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Rhodium-Catalyzed Intramolecular Silylformylation of Acetylenes: A Vehicle for Complete Regio- and Stereoselectivity in the Formylation of Acetylenic Bonds

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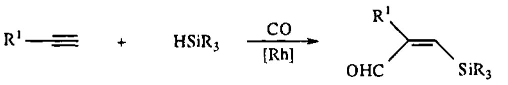
Catalytic hydroformylation is widely used for the incorporation of carbon monoxide into various unsaturated substrates.[1] Replacement of hydrogen by a trialkylsilane was first effected by Murai's group using $Co_2(CO)_8$.[2−4] Recently, we[5] and Ojima's group[6] independently reported the silylformylation of alkynes catalyzed by rhodium complexes, and this process has been extensively studied[7,8] in the past few years. Treatment of terminal alkynes with a hydrosilane and carbon monoxide usually results in formylation at the internal sp carbon, affording (*Z*)-3-silyl-2-alkenals **1** in high yields and with a high degree of regio- and stereochemical control (eq 1).



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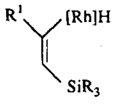
(1)

The silylformylation of internal alkynes gives rise to lower regioselectivity (up to 89% selectivity).[5] Specifically, the silylformylation of both 2-hexyne and 1-phenylpropyne indicates that the sp carbon bearing the larger substituent was preferably formylated. These reactions may proceed by a pathway involving oxidative addition of R_3SiH to rhodium, *cis* addition of the Rh−Si to the triple bond to give **2**, and CO insertion into the Rh−C bond to form **3**.



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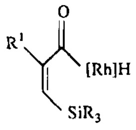

3

To our knowledge, although several examples of silylcarbocyclization reactions have been described in the literature,[7a−d] genuine *intramolecular* silylformylation with acetylenic and hydrosilane groups belonging to the same molecule has never been reported. On the basis of the intermediates **2** and **3** noted above, as well as several publications on intramolecular hydrosilation and cyanosilation reactions,[8] it seemed reasonable to assume that alkynyldiorganylsilanes could react with CO in an intramolecular fashion. We report herein important results obtained, using rhodium complexes as catalysts, for the regio- and stereospecific intramolecular silylformylation of acetylenic bonds.

Reaction of pent-4-ynylmethylphenylsilane (**4a**)[9] with CO (20 atm) and a catalytic amount of either the zwitterionic complex **5** ($(\eta^6\text{-}C_6H_6BPh_3)^-Rh^+(1,5\text{-COD})$)[11] (COD = cyclooctadiene) (1 mol %), or $Rh_4(CO)_{12}$ (0.5 mol %) and triethylamine (equimolar with respect to **4a**), gave the corresponding aldehyde **6a** in 43% or 56% isolated yield, respectively. As summarized in Table 1, the carbonylation of compounds **4a−d** in the presence of **5** gave the silylformylated compounds **6a−d** in 37−56% yields of pure products.[12] The yield of aldehyde is affected by the substituents attached to the silicon atom. Higher product yields are obtained when starting from alkynylmethylphenylsilanes rather than alkynyldiphenylsilanes. The scope of this intramolecular silylformylation also seems to depend on the size of the silacycloalkane framework. The six-membered ring silacycles **6b,d** were isolated in higher yields than their five-membered ring silacycles analogs (compare entries 2 and 3 or 4 and 5),

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[†] University of Ottawa.

[‡] Nagoya University.

(1) (a) Pino, P.; Braca, G. In *Organic Synthesis via Metal Carbonyls;* Wender, I., Pino, P., Eds.; John Wiley & Sons: New York, 1977; Vol. 2, p 419. (b) Pino, P.; Piacenti, F.; Bianchi, M. In *Organic Synthesis via Metal Carbonyls;* Wender, I., Pino, P., Eds.; John Wiley & Sons: New York, 1977; Vol. 2, p 43. (c) Colquhoun, H. M.; Thompson, D. J.; Twigg, M. V. *Carbonylation*; Plenum Press: New York, 1991.

(2) Seki, Y.; Hidaka. A.; Makino, S.; Murai, S.; Sonoda, N. *J. Organomet. Chem.* **1977**, *140*, 361.

(3) (a) Seki, Y.; Murai, S.; Hidaka, A.; Sonoda, N. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 881. (b) Seki, Y.; Hidaka, A.; Murai, S.; Sonoda, N. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 174.

(4) (a) Murai, S.; Kato, T.; Sonoda, N.; Seki, Y.; Kawamoto, K. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 393. (b) Murai, S.; Sonoda, N. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 837.

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

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

(7) (a) Matsuda, I.; Ogiso, A.; Sato, S. *J. Am. Chem. Soc.* **1990,** *112*, 6120. (b) Matsuda, I.; Sakakibara, J.; Nagashima, H. *Tetrahedron Lett.* **1991**, *32*, 7431. (c) Ojima, I.; Donovan, R. J.; Shay, W. R. *J. Am. Chem. Soc.* **1992**, *114*, 6580. (d) Ojima, I.; Tzamarioudaki, M.; Tsai C. Y. *J. Am. Chem. Soc.* **1994**, *116*, 3643. (e) Matsuda, I.; Sakakibara, J.; Inoue, H.; Nagashima, H. *Tetrahedron Lett.* **1992**, *33*, 5799. (f) Eguchi, M.; Zeng, Q.; Korda, A.; Ojima, I. *Tetrahedron Lett.* **1993**, *34*, 915. (g) Ojima, I.; Donovan, R. J.; Eguchi. M.; Shay, W. R.; Ingallina, P.; Korda, A.; Zeng, Q. *Tetrahedron* **1993**, *49*, 5431. (h) Wright, M. E.; Cochran, B. B. *J. Am. Chem. Soc.* **1993**, *115*, 2059. (i) Doyle, M. P.; Shanklin, M. S. *Organometallics* **1993**, *12*, 11. (j) Zhou, J. Q.; Alper, H. *Organometallics* **1994**, *13*, 1586.

(8) (a) Tamao, K.; Maeda, K.; Tanaka, T.; Ito, Y. *Tetrahedron Lett.* **1988**, *29*, 6955. (b) Steinmetz, M. G.; Udayakumar, B. S. *J. Organomet. Chem.* **1989**, *378*, 1. (c) Suginome, M.; Kinugasa, H.; Ito, Y. *Tetrahedron Lett.* **1994**, *35*, 8635. Also note that intramolecular hydrosilation has been reported for other systems, including olefins (Bergens, S. H.; Noheda, P.; Whelan, J.; Bosnich, B. *J. Am. Chem. Soc.* **1992**, *114*, 2121) and hydroxyketones (Burk, M. J.; Feaster, J. E. *Tetrahedron Lett.* **1992**, *33*, 2099).

(9) The ω-alkynyldiorganylsilanes **4a−d**, containing methyl and/or phenyl substituents on the silicon atom, and in which the reacting acetylenic and hydrosilane groups are separated by three or four methylene units, were synthesized according to a procedure reported for the preparation of alkenylsilanes involving an alkenylmagnesium bromide.[10] They are all new compounds and were characterized by (^1H,^{13}C) NMR, IR (neat), and high-resolution mass spectroscopy (see supplementary material).

(10) Barton, T. J.; Revis, A. *J. Am. Chem. Soc.* **1984**, *106*, 3802.

(11) (a) Amer, I.; Alper, H. *J. Am. Chem. Soc.* **1990**, *112*, 3674. (b) Alper, H.; Zhou, J. Q. *J. Org. Chem.* **1992**, *57*, 3729. (c) Zhou, J. Q.; Alper, H. *J. Chem. Soc., Chem. Commun.* **1991**, 233. (d) Zhou, J. Q.; Alper, H. *J. Org. Chem.* **1992**, *57*, 3328. (e) Alper, H.; Zhou, J. Q. *J. Chem. Soc., Chem. Commun.* **1993**, 316. (f) Totland, K.; Alper, H. *J. Org. Chem.* **1993**, *58*, 3326.

(12) The general procedure for the zwitterionic rhodium(I)-catalyzed intramolecular silylformylation reaction was as follows. The ω-alkynyldiorganylsilane (1 mmol), dichoromethane (20 mL), and **5** (0.010 mmol) were placed in a 40-mL autoclave. The reactor was flushed three times with carbon monoxide and pressurized to 20 atm of CO. The reaction mixture was stirred for 24 h at 40 °C and then cooled to room temperature. The solvent was removed by rotary evaporation, and the residue was purified by recycling HPLC (column JAIGEL 2H). The silylalkenals **6a−d** are new compounds characterized by (^1H,^{13}C) NMR, IR (neat), and high-resolution mass spectroscopy as well as by elemental analyses (C,H) (see supplementary material). The $Rh_4(CO)_{12}$-catalyzed intramolecular silylformylation was carried out as follows. A glass tube fitted with a stir bar was charged with $Rh_4(CO)_{12}$ (0.0042 g, 0.0056 mmol) and benzene (5 mL), saturated with CO. The tube was put in a 100-mL stainless steel autoclave, which was pressurized to 20 atm of CO. After the mixture was stirred for 5 min and the CO was purged, the silanes **4a**,**e**−i(1.20 mmol) in C_6H_6 (1 mL) and NEt_3 (0.121 g, 1.20 mmol) were placed in the autoclave, which was then pressurized again by CO to 20 atm. The mixture was stirred for 3 h at 90 °C and cooled at ambient temperature. After excess CO was removed (fume hood), the reaction mixture was concentrated under reduced pressure, and the residual oily liquid was purified by column chromatography on silica gel using hexane/EtOAc (97/3) as an eluant to give the silylalkenals **6a**,**f**−i. The silylalkenals **6f**−i are new compounds characterized by (^1H,^{13}C) NMR and IR (CCl_4) spectroscopy and by elemental analyses (C,H) (see supplementary material).

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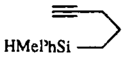
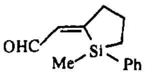
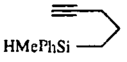
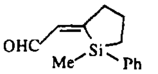
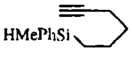
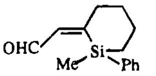
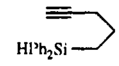
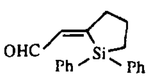
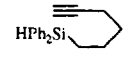
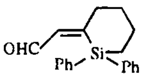
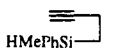
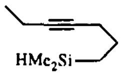
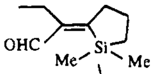
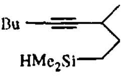
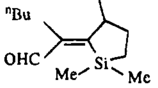
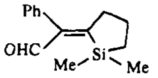
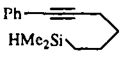
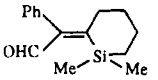
Table 1. Rhodium-Catalyzed Intramolecular Silylformylation of **4**

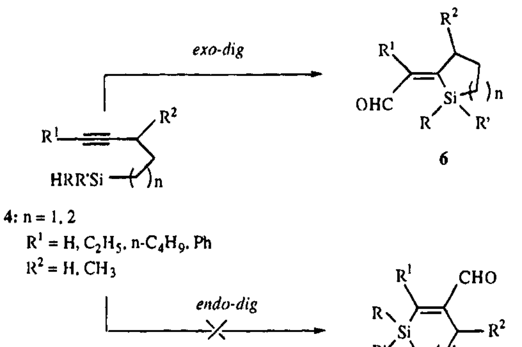
entry		alkynylsilane **4**	catalyst[a]		product **6**[b]	yield (%)[c]
1	a		$Rh_4(CO)_{12}$	a		56
2	a		**5**	a		43
3	b		**5**	b		56
4	c		**5**	c		37
5	d		**5**	d		49
6	e		$Rh_4(CO)_{12}$	e		
7	f		$Rh_4(CO)_{12}$	f		83
8	g		$Rh_4(CO)_{12}$	g		71
9	h		$Rh_4(CO)_{12}$	h		79
10	i		$Rh_4(CO)_{12}$	i		69

[a] See footnote 12 for general procedures. [b] All products gave satisfactory elemental analyses, (^1H,^{13}C) NMR, and IR spectra. [c] Isolated yield.

while but-3-ynylmethylphenylsilane (**4e**),[13] containing only two methylene units, gave a complex mixture of unidentified products.

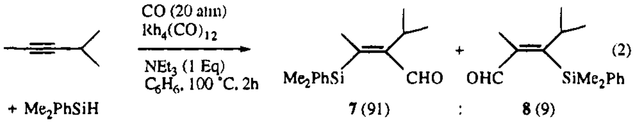
This type of internal silylformylation proceeded smoothly for internal alkynylsilanes. For example, when hept-4-ynyldimethylsilane (**4f**) was subjected to conditions similar to those employed for **4a**,[12] the formylated product **6f** was isolated in 83% yield as the sole carbonylated product. Different internal alkynylsilanes **4f–i**,[15] in which three or four methylene units separated the reacting centers, were readily carbonylated to form the corresponding aldehydes **6f–i** in good yields, somewhat higher than those of terminal alkynylsilanes (Table 1). Of particular note is the observation that **4g**, which contains two sterically discriminating substituents, affords **6g** as the only product. Regardless of the substituents, both alkyl and aryl acetylenes undergo reaction in an identical process.

Scheme 1



A significant finding was the formation of *only* the exocyclic regioisomer in all cases with the occurrence of net *cis* addition of the aldehyde and silyl units (Scheme 1). The stereochemistry of the silylformylation products was determined by NOE experiments. Such complete regioselectivity is remarkable by this simple operation. In contrast to the intermolecular reaction, it is not the internal sp carbon which is selectively formylated but the terminal one in the case of terminal alkynylsilanes. This is the first example of reverse regioselectivity in the silylformylation of terminal alkynes. These results demonstrate that, as a result of selective *exo–dig* ring closure, this silylformylation process can distinguish between the two sp carbons of the acetylenic bond.

The regioselectivity observed, starting from internal alkynylsilanes, contrasts with that found for the intermolecular reaction. Indeed, when 4-methyl-2-pentyne is reacted under the same conditions, silylation occurs predominantly at the sterically less hindered site (i.e., **7** as the major product in eq 2).



In conclusion, alkynyldiorganylsilanes **4** undergo intramolecular silylformylation reactions upon exposure to carbon monoxide in the presence of the rhodium complexes (the zwitterionic complex and $Rh_4(CO)_{12}$ are comparable in effectiveness). This process provides a new method to distinguish specifically between the two sp carbons of the acetylenic bond independent of the steric factor of the substituents. The reaction is totally regio- and stereospecific and results in the formation of previously unknown (*Z*)-2-(formylmethylidene)-1-silacycloalkanes **6**. These compounds are of considerable potential in organic and polymer synthesis due to their stereochemical features and novel structure. An investigation of the chemistry of the 2-(formylmethylene)-1-silacycloalkanes **6** is in progress.

Acknowledgment. We are grateful to the Natural Sciences and Engineering Research Council of Canada and to the Ministry of Education, Science and Culture of Japan for support of this research.

Supplementary Material Available: General experimental details, list of materials, general procedures, and spectroscopic characterization of compounds **4a–i**, **6a–d** and **6f–i** (9 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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(13) But-3-ynylmethylphenylsilane was prepared by zinc–copper coupling of 4-iodobut-1-yne and HMePhSiCl according to a literature method.[14] It is a new compound characterized by (^1H,^{13}C) NMR and IR (CCl_4) (see supplementary material).

(14) Knoess, H. P.; Furlong, M. T.; Rozema, M. J.; Knochel, P. *J. Org. Chem.* **1991**, *56*, 5974.

(15) Alkynylsilanes **4f–i** were prepared by substitution reactions of the corresponding alkynyl iodide with HMe_2SiCH_2MgCl derived from HMe_2SiCH_2Cl and Mg metal. They are new compounds characterized by (^1H,^{13}C) NMR and IR (CCl_4) (see supplementary material).