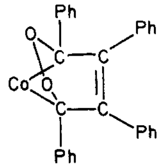
reactions of related complexes. An excited form of 1 could add O_2 to generate an endo peroxide[50] intermediate



Further studies will be necessary to resolve the mechanism of the oxidation process.

Acknowledgment. We thank the National Science Foundation for research support (Grants CHE 78-01615 and 81-05069 to W.C.T. and Grant CHE 80-09671 to J. A.I.).

Registry No. 1, 12124-09-3; 2, 79953-72-3; 3, 1278-02-0; (*Z*)-dibenzoylstilbene, 6313-26-4.

Supplementary Material Available: A listing of observed and calculated structure amplitudes (18 pages). Ordering information is given on any current masthead page.

Organofluorosilicates in Organic Synthesis. 14.[1] Carbon–Carbon Bond Formation Promoted by Palladium Salts

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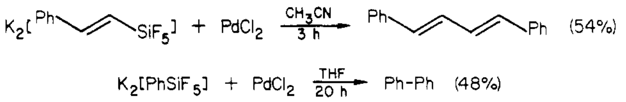
Five types of palladium-promoted carbon–carbon bond forming reactions have been achieved with potassium (*E*)-alkenylpentafluorosilicates which are readily available from alkynes by hydrosilylation followed by silicate formation. (1) The homocoupling reaction of styryl- and phenylsilicates gives 1,4-diphenylbutadiene and biphenyl, respectively. (2) The cross-coupling reaction with activated olefins such as methyl acrylate giving unsymmetrical 1,3-dienes is promoted by palladium acetate. (π-Allyl)palladium complexes are obtained with palladium chloride. (3) The palladium-catalyzed cross-coupling reaction with allylic halides gives (*E*)-1,4-dienes and has been applied to the synthesis of a key intermediate for total synthesis of (±)-recifeiolide. (4) A facile carbonylation occurs in methanol to give α,β-unsaturated carboxylic esters. (5) A limited number of cross-coupling reactions occur with $C(sp^2)$ halides in the presence of palladium complexes as catalysts under forced conditions. The products of these reactions may be interpreted in terms of the chemistry expected of alkenylpalladium intermediates, arising from transfer of the alkenyl group from silicon to palladium.

The formation of carbon–carbon bonds is one of the most fundamental problems in organic chemistry, and numerous selective reactions have been explored by the use of transition-metal compounds.[2] In our previous papers organopentafluorosilicates have been shown to be useful intermediates for functional group transformations.[1,3] Preliminarily we have reported several types of carbon–carbon bond forming reactions of organopentafluorosilicates under the influence of palladium,[4,5] copper,[6] and silver[7] salts. This paper describes the full details of the palladium-promoted carbon–carbon bond forming reactions. Since only the potassium salts of organopentafluorosilicates are used throughout the present study, the countercation will be omitted from the individual names of the silicates.

Results and Discussion

Homocoupling Reaction. The reaction of (*E*)-styrylpentafluorosilicate with 1 equiv of palladium chloride in acetonitrile at room temperature gave (*E*,*E*)-1,4-diphenyl-1,3-butadiene in 54% yield. The reaction was quite rapid and a black mixture resulted, probably indicating the formation of the palladium metal. Other alkenylsilicates such as 1-hexenylsilicate did not undergo a similar coupling reaction when treated with palladium chloride under various conditions but gave several minor products which were not characterized. The reason why other alkenylsilicates gave no coupling products is not clear at the present time. The phenylsilicate, however, reacted with palladium chloride to produce biphenyl in moderate yield.



The palladium-promoted homocoupling reaction may have possibly proceeded via intermediacy of the organopalladium species, arising from the metal-exchange reaction between the organosilicate and the palladium salt, by a mechanism analogous to that proposed for similar palladium-promoted coupling of alkenylmercuric chlorides[8] and styryltrimethylsilane,[9] a tetracoordinate alkenylsilane.

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[1] For part 13, see: Yoshida, J.; Tamao, K.; Kakui, T.; Kurita, A.; Murata, M.; Yamada, K.; Kumada, M. *Organometallics* 1982, *1*, 369–380.

[2] For example: (a) Noyori, R. In "Transition Metal Organometallics in Organic Synthesis"; Alper, H., Ed.; Academic Press: New York, 1976; Vol. 1, p 93. (b) Tsuji, J. "Organic Synthesis with Palladium Compounds", Springer-Verlag: Heidelberg, New York, 1980. (c) Collman, J. P.; Hegedus, L. S. "Principles and Applications of Organotransition Metal Chemistry", University Science Books: Mill Valley, CA, 1980.

[3] Tamao, K.; Yoshida, J.; Yamamoto, H.; Kakui, T.; Matsumoto, H.; Takahashi, M.; Kurita, A.; Murata, M.; Kumada, M. *Organometallics*, preceding article in this issue (part 12) and references cited therein.

[4] Yoshida, J.; Tamao, K.; Takahashi, M.; Kumada, M. *Tetrahedron Lett.* **1978**, 2161.

[5] Tamao, K.; Kakui, T.; Kumada, M. *Tetrahedron Lett.* **1979**, 619.

[6] Yoshida, J.; Tamao, K.; Kakui, T.; Kumada, M. *Tetrahedron Lett.* **1979**, 1141.

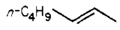
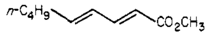
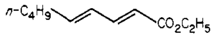
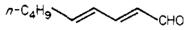
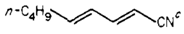
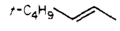
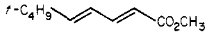
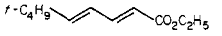
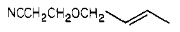
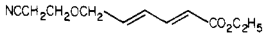
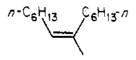
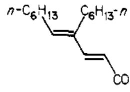
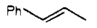
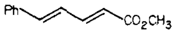
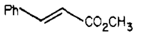
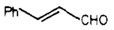
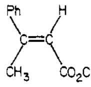
[7] Tamao, K.; Matsumoto, H.; Kakui, T.; Kumada, M. *Tetrahedron Lett.* **1979**, 1137.

[8] Larock, R. C. *J. Org. Chem.* **1976**, *41*, 2241.

[9] Weber, W. P.; Felix, R. A.; Willard, A. K.; Koenig, K. E. *Tetrahedron Lett.* **1971**, 4701.

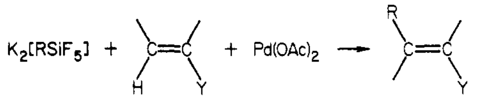
0276-7333/82/2301-0542$01.25/0 © 1982 American Chemical Society

Table I. Cross-Coupling Reaction of Organopentafluorosilicates with Activated Olefins[a]

R in $K_2[RSiF_5]$	olefin	time, h	product	yield,[b] %
	$CH_2=CHCO_2CH_3$	47		37
	$CH_2=CHCO_2C_2H_5$	20		48
	$CH_2=CHCHO$	4		20
	$CH_2=CHCN$	45		43
	$CH_2=CHCO_2CH_3$	28		(61)
	$CH_2=CHCO_2C_2H_5$	20		38
	$CH_2=CHCO_2C_2H_5$	20		23
	$CH_2=CHCO_2C_2H_5$	48		28
	$CH_2=CHCO_2CH_3$[d]	9		(35)
Ph-	$CH_2=CHCO_2CH_3$[d]	19		(69)
	$CH_2=CHCHO$[d]	29		(27)
	(E)-$CH_3CH=CHCO_2CH_3$[d]	32		53 (60)

[a] The reactions were carried out on 1-2-mmol scale with 1 part of $K_2[RSiF_5]$, 1 part of $Pd(OAc)_2$, 10 parts of an olefin, and 5.0 mL/mmol of THF at room temperature unless otherwise stated. [b] Isolated yields. The yields determined by GLC are given in parentheses. [c] A mixture of E,E and Z,E isomers. [d] The reaction was carried out in acetonitrile under reflux.

Cross-Coupling Reaction with Activated Olefins. Alkenyl- and phenylpentafluorosilicates were found to react with activated olefins such as methyl acrylate, acrylonitrile, acrolein, and methyl crotonate in the presence of palladium acetate producing alkenyl- and phenyl-substituted olefins, respectively (eq 1). After the reaction a palladium mirror appeared. The reaction, therefore, requires a stoichiometric amount of palladium acetate. The results are summarized in Table I. The reaction of (*E*)-alkenylsilicates with methyl or ethyl acrylate and acrolein is highly stereoselective and only *E,E* dienes were obtained. A similar coupling reaction of an internal alkenylsilicate proceeded rather slowly, the stereochemistry of the product being analogously assigned to be an *E,E* diene. The phenylsilicates also reacted with these olefins stereoselectively to give (*E*)-phenyl-substituted olefins. However, the reaction of the hexenylsilicate with acrylonitrile is nonstereoselective and a mixture of *E,E* and *Z,E* dienes was obtained. Unfortunately, the yields could not be improved by the variation in reaction conditions.



(1)

Y = CO$_2$R', CHO, CN

There have been reported similar coupling reactions of organometallic compounds with activated olefins under the influence of palladium salts. Organopalladium species prepared in situ from organomercuric salts,[10] alkenylboronic acids[11a] or organic halides[11] have been known to react with activated olefins to give the cross-coupling products, and a mechanism involving addition of the organopalladium species followed by elimination of the hydridopalladium group has been proposed. Tetracoordinate styryltrimethylsilane was also reported to react with methyl acrylate in the presence of palladium chloride to give the cross-coupling product, and a mechanism involving the styrylpalladium intermediate was proposed.[9] The present reaction can also be explained by a similar mechanism.

Stereoselective formation of methyl (*E*)-3-phenylcrotonate in the reaction of the phenylsilicate with methyl crotonate may suggest that the reaction proceeds by the syn addition of the organopalladium species followed by the syn elimination of the hydridopalladium group. Loss of stereoselectivity observed in the reaction of the hexenylsilicate with acrylonitrile may resemble the low stereoselectivity of the reaction of a phenylpalladium species with acrylonitrile.[10]

The present reaction does not give very high yields but may provide an alternative to some elegant procedures for the preparation of unsymmetrical 1,3-dienes using hydroboration,[12] hydroalumination,[13] or hydrozirconation[14] of alkynes.

Formation of (π-Allyl)palladium Compounds. In connection with the reaction of the alkenylsilicates with activated olefins, we have found that (π-allyl)palladium complexes can be isolated when palladium chloride is used in place of palladium acetate. The result affords direct evidence for transfer of the alkenyl group from silicon to palladium.

(*E*)-1-Hexenylpentafluorosilicate reacted with ethyl acrylate in the presence of 1.1 equiv of palladium chloride at 0 °C to produce di-μ-chloro-bis(1-(ethoxycarbonyl)-oct-2-enyl)dipalladium(II) in 38% yield. As shown in Table II the reaction of (*E*)-1-hexenylsilicate with styrene and methyl vinyl ketone also proceeded smoothly at 0 °C to give the corresponding (π-allyl)palladium compounds.

The following observations are noteworthy. When the reaction of the 1-hexenylsilicate with ethyl acrylate and palladium chloride was carried out at 50 °C, the yield of

---

(10) (a) Heck, R. F. *J. Am. Chem. Soc.* **1968**, *90*, 5518. (b) *Ibid.* **1969**, *91*, 6707.

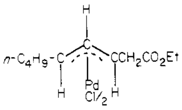
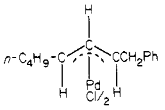
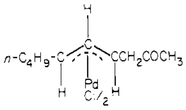
(11) (a) Dieck, H. A.; Heck, R. F. *J. Org. Chem.* **1975**, *40*, 1083. (b) Heck, R. F.; Nolley, J. P. *Ibid.* **1972**, *37*, 3220. (c) Dieck, H. A.; Heck, R. F. *J. Am. Chem. Soc.* **1974**, *96*, 1133. (d) Heck, R. F. *Acc. Chem. Res.* **1979**, *12*, 146.

(12) Yatagai, H. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 1670.

(13) Baba, S.; Negishi, E. *J. Am. Chem. Soc.* **1976**, *98*, 6729.

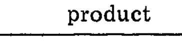
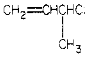
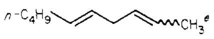
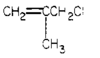
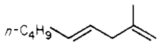
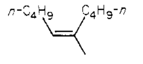
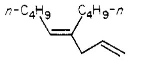
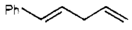
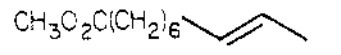
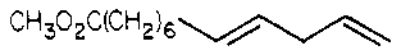
(14) Okukado, N.; VanHorn, D. E.; Klima, W. L.; Negishi, E. *Tetrahedron Lett.* **1978**, 1027.

Table II. Formation of (π-Allyl)palladium Compounds in the Reaction of 1-Hexenylpentafluorosilicate with Palladium Chloride and Olefins[a]

olefin	temp, °C	time, h	product	yield,[b] %
$CH_2{=}CHCO_2Et$	50	0.5		25
	0	6		38
	−20	9		6
$CH_2{=}CHPh$	0	2.5		19
$CH_2{=}CHCOCH_3$	0	5		80

[a] The reactions were carried out with 1.0 mmol of 1-hexenylpentafluorosilicate, 1.1 mmol of palladium chloride, 1.1 mmol of an olefin, and 5.0 mL of dry THF. [b] Isolated yield and based on the 1-hexenylsilicate.

Table III. Cross-Coupling Reaction of Alkenylsilicates with Allylic Substrates[a]

R in $K_2[RSiF_5]$	allylic substrate	equiv	solvent	product	yield,[b] %
	$CH_2{=}CHCH_2Cl$	1.0	Et_2O		38
		2.0	Et_2O		60
		5.0	Et_2O		66
		10.0	Et_2O		69
		10.0	THF		71
		10.0	CH_3CN		50
		10.0	C_6H_6		50
		10.0[c]	THF		39
		10.0[d]	THF		trace
	$CH_2{=}CHCH_2Br$	10.0	THF		60
	$CH_2{=}CHCH_2OAc$	10.0	THF		4
	$CH_2{=}CHCH_2OTs$	10.0	THF		24
	 $CH_2{=}CH\underset{CH_3}{\underset{\vert}{C}}HCl$	10.0	THF		59
	 $CH_2{=}\underset{CH_3}{\underset{\vert}{C}}CH_2Cl$	10.0	THF		35[f]
	$CH_3CH{=}CHCH_2Cl$	10.0	THF		g
	$CH_2{=}CHCH_2Cl$	10.0	THF		66
	$CH_2{=}CHCH_2Cl$	10.0	THF		40[h]
	$CH_2{=}CHCH_2Cl$	10.0	THF		55[i]

[a] Unless otherwise noted, the reactions were carried out with 1.0 mmol of $K_2[RSiF_5]$ in the presence of $Pd(OAc)_2$ (10 mol %) in 5.0 mL of a solvent at room temperature for 24 h. [b] Determined by GLC analysis. [c] $PdCl_2$ (10 mol %) was used. [d] $Pd(acac)_2$ (10 mol %) was used. [e] A mixture of (2*E*,5*E*)- and (2*Z*,5*E*)-decadiene was obtained. [f] Refluxed for 4 h. [g] Trace amounts of unidentified products were obtained. [h] The reaction was carried out for 7 h. [i] Isolated yield.

the (π-allyl)palladium compound decreased and palladium metal was deposited. Probably the (π-allyl)palladium compound decomposed at this temperature. When the reaction was carried out at −20 °C, most of the alkenylsilicate was consumed at the end of the reaction, indicating that the transfer of the alkenyl group from silicon to palladium occurred smoothly even at this temperature. But the yield of the (π-allyl)palladium compound was also low probably because of the slow addition of the alkenylpalladium intermediate to the olefin.

Larock et al. have reported that alkenylmercuric chlorides readily reacted with palladium chloride and olefins to give (π-allyl)palladium compounds in high yield and proposed a mechanism involving the addition of alkenylpalladium intermediates to olefins followed by palladium hydride rearrangement.[15] Most probably the present reaction also proceeds by a similar mechanism, as shown in Scheme I.

The present results may not only offer evidence for the transfer of the alkenyl group of the silicate from silicon to palladium but also provide a new route to (π-allyl)palladium compounds.[16]

Cross-Coupling with Allylic Halides. In the previous sections it has been shown that the reaction of alkenyl- and phenylsilicates with palladium salts may proceed through organopalladium intermediates. Since the aryl-[17a] and alkenylpalladium[17b] species are known to react with allylic halides producing the cross-coupling product, we have examined the reaction of the (*E*)-alkenylsilicates with

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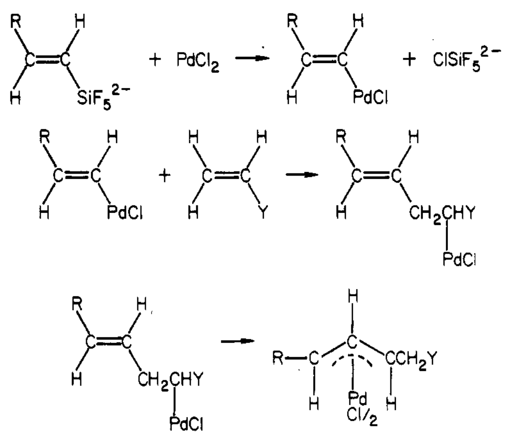
[15] Larock, R. C.; Mitchell, M. A. *J. Am. Chem. Soc.* **1978**, *100*, 180.

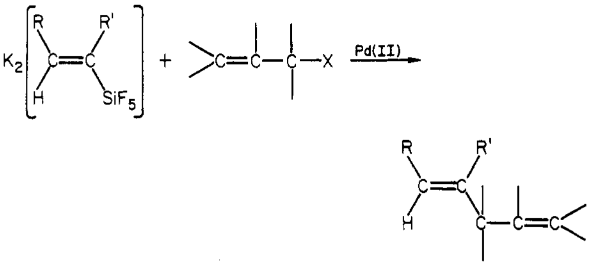
[16] (a) Huttel, R. *Synthesis* **1979**, 228. (b) Trost, B. M. *Tetrahedron* **1977**, *33*, 2615.

[17] (a) Heck, R. F. *J. Am. Chem. Soc.* **1968**, *90*, 5531. (b) Larock, R. C.; Bernhardt, J. C.; Briggs, R. J. *J. Organomet. Chem.* **1978**, *156*, 45.

Scheme I



allylic halides in the presence of catalytic amounts of palladium salts (eq 2). As shown in Table III the corresponding cross-coupling products *E* 1,4-dienes were obtained stereoselectively in good yields. For example, (*E*)-1-hexenylpentafluorosilicate reacted with allyl chloride in the presence of palladium acetate (10 mol %) in THF to give (*E*)-1,4-nonadiene in 71% yield. Although the reaction proceeded with 1 equiv of allyl chloride, the yield of the product increased by increasing the amount of allyl chloride and the most satisfactory yield was obtained when 10 equiv of allyl chloride was used. The nature of the reaction medium did not significantly affect the yield, but THF seems to be the most suitable solvent. Palladium acetate was the most effective of the examined catalysts. Palladium chloride was also effective, but palladium acetylacetonate was almost inactive.

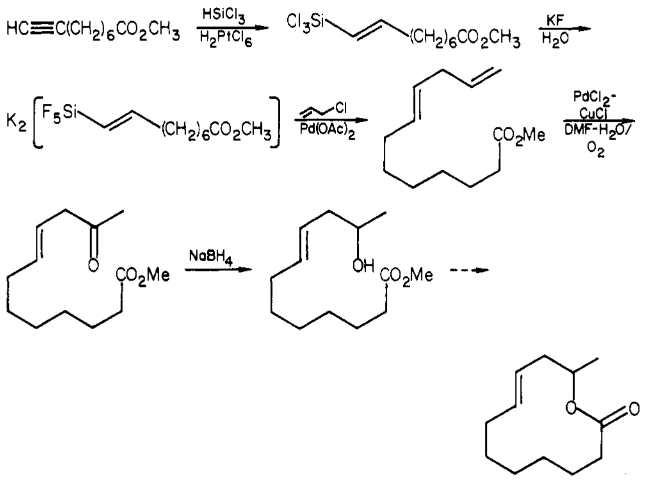


(2)

With the use of optimum reaction conditions the scope and limitations of this cross-coupling reaction were then studied with several types of allylic substrates and alkenylsilicates. As an allylic substrate allyl chloride was the most satisfactory. Allyl bromide was less effective. When allyl acetate or allyl tosylate was used, the yield of the cross-coupling product decreased conspicuously. In the reaction with 3-chloro-1-butene the carbon–carbon bond formation occurred exclusively at the γ-position and a mixture of (2*E*,5*E*)- and (2*Z*,5*E*)-2,5-decadiene was obtained. Methallyl chloride also reacted with the alkenylsilicate but the yield of the cross-coupling product was low, indicating that the present reaction is subject to the steric hindrance around the double bond in the allylic substrate. Crotyl chloride was almost inactive, and only trace amounts of unidentified products were obtained.

Both terminal and internal (*E*)-alkenylsilicates reacted smoothly with allyl chloride to give the cross-coupling products. In all cases the reaction is highly regioselective and an allyl group is introduced onto the carbon to which the silicon atom has been attached. The *E* stereochemistry of the alkenylsilicates is retained during the reaction and *E* 1,4-dienes are obtained stereoselectively. Mechanisms of the reaction of organopalladium with allylic halides have already been discussed in detail by Heck and Larock.[17]

Scheme II



Analogously, the present reaction may involve the following processes. The alkenyl group of the alkenylsilicate transfers from silicon to palladium, producing the alkenylpalladium species which adds to the allylic double bond. The (1-alkenyl-3-chloro-2-propyl)palladium species then decomposes by eliminating palladium chloride to give the *E*-1,4-dienes. Palladium chloride thus formed may again react with the alkenylsilicate, and the overall reaction proceeds catalytically in palladium.

The synthesis of the 1,4-diene structure has received increasing attention, and several cross-coupling reactions of vinylic organometallics with allylic substrates have been developed as useful routes from alkynes. These involve the palladium-promoted coupling of alkenylmercury[17b] and -boron compounds,[12,18d] coupling of organocopper[18f] or copper-induced coupling of organoboron,[18] and direct coupling of alkenylaluminum reagents.[19] Of these procedures, the alkenylmercurial route gives higher yields of 1,4-dienes but is applicable only to the terminal alkenyl derivatives. The present procedure, like the alkenylboron routes, can be applied to both the terminal and internal alkenyl derivatives. Although the present procedure does not give very high yields and requires 10 equiv of allylic halide, it requires only 10 mol % of palladium chloride like the other palladium-promoted reactions mentioned above, retains the *E* configuration of the double bond, and is capable of tolerating some functional groups such as an alkoxycarbonyl group incompatible with hydroalumination.

To illustrate one of the unique synthetic applications of the present coupling reaction, we have developed a new route to methyl (±)-11-hydroxy-(*E*)-8-dodecenoate, a precursor of recifeiolide, the naturally occurring macrolide from *Cephalosporium recifei*[20] (Scheme II). The high *E*

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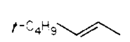
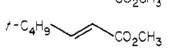
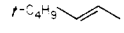
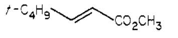
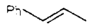
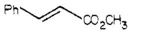
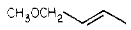
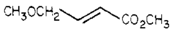
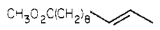
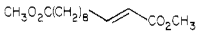
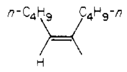
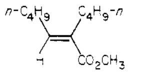
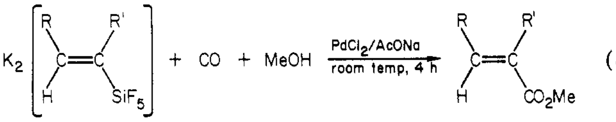
Table IV. Carbomethoxylation of $K_2[RSiF_5]$[a]

R in $K_2[RSiF_5]$	product	yield,[b] %
		91 (83)[c]
		90
		76
		61 (57)[c]
		72
		88
Ph-	$PhCO_2CH_3$	trace
$PhCH_2$-	$PhCH_2CO_2CH_3$	trace

[a] Carried out by using 1 mmol of silicate, $PdCl_2$ (1.1 mmol), CH_3CO_2Na (ca. 2 mmol), and methanol (5 mL) under atmospheric pressure of CO at room temperature for 4 h, unless otherwise noted. [b] Yields were determined by GLC based on the silicate. [c] A 3-mmol scale reaction, the product being isolated by distillation.

stereoselectivity and the functional group compatibility should be noted here. The silicate $K_2[F_5SiCH{=}CH(CH_2)_6CO_2CH_3]$, prepared by hydrosilylation of methyl 8-nonynoate followed by treatment with aqueous KF (62% yield), was allowed to react with allyl chloride in the presence of palladium acetate. Methyl (*E*)-8,11-dodecadienoate thus obtained (55% yield) was oxidized by the Wacker process ($PdCl_2$–CuCl/DMF–H_2O/O_2 system)[21] to give methyl 11-oxo-(*E*)-8-dodecenoate in 67% yield. Reduction with $NaBH_4$ gave isomerically pure methyl (±)-11-hydroxy-(*E*)-8-dodecenoate in 93% yield. Several elegant cyclization methods for the macrolide synthesis have been developed.[22]

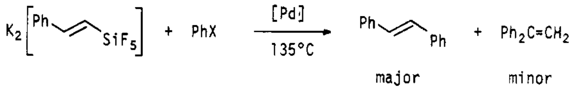
Carbonylation. We find that (*E*)-alkenylpentafluorosilicates readily react with carbon monoxide (atmospheric pressure) in the presence of palladium salts and sodium acetate in methanol to give *E* α,β-unsaturated carboxylic esters in excellent yields. This reaction (eq 3) is indeed the first case of carbonylation of organosilicon compounds.


(3)

The use of sodium acetate as a base afforded the most satisfactory results; tertiary amines in place of sodium acetate gave only moderate to poor yields, e.g., the yield of methyl 2-nonenoate was 40% with Et_3N and 20% with pyridine. While $PdCl_2$ and $PdBr_2$ exhibited similar reactivities, $Pd(OAc)_2$ was somewhat less active and no carbonylation occurred with $PdCl_2(PPh_3)_2$. The carbonylation proceeded smoothly at room temperature (around 25 °C) but very slowly at 0 °C. The results summarized in Table IV were obtained under the typical reaction conditions: $PdCl_2$/AcONa/MeOH/CO (1 atm)/25 °C. The present carbonylation proceeds highly stereoselectively with both the terminal and internal alkenylsilicates and is capable of tolerating some functional groups such as ester and ether. Phenyl- and alkylsilicates, unfortunately, gave only trace amounts of carbonylation products.

Preparation of α,β-unsaturated carboxylic esters via carbonylation of organometallics has so far been known only for the palladium-catalyzed reaction of alkenylmercurials.[23] Quite recently, alkenylboranes have also been reported to be carbonylated under similar conditions to our present system.[24] These carbonylations proceed catalytically in palladium if copper(II) halide or *p*-benzoquinone is used as a reoxidant. The present reaction, unfortunately, requires a stoichiometric amount of palladium salt, since copper(II) salts react readily with alkenylsilicates[1] and hence cannot be used as a reoxidant. While carbonylation of alkenyl halides with nickel carbonyl proceeds with retention of configuration,[25] palladium-catalyzed reactions suffer from rather low stereoselectivity.[26] Our present procedure may provide a convenient, efficient, and stereoselective route to *E* α,β-unsaturated carboxylic esters from acetylenes.

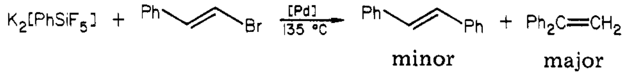
Cross-Coupling Reaction with C(sp^2) Halides. Cross-coupling reactions between organic halides and organometallics have recently been accomplished in the presence of transition-metal complexes.[27] The aforementioned reactions involving the alkenyl group transfer from silicon to palladium suggest the possibility of the cross-coupling of organopentafluorosilicates with organic halides. We find that the styrylsilicate couples with iodo- or bromobenzene in the presence of palladium complexes as catalysts under rather drastic conditions (135 °C) to give (*E*)-stilbene in fair yields, together with 1,1-diphenylethylene, no (*Z*)-stilbene being formed (eq 4).



(4)

Results are summarized in Table V. The reaction occurred with either Pd(0) or Pd(II) catalyst precursors regardless of the nature of the ligands. Unfortunately, the yield could not be improved by variation of conditions and catalysts. A somewhat improved yield was observed in the presence of triethylamine, but it might have resulted from the Heck reaction[11] between iodobenzene and styrene which was formed in all cases as a byproduct. Lower yields were obtained with bromobenzene. (*E*)-1-Hexenylsilicate gave a complex mixture of products. No reaction was observed under refluxing conditions in THF or with $NiCl_2$(dppp) (dppp = $Ph_2P(CH_2)_3PPh_2$) as a catalyst at 135 °C.

A similar reaction between phenylsilicate and bromostyrene gave 1,1-diphenylethylene as a major product, along with a trace amount of (*E*)-stilbene. This reaction occurred only in the presence of THF.



Formation of (*E*)-stilbene may be explained by a mechanism similar to that proposed for palladium-[28] or nickel-catalyzed[29] cross-coupling of active organometallics

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[21] Tsuji, J.; Shimizu, I.; Yamamoto, K. *Tetrahedron Lett.* **1976**, 2975.

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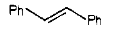
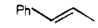
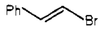
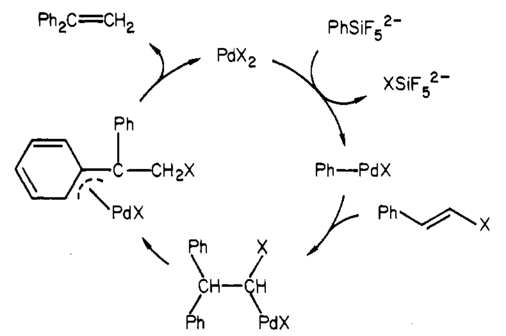
[29] Tamao, K.; Sumitani, K.; Kiso, Y.; Zembayashi, M.; Fujioka, A.; Kodama, S.; Nakajima, I.; Minato, A.; Kumada, M. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 1958.

Table V. Cross-Coupling Reactions of Phenyl- and Styrylsilicate with C(sp^2) Halides[a]

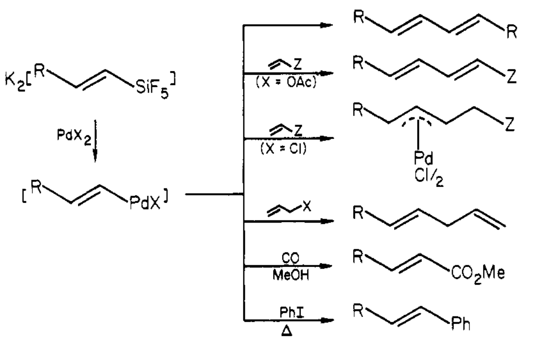
R in $K_2[RSiF_5]$	halide	catalyst,[b] 5 mol %	time, h	% yield of products[c]	
					$Ph_2C{=}CH_2$
	PhI	PdL_4	20	28	7
		$PdCl_2$	5	36	9
		$PdCl_2$[d]	5	38	9
		$Pd(OAc)_2/2L/Et_3N$	20	51	8
		$Pd(OAc)_2$/dppb	20	39	5
		$Pd_2(DBA)(CHCl_3)$[e]	5	40	4
		$Pd_2(DBA)(CHCl_3)/4L$[e]	5	41	6
		$Pd_2(DBA)(CHCl_3)$/2dppp[e]	5	33	8
		$Pd_2(DBA)(CHCl_3)$/2dppb[e]	5	39	6
	PhBr	$Pd_2(DBA)(CHCl_3)$[e]	5	18	4
		$Pd_2(DBA)(CHCl_3)/4L$[e]	5	33	3
Ph-		$Pd(OAc)_2$/dppb[f]	5	trace	23

[a] Carried out in a sealed glass tube at 135 °C in the absence of solvent, unless otherwise stated. [b] L = PPh_3, dppp = $Ph_2P(CH_2)_3PPh_2$, dppb = $Ph_2P(CH_2)_4PPh_2$, and DBA = dibenzylideneacetone. [c] Determined by GLC. [d] In heptane. [e] One mol % of the catalyst precursor was used. [f] In THF.

Scheme III



Scheme IV



with organic halides. Thus, the reaction might involve oxidative addition of an organic halide, organic group-transfer from silicon to the palladium(II) species, and reductive elimination of the coupling product. Production of a palladium(0) species from a palladium(II) catalyst precursor may be attained by homocoupling of an organosilicate as mentioned above.

Formation of 1,1-diphenylethylene lacks a ready explanation, but speculatively, at least, the reaction of phenylsilicate and styryl bromide might proceed through an addition–elimination mechanism as visualized in Scheme III. The hydride–palladium rearrangement process may result in the formation of a (π-benzyl)palladium species,[30] reminiscent of the formation of (π-allyl)palladium complexes (Scheme I).

Although similar coupling reactions involving the rearrangement of an alkenyl group have been observed in the palladium-promoted head-to-tail coupling of alkenylmercurials[31] and -boranes,[24b] a detailed mechanism remains obscure.

Summarizing Remarks

Palladium-promoted reactions of alkenylpentafluorosilicates presented herein are summarized in Scheme IV. While the coupling reactions with allylic and aryl halides are catalytic in palladium, other reactions require a stoichiometric amount of a palladium salt. In view of the ready accessibility of (*E*)-alkenylsilicates, the present reactions may be useful for the preparation of a variety of olefinic compounds containing an *E* alkenyl moiety. These reactions are all characteristic of organopalladium complexes. One of the most important features from a mechanistic standpoint is that an alkenyl or aryl group readily transfers from silicon to a palladium(II) salt. It should be noted here that most reactions occur only with the palladium(II) halides or acetate not coordinated by phosphine ligands. This feature strongly suggests that an interaction between an alkenyl group and a rather naked palladium(II) species may play an important role in the alkenyl group transfer step and is reminiscent of the mechanism of the copper(II)-induced cleavage reactions of alkenylsilicates.[1] Delineation of a detailed mechanism, however, must wait for further studies.

Experimental Section

General Remarks. Infrared spectra were recorded on a Hitachi EPI-G3 grating infrared spectrometer. ^1H NMR spectra were determined with a JEOL JNM-MH-100 (100-MHz) spectrometer in carbon tetrachloride. Chemical shifts (δ) are recorded in parts per million downfield from Me_4Si. Mass spectra were measured on a JEOL JMS-D300 mass spectrometer connected with a JEOL LGC-20K gas chromatograph, equipped with a 1-m glass column packed with OV-17 (1%) on Chromosorb B, and JMA-2000 data processing system. Ionization voltage was 24 eV for all compounds. GLC analyses and preparative purification were performed on a Shimadzu GC-4B gas chromatograph, equipped with a 3-m column packed with 30% Silicone DC550 on Chromosorb B or Celite 545. GC peak integrals were recorded by using a Shimadzu Chromotopac C-E1B integrator.

Materials. Organopentafluorosilicates were prepared as described previously.[3] Palladium chloride and palladium acetate of ordinary commerical grade were used without further purification. $Pd_2(DBA)(CHCl_3)$[32] and allyl tosylate[33] were prepared according to the published procedures. Methyl 8-nonynoate was prepared by the acid-catalyzed esterification of 8-nonynoic acid.[34]

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(30) (a) Stevens, P. S.; Shier, G. D. *J. Organomet. Chem.* **1970**, *21*, 495. (b) Roberts, J. S.; Klabunde, K. J. *J. Am. Chem. Soc.* **1977**, *99*, 2509. (c) Becker, Y.; Stille, J. K. *Ibid.* **1978**, *100*, 845.

(31) Larock, R. C.; Riefling, B. *J. Org. Chem.* **1978**, *43*, 1468.

(32) Ukai, T.; Kawazura, H.; Ishii, Y.; Bonnet, J. J.; Ibers, J. A. *J. Organomet. Chem.* **1974**, *65*, 253.

(33) Johnson, C. R.; Dutra, G. A. *J. Am. Chem. Soc.* **1973**, *95*, 7777.

All solvents were dried in the usual manner and distilled before use. Other chemicals and nitrogen were used directly as obtained commercially.

Homocoupling Reaction of Organopentafluorosilicates. The homocoupling reaction of styrylpentafluorosilicate was carried out as follows. A mixture of the styrylsilicate (327 mg, 1.07 mmol), palladium chloride (188 mg, 1.06 mmol), and acetonitrile (2.0 mL) was stirred at room temperature for 3 h. The black mixture was filtered, and the solid product was washed with benzene. The combined filtrate was concentrated by evaporation. Column chromatgraphy on silica gel (petroleum ether/benzene, 1:1) of the brown solid residue yielded 59 mg (54% yield) of 1,4-diphenylbutadiene, which was identified by comparison of its spectral data with those of an authentic material.[7]

The homocoupling reaction of the phenylsilicate (310 mg, 1.12 mmol) in the presence of palladium chloride (191 mg, 1.08 mmol) in 3.0 mL of THF was carried out at room temperature in a similar fashion. After 20 h GLC analysis of the reaction mixture showed the formation of biphenyl in 48% yield based on palladium chloride. The product was isolated and identified by comparison of its spectral data with those of an authentic meterial.

Cross-Coupling Reaction of Organopentafluorosilicates with Activated Olefins. General Procedure. A mixture of an organopentafluorosilicate (1.0 mmol), palladium acetate (224 mg, 1.0 mmol), an activated olefin (10.0 mmol), and a given solvent (5.0 mL) was stirred at room temperature for a given period of time (see Table I). After the reaction methylene chloride was added and the insoluble material was removed by filtration. The product was isolated, after evaporation of the solvent, by preparative TLC or column chromatography and characterized by ^{1}H NMR, IR, and mass spectroscopy and elemental analyses.

Formation of (π-Allyl)palladium Compounds. The following preparation of di-μ-chloro-bis(1-(ethoxycarbonyl)oct-2-enyl)dipalladium(II) is representative of the procedure used in determining the isolated yields reported in Table II.

Di-μ-chloro-bis(1-(ethoxycarbonyl)oct-2-enyl)dipalladium(II). Nitrogen was bubbled into a mixture of (*E*)-1-hexenylpentafluorosilicate (286 mg, 1.0 mmol) and dry THF (5.0 mL). After addition of palladium chloride (195 mg, 1.1 mmol) and ethyl acrylate (1.1 mL, 10 mmol) the mixture was stirred at 0 °C for 6 h. Ether was added and insoluble matters were removed by filtration. Evaporation of the yellow filtrate gave 123 mg (38% yield) of the (π-allyl)palladium compound. Recrystallization of the crude product from ethanol–hexane (1:1) gave pale yellow crystals: mp 115–117 °C (lit.[15] 116–117 °C dec); IR (KBr) 2960, 2930, 2860, 1735, 1520, 1465, 1367, 1328, 1190, 1030 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.95 (t, J = 6 Hz, 3 H), 1.2–1.9 (m, 6 H), 1.25 (t, J = 7 Hz, 3 H), 2.52 (dd, J = 9 and 16 Hz, 1 H), 2.81 (dd, J = 5 and 16 Hz, 1 H), 3.5–4.0 (m, 2 H), 4.16 (q, J = 6 Hz, 2 H), 5.12 (t, J = 11 Hz, 1 H). The spectral data of the reaction product accorded with those of an authentic sample reported in the literature:[15] IR (KBr) 1728 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.8–1.9 (m, 9 H), 1.20 (t, J = 7 Hz, 3 H), 2.48 (dd, J = 9 and 17 Hz, 1 H), 2.78 (dd, J = 5 and 17 Hz, 1 H), 3.5–4.0 (m, 2 H), 4.12 (q, J = 7 Hz, 2 H), 5.18 (t, J = 11 Hz, 1 H). Anal. Calcd for $C_{11}H_{19}ClO_2Pd$: C, 40.64; H, 5.89. Found: C, 40.86; H, 6.12.

The following (π-allyl)palladium compounds were prepared in a similar fashion.

Di-μ-chloro-bis(2-oxodec-4-enyl)dipalladium(II) was recrystallized from hexane–$CHCl_3$ (20:1): mp 133–135 °C dec; IR (KBr) 3000, 2955, 2930, 2860, 1715, 1515, 1463, 1420, 1380, 1360, 1168, 1025 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.90 (t, J = 6 Hz, 3 H), 1.1–1.9 (m, 6 H), 2.18 (s, 3 H), 2.65 (dd, J = 9 and 17 Hz, 1 H), 2.98 (dd, J = 5 and 17 Hz, 1 H), 3.5–4.0 (m, 2 H), 5.16 (t, J = 11 H, 1 H). Anal. Calcd for $C_{10}H_{17}ClOPd$: C, 40.70; H, 5.81. Found: C, 40.99; H, 5.72.

Di-μ-chloro-bis(1-phenyloct-2-enyl)dipalladium(II) was recrystallized from hexane: mp 116–118 °C; IR (KBr) 3025, 2955, 2930, 2860, 1600, 1510, 1492, 1450, 1100, 1075, 1030, 975, 750, 700 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.90 (t, J = 6 Hz, 3 H), 1.1–1.9 (m, 6 H), 2.96 (d, J = 6 Hz, 2 H), 3.6–4.0 (m, 2 H), 5.04 (t, J = 11 Hz, 1 H), 7.23 (br s, 5 H). Anal. Calcd for $C_{14}H_{19}ClPd$: C, 51.09; H, 5.82. Found: C, 50.05; H, 5.50.

Cross-Coupling Reaction of Alkenylsilicates with Allylic Halides. The following preparation of (*E*)-1,4-nonadiene is representative of the procedure for the reaction of alkenylsilicates with allylic substrates catalyzed by palladium(II) salts.

(*E*)-1,4-Nonadiene. A mixture of (*E*)-1-hexenylpentafluorosilicate (1.422 g, 5.0 mmol), allyl chloride (4.10 mL, 50 mmol), palladium acetate (112 mg, 0.50 mmol), and dry THF (10 mL) was stirred at room temperature for 24 h. After addition of pentane (20 mL) insoluble material was removed by filtration and the solvent was evaporated. The residue was distilled (bulb-to-bulb distillation) to give 259 mg (42% yield) of (*E*)-1,4-nonadiene: $n^{20}{}_D$ 1.4306 (lit.[18a] $n^{25}{}_D$ 1.4301); IR (CCl_4) 3075, 2950, 2925, 2870, 2850, 1643, 1468, 1458, 1435, 1380, 1100, 989, 967, 911 cm^{-1}; ^{1}H NMR δ 0.90 (t, J = 6 Hz, 3 H), 1.1–1.5 (m, 4 H), 1.8–2.15 (m, 2 H), 2.3–2.5 (m, 2 H), 4.8–5.05 (m, 2 H), 5.25–5.4 (m, 2 H), 5.45–5.95 (m, 1 H); mass spectrum, m/e (%) 125 (M^+ + 1, 2), 124 (M^+, 16), 82 (34), 81 (49), 54 (100); high resolution mass spectrum, m/e 124.1257 (calcd for C_9H_{16}, m/e 124.1253).

An authentic sample of (*Z*)-1,4-nonadiene was prepared according to Normant's method.[35] *n*-Butylcopper prepared from *n*-butylmagnesium bromide and cuprous bromide was allowed to react with acetylene followed by treatment with allyl bromide in the presence of HMPA and triethyl phosphite to give (*Z*)-1,4-nonadiene: IR (CCl_4) 3084, 3020, 1643, 988, 908 cm^{-1}; ^{1}H NMR δ 0.95 (t, J = 6 Hz, 3 H), 1.1–1.6 (m, 4 H), 1.8–2.3 (m, 2 H), 2.75–2.85 (m, 2 H), 4.8–5.1 (m, 2 H), 5.1–5.5 (m, 2 H), 5.5–6.0 (m, 1 H). GLC analysis (QF-1 30% on Celite 545, 3 m) of the product from (*E*)-1-hexenylsilicate and allyl chloride showed a single sharp peak which could be separated from that of the authentic *Z* isomer. Thus the stereochemical purity of the reaction product was assigned to be 100% *E*.

All other 1,4-dienes were prepared in a similar fashion.

(8-(Methoxycarbonyl)-1-octenyl)pentafluorosilicate. Methyl 8-nonynoate (3.36 g, 20.0 mmol) was allowed to react with trichlorosilane (2.50 mL, 24.8 mmol) in the presence of chloroplatinic acid (0.10 M solution in 2-propanol, 200 μL, 0.020 mmol) at 5 °C for 24 h. Distillation (130 °C (5mmHg)) of the reaction mixture gave 4.576 g (76% yield) of ((*E*)-8-(methoxycarbonyl)-1-octenyl)trichlorosilane: ^{1}H NMR δ 1.1–1.8 (m, 8 H), 2.1–2.5 (m, 4 H), 3.61 (s, 3 H), 5.77 (d, J_{trans} = 19 Hz, 1 H), 6.65 (dt, J_{trans} = 19 Hz (d) and 7 Hz (t), 1 H). The alkenylsilane (4.576 g, 15.1 mmol) was treated with potassium fluoride (23.2 g, 400 mmol) in 30 mL of water at 0 °C in the usual manner. White precipitate was separated by filtration followed by washing with water, ethanol, and ether. After the mixture was dried in vacuo, 4.074 g (73% yield) of ((*E*)-8-(methoxycarbonyl)-1-octenyl)pentafluorosilicate was obtained: IR (KBr) 2920, 2850, 1745, 1622, 1438, 1260, 1200, 1167, 1000, 775, 738, 657, 549, 453 cm^{-1}. Although satisfactory elemental analysis was not obtained, the silicate was used in the subsequent reaction without further purification.

(*E*)-11-(Methoxycarbonyl)-1,4-undecadiene: A mixture of ((*E*)-8-(methoxycarbonyl)-1-octenyl)pentafluorosilicate (1.12 g, 3.0 mmol), allyl chloride (2.46 mL, 30.0 mmol), palladium acetate (67 mg, 0.30 mmol), and dry THF (10 mL) was stirred at room temerature for 20 h. Ether (20 mL) was added, and the insoluble matters were removed by filtration followed by evaporation of the solvent. Bulb-to-bulb distillation under reduced pressure (1mmHg) gave 344 mg (55% yield) of (*E*)-11-(methoxycarbonyl)-1,4-undecadiene: $n^{20}{}_D$ 1.4563; IR (liquid film) 3075, 2920, 2850, 1745, 1642, 1452, 1435, 1362, 1255, 1200, 1167, 990, 965, 907 cm^{-1}; ^{1}H NMR 1.1–1.75 (m, 8 H), 1.8–2.1 (m, 2 H), 2.21 (t, J = 7 Hz, 2 H), 2.6–2.8 (m, 2 H), 3.58 (s, 3 H), 4.8–5.1 (m, 2 H), 5.25–5.4 (m, 2 H), 5.45–5.95 (m, 1 H); mass spectrum m/e (%) 211 (M^+ + 1, 1), 210 (M^+, 10), 178 (25), 136 (27), 95 (60), 81 (81), 68 (100). Anal. Calcd for $C_{13}H_{22}O_2$: C, 74.24; H, 10.54. Found: C, 73.94; H, 10.79.

Methyl (*E*)-11-Oxo-8-dodecenoate. A mixture of (*E*)-11-(methoxycarbonyl)-1,4-undecadiene (163 mg, 0.776 mmol), cuprous chloride (79 mg, 0.800 mmol), palladium chloride (14 mg, 0.079 mmol), DMF (5.0 mL), and water (0.6 mL) was stirred under an atmosphere of oxygen. After 15 h palladium chloride (14 mg) was added and the mixture was stirred for 2 h. The mixture was

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(34) Sood, R.; Nagasawa, M.; Sih, C. J. *Tetrahedron Lett.* **1974**, 423.

(35) Normant, J. F.; Cahiez, G.; Chuit, C. *J. Organomet. Chem.* **1974**, *77*, 269.

poured into aqueous HCl, and the organic matters were extracted with ether. The extracts were dried over Na_2SO_4 and concentrated by evaporation. Bulb-to-bulb distillation of the residue gave 117 mg (67% yield) of methyl (*E*)-11-oxo-8-dodecenoate: IR (liquid film) 2925, 2850, 1745, 1723, 1460, 1438, 1360, 1255, 1160, 1008, 965 cm^{-1}; ^1H NMR δ 1.2–1.8 (m, 8 H), 1.9–2.2 (m, 2 H), 2.05 (s, 3 H), 2.22 (t, $J = 7$ Hz, 2 H), 2.95–3.05 (m, 2 H), 3.60 (s, 3 H), 5.35–5.55 (m, 2 H); mass spectrum, *m/e* (%) 227 ($M^+ + 1$, 1), 226 (M^+, 33), 208 (24), 136 (100). Although the product was contaminated with small amounts of impurities (GLC), it was used in the subsequent reaction without further purification.

Methyl (±)-(*E*)-11-Hydroxy-8-dodecenoate. To a solution of methyl (*E*)-11-oxo-8-dodecenoate (117 mg, 0.52 mmol) in ethanol (5.0 mL) was added sodium borohydride (70 mg, 1.85 mmol), and the mixture was stirred at room temperature overnight. After addition of dilute aqueous HCl the product was extracted with ether, dried over Na_2SO_4, and concentrated by evaporation. Bulb-to-bulb distillation of the residue gave 110 mg (93% yield) of methyl (±)-(*E*)-11-hydroxy-8-dodecenoate: $n^{20}{}_D$ 1.4600; IR (liquid film) 3400, 2925, 2850, 1748, 1460-1000 (broad absorptions including maximum at 1440, 1378, 1330, 1260, 1200, 1170, 1070, 1010), 965, 935 cm^{-1}; ^1H NMR δ 1.0-1.8 (m, 8 H), 1.10 (d, $J = 6.5$ Hz, 3 H), 1.8–2.2 (m, 4 H), 2.20 (t, $J = 8$ Hz, 2 H), 3.59 (s, 3 H), 3.5–3.8 (m, 1 H), 5.3–5.5 (m, 2 H); mass spectrum, *m/e* (%) 210 ($M^+ - 18$, 5), 184 ($M^+ - 44$, 16), 152 (53), 84 (100). Anal. Calcd for $C_{13}H_{24}O_3$: C, 68.38; H, 10.59. Found: C, 68.61; H, 10.53. The spectral data of the reaction product accorded with those reported for methyl (+)-(*S*)-(*E*)-11-hydroxy-8-dodecenoate.[20b]

Carbonylation of Alkenylsilicates. A typical procedure is as follows.

Methyl (*E*)-2-Nonenoate. To a mixture of (*E*)-1-octenylpentafluorosilicate (936 mg, 3.0 mmol), sodium acetate (480 mg, 5.9 mmol), and anhydrous methanol (15 mL), through which had been bubbled carbon monoxide for 5 min, was added palladium chloride (585 mg, 3.3 mmol). The mixture was stirred under the carbon monoxide atmosphere (a CO balloon) at room temperature (ca. 25 °C) for 4 h. Almost immediately the color changed from brown to black (possibly palladium black). Ether was added and the mixture filtered. The filtrate was washed three times with 10% NaCl aqueous solution, dried over magnesium sulfate, and distilled (bulb-to-bulb) to give 424 mg (83% yield) of methyl (*E*)-2-nonenoate: $n^{20}{}_D$ 1.4459; IR (liquid film) 2920, 2850, 1730, 1660, 1470, 1460, 1440, 1382, 1315, 1275, 1190, 1170, 1125, 1037, 974, 845 cm^{-1}; ^1H NMR δ 0.91 (t, $J = 6$ Hz, 3 H), 1.15–1.6 (m, 8 H), 2.20 (br q, $J = 7$ Hz, 2 H), 3.67 (s, 3 H), 5.72 (dt, $J = 16$ and 1 Hz, 1 H), 6.86 (dt, $J = 16$ and 7 Hz, 1 H); mass spectrum, *m/e* (%) 170 (M^+, 3), 87 (100). Anal. Calcd for $C_{10}H_{18}O_2$: C, 70.55; H, 10.66. Found: C, 70.69; H, 10.90.

Reaction of an Organopentafluorosilicate with an Organic Halide. Typical Procedure. A mixture of (*E*)-styrylpentafluorosilicate (306 mg, 1 mmol), palladium chloride (8.7 mg, 0.05 mmol), and iodobenzene (0.15 mL, 1.3 mmol) was sealed in a glass tube and heated at 135 °C for 5 h. GLC analysis of the mixture showed that (*E*)-stilbene and 1,1-diphenylethylene were formed in 36% and 9% yields, respectively. Styrene was also detected, but the yield was not determined. After filtration and flash distillation the products were isolated by preparative GLC and identified by spectral data superimposable with those of authentic samples. The insoluble filter cake showed an IR spectrum corresponding to hexafluorosilicate.

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Registry No. $K_2[PhCH{=}CHSiF_5]$, 68901-41-7; $K_2[PhSiF_5]$, 5507-59-5; $K_2[CH_3O_2C(CH_2)_6CH{=}CHSiF_5]$, 68757-55-1; $K_2[n\text{-}C_6H_{13}CH{=}CHSiF_5]$, 70995-82-3; $K_2[t\text{-}C_4H_9CH{=}CHSiF_5]$, 70995-83-4; $K_2[NCCH_2CH_2OCH_2CH{=}CHSiF_5]$, 74463-90-4; $K_2[n\text{-}C_6H_{13}CH{=}C(n\text{-}C_6H_{13})SiF_5]$, 71686-45-8; $K_2[n\text{-}C_4H_9CH{=}CHSiF_5]$, 68732-24-1; $K_2[n\text{-}C_4H_9CH{=}C(n\text{-}C_4H_9)SiF_5]$, 70995-87-8; $K_2[CH_3O_2C(CH_2)_8CH{=}CHSiF_5]$, 70995-86-9; $K_2[PhCH_2SiF_5]$, 71782-41-7; $K_2[CH_3OCH_2CH{=}CHSiF_5]$, 70995-85-6; $PhCH{=}CH{-}CH{=}CHPh$, 538-81-8; $CH_2{=}CHCHO$, 107-02-8; $CH_2{=}CHCN$, 107-13-1; (*E*)-$CH_3CH{=}CHCO_2CH_3$, 623-43-8; $CH_2{=}CHCO_2Et$, 140-88-5; $CH_2{=}CHPh$, 100-42-5; $CH_2{=}CHCOCH_3$, 78-94-4; $CH_2{=}CHCH_2Cl$, 107-05-1; $CH_2{=}CHCH_2Br$, 106-95-6; $CH_2{=}CHCH_2OAc$, 591-87-7; $CH_2{=}CHCH_2OTs$, 4873-09-0; $CH_2{=}CHCH(CH_3)Cl$, 563-52-0; $CH_2{=}C(CH_3)CH_2Cl$, 927-73-1; $CH_3CH{=}CHCH_2Cl$, 591-97-9; PhI, 591-50-4; PhBr, 108-86-1; $PhCH{=}CHBr$, 588-72-7; Ph—Ph, 92-52-4; $CH_3O_2C(CH_2)_6CH{=}CHCH_2CH{=}CH_2$, 68712-26-5; $CH_3O_2C(CH_2)_6CH{=}CHCH_2COCH_3$, 68712-27-6; (±)-$CH_3O_2C(CH_2)_6CH{=}CHCH_2CH(OH)CH_3$, 68779-88-4; $CH_3O_2CCH{=}CH(CH_2)_5CH_3$, 14952-06-8; $n\text{-}C_4H_9CH{=}CHCH{=}CHCO_2CH_3$, 54354-51-7; $n\text{-}C_4H_9CH{=}CHCH{=}CHCO_2C_2H_5$, 53434-79-0; $n\text{-}C_4H_9CH{=}CHCH{=}CHCHO$, 5910-87-2; (*E,E*)-$n\text{-}C_4H_9CH{=}CHCH{=}CHCN$, 79803-68-2; (*Z,E*)-$n\text{-}C_4H_9CH{=}CHCH{=}CHCN$, 53378-99-7; $t\text{-}C_4H_9CH{=}CHCH{=}CHCO_2CH_3$, 79803-69-3; $t\text{-}C_4H_9CH{=}CHCH{=}CHCO_2C_2H_5$, 21016-49-9; $NCCH_2CH_2OCH_2CH{=}CHCH{=}CHCO_2C_2H_5$, 79803-70-6; $n\text{-}C_6H_{13}CH{=}C(n\text{-}C_6H_{13})CH{=}CHCO_2C_2H_5$, 79803-71-7; $PhCH{=}CHCH{=}CHCO_2CH_3$, 24196-39-2; $PhCH{=}CHCO_2CH_3$, 1754-62-7; $PhCH{=}CHCHO$, 14371-10-9; $PhC(CH_3){=}CHCO_2CH_3$, 3461-50-5; $[PdCl(n\text{-}C_4H_9CHCH{=}CHCH_2CO_2Et)]_2$, 65653-16-9; $[PdCl(n\text{-}C_4H_9CHCH{=}CHCH_2Ph)]_2$, 79816-40-3; $[PdCl(n\text{-}C_4H_9CHCH{=}CHCH_2COCH_3)]_2$, 79839-77-3; $n\text{-}C_4H_9CH{=}CHCH_2CH{=}CH_2$, 60835-96-3; (*E,E*)-$n\text{-}C_4H_9CH{=}CHCH_2CH{=}CHCH_3$, 68712-23-2; (*Z,E*)-$n\text{-}C_4H_9CH{=}CHCH_2OH{=}CHCH_3$, 68712-24-3; $n\text{-}C_4H_9CH{=}CHCH_2C(CH_3){=}CH_2$, 68712-25-4; $n\text{-}C_4H_9CH{=}C(n\text{-}C_4H_9)CH_2CH{=}CH_2$, 60835-98-5; $PhCH{=}CHCH_2CH{=}CH_2$, 55666-17-6; $t\text{-}C_4H_9CH{=}CHCO_2CH_3$, 20664-51-1; $PhCH{=}CHCO_2CH_3$, 103-26-4; $CH_3OCH_2CH{=}CHCO_2CH_3$, 13168-99-5; $CH_3O_2C(CH_2)_8CH{=}CHCO_2CH_3$, 13038-20-5; $n\text{-}C_4H_9CH{=}C(n\text{-}C_4H_9)CO_2CH_3$, 70980-01-7; $PhCO_2CH_3$, 93-58-3; $PhCH_2CO_2CH_3$, 101-41-7; $PhCH{=}CHPh$, 103-30-0; $Ph_2C{=}CH_2$, 530-48-3; Pd, 7440-05-3; $CH_3O_2C(CH_2)_6C{\equiv}CH$, 7003-48-7; $HSiCl_3$, 10025-78-2; ((*E*)-8-(methoxycarbonyl)-1-octenyl)trichlorosilane, 79803-72-8.

Supplementary Material Available: Characterizing data (^1H NMR, IR, and mass spectra, refractive indexes, and C/H analyses) for organic products of these reactions (7 pages). Ordering information is given on any current masthead page.