Andy Muir of ICI Specialties and ICI Chemicals and Polymers, Runcorn, UK, for providing 3,5-cyclohexadiene-*cis*-1,2-diol and Viscotek GPC analysis. We thank Dr. Greg Fu for helpful discussions. D.L.G. thanks NSERC Canada for a predoctoral fellowship.

Registry No. 1b, 144193-12-4; **1b** (homopolymer), 144193-14-6; PPV, 26009-24-5.

Supplementary Material Available: Listing of ^{1}H and ^{13}C NMR spectroscopic and analytical data for synthetic intermediates in Scheme I (2 pages). Ordering information is given on any current masthead page.

Conversion of Alkenes to Enol Silyl Ethers of Acylsilanes by Iridium-Catalyzed Reaction with a Hydrosilane and Carbon Monoxide

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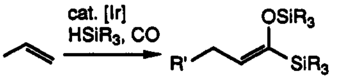
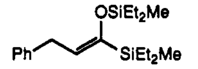
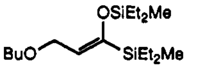
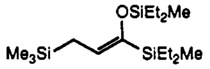
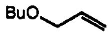
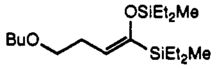
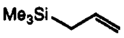
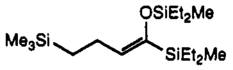
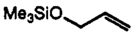
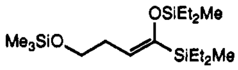
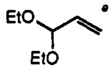
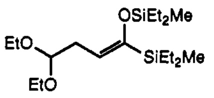
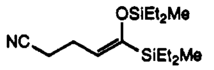
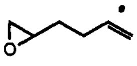
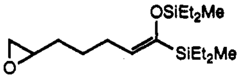
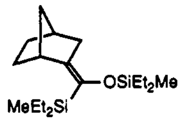
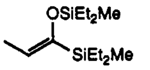
We wish to report that iridium complexes ($[IrCl(CO)_3]_n$ and $Ir_4(CO)_{12}$) catalyze the reaction of alkenes with a hydrosilane ($HSiR_3$) and carbon monoxide (eq 1) to yield enol silyl ethers of acylsilanes. This unprecedented reaction results in regioselective introduction of carbon monoxide into the terminal carbon atom of alkenes, forming a siloxy(silyl)methylene unit ($=C(SiR_3)OSiR_3$). The possibility that an acylsilane or its derivative can be a product of a catalytic reaction using $HSiR_3$ and CO has been pointed out.[1] Since then, a number of new catalytic reactions with $HSiR_3$ and CO have been reported.[2] Nevertheless, the present Ir-catalyzed reaction represents the first example of formation of acylsilane[3,4] derivatives from the $HSiR_3$/CO combination.[5]



(1)

1: R' = Bu
2: R' = Cy
3: R' = *t*-Bu

Table I. Iridium-Catalyzed Reaction of Alkenes with $HSiEt_2Me$ and CO[a]

alkene	product	yield, %[b]	*E*/*Z* ratio[c]
		(50)[d]	72/28
		67	57/43
		73	73/27
		75	68/32
		53	79/21
		67	67/33
 [e]		58	73/27
 [e]		45	73/27
 [e]		56	65/35
		85	36/64[f]
 [g]		67	66/34

[a] Reaction conditions: alkene (10 mmol), $HSiEt_2Me$ (1 mmol), $[IrCl(CO)_3]_n$ (0.02 mmol), CO (50 atm), C_6H_6 (2 mL), 140 °C, 48 h. Characterization of the products obtained is given in the supplementary material. [b] Isolated yields based on $HSiEt_2Me$. GLC yield is in parentheses. [c] Determined by ^{1}H NMR. [d] Dimerization and polymerization of styrene also took place. [e] An alkene (5 mmol) was used. [f] The assignment of the stereochemistry is tentative. [g] Ethylene (10 atm, initial pressure at 25 °C) was used.

Typically, the reaction was carried out with alkene (10 equiv) and $HSiEt_2Me$ (1 equiv) in benzene (2 mL) at 140 °C under 50

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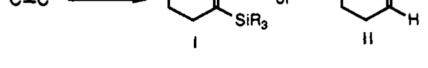
(3) Formal analogy to hydroformylation would suggest that i and ii could be products. Recently, catalytic reactions of acetylenes with $HSiR_3$ and CO to give products relating to ii have been reported.[2c–h]



(4) The product has functionalities of vinylsilane, enol silyl ether, and masked acylsilane. All of these functional groups are quite useful in organic synthesis. For reviews, see: Colvin, E. W. *Silicon in Organic Synthesis*; Butterworths: London, 1981. Magnes, P. D.; Sarkar, T.; Djurie, S. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W.; Eds.; Pergamon: Oxford, 1982; Vol. 7, Chapter 48. Weber, W. P. *Silicon Reagents for Organic Synthesis*; Springer-Verlag: New York, 1983.

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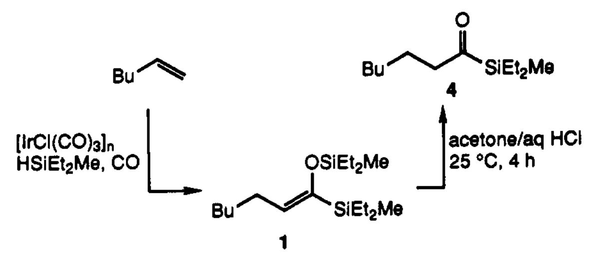
Scheme I



atm (initial pressure at 25 °C) of carbon monoxide for 48 h in the presence of $[IrCl(CO)_3]_n$ (2 mol %) as a catalyst. Incorporation of a siloxy(silyl)methylene unit, derived from one molecule of CO and two molecules of $HSiEt_2Me$, into the terminal carbon atom of the alkene took place to afford a 1-silyl enol silyl ether (**1**, R′ = Bu, 74% (*E*/*Z* = 79/21); **2**, R′ = Cy, 66% (*E*/*Z* = 86/14); **3**, R′ = *t*-Bu, 60% (*E*/*Z* = 69/31)) as the sole product.[6] No regioisomer was detected. Dimethylphenylsilane ($HSiPhMe_2$) and triethylsilane ($HSiEt_3$) can also be used for the reaction of 1-hexene to give the corresponding products in 65% (*E*/*Z* = 87/13) and 50% yields (*E*/*Z* = 66/34), respectively. Several iridium complexes were examined for their catalytic activity. While neither $IrCl(CO)(PPh_3)_2$ nor $IrH(CO)(PPh_3)_3$ was effective, $Ir_4(CO)_{12}$ exhibited catalytic activity affording **1** in 65% yield.

The new catalytic reaction can be applied to a wide variety of terminal alkenes (Table I). Note that functional groups, such as acetal,[7] cyano,[8] and epoxide,[9] known to react in transition metal catalyzed reactions with $HSiR_3$ or with $HSiR_3$/CO remain intact. While norbornene was reactive, cyclohexene reacted only sluggishly under those conditions. The multifunctionality of the products is synthetically attractive and will no doubt find application in the future. The products obtained can be easily hydrolyzed to acylsilanes.[5i,10] For example, treatment of **1** with acid (acetone/HCl (0.2 M) = 4/1) at 25 °C for 4 h gave an acylsilane **4** in quantitative yield (Scheme I).

The stoichiometry of the reaction 1 indicates that two hydrogen atoms in reactants are not incorporated in the product. These are incorporated into another molecule of the starting alkene. Thus reaction of vinylcyclohexene gave ethylcyclohexane (64% yield based on $HSiEt_2Me$) in addition to **2** (66%).[11]

The mechanism of the catalytic reaction is not known at present. The possibility that an acylsilane intermediate gives the observed product by dehydrogenative silylation was eliminated. Thus reaction of **4** with 1 equiv of $HSiEt_2Me$ in the presence of $[IrCl(CO)_3]_n$ resulted in 93% recovery of **4**.[12] We are now examining the possible intervention of a siloxycarbyne complex ($Ir{\equiv}COSiR_3$) intermediate.

Acknowledgment. This work is supported by a Grant-in-Aid for Scientific Research on a Priority Area, Activation of Unreactive Small Molecules, Grant No. 04241106, from the Ministry of Education, Science, and Culture, Japan. We thank the Instrumental Analysis Center, Faculty of Engineering, Osaka University, for use of the facilities.

Supplementary Material Available: Listings of spectral data and elemental analyses for the products (13 pages). Ordering information is given on any current masthead page.

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(6) All new compounds were characterized by NMR, IR, and mass spectral data and by elemental analyses or high-resolution mass spectra. See the supplementary material. The reaction was slow at 80 °C. A decrease in the ratio of 1-hexene/$HSiEt_2Me$ to 3/1 resulted in a decrease in the yield of **1** to 34%. The reactions run equally well in toluene as a solvent. The use of CH_2Cl_2 or THF in place of benzene gave **1** as a main product along with many unidentified products.

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(11) In this reaction, ethylidenecyclohexane was also obtained in 52% yield (based on vinylcyclohexane) as the result of isomerization of vinylcyclohexane, and 41% of vinylcyclohexane was recovered.

(12) The reaction of **4** with $HSiEt_2Me$ and CO even in the presence of an excess amount of 1-octene under the same reaction conditions also resulted in the recovery of **4** in 85% along with the CO incorporation product derived from 1-octene (**1**, R′ = hex, SiR_3 = $SiEt_2Me$, 73% yield).

Nucleotide and Deduced Amino Acid Sequences of the Oxidosqualene Cyclase from *Candida albicans*

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Oxidosqualene lanosterol-cyclase (EC 5.4.99.7) catalyzes a remarkable and crucial cyclization/rearrangement reaction during the course of sterol biosynthesis in fungi and animals (Figure 1).[1] The underlying mechanism of this and related polyene–polycycle conversions has intrigued scientists since the elucidation of the structure of cholesterol.[2] Decades of synthetic and bioorganic investigations,[3] culminating with the most recent work from the Corey laboratory,[4] have provided a detailed understanding of the substrate structural requirements, specificity, and stereochemistry of cyclization/rearrangement. In stark contrast, little is known about oxidosqualene cyclase enzymes, as they have only recently yielded to complete purification.[5] We have initiated a program

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* Author to whom correspondence should be addressed; phone, (415) 723-3625.

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