydes, epoxides, and cyclic ethers.[1] More recently Matsuda and Ojima independently discovered the silylformylation of alkynes catalyzed by rhodium and mixed rhodium−cobalt catalysts, respectively (eq 1).[2,3] By contrast, the same reaction conditions applied to alkenes do not result in silylformylation; rather the silyl enol ether of the formylated alkene is produced (eq 2).[4,5]

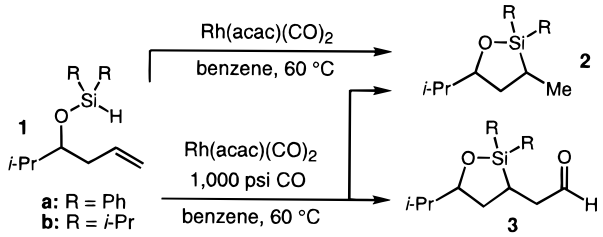



Our own interest in silylformylation derives from a desire to develop methods to control the regiochemistry of olefin carbonylation.[6] Thus, we wondered whether an intramolecular variant might lead to alkene silylformylation with concomitant control of regioselectivity (eq 3).[7] Herein we report that this is indeed the case and present the first examples of silylformylation of alkenes.

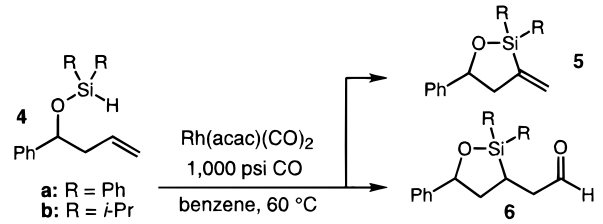



We focused our investigation initially on the homoallylic alcohol class of substrates for the simple reason that they are generally well-behaved in intramolecular hydrosilylation, giving clean and highly regioselective reactions.[8] Thus, subjection of siloxy olefin **1a** to hydrosilylation with $Rh(acac)(CO)_2$ as catalyst resulted in the clean formation of siloxane **2a** as a 4:1 mixture (*cis:trans*) of diastereomers (Scheme 1). Resubjection of **1a** to the same conditions with the addition of 1000 psi of CO led principally to slow formation of aldehyde **3a** as a 6:1 mixture (*cis:trans*) of diastereomers[9] along with a small amount of **2a**. In contrast, subjection of **1b** to the same conditions led only to slow hydrosilylation.

**Scheme 1**




**Scheme 2**




As part of an effort to establish the generality of this discovery we prepared siloxy olefins **4a** and **4b** bearing a phenyl group at the homoallylic position. In an interesting reversal from the chemistry of substrates **1**, **4b**, bearing isopropyl groups on silicon, underwent silylformylation to produce aldehyde **6b** as a 7:1 mixture (*cis:trans*) of diastereomers along with a small amount of vinylsilane **5b** (Scheme 2). Subjection of **4a** to the same conditions led only to slow hydrosilylation accompanied by substantial decomposition.

Following the discovery that successful silylformylation of these substrates depends acutely on the nature of the silicon substituents, we carried out an investigation of the scope of the process (Table 1). In every case (except entry 6) the diastereomeric aldehydes were found to be the major product as determined by $^1H$ NMR and GC analysis. Small amounts (∼10−25%) of the diastereomeric hydrosilylation products were observed as well and were generally the only byproduct produced to any significant extent. Since the aldehyde products, while quite stable, often proved difficult to isolate in analytically pure form[10] they were reduced and protected for the purposes of obtaining isolated yields and spectroscopic characterization. The first trend that emerged was that substitution at the homoallylic position ($R^1$) favors silylformylation. Whereas we observed essentially no carbonylation (all hydrosilylation) of the completely unsubstituted case ($R^1$, $R^2$ = H, $R^3$ = Ph), placement of methyl, allyl, isopropyl, 2-siloxyethyl, and phenyl groups at the homoallylic position all resulted in silylformylation in moderate to good yields (entries 1−5). Substitution at the

(1) (a) Murai, S.; Sonoda, N. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 837−846. (b) Fukumoto, Y.; Chatani, N.; Murai, S. *J. Org. Chem.* **1993**, *58*, 4187−4188. (c) Chatani, N.; Murai, S. *Synlett* **1996**, 414−424.

(2) Matsuda, I.; Ogiso, A.; Sato, S.; Izumi, Y. *J. Am. Chem. Soc.* **1989**, *111*, 2332−2333.

(3) Ojima, I.; Ingallina, P.; Donovan, R. J.; Clos, N. *Organometallics* **1991**, *10*, 38−41.

(4) (a) Colleuille, Y. *Chem. Abstr.* **1966**, *65*, 8959d. (b) Chalk, A. J.; Harrod, J. F. *J. Am. Chem. Soc.* **1967**, *89*, 1640−1647.

(5) (a) Seki, Y.; Hidaka, A.; Makino, S.; Murai, S.; Sonada, N. *J. Organomet. Chem.* **1977**, *140*, 361−378. (b) Seki, Y.; Hidaka, A.; Murai, S.; Sonada, N. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 174−175. (c) Seki, Y.; Murai, S.; Hidaka, A.; Sonada, N. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 881−882. (d) Chatani, N.; Ikeda, S.; Ohe, K.; Murai, S. *J. Am. Chem. Soc.* **1992**, *114*, 9710−9711.

(6) Control over the regiochemistry of olefin carbonylation has been acheived by using substrate directing effects. For a review and lead references see: Hoveyda, A. H.; Evans, D. A.; Fu, G. C. *Chem. Rev. (Washington, D.C.)* **1993**, *93*, 1307−1370.

(7) For regioselective intramolecular silylformylation of alkynes see: (a) Monteil, F.; Matsuda, I.; Alper, H. *J. Am. Chem. Soc.* **1995**, *117*, 4419−4420. (b) Ojima, I.; Vidal, E.; Tzamarioudaki, M.; Matsuda, I. *J. Am. Chem. Soc.* **1995**, *117*, 6797−6798. (c) Ojima, I.; Donovan, R. J.; Shay, W. R. *J. Am. Chem. Soc.* **1992**, *114*, 6580−6582. (d) Ojima, I.; Tzamarioudaki, M.; Tsai, C.-Y. *J. Am. Chem. Soc.* **1994**, *116*, 3643−3644. (e) Ojima, I.; McCullagh, J. V.; Shay, W. R. *J. Organomet. Chem.* **1996**, *521*, 421−423.

(8) (a) Tamao, K.; Tanaka, T.; Nakajima, T.; Sumiya, R.; Arai, H.; Ito, Y. *Tetrahedron Lett.* **1986**, *27*, 3377−3380. (b) Tamao, K.; Nakajima, T.; Sumiya, R.; Arai, H.; Higuchi, N.; Ito, Y. *J. Am. Chem. Soc.* **1986**, *108*, 6090−6093.

(9) Determined by $^1H$ NMR spectroscopy of the unpurified reaction mixture. For details of the stereochemical determinations see the Supporting Information.

(10) The aldehydes proved somewhat unstable to chromatography on silica gel. Hoveyda has documented detailed observations on the stability of several $\beta$-silyl aldehydes: Young, D. G. J.; Hale, M. R.; Hoveyda, A. H. *Tetrahedron Lett.* **1996**, *37*, 827−830.

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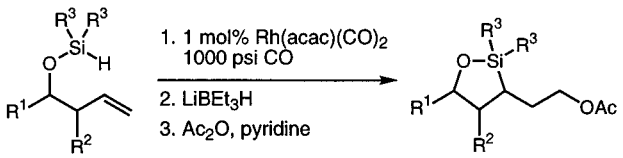
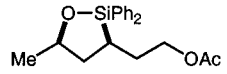
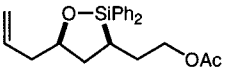
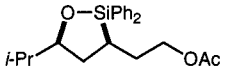
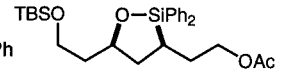
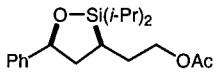
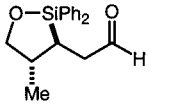
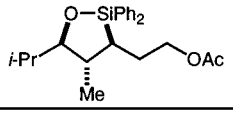
**Table 1.** Rhodium-Catalyzed Intramolecular Silylformylation of $\beta$-Siloxy Alkenes[a]



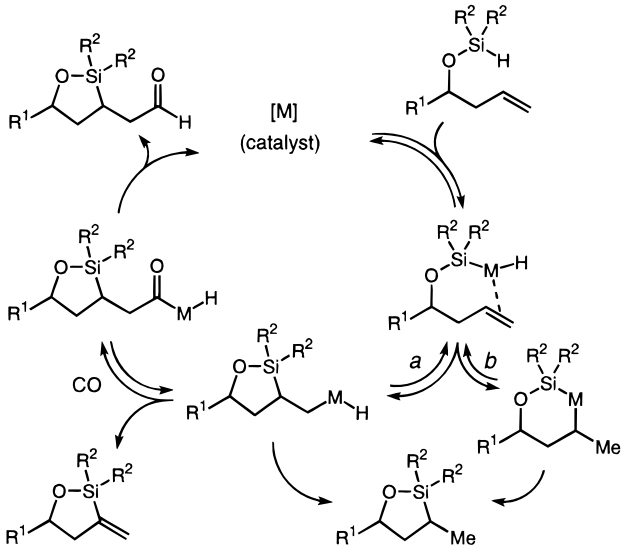

| entry | $R^1$ | $R^2$ | $R^3$ | major product | ds[b] | y (%)[c] |
|---|---|---|---|---|---|---|
| 1 | Me | H | Ph |  | 4.5:1 | 67 |
| 2 | allyl | H | Ph |  | 4:1 | 64 |
| 3 | *i*-Pr | H | Ph |  | 6:1 | 79 |
| 4 | TBSO $CH_2CH_2$ | H | Ph |  | 4:1 | 60 |
| 5 | Ph | H | *i*-Pr |  | 7:1 | 54 |
| 6 | H | Me | Ph |  | 11:1 | 10[d] |
| 7[e] | *i*-Pr | Me | Ph |  | 10:1 | 71 |

[a] All silylformylations were conducted on a 2.0 mmol scale in 10.0 mL of benzene at 60 °C for 24−48 h. [b] Diastereoselectivity (*cis*:*trans*, oxygen- and silicon-bearing stereocenters) determined by $^1$H NMR analysis of the unpurified reaction mixtures. [c] Isolated yield of diastereomerically enriched (>10:1) major product over three steps. [d] GC yield of unpurified aldehyde. The major product was the hydrosilylation product. The stereochemistry was tentatively assigned by analogy to the hydrosilylation product. [e] The starting material was the *anti* diastereomer.

allylic position also promotes silylformylation, but the effect is not as pronounced (entry 6). The confluence of homoallylic and allylic substituents leads to a particularly diastereoselective reaction (entry 7).

On the basis of the similarity of the reaction conditions employed here to hydrosilylation, and the observation of hydrosilylation products in these reactions, the broad outlines of a plausible mechanism for the present silylformylation are presented in Scheme 3. Following oxidative addition of the Si−H bond to the catalyst, two olefin insertion steps are possible: metal−silyl insertion (path *a*) and metal−hydride insertion (path *b*). That both pathways can, in principle, lead to the observed hydrosilylation products by way of alkyl−hydride and alkyl−silyl reductive eliminations respectively forms the basis of an interesting mechanistic question in intramolecular olefin hydrosilylation.[11] Silylformylation, however, would seem to require the intermediacy of path *a* followed by CO insertion and reductive elimination. Thus, to the extent that this mechanism can be supported, it provides evidence for the feasibility of the silyl−metal olefin insertion step in a system

**Scheme 3**




with close analogy to hydrosilylation. Analogously, the production of vinylsilanes in rhodium-catalyzed hydrosilyation has been taken to support the silyl−metal olefin insertion pathway.[12]

In terms of potential synthetic utility this methodology holds promise for the stereoselective synthesis of both polyacetate- and polypropionate-derived polyol fragments by way of oxidative cleavage of the $RO(Ph)_2Si-C$ bond.[13] Prior to oxidation, the siloxanes may be useful for inducing acyclic stereocontrol in extending the polyol chain. Hoveyda has recently reported several examples of such stereocontrol, demonstrating the feasibility of such a strategy.[14] Among the mechanistic issues to be addressed are the dramatic effects of substitution at the homoallylic position and variation of the silicon substituents. An understanding of these effects could lead to expanded generality and synthetic utility of this methodology. Such synthetic and mechanistic efforts are in progress.

**Acknowledgment.** We gratefully acknowledge Columbia University and the Exxon Education Foundation for their support of this work. The National Science Foundation (CHE-96-14117) is acknowledged as well.

**Supporting Information Available:** Experimental procedures and spectral data for all silylformylation products in Table 1 as well as details of the stereochemical proofs (8 pages). See any current masthead page for ordering and Internet access instructions.

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(11) Evidence for both pathways has been presented in the case of hydrosilylation of allylic alcohol-derived substrates. See: (a) Bergens, S. H.; Noheda, P.; Whelan, J.; Bosnich, B. *J. Am. Chem. Soc.* **1992**, *114*, 2128−2135. (b) Tamao, K.; Nakagawa, Y.; Ito, Y. *Organometallics* **1993**, *12*, 2297−2308.

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(13) An excellent review has recently appeared: Jones, G. R.; Landais, Y. *Tetrahedron* **1996**, *52*, 7599−7662.

(14) (a) Hale, M. R.; Hoveyda, A. H. *J. Org. Chem.* **1992**, *57*, 1643−1645. (b) Hale, M. R.; Hoveyda, A. H. *J. Org. Chem.* **1994**, *59*, 4370−4374.