Organofluorosilicates in Organic Synthesis. 13.[1] Copper(II) Oxidation of Organopentafluorosilicates

Jun-ichi Yoshida, Kohei Tamao, Toshio Kakui, Atsushi Kurita, Masao Murata, Kozaburo Yamada, and Makoto Kumada*

Department of Synthetic Chemistry, Faculty of Engineering, Kyoto University, Yoshida, Kyoto 606, Japan

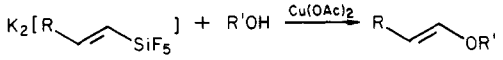
Received July 30, 1981

The carbon–silicon bond in organopentafluorosilicates ($K_2[RSiF_5]$, R = alkyl, alkenyl, and phenyl) has been found to be cleaved by copper(II) chloride or bromide to give the corresponding organic halides in high yields. The reaction obeys a stoichiometry of $K_2[RSiF_5]/CuX_2 = 1/2$. A halogen atom is regioselectively introduced to the carbon atom to which the silicon atom has been attached. (*E*)-Alkenyl halides are obtained stereoselectively from (*E*)-alkenylsilicates. Since organopentafluorosilicates can be readily prepared from olefins and acetylenes, the present reaction provides a synthetically useful route to organic halides. A two-step mechanism involving initial formation of an organic radical followed by ligand transfer from CuX_2 has been suggested by (1) spin trapping of the alkyl radical intermediate, (2) formation of an aldehyde in the presence of oxygen, and (3) stereochemical scrambling in the reaction of *exo*- and *endo*-2-norbornylpentafluorosilicates. Alkylsilicates undergo conjugate addition to α,β-enones in the presence of copper(II) acetate under rather forced conditions. In contrast to the inertness of alkylsilicates, alkenylsilicates react with some copper(II) pseudohalides. The reaction of (*E*)-alkenylsilicates with copper(II) thiocyanate gives (*E*)-alkenyl thiocyanates. The reaction with copper(II) selenocyanate prepared from $Cu(OAc)_2$ and KSeCN in situ gives a dialkenyl selenide. Copper(II) acetate induces the oxidative solvolytic cleavage of the carbon–silicon bond in alkenylsilicates. The reaction in the presence of an alcohol or water gives the alkenyl ethers or aldehydes, respectively.

In another paper,[1] we report full details of the cleavage reactions of the carbon–silicon bonds in hexacoordinate organopentafluorosilicates, $M_2[RSiF_5]$, by halogens and *N*-bromosuccinimide which do not affect those in neutral tetracoordinate silanes. This paper deals with the oxidative cleavage of organopentafluorosilicates by copper(II) salts. We have recently reported that copper(II) chloride and bromide cleave the carbon–silicon bond to produce the corresponding organic halides in good yields (eq 1).[2]

$$K_2[RSiF_5] + CuX_2 \rightarrow R\text{–}X \ (X = Cl, Br, SCN) \quad (1)$$

Copper(II) thiocyanate has also been found to react with alkenylpentafluorosilicates to give alkenyl thiocyanates (eq 1).[3] We have recently found also that copper(II) acetate induces the solvolytic cleavage of alkenylpentafluorosilicates to form, with alcohols, the corresponding alkenyl ethers (eq 2).[4]



(2)

Although copper(II) cleavage of the silicon–hydrogen[5] and silicon–aryl bonds[6] has been known, the former reaction (eq 1) is the first case of the copper(II) cleavage of silicon–alkyl and –alkenyl bonds involving a ligand transfer from copper to the organic group. The latter reaction (eq 2) is also the first example of copper(II) induced solvolytic cleavage of the carbon–silicon bond.[7] Investigation into the reaction of organopentafluorosilicates with copper(II) salts may not only provide a synthetically useful route to a variety of functionalyzed organic compounds but also contribute to the elucidation of a whole view of copper(II) cleavage of carbon–metal bonds.

Table I. Reaction of Octylpentafluorosilicate with Copper(II) Chloride and Bromide in Ether[a]

molar ratio of $CuX_2/K_2[C_8H_{17}SiF_5]$	yield of $C_8H_{17}X$, %[b] X = Cl	X = Br
1.0	58	62
1.3	65	65
2.0	70[c]	70
4.0[d]	73[e]	69

[a] The reactions were carried out on a 1-mmol scale in 5.0 mL of dry ether at room temperature for 2 h (for $CuCl_2$) or 5 h (for $CuBr_2$). [b] Yields were determined by GLC and based on the octylsilicate. [c] Octyltrifluorosilane was formed in 3% yield. [d] For $CuCl_2$ the ratio was 4.1. [e] Octyltrifluorosilane was formed in 30% yield.

Copper(II) cleavages of carbon–metal bonds have been intensively investigated for a variety of metals including boron,[8] aluminum,[9] lead,[10] zirconium,[11] cobalt,[12] palladium,[11,13,14] mercury,[11,15] and thallium.[16] The reactions, in most cases, are undoubtedly of the redox type and are considered to proceed by a two-step mechanism.[17] First an organic radical is formed by the reaction of organometallic compounds with a copper(II) salt (eq 3), and in

(1) For part 12, see: Tamao, K.; Yoshida, J.; Yamamoto, H.; Kakui, T.; Matsumoto, H.; Takahashi, M.; Kurita, A.; Murata, M.; Kumada, M. *Organometallics*, preceding paper in this issue.
(2) Yoshida, J.; Tamao, K.; Kurita, A.; Kumada, M. *Tetrahedron Lett.* **1978**, 1809.
(3) Tamao, K.; Kakui, T.; Kumada, M. *Tetrahedron Lett.* **1980**, *21*, 111.
(4) Tamao, K.; Kakui, T.; Kumada, M. *Tetrahedron Lett.* **1980**, *21*, 4105.
(5) (a) Cunico, R. F.; Dexheimer, E. M. *Synth. React. Inorg. Met.-Org. Chem.* **1974**, *4*, 23. (b) Anderson, H. H. *J. Am. Chem. Soc.* **1958**, *80*, 5083.
(6) Akhrem, I. S.; Vertanyan, R. S.; Topuzyan, V. O.; Vol'pin, M. E. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1975**, 1387.
(7) The only documented oxidative solvolysis of the carbon–silicon bond is methanolysis of (ferrocenylmethyl)trimethylsilane and its derivatives induced by Fe(III), giving ferrocenylmethyl methyl ether. Kondo, T.; Yamamoto, K.; Omura, T.; Kumada, M. *J. Organomet. Chem.* **1973**, *60*, 287. Kondo, T.; Yamamoto, K.; Kumada, M. *Ibid.* **1973**, *60*, 303.
(8) Lane, C. F. *J. Organomet. Chem.* **1971**, *31*, 421.
(9) Sato, F.; Mori, Y.; Sato, M. *Chem. Lett.* **1978**, 833.
(10) Clinton, N. A.; Kochi, J. K. *J. Organomet. Chem.* **1973**, *56*, 243.
(11) Budnik, R. A.; Kochi, J. K. *J. Organomet. Chem.* **1976**, *116*, C3.
(12) Yamamoto, H.; Yokoyama, T.; Kwan, T. *Chem. Pharm. Bull.* **1975**, *23*, 2186.
(13) Henry, R. M. *J. Org. Chem.* **1974**, *39*, 3871.
(14) Backvall, J. E.; Nordberg, R. E. *J. Am. Chem. Soc.* **1980**, *102*, 393, and references cited therein.
(15) Beletskaya, I. P.; Artamikina, Y. A.; Reutov, O. A. *J. Organomet. Chem.* **1975**, *99*, 343.
(16) Uemura, S.; Toshimitsu, A.; Okano, M.; Ichikawa, K. *Bull. Chem. Soc. Jpn.* **1975**, *48*, 1925.
(17) Kochi, J. K. "Organometallic Mechanism and Catalysis"; Academic Press: New York, 1978; Chapter 2.

0276-7333/82/2301-0369$01.25/0 © 1982 American Chemical Society

$$R\text{-}M + Cu^{II}X_2 \rightarrow R\cdot + Cu^{I}X + M\text{-}X \quad (3)$$

the second step the radical is oxidized by another copper(II) salt via the ligand-transfer or the electron-transfer process, depending on the nature of the organic group and the copper(II) salt (eq 4). The present results will be

$$R\cdot + Cu^{II}X_2 \rightarrow R\text{-}X \text{ or } R_{ox} + Cu^{I}X \quad (4)$$

$$R_{ox} = R(\text{-}H) \text{ etc.}$$

discussed in the light of these mechanistic aspects, with emphasis on the high susceptibility of organopentafluorosilicates to the carbon–silicon bond cleavage by copper(II) salts.

Throughout this paper, only potassium organopentafluorosilicates, $K_2[RSiF_5]$, have been used, and hence the countercation will be omitted from the individual name of the silicates.

Results and Discussion

I. Reaction of Organopentafluorosilicates with Copper(II) Halides. A. Stoichiometry. When a mixture of octylpentafluorosilicates and anhydrous copper(II) chloride or bromide was stirred in dry ether at room temperature, the color of the reaction mixture gradually faded, possibly indicating the reduction of copper(II) to copper(I), and octyl chloride or bromide respectively, was produced. The yields of organic halides increased with an increase in the amount of copper(II) halide (Table I). In order to elucidate the stoichiometry, we determined the amount of copper(I) produced during the reaction. Thus octylpentafluorosilicate (1 part) was allowed to react with copper(II) chloride (2 parts) in acetonitrile, and the amount of the resulting soluble copper(I) was determined by titration.[18] The amount of copper(I) was found to be essentially equal to twice the amount of octyl chloride (see Experimental Section for details). Therefore the present reaction is reasonably considered to obey a stoichiometry (eq 5) analogous to that previously reported for the cop-

$$K_2[RSiF_5] + 2Cu^{II}X_2 \rightarrow RX + 2Cu^{I}X + K_2[XSiF_5] \quad (5)$$

per(II) oxidation reactions of other organometallic compounds.[17] When 1 equiv of copper(II) halide was used, the yield of the organic halide exceeded 50% (Table I) against the stoichiometry (eq 5). This is probably due to the oxidation of copper(I) to copper(II) by molecular oxygen under the reaction conditions. The regenerated copper(II) might again react with the organosilicate. Indeed the reaction under a nitrogen atmosphere with 1 equiv of copper(II) chloride resulted in reduction of the yield of octyl chloride to 50%.

B. Solvent Effect. Yields of organic halides were greatly dependent upon the nature of the solvent as shown in Table II. In nonpolar solvents such as carbon tetrachloride and benzene the yield of octyl chloride was very low and most of the organosilicate was recovered unchanged. Ether was the most suitable solvent among those examined for the reaction of the octylsilicate with copper(II) chloride. The choice of solvent, however, also depends upon the nature of the organosilicate. Generally the reaction of the alkylsilicates seems to proceed most smoothly in ether or THF, whereas methanol seems to be better for the alkenylsilicates.

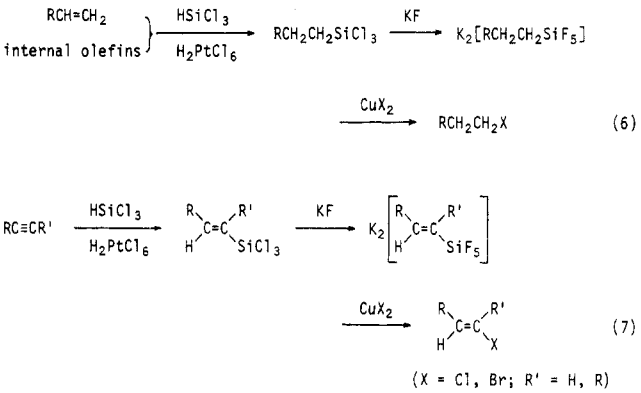
C. Synthetic Applications. The present reaction has been applied to various types of organopentafluorosilicates

Table II. Solvent Effect on the Reaction of Octylpentafluorosilicate with Copper(II) Chloride[a]

solvent	yield of octyl chloride, %[b]
CCl_4	3
C_6H_6	4
Et_2O	70
THF	51
CH_3CN	60
CH_3OH	20

[a] Octylpentafluorosilicate (1.0 mmol) was allowed to react with 2.0 mmol of copper(II) chloride in 5.0 mL of a solvent at room temperature for 2 h. [b] The yields are based on the octylsilicate and were determined by GLC.

such as primary alkyl-, secondary alkyl-, alkenyl-, and arylpentafluorosilicates, and the corresponding organic halides have been obtained in high yields. The results are summarized in Table III. As mentioned in the previous paper, alkyl- and alkenylsilicates are readily obtainable via regio- and stereoselective hydrosilylation of olefins and acetylenes,[19] and a halogen atom is selectively introduced onto the carbon atom to which the silicon atom has been attached. Therefore the present method provides a new regio- and stereoselective route to organic halides from olefins and acetylenes (eq 6 and 7), an attractive alternative



to the conventional hydrohalogenation procedures using organoboron, organoaluminum, and organozirconium compounds[20] and also the NBS cleavage of organosilicates mentioned elsewhere.[1] An efficient preparation of the anti-Markovnikov alkyl chloride should be noted, since alkylsilicates are not cleaved by *N*-chlorosuccinimide, as described previously.[1]

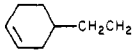
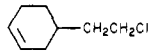
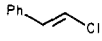
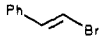
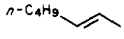
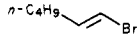
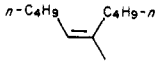
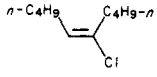
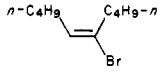
The reaction of organopentafluorosilicates with copper(II) halides was compatible with a number of functional

(18) (a) Knop, J. *J. Am. Chem. Soc.* **1924**, *46*, 263. (b) Jenkins, C. L.; Kochi, J. K. *Ibid.* **1972**, *94*, 843. (c) Jenkins, C. L.; Kochi, J. K. *Ibid.* **1972**, *94*, 856.

(19) (a) Eaborn, C.; Bott, R. W. In "Organometallic Compounds of the Group IV Elements"; MacDiarmid, A. G., Ed.; Marcel Dekker: New York, 1968; Vol. 1, p 105. (b) Lukevits, E. Y.; Voronkov, M. G. "Organic Insertion Reactions of Group IV Elements"; Consultants Bureau: New York, 1966. (c) Lukevits, E.; Belyakova, Z. V.; Pomerantseva, M. G.; Voronkov, M. G. *J. Organomet. Chem. Libr.* **1977**, *5*, 1. (d) Speier, J. L. *Adv. Organomet. Chem.* **1979**, *17*, 407.

(20) Hydroboration: (a) Brown, H. C.; Rathke, M. W.; Rogic, M. M. *J. Am. Chem. Soc.* **1968**, *90*, 5038. (b) Brown, H. C.; Lane, C. F. *Ibid.* **1970**, *92*, 6660. (c) Lane, C. F.; Brown, H. C. *Ibid.* **1970**, *92*, 7212. (d) Brown, H. C.; Hamaoka, T.; Ravindran, N. *Ibid.* **1973**, *95*, 5786. (e) Brown, H. C.; Hamaoka, T.; Ravindran, N. *Ibid.* **1973**, *95*, 6456. (f) Brown, H. C. "Organic Syntheses via Boranes"; Wiley: New York, 1978. See also ref 8. Hydroalumination: (g) Isagawa, K.; Tatsumi, K.; Otsuji, Y. *Chem. Lett.* **1976**, 1145. (h) Sato, F.; Sato, S.; Sato, M. *J. Organomet. Chem.* **1976**, *122*, C25. (i) Sato, F.; Sato, S.; Sato, M. *Ibid.* **1977**, *131*, C26. (j) Sato, F.; Sato, S.; Kodama, H.; Sato, M. *Ibid.* **1977**, *142*, 71. (k) Zweifel, G.; Whitney, C. C. *J. Am. Chem. Soc.* **1967**, *89*, 2753. (l) Zweifel, G.; Steele, R. B. *Ibid.* **1967**, *89*, 5085. See also ref 9. Hydrozirconation: (m) Hart, D. W.; Schwartz, J. *Ibid.* **1974**, *96*, 8115. (n) Hart, D. W.; Blackburn, F. F.; Schwartz, J. *Ibid.* **1975**, *97*, 679. (o) Schwartz, J. In "New Applications of Organometallic Reagents in Organic Synthesis"; Seyferth, D., Ed.; Elsevier: Amsterdam, 1976, p 461. (p) Schwartz, J. *Angew. Chem.* **1976**, *88*, 402.

Table III. Reaction of Organopentafluorosilicates with Copper(II) Halides[a]

R in $K_2[RSiF_5]$	X in CuX_2	solvent	time, h	product	yield, %[b]
n-C_8H_{17}	Cl	Et_2O	2	n-$C_8H_{17}Cl$	(70)
	Br	Et_2O	5	n-$C_8H_{17}Br$	(70)
	Br	THF	20	n-$C_8H_{17}Br$	(88)
$CH_3O_2C(CH_2)_{10}$	Cl	Et_2O	1	$CH_3O_2C(CH_2)_{10}Cl$	70
$CH_3CO(CH_2)_4$	Cl	Et_2O	2	$CH_3CO(CH_2)_4Cl$	46 (66)
$Br(CH_2)_{11}$	Cl	Et_2O	2	$Br(CH_2)_{11}Cl$	60
	Cl	Et_2O	20		51 (73)
$CH_2{=}CHCH_2O(CH_2)_3$	Br	THF	4	$CH_2{=}CHCH_2O(CH_2)_3Br$	45 (52)
$CH_2{=}CH(CH_2)_4$	Br	THF	5	$CH_2{=}CH(CH_2)_4Br$	45
	Cl	Et_2O	2		(18)
			54		(58)
	Cl	THF	2		(46)
	Br	MeOH	4		59[c]
	Br	MeOH	4		(61)[d]
	Cl	MeOH	2		(76)
	Br	MeOH	2		(55)[e]
Ph	Cl	THF	14	PhCl	(75)
	Br	THF	14	PhBr	(79)

[a] The reactions were carried out on a ~1-5-mmol scale with 2 equiv of CuX_2 at room temperature. [b] Isolated yield, based on the organopentafluorosilicate. Yields determined by GLC analysis are given in parentheses. [c] E 100% by GLC. [d] E 99% by GLC. [e] E >95% by ^1H NMR.

groups, such as bromo, oxo, alkoxy, alkoxycarbonyl, and alkenyl groups, as shown in Table III. Since both the hydrosilylation and silicate preparation are also compatible with these functional groups, the overall transformation can be applied to various olefins and acetylenes containing these functional groups.

It should also be mentioned that the copper(II) cleavage of alkenylsilicates occurs with retention of configuration of the alkenyl group and the stereoselectivity is higher than the halogenation by NBS and halogen. For example, (E)-1-hexenyl bromide is formed in >99% isomeric purity with $CuBr_2$ and in 91% with NBS in benzene.[1] It seems interesting to note here that while the stereochemistry of the alkenyl group is predominantly retained, almost complete stereochemical scrambling has been observed in the cleavage of alkylsilicates (vide infra).

D. Mechanistic Studies. On the basis of the stoichiometry the present reaction seems to proceed by the following mechanism. In the first step an alkyl radical is formed by alkyl transfer or electron transfer from the alkylsilicate to copper(II) (eq 8). In the second step a

$$[RSiF_5]^{2-} + Cu^{II}X_2 \rightarrow R\cdot + [XSiF_5]^{2-} + Cu^{I}X \quad (8)$$

$$R\cdot + Cu^{II}X_2 \rightarrow R\text{–}X + Cu^{I}X \quad (9)$$

ligand transfer from another copper(II) halide to the alkyl radical takes place, producing an alkyl halide (eq 9). In order to obtain further information on the reaction mechanism, we performed stereochemical studies and studies on trapping of the alkyl radical intermediate.

Spin Trapping of the Alkyl Radical Intermediate. A successful spin trapping of the alkyl radical intermediate gave a support to the proposed two-step mechanism. Shaking a mixture of octylpentafluorosilicate, copper(II) chloride, 2,3,5,6-tetrakis(trideuteriomethyl)nitrosobenzene, and ether in an ESR sample tube at room temperature gave ESR absorptions. The spectrum (a_N = 13.4 mT, a_H = 10.5 mT, g = 2.0061) was clearly assigned to a n-alkyl, in our present case undoubtedly the n-octyl, radical adduct of the nitroso compound[21] (eq 10 and Figure 1).

$$[n\text{-}C_8H_{17}SiF_5]^{2-} + Ar\text{–}NO \xrightarrow{CuCl_2} n\text{-}C_8H_{17}\text{–}\overset{\overset{O\cdot}{|}}{N}\text{–}Ar \quad (10)$$

In order to test whether the trapped alkyl radical is the intermediate of the main reaction leading to the alkyl halide or only the intermediate of a side reaction, we examined the effect of a nitroso compound on the yield of an organic halide. If the alkyl radical is the intermediate of the main reaction, the yield of the organic halide must decrease in the presence of the trapping agent. Table IV summarizes a comparison of the yields of organic halides in the reaction of several organopentafluorosilicates with copper(II) halides carried out in the presence or absence of nitrosobenzene or 2,4,6-tri-*tert*-butylphenol. In all cases except cyclohexylsilicate, notrosobenzene caused a great decrease in the yields of the organic halides, indicating that the main reaction proceeded through the organic radical intermediate. A radical-chain mechanism may be ruled out by the fact that an inhibitor such as 2,4,6-tri-*tert*-butylphenol did not affect the yield of the organic halide. In the reaction of cyclohexylsilicate with a copper(II) halide the yield of cyclohexyl halide did not change appreciably in the presence of nitrosobenzene. The reason is not clear at present. It should be noted that also in the case of the alkenylsilicates nitrosobenzene caused a decrease in the

(21) Terabe, S.; Kuruma, K.; Konaka, R. *J. Chem. Soc., Perkin Trans. 2* **1973**, 1252, and references cited therein.

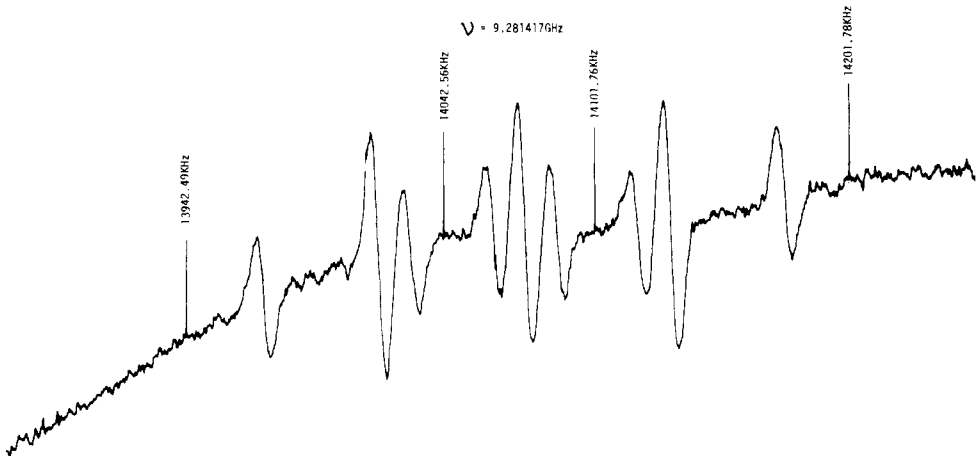
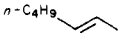


Figure 1. ESR spectrum of the spin adduct of *n*-octyl radical and 2,3,5,6-tetrakis(trideuteriomethyl)nitrosobenzene during the reaction of $K_2[n\text{-}C_8H_{17}SiF_5]$ with $Cu^{II}X_2$ in ether.

Table IV. Reaction of Organopentafluorosilicates with Copper(II) Halides in the Presence of a Radical Trapping Agent[a]

R in $K_2[RSiF_5]$	CuX_2	trapping agent[b]	solvent	time, h	yield of RX, %[c]
$n\text{-}C_8H_{17}$	$CuBr_2$		THF	6	61
		PhNO			22
		TBP[d]			57
		TBP[e]			59
$n\text{-}C_{12}H_{25}$	$CuCl_2$		Et_2O	4	54
		PhNO			19
	$CuCl_2$		Et_2O	50	47
		PhNO			41
	$CuBr_2$		THF	48	42
		PhNO			48
	$CuBr_2$		THF[f]	4	42
		PhNO			30
	$CuBr_2$		THF[f]	4	37
		PhNO			19
	$CuBr_2$		MeOH	4	61[g]
		PhNO			31[g]

[a] Reactions were carried out on a 1-mmol scale in 5.0 mL of a solvent at room temperature unless otherwise stated. [b] One equivalent of a trapping agent was used. [c] Yields are based on the organosilicate and were determined by GLC analysis. [d] 2,4,6-Tri-*tert*-butylphenol (0.01 equiv) was used. [e] 2,4,6-Tri-*tert*-butylphenol (1.0 equiv) was used. [f] The reaction was carried out at 50 °C. [g] (*E*)-1-Hexenyl bromide was formed in 99% stereoselectivity.

yield of the alkenyl halide whereas the halogen transfer reaction occurs with a high stereoselectivity ($E \geq 91\%$). If the reaction proceeded through the alkenyl radical intermediate, isomerization should occur to produce a mixture of the (*E*)- and (*Z*)-alkenyl halide.[22] The reason cannot readily be explained, but there might be a possibility that while the halogenation reaction is a rapid cage process, possibly keeping an interaction between the alkenyl group and a copper species (vide infra), the addition of nitrosobenzene has influenced the course of the reaction, giving rise to the formation of the spin-trapping product.

Table V. Reaction of Octylpentafluorosilicate with Copper(II) Chloride under an Atmosphere of Molecular Oxygen[a]

conditions	time, h	yield, %[b] $n\text{-}C_8H_{17}Cl$	yield, %[b] $n\text{-}C_7H_{15}CHO$
in Et_2O under N_2	2	67	0
in Et_2O under O_2	2	62	6
in MeOH under N_2	2	21	0
in MeOH under O_2	2	4	14
in MeOH under O_2	50	0	18
in MeOH under O_2[c]	50	0	35

[a] $K_2[n\text{-}C_8H_{17}SiF_5]$ (1.0 mmol) was allowed to react with 2.0 mmol of $CuCl_2$ in 5.0 mL of a solvent under an atmospheric pressure of nitrogen or oxygen unless otherwise stated. [b] Yields are based on the octylsilicate and were determined by GLC analysis. [c] The reaction was carried out with 0.5 mmol of $CuCl_2$.

Molecular Oxygen as a Scavenger for the Alkyl Radical Intermediate. Alkyl radicals have been known to be trapped by molecular oxygen at diffusion-controlled rates to produce alcohols, ketones, aldehydes, and/or peroxides, depending on their structure.[23] In our case, the alkyl radical intermediate was indeed scavenged by molecular oxygen to produce the corresponding aldehyde (eq 11). Table V summarizes the results of the reaction of

$$K_2[n\text{-}C_8H_{17}SiF_5] + CuCl_2 + O_2 \xrightarrow{MeOH} n\text{-}C_7H_{15}CHO \quad (11)$$

octylpentafluorosilicate with copper(II) chloride under an atmospheric pressure of oxygen in ether or methanol. While in ether octanal was formed in only 6% yield together with octyl chloride (62% yield), in methanol the chlorine transfer was greatly retarded and the oxygenation became the major course of the reaction to produce octanal in 35% yield.

(22) The configurational stability of alkenyl radicals is very low. The rate constant of inversion of 1-propenyl radical has been estimated as ca. 10^9 s^{-1} at 25 °C. The mechanism of decomposition of alkenyl–copper complexes has also been studied. Whitesides, G. M.; Casey, C. P.; Krieger, J. K. *J. Am. Chem. Soc.* **1971**, *93*, 1379.

(23) (a) Chen, J. Y.; Fardner, H. C.; Kochi, J. K. *J. Am. Chem. Soc.* **1976**, *98*, 6150. (b) Chen, J. Y.; Kochi, J. K. *Ibid.* **1977**, *99*, 1450.

Table VI. Reaction of *exo*- and *endo*-2-Norbornylpentafluorosilicates with Copper(II) Bromide[a]

solvent	exo/endo ratio[b] and yield (%)[c] of 2-norbornyl bromide: from *exo*-silicate	from *endo*-silicate[d]
MeOH	71/29 (39)	78/22 (20)
THF	73/27 (51)	76/24 (48)
C_6H_6	70/30 (46)	84/16 (38)
CCl_4	80/20 (35)	87/13 (18)

[a] The reactions were carried out on a 2-mmol scale at 50 °C for 4 h. [b] Determined by ^{1}H NMR (≤±5%). [c] The yields (given in parentheses) are based on the norbornyl silicate and were determined by GLC analysis. [d] The isomeric purity of the silicate was 95% endo. The product ratios are corrected based on this purity.

The result is consistent with the following sequence of reactions involving the trapping of the octyl radical by molecular oxygen (eq 12, 13). The absence of octyl alcohol

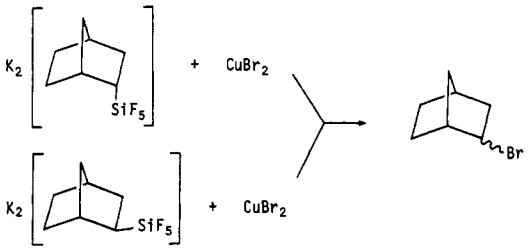
$$n\text{-}C_8H_{17}\cdot + O_2 \rightarrow n\text{-}C_8H_{17}OO\cdot \quad (12)$$

$$2n\text{-}C_8H_{17}OO\cdot \rightarrow n\text{-}C_7H_{15}CHO + n\text{-}C_8H_{17}OH + O_2 \quad (13)$$

may be attributed to further oxidation of the alcohol under the reaction conditions.

It should be noted here that the present oxidation is the first example of metal-assisted oxygenation of an alkylsilicon bond and the overall result corresponds to the conversion of an olefin to a terminal aldehyde. Our efforts to improve the yield of the aldehyde were unfortunately fruitless, possibly owing to the susceptibility of the aldehyde to copper(II) salts.[24]

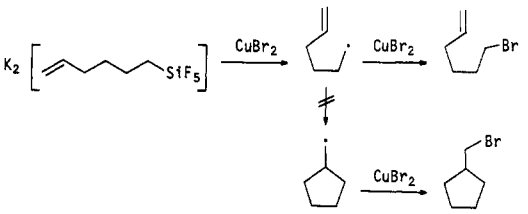
Stereochemistry at Carbon. The mechanism involving the alkyl radical intermediate also receives support from stereochemical studies. We have examined the stereochemistry of cleavage of the carbon–silicon bond in *exo*- and *endo*-2-norbornylpentafluorosilicates[1] by copper(II) bromide. The cleavage proceeded nonstereospecifically at carbon to form a mixture of *exo*- and *endo*-2-norbornyl bromide in an exo/endo ratio of (70–87)/(30–13) (eq 14). Table VI summarizes the results. The ratio was



(14)

essentially independent of the stereochemistry of the starting material and of the nature of the solvent. The complete loss of the stereospecificity clearly indicates that a norbornyl radical is involved in the stereochemistry-determining step, consistent with the proposed mechanism. The exo/endo ratios observed here are essentially the same as those shown in the reactions of norbornyl and substituted norbornyl radicals with halogenating agents.[25] Stereochemical scrambling at carbon has also been reported for the copper(II) bromide cleavage of alkyl–zirconium, alkyl–mercury, and alkyl–palladium bonds in the 3,3-dimethylbutyl-*1,2-d*$_2$ and tricyclo[2.2.1.0^{2,6}]heptyl systems.[11]

Reaction of 5-Hexenylpentafluorosilicate with Copper(II) Bromide. The irreversible intramolecular cyclization of the 5-hexenyl radical to the cyclopentylmethyl radical has been used to examine the behavior of radical intermediates in a number of systems,[26] and the rate of the isomerization has been reported to be 1×10^5 s^{-1} at 25 °C.[26] 5-Hexenylpentafluorosilicate was thus allowed to react with copper(II) bromide (Table III). No cyclization product was detected (eq 15). Therefore the



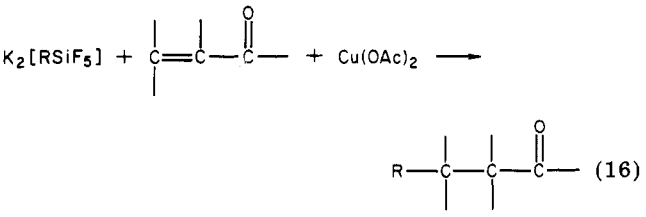
(15)

rate of bromine transfer to the 5-hexenyl radical intermediate is considered to be too fast for the cyclization to compete effectively. The present observation is consistent with the results reported by Kochi and his co-workers for the reaction of 5-hexenyl radical from 6-heptenoyl peroxide with copper(II) bromide.[27]

II. Reaction of Organopentafluorosilicates with Copper(II) Pseudohalides and Acetate. In order to explore the scope of the reaction of organopentafluorosilicates with copper(II) salts, we examined their reactions with some copper(II) pseudohalides and acetate.

A. Reaction of Alkylpentafluorosilicates with Copper(II) Triflate, Copper(II) Acetate, and Copper(II) Thiocyanate. Copper(II) triflate caused merely dissociation of the alkylsilicate. Thus, when octylpentafluorosilicate was allowed to react with copper(II) triflate in ether, octyltrifluorosilane was formed as the only detectable product in 66% yield. With copper(II) acetate or copper(II) thiocyanate in ether under the usual conditions, the octylsilicate was recovered unchanged and no other product was detected. It follows that the alkyl carbon–silicon bond in organopentafluorosilicates is cleaved only by copper(II) halides, but not with copper(II) thiocyanate, acetate, and triflate. The crucial step of the copper(II) cleavage reaction of alkylsilicates may be the initial step in which an alkyl radical species is oxidatively released (cf. eq 8).

B. Conjugate Addition of Alkylpentafluorosilicates to α,β-Unsaturated Ketones Induced by Copper(II) Acetate. Under forced conditions alkylsilicates have also been found to be cleaved by copper(II) acetate, conjugate addition products being formed with α,β-unsaturated ketones. Thus a heterogeneous mixture of octylpentafluorosilicate, methyl vinyl ketone, and copper(II) acetate was heated at 135 °C for 3 h in a sealed tube (eq 16). After

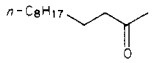
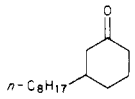
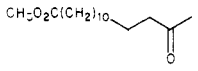


(16)

hydrolytic workup, 2-dodecanone, the conjugate addition

(24) Nigh, W. G. In "Oxidation in Organic Chemistry"; Trahanovsky, W. S., Ed.; Academic Press: New York, 1973; Part B, Chapter 1, p 1.
(25) (a) Bartlett, R.; Fickers, G.; Haupt, F.; Helgeson, R. *Acc. Chem. Res.* **1970**, *3*, 177. (b) Kooyman, E. C.; Vegter, G. C. *Tetrahedron* **1958**, *4*, 382. (c) Cristol, S. J.; Gaston, L. K.; Tiedeman, T. *J. Org. Chem.* **1964**, *29*, 1279. (d) Green, F. D.; Chu, C. C.; Walia, J. *Ibid.* **1964**, *29*, 1285.
(26) Lal, D.; Griller, D.; Husband, S.; Ingold, K. U. *J. Am. Chem. Soc.* **1974**, *96*, 6355, and references cited therein.
(27) Jenkins, C. L.; Kochi, J. K. *J. Org. Chem.* **1971**, *36*, 3103.

Table VII. Conjugate Addition of Alkylpentafluorosilicate to α,β-Unsaturated Ketones in the Presence of Copper Salts[a]

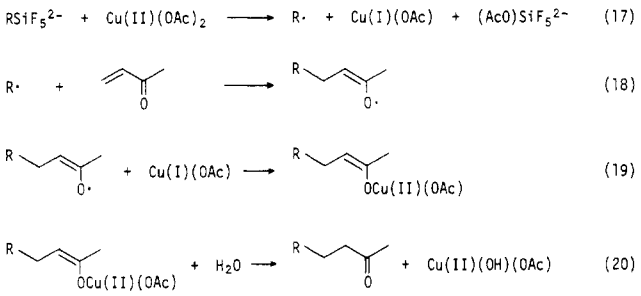
R in $K_2[RSiF_5]$	α,β-enone	copper salt	product	yield, %[b]
n-C_8H_{17}	$CH_2{=}CHCOCH_3$	$Cu(OAc)_2$		70
		CuCl		28
		CuI		4
		$Cu(OAc)_2$		16
$CH_3O_2C(CH_2)_{10}$	$CH_2{=}CHCOCH_3$	$Cu(OAc)_2$		43

[a] A mixture of $K_2[RSiF_5]$ (1.0 mmol), an α,β-unsaturated ketone (20.0 mmol), and a copper salt (1.0 mmol) was heated at 135 °C for 3 h in a sealed tube. [b] Yields are based on $K_2[RSiF_5]$ and were determined by GLC analysis.

product, was obtained in 70% yield. IR analysis of the solid residue showed only characteristic bands of the hexafluorosilicate. Although the reaction occurred with copper(I) chloride and iodide, copper(II) acetate was the most effective among the examined substrates, as shown in Table VII.

Cyclohexenone also reacted with the octylsilicate under similar conditions to give 3-octylcyclohexanone, but the yield was low. The present reaction is compatible with an alkoxycarbonyl group. 10-(Methoxycarbonyl)decanylsilicate reacted with methyl vinyl ketone to produce methyl 2-oxopentadecanoate in 43% yield. The alkenylsilicate did not undergo a similar conjugate addition reaction.

A conjugate addition of organocopper(I) species to α,β-enones has been well-known.[28] Although a mechanism involving an alkylcopper species cannot be ruled out at the present time, we favor the following radical mechanism (eq 17–20) for our present system in the light of the aforementioned discussion concerning the copper(II) induced formation of an alkyl radical from an alkylsilicate. The proposed mechanism is reminiscent of that of the Meerwein arylation reaction.[29]



C. Reaction of Alkenylpentafluorosilicates with Copper(II) Thiocyanate. In contrast to the inertness of alkylpentafluorosilicates, alkenylsilicates were found to react with copper(II) thiocyanate to give the corresponding alkenyl thiocyanates.[3] When a mixture of (*E*)-1-octenylpentafluorosilicate, copper(II) thiocyanate, and DMF was stirred at room temperature, the color of the reaction mixture changed from black to yellow-brown, indicative of the reduction of copper(II) to copper(I) (eq 21). After the workup, (*E*)-1-octenyl thiocyanate was obtained in 67% yield. The nature of the solvent influenced the yield of the product, and DMF was the most suitable solvent among those examined, i.e., the yield of octenyl thiocyanate in the reaction of octenylsilicate with 2 equiv of $Cu(NCS)_2$ was 33% in benzene, 40–45% in ethanol, acetonitrile, or ether, 51% in acetone, and 59% in DMF. The use of 3 equiv of $Cu(NCS)_2$ improved the yield to 74% in DMF. Thus, the most satisfactory results were obtained under the conditions where an alkenylsilicate was allowed to react with 3 equiv of $Cu(NCS)_2$ in DMF at room temperature.

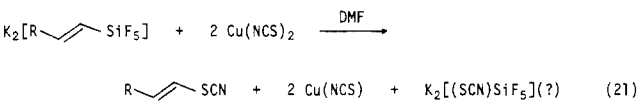
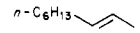
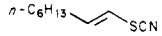
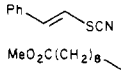
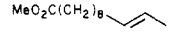
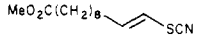
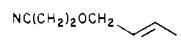
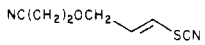
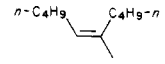
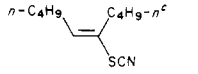


Table VIII. Reaction of Organopentafluorosilicates with Copper(II) Thiocyanate[a]

R in $K_2[RSiF_5]$	product	yield, %[b]
		67 (74)
		53
		70
		49
		78
Ph	PhSCN	49
n-C_8H_{17}	n-$C_8H_{17}SCN$	trace

[a] An organopentafluorosilicate (3.0 mmol) was allowed to react with copper(II) thiocyanate (9.0 mmol) in 10 mL of DMF at room temperature for 3 h. [b] Isolated yields based on the organosilicates. The yield in parenthesis was determined by GLC analysis. [c] Contaminated with 7% of the other isomer.

The present reaction was successfully applied to some alkenyl- and phenylsilicates, and the corresponding organic thiocyanates were obtained in high yields, as summarized in Table VIII. The reaction is highly stereoselective at least for terminal (*E*)-alkenylsilicates, isomerically pure (*E*)-alkenyl thiocyanates being selectively produced. The product from 1-butyl-1-hexenylsilicate was also assigned analogously to the *E* isomer, which was contaminated with a small amount (ca. 7%) of the other isomer which was not fully characterized. The phenylsilicate also formed phenyl thiocyanate in 42% yield.

The IR spectra of alkenyl thiocyanates exhibit, in addition to a sharp strong band at 2155 cm^{-1} due to thiocyanate, a weak to medium broad band in the 2100-cm^{-1} region, which is characteristic of isothiocyanate. However, GLC analysis, ^1H NMR and mass spectral data, and a comparison with literature data of the known compound ($PhCH{=}CHSCN$)[30] were inconsistent with the presence of any isothiocyanate as an impurity. The infrared behavior remains to be further examined.

(28) Posner, G. H. *Org. React. (N. Y.)* **1972**, *19*, 1.
(29) Rondestvedt, C. S. *Org. React. (N. Y.)* **1960**, *11*, 189; **1976**, *24*, 225.
(30) Guy, R. G.; Pearson, I. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 2310.

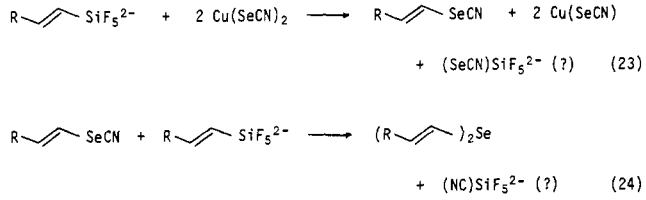
The mechanism is not clear, but may be similar to that for the halogen transfer from copper(II) halides to organopentafluorosilicates and other organometallics. The reaction may obey the stoichiometry $RSiF_5^{2-}/Cu(NCS)_2 = 1/2$, but an excess amount (3 equiv) of the latter may be required, owing to its great tendency to decompose into Cu(NCS) and $(SCN)_2$.[18b] The main difference from the halogen transfer reaction is that copper(II) thiocyanate does not react with alkylsilicates.

While there have been many methods for the preparation of alkyl thiocyanates,[31] only a few methods have been developed for the preparation of alkenyl derivatives. The present reaction provides a simple and general method for the preparation of alkenyl thiocyanates which are expected to be versatile in organic synthesis.[31]

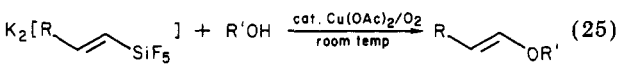
D. Reaction of Alkenylpentafluorosilicate with Copper(II) Selenocyanate. (*E*)-1-Hexenylsilicate was allowed to react in DMF with copper(II) selenocyanate prepared from copper(II) acetate (2 equiv) and KSeCN (4 equiv) in situ to form (*E*,*E*)-di-1-hexenyl selenide in 58% yield (eq 22). Hexenyl selenocyanate was not obtained.

The nature of the solvent influenced the yield of the product, and DMF was the most suitable among the examined solvents, as in the reaction with copper(II) thiocyanate; the yield in benzene, acetonitrile, and ether was 34%, 25%, and 17%, respectively. The use of either an excess amount or 1 equiv of $Cu(SeCN)_2$ was also less satisfactory.

Although the reaction mechanism is not clear, the alkenyl selenocyanate was possibly produced by the reaction of the alkenylsilicate with copper(II) selenocyanate in the first step. Then the alkenyl selenocyanate may be attacked by a further equiv of alkenylsilicate to give the dialkenyl selenide (eq 23 and 24).



E. Oxidative Solvolysis of Alkenylpentafluorosilicates Catalyzed by Copper(II) Acetate. Copper(II) acetate was also found to cleave alkenylpentafluorosilicates. For example, the reaction of 1-octenylpentafluorosilicate with copper(II) acetate in DMF gave 1-octenyl acetate[32] in 30% yield. In alcoholic solvents the reaction course has been dramatically changed. Thus, we find that isomerically pure (*E*)-alkenyl ethers are obtained from (*E*)-alkenylpentafluorosilicates by treatment with a catalytic amount of copper(II) acetate in alcohol under an oxygen atmosphere (eq 25). Since the starting silicates are readily



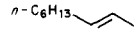
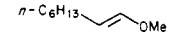
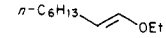
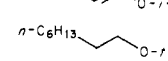
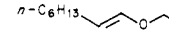
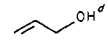
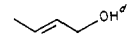
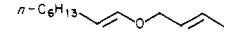
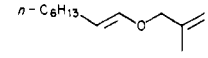
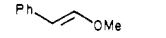
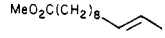
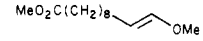
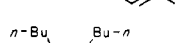
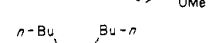
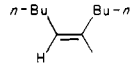
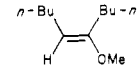
obtained from acetylenes via hydrosilylation, the overall reaction is regarded as a regio- and stereoselective transformation of acetylenes to (*E*)-alkenyl ethers. Data in Table IX reveal that the reaction requires only a catalytic amount of copper(II) acetate, provided it is conducted under an air or oxygen atmosphere.

Table IX. Reaction of 1-Octenylpentafluorosilicate with Copper(II) Acetate in Ethanol[a]

$Cu(OAc)_2$, mmol	condition	1-octenyl ethyl ether yield, %[b]
2.0	under air[c]	44
1.0	under air[c]	46
0.50	under air[c]	64
0.25	under air[c]	64
0.25	under O_2[d]	66
0.125	under O_2[d]	59

[a] 1-Octenylpentafluorosilicate (1.0 mmol) was allowed to react with $Cu(OAc)_2$ in 5.0 mL of ethanol. [b] Yields are based on the octenylsilicate and determined by GLC analysis. [c] The reactions were carried out in an open flask. [d] The reactions were carried out under an atmospheric pressure of oxygen.

Table X. Alcoholysis of $K_2[RSiF_5]$ Catalyzed by $Cu(OAc)_2$[a]

R in $K_2[RSiF_5]$	alcohol	product	yield, %[b]
	MeOH		56 (66)
	EtOH		(64)[c]
	i-PrOH		(23)[c]
	t-BuOH		(0)[c]
			50 (62)[c]
			55
			31
	MeOH		51 (55)
	MeOH		67[e]
	MeOH		55
	MeOH		52[f]

[a] Unless otherwise noted, a mixture of $K_2[RSiF_5]$ (3 mmol), dry alcohol (10 mL), and $Cu(OAc)_2$ (0.75 mmol, 25 mol%) was stirred at room temperature for 21 h under air to maintain the blue color of the reaction mixture. [b] Isolated yield based on the silicate (column chromatography, silica gel, pentane or pentane/benzene). GLC yields are given in parentheses. [c] As byproducts, n-$C_6H_{13}CH{=}CHOAc$ (2–8%) and/or octanal (2–23%) were formed. [d] In these reactions, 5 mL of alcohol was used. [e] As a byproduct, $MeO_2C(CH_2)_8CH{=}CH_2$ was isolated in 16% yield. [f] Isolated by distillation. As a byproduct, (*Z*)-5-decene was formed in 16% yield. GLC purification caused partial cis/trans isomerization of the product.

Representative results on the synthetic applications are summarized in Table X. There are several significant features. (1) The transformation is highly stereoselective and gives (*E*)-alkenyl ethers in isomeric purities over 99%. (2) The reaction is sensitive to the steric bulkiness of alcohols. The yields of alkenyl ethers decrease in the order MeOH > EtOH > *i*-PrOH ≫ *t*-BuOH (with *t*-BuOH no alkenyl ether was formed). (3) Allylic alcohols gave allyl alkenyl ethers, useful synthetic intermediates which undergo the Claisen rearrangement.[33] (4) Some functional

(31) (a) Guy, R. G. "The Chemistry of Cyanates and Their Thio Derivatives"; Patai, S., Ed.; Wiley: New York, 1977; Part 2, Chapter 18, pp 819–886. (b) Arase, A.; Masuda, Y.; Suzuki, A. *Bull. Chem. Soc. Jpn.* **1974**, *47*, 2511.

(32) Enol esters have been known to be valuable intermediates in organic synthesis. See: Larock, R. C.; Oertle, K.; Beatty, K. M. *J. Am. Chem. Soc.* **1980**, *102*, 1966, and references cited therein.

groups such as ester and cyano groups are compatible with the present reaction. (5) An internal alkenyl ether is also prepared with comparable efficiency.

The present reaction is quite different from other copper(II) cleavage reactions of alkenylsilicates in that while copper(II) chloride, bromide, thiocyanate, and selenocyanate yield the ligand-transfer products, copper(II) acetate induces a solvolytic cleavage of the carbon–silicon bond. Although the mechanism of the present novel solvolytic cleavage has not yet been fully clarified, several points should be mentioned. (1) If the reaction is carried out under an inert-gas atmosphere, copper(II) acetate is reduced to a copper(I) species. The stoichiometry could not be determined, but the formation of a Cu(I) species was confirmed by titration.[18] Under an oxygen atmosphere the resulting Cu(I) is oxidized to regenerate a copper(II) salt, making the reaction to proceed catalytically with respect to copper(II) acetate. (2) Since no alkenyl ether was formed when a mixture of alkenyl acetate, copper(II) acetate, and methanol was stirred under similar conditions, the observed alkenyl ether is considered to be the direct reaction product, not via the ligand-transfer product. (3) Reaction with CH_3OD gave no deuterium-incorporated product. The result may rule out, at the least, the mechanism involving the trans addition of alcohol–anti elimination of a silicon hydride species.

In the light of these observations, coupled with aforementioned mechanistic aspects on the copper(II) oxidation of organosilicates and Kochi's works of the oxidative solvolysis of alkyl radicals by copper(II) salts,[17,18b] the present reaction may be visualized by the mechanism shown in eq 26–29. Thus, the reaction may proceed

$$RSiF_5^{2-} + Cu(OAc)_2 \rightarrow RSiF_5^{-}\cdot + Cu(OAc) + OAc^- \quad (26)$$

$$RSiF_5^{-}\cdot + Cu(OAc)_2 \rightarrow RCu(OAc)_2 + SiF_5^- \quad (27)$$

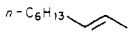
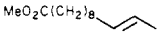
$$RCu(OAc)_2 + R'OH \rightarrow ROR' + Cu(OAc) + AcOH \quad (28)$$

$$RSiF_5^{2-} + R'OH + 2Cu(OAc)_2 \rightarrow ROR' + 2Cu(OAc) + AcOH + SiF_5(OAc)^{2-} \quad (29)$$

through one-electron transfer from silicate to copper(II) species (eq 26) followed by transfer of the organic group from silicon to copper, forming an organocopper(III) species (eq 27) from which may be formed the observed solvolytic product together with the copper(I) species (eq 28). Since the reaction is highly stereoselective, no free radical can be involved. The present oxidative solvolysis is observed only with alkenylsilicates, but not with alkylsilicates. Therefore, there may be an interaction (complex formation) between the alkenyl group and a copper species throughout the reaction.

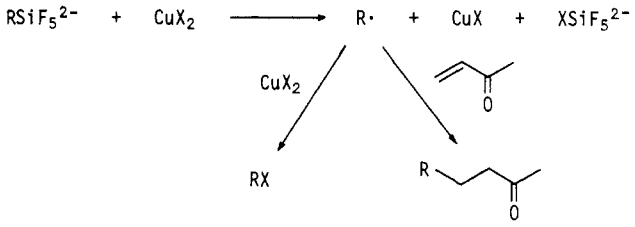
While alkenyl ethers have been prepared mainly from the corresponding carbonyl compounds, there have also been a few methods for their preparation from acetylenes.[34] They involve solvomercuration–demercuration of terminal acetylenes producing 2-alkoxy-1-alkenes,[34c] addition of alcohols to certain electron withdrawing group substituted acetylenes,[34b] and acidic solvolysis of α,β-epoxysilanes,[34a,35] the last being probably the most general method so far developed. Our present method provides a useful alternative to these existing procedures.

Table XI. Reaction of Alkenylpentafluorosilicates with Copper(II) Acetate in the Presence of Water[a]

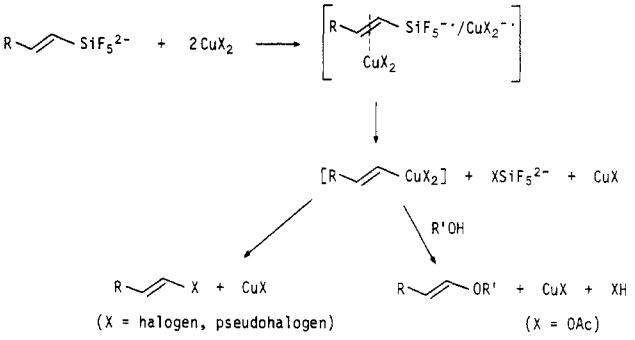
R in $K_2[RSiF_5]$	solvent	H_2O, μL	product	yield, %[b]
	C_6H_6	200	n-$C_6H_{13}CH_2CHO$	trace
	DMF	200		13
	THF	200		42
	i-PrOH	200		46
	CH_3CN	200		50
	CH_3CN	100		52
	CH_3CN	50		45
	CH_3CN	100	$MeO_2C(CH_2)_8CH_2CHO$	50

[a] Alkenylpentafluorosilicates (1.0 mmol) were allowed to react with copper(II) acetate (0.25 mmol) in the presence of water in 5.0 mL of a solvent under air at room temperature for 2 days. [b] Yields were based on the alkenylsilicate and determined by GLC analysis.

Scheme I



Scheme II



Oxidative hydrolysis of alkenylsilicates has also been observed. Thus, in the presence of a catalytic amount of copper(II) acetate (25 mol %) an alkenylsilicate reacted with water under an air atmosphere in acetonitrile at room temperature in 2 days to give an aldehyde (eq 30). As

$$K_2[RCH{=}CHSiF_5] + H_2O \xrightarrow[CH_3CN]{Cu(OAc)_2} RCH_2CHO \quad (30)$$

shown in Table XI, acetonitrile was the most suitable among the examined solvents. The reaction may apparently proceed through the formation of an enol.

Summarizing Remarks

Several copper(II) induced cleavage reactions of organopentafluorosilicates have been presented. Alkylsilicates give alkyl halides and undergo conjugate addition to α,β-unsaturated ketones. Alkenylsilicates afford alkenyl halides, thiocyanates, selenides, and ethers. We have demonstrated that these reactions are initiated by one-electron transfer from silicate to copper(II) species. In the case of alkylsilicates an alkyl radical is considered to be a crucial species responsible for the observed ligand-transfer products and conjugate addition to α,β-enones (Scheme I).

(33) Rhoads, S. J.; Raulins, N. R. *Org. React (N. Y.)* **1975**, *22*, 1.
(34) (a) Hudrlik, P. F.; Hudrlik, A. M. "The Chemistry of the Carbon–Carbon Triple Bond"; Patai, S., Ed.; Wiley: New York, 1978; Part 1, Chapter 7, pp 199–273. (b) Dickstein, J. I.; Meller, S. I. *Ibid.*; Part 2, Chapter 19, pp 813–955. (c) Hudrlik, P. F.; Hudrlik, A. M. *J. Org. Chem.* **1973**, *38*, 4254.
(35) Hudrlik, P. F.; Hudlik, A. M.; Rona, R. J.; Misra, R. N.; Withers, G. P. *J. Am. Chem. Soc.* **1977**, *99*, 1993.

In the case of alkenylsilicates an alkenyl radical might not be involved, but an alkenyl–copper species may play an important role in the observed reactions, in the light of the reactivity and stereochemical differences between alkyl- and alkenylsilicates. The mechanistic difference may arise from the complex formation between a silicate and copper(II) species, possibly through the carbon–carbon double bond (Scheme II).

Experimental Section

General. Infrared spectra were recorded on a Hitachi EPI-G3 grating infrared spectrometer. ^{1}H NMR spectra were determined with a JEOL JNM-MH-100 (100 MHz) spectrometer in carbon tetrachloride. Chemical shifts (δ) are recorded in ppm 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 a JMA-2000 data processing system. Ionization voltage was 24 eV for all compounds. ESR spectra were observed on a JEOL-PE2X spectrometer modified with a JEOL ES-SCXA gun diode microwave unit. GLC analyses and preparative purification were performed on a Shimadzu GC-4B gas chromtograph, equipped with a 3-m column packed with 30% Silicone DC550 on Chromosorb B or Celite 545. GC peak integrals were recorded with a Shimadzu Chromatopac C-E1B integrator.

Materials. Organopentafluorosilicates except 5-hexenylpentafluorosilicate were prepared as described elsewhere.[1] Copper(II) chloride and bromide of ordinary commercial grade were used without further purification. Anhydrous copper(II) acetate was obtained by refluxing copper(II) acetate hydrate with acetic anhydride.[36] Copper(II) triflate[18b] and thiocyanate[18b] and 5-hexenyl bromide[37] were prepared according to the published procedures. All solvents were dried in the usual manner and distilled before use.

Titration of Copper(I). A mixture of octylpentafluorosilicate (200 mg, 0.636 mmol), copper(II) chloride (180 mg, 1.339 mmol), and acetonitrile (20 mL) was stirred at room temperature under a nitrogen atmosphere for 17 h. GLC analysis of the reaction mixture showed that 0.403 mmol (63% yield) of octyl chloride was formed. After addition of 80 mL of acetonitrile a 20-mL aliquot of the reaction mixture was titrated as follows.[18] The aliquot was poured into a mixture of $FeCl_3 \cdot 6H_2O$ (1.09 g) in 18 mL of 2 N H_2SO_4. This was followed by addition of concentrated H_2SO_4 (2.0 mL), H_3PO_4 (2.0 mL), and water (114 mL). The mixture was titrated with 0.10 N $K_2Cr_2O_7$ with diphenylamine as indicator. The titration showed that 0.825 mmol of copper(I) had been formed in the reaction mixture.

Reaction of Organopentafluorosilicate with Copper(II) Halides. General Procedure. A mixture of organopentafluorosilicate (5.0 mmol), copper(II) halide (10.0 mmol), and solvent (10 mL) was stirred at room temperature for a given period of time. After addition of pentane (20 mL), the mixture was filtered and the insoluble precipitate was washed with pentane. The combined filtrate was washed with water, dried over Na_2SO_4, and evaporated. The product was isolated by distillation. Further purification, if necessary, was carried out by preparative GLC or column chromatography. Spectral and elemental analytical data of some organic halides are given below. The other organic halides were identified by comparison of their ^{1}H NMR and IR spectra and their retention time on GLC with those of authentic materials.

Methyl 11-chloroundecanoate (isolated by bulb-to-bulb distillation): n^{20}_D 1.4487; IR (liquid film) 2920, 2845, 1745, 1469, 1437, 1360, 1250, 1195, 1171, 883, 720 cm^{-1}; ^{1}H NMR 1.1–1.9 (m, 16 H), 2.22 (t, J = 7 Hz, 2 H), 3.45 (t, J = 7 Hz, 2 H), 3.59 (s, 3 H); MS, m/e (%) 87 (34), 74 (100), 55 (55), 41 (59); high-resolution MS, m/e 234.1353 (calcd for $C_{12}H_{23}{}^{35}ClO_2$, 234.1381), 236.1400 (calcd for $C_{12}H_{23}{}^{37}ClO_2$, 236.1351). (The molecular peak was detected only at higher ion multiplicity, around 300.)

1-Chloro-5-hexanone (isolated by bulb-to-bulb distillation): n^{20}_D 1.4405; IR (liquid film) 2995, 2950, 2870, 1712, 1441, 1406, 1360, 1310, 1278, 1165, 950, 797, 725, 645 cm^{-1}; ^{1}H NMR 1.5–1.9 (m, 4 H), 2.09 (s, 3 H), 2.42 (t, J = 7 Hz, 2 H), 3.51 (t, J = 6 Hz, 2 H); MS, m/e (%) 121 (0.7), 119 (2), 99 (M$^+$ – Cl, 4), 98 (15), 58 (28), 55 (13), 43 (100); high-resolution MS, m/e 134.0531 (calcd for $C_6H_{11}{}^{35}ClO$, 134.0496), 136.0544 (calcd for $C_6H_{11}{}^{37}ClO$, 136.0466). (The molecular peak was detected only at higher ion multiplicity, around 300.)

1-Bromo-11-chloroundecane [isolated by column chromatography on silica gel (pentane)]: n^{20}_D 1.4777; IR (liquid film) 2910, 2845, 1460, 1300, 1285, 1250, 719, 645, 557 cm^{-1}; ^{1}H NMR 1.1–1.6 (m, 14 H), 1.6–2.1 (m, 4 H), 3.35 (t, J = 6 Hz, 2 H), 3.47 (t, J = 6 Hz, 2 H); MS, m/e (%) 270 (M$^+$ + 2, 0.3), 191 (2), 189 (7), 151 (12), 149 (14), 137 (95), 135 (100). Anal. Calcd for $C_{11}H_{22}BrCl$: C, 49.00; H, 8.22. Found: C, 48.72; H, 8.33.

4-(2-Chloroethyl)cyclohexene (isolated by bulb-to-bulb distillation): n^{20}_D 1.4822; IR (liquid film) 3020, 2910, 2830, 1651, 1449, 1432, 1368, 1332, 1312, 1292, 1280, 1262, 1208, 1140, 1067, 1040, 1030, 895, 862, 850, 773, 740, 715, 649 cm^{-1}; ^{1}H NMR 1.0–2.4 (m, 9 H), 3.53 (t, J = 7 Hz, 2 H), 5.4–5.7 (m, 2 H); MS, m/e (%) 146 (M$^+$ + 2, 5), 144 (M$^+$, 18), 81 (100); high-resolution MS, m/e 144.0699 (calcd for $C_8H_{13}{}^{35}Cl$, 144.0703), 146.0660 (calcd for $C_8H_{13}{}^{37}Cl$, 146.0673).

3-(3-Bromopropoxy)prop-1-ene (isolated by bulb-to-bulb distillation): n^{20}_D 1.4651; IR (liquid film) 3075, 3010, 2850, 1648, 1475, 1342, 1285, 1255, 1210, 1140, 1105, 1080, 990, 920 cm^{-1}; ^{1}H NMR 2.09 (tt, J = 6 and 7 Hz, 2 H), 3.48 (t, J = 7 Hz, 2 H), 3.51 (t, J = 6 Hz, 2 H), 3.8–4.1 (m, 2 H), 5.0–5.4 (m, 2 H), 5.6–6.1 (m, 1 H); MS, m/e (%) 180 (M$^+$ + 2, 2), 178 (M$^+$, 2), 123 (16), 121 (17), 58 (98), 41 (100); high-resolution MS, m/e 177.9977 (calcd for $C_6H_{11}{}^{79}BrO$, 177.9990), 180.0000 (calcd for $C_6H_{11}{}^{81}BrO$, 179.9970).

(*E*)-5-Chloro-5-decene (isolated by preparative GLC): n^{20}_D 1.4458; IR (liquid film) 3030, 2955, 2925, 2865, 1654, 1470, 1383, 1218, 1144, 1105, 953, 847, 745, 680 cm^{-1}; ^{1}H NMR 0.7–1.1 (m, 6 H), 1.1–1.7 (m, 8 H), 1.9–2.2 (m, 2 H), 2.29 (t, J = 7 Hz, 2 H), 5.49 (t, J = 8 Hz, 1 H); MS, m/e (%) 176 (M$^+$ + 2, 13), 174 (M$^+$, 41), 83 (100). Anal. Calcd for $C_{10}H_{19}Cl$: C, 68.75; H, 10.96; Cl, 20.29. Found: C, 68.65; H, 11.10; Cl, 20.13.

Isomeric Purity of Alkenyl Halides. Isomeric purities of 1-hexenyl bromide and 5-bromo-5-decene were determined as described previously.[1] The results are given in Table III. The isomeric purity of 5-chloro-5-decene was not fully determined, but its spectral data showed that only a single isomer had been formed.

Spin Trapping. Shaking an Ar-bubbled mixture of octylpentafluorosilicate, copper(II) chloride, 2,3,5,6-tetrakis(trideuteriomethyl)nitrosobenzene, and dry ether in an ESR sample tube at room temperature gave ESR absorptions (a_N = 13.4 mT, a_H = 10.5 mT, g = 2.0061) due to the spin adduct of a n-alkyl radical. They coincide with the ESR spectrum of the spin adduct of ethyl radical with tetramethylnitrosobenzene (a_N = 13.68 mT, a_H = 10.97 mT, g = 2.0061).[21]

Reaction of Octylpentafluorosilicate with Copper(II) Chloride in the Presence of Molecular Oxygen. Oxygen was bubbled into a mixture of copper(II) chloride (269 mg, 2.0 mmol) in 5.0 mL of a solvent. Octylpentafluorosilicate (315 mg, 1.0 mmol) was then added, and the mixture was stirred at room temperature for a given period of time under an atmosphere of oxygen. After the reaction was complete, the mixture was analyzed by GLC. The products, octanal and/or octyl chloride, were isolated by preparative GLC and identified by comparison of their spectral data with those of authentic materials. Results are summarized in Table V.

Reaction of *exo*- and *endo*-2-Norbornylpentafluorosilicates with Copper(II) Bromide. A mixture of *exo*- or *endo*-2-norbornylpentafluorosilicate[1] (592 mg, 2.0 mmol), copper(II) bromide (893 mg, 4.0 mmol), and a solvent (10 mL) was stirred at 50 °C for 4 h. Pentane (30 mL) was added and the insoluble matters were removed by filtration. The filtrate was washed with water, dried over Na_2SO_4, and evaporated. The residue, crude 2-norbornyl bromide, was submitted to ^{1}H NMR analysis. The exo/endo ratio of the product was determined by relative intensities of 2-methine protons (see ref 1). The results are summarized in Table VI.

Preparation of 5-Hexenylpentafluorosilicate. To a solution of silicon tetrachloride (4.0 mL, 35.0 mmol) in 20 mL of dry ether

(36) Fieser, L. F.; Fieser, M. "Reagents for Organic Synthesis"; Wiley: New York, 1967; Vol. 1, p 159.
(37) Lyle, R. E.; DeWitt, E. J.; Pattison, I. C. *J. Org. Chem.* **1956**, *21*, 61.

was added at 0 °C 5-hexenylmagnesium bromide which was prepared from 5-hexenyl bromide (2.44 g, 15.0 mmol) and magnesium (400 mg, 16.5 mmol) in 15 mL of dry ether. After stirring at room temperature for 2 h, white precipitate was removed by filtration. Distillation of the filtrate gave 1.75 g (54% yield) of 5-hexenyltrichlorosilane: ^{1}H NMR 0.9–1.9 (m, 6 H), 1.9–2.3 (m, 2 H), 4.8–5.2 (m, 2 H), 5.5–6.0 (m, 1 H). 5-Hexenyltrichlorosilane (1.245 g, 5.7 mmol) was added dropwise to a solution of KF (7.25 g, 125 mmol) in 11 mL of deionized water at 0 °C. After the addition was completed the mixture was stirred at room temperature for 5 h. 5-Hexenylpentafluorosilicate (1.505 g, 65% yield) was obtained as white powder which was separated by filtration, washed with water, THF, and ether, and dried in vacuo: IR (KBr) 3070 (w), 2915 (m), 1634 (m), 918 (m), 747 (s), 650 (s), 523 (m), 478 (m), 446 (m) cm^{-1}. The product was not analytically pure, but was used in the following cleavage reaction without further purification.

Reaction of 5-Hexenylpentafluorosilicate with Copper(II) Bromide. 5-Hexenylpentafluorosilicate (569 mg, 2.0 mmol) was allowed to react with copper(II) bromide (893 mg, 4.0 mmol) in 10 mL of THF at room temperature for 5 h. Pentane (30 mL) was added and the mixture was filtered. The filtrate was washed with water and dried over Na_2SO_4. After evaporation of the solvent, bulb-to-bulb distillation of the residue gave 146 mg (45% yield) of 5-hexenyl bromide. The product was identified by comparison of its ^{1}H NMR and IR spectra with those of an authentic sample. Cyclopentylmethyl bromide was not detected by GLC.

Reaction of Octylpentafluorosilicate with Copper(II) Pseudohalides and Acetate. A mixture of octylpentafluorosilicate (315 mg, 1.0 mmol), copper(II) triflate, and 5.0 mL of ether was stirred at room temperature for 2 h. GLC analysis of the reaction mixture showed the formation of octyltrifluorosilane in 66% yield. After workup octyltrifluorosilane[1] was isolated by preparative GLC and identified by comparison of its ^{1}H NMR and IR spectra and their retention time on GLC with those of an authentic material.

Reaction of octylpentafluorosilicate with copper(II) thiocyanate and copper(II) acetate was also attempted in a similar fashion, but in neither case was product observed by GLC analysis of the reaction mixture. The insoluble matters which were separated by filtration from the reaction mixture showed an IR absorption only due to the octylsilicate, and no absorption due to hexafluorosilicate was detected, indicating that most of the octylsilicate remained unchanged.

Conjugate Addition of Alkylpentafluorosilicates to α,β-Unsaturated Ketones in the Presence of a Copper Salt. General Procedure. A heterogeneous mixture of an alkylpentafluorosilicate (1.0 mmol), α,β-unsaturated ketone (20.0 mmol), and a copper salt (1.0 mmol) was heated at 135 °C for 3 h in a sealed tube. After the reaction was completed, ether and water were added and the organic layer was analyzed by GLC. After filtration, extraction with ether, and evaporation of the solvent, the product was isolated by preparative GLC. Spectral data and elemental analyses of the conjugate addition products are given below.

2-Dodecanone: n^{20}_D 1.4330; IR (liquid film) 2955, 2925, 2855, 1720, 1465, 1410, 1355, 1165 cm^{-1}; ^{1}H NMR 0.88 (t, J = 6 Hz, 3 H), 1.1–1.7 (m, 16 H), 2.03 (s, 3 H), 2.32 (t, J = 7 Hz, 2 H); MS, m/e (%) 185 (M$^+$ + 1, 2) 184 (M$^+$, 11), 169 (4), 126 (9), 85 (10), 71 (32), 59 (36), 58 (100). Anal. Calcd for $C_{12}H_{24}O$: C, 78.20; H, 13.12. Found: C, 78.00; H, 13.11.

Methyl 14-oxopentadecanoate: mp 34–35 °C; IR (KBr) 2920, 2850, 1737, 1710, 1467, 1438, 1375, 1357, 1307, 1252, 1230, 1205, 1175 cm^{-1}; ^{1}H NMR 1.1–1.75 (m, 20 H), 2.02 (s, 3 H), 2.22 (t, J = 7 Hz, 2 H), 2.32 (t, J = 7 Hz, 2 H), 3.61 (s, 3 H); MS, m/e (%) 270 (M$^+$, 12), 239 (34), 213 (100), 181 (70), 98 (56). Anal. Calcd for $C_{16}H_{30}O_3$: C, 71.07, H, 11.18. Found: C, 71.01; H, 11.19.

3-Octylcyclohexanone: IR (liquid film) 2960, 2925, 2855, 1715, 1450, 1225 cm^{-1}; ^{1}H NMR 0.90 (t, J = 6 Hz, 3 H), 1.28 (br s, 14 H), 1.5–2.4 (m, 5 H); MS, m/e (%) 211 (M$^+$ + 1, 4), 210 (M$^+$, 24), 167 (31), 96 (100). Anal. Calcd for $C_{14}H_{26}O$: C, 79.93; H, 12.46. Found: C, 79.96; H, 12.62.

Reaction of Alkenylpentafluorosilicates with Copper(II) Thiocyanate. The following preparation of (E)-1-octenyl thiocyanate is representative of the procedure for the reaction of the alkenylsilicates with copper(II) thiocyanate.

(E)-1-Octenyl Thiocyanate. A mixture of (E)-1-octenylpentafluorosilicate (936 mg, 3.0 mmol), copper(II) thiocyanate (1.620 g, 9.0 mmol), and dry DMF (10 mL) was stirred at room temperature for 3 h. After the addition of ether, the mixture was filtered. The filtrate was washed with water and 10% brine and dried over $MgSO_4$. After evaporation of the solvent, bulb-to-bulb distillation of the residue under reduced pressure gave 338 mg (67% yield) of (E)-1-octenyl thiocyanate as a colorless liquid: n^{20}_D 1.4815; IR (liquid film) 3040, 2950, 2920, 2850, 2155, 1468, 1460, 1380, 945 cm^{-1}; ^{1}H NMR 0.88 (t, J = 6 Hz, 3 H), 1.32 (br s, 8 H), 2.18 (q, J = 6 Hz, 2 H), 5.74 (q, J = 16 Hz, 1 H), 6.16 (dt, J = 16 and 6 Hz, 1 H); MS, m/e (%) 169 (M$^+$, 28), 99 (23), 86 (32), 83 (35), 68 (100). Anal. Calcd for $C_9H_{15}NS$: C, 63.85; H, 8.93. Found: C, 64.14; H, 8.73.

The following organic thiocyanates were prepared in a similar fashion.

2-Phenylethenyl thiocyanate [isolated by column chromatography on silica gel, pentane/benzene (1:1)]: n^{20}_D 1.6226 (lit.[30] n^{24}_D 1.6178); IR (liquid film) 3060, 2155, 2100, 1610, 1570, 1494, 1444, 1230, 1073, 947, 850, 783, 738, 690 cm^{-1}; ^{1}H NMR 6.43 (d, J = 15 Hz, 1 H), 6.94 (d, J = 15 Hz, 1 H), 7.30 (s, 5 H); MS, m/e (%) 161 (M$^+$, 100), 134 (48), 117 (41), 91 (23), 77 (22). Anal. Calcd for C_9H_7NS: C, 67.05; H, 4.38. Found: C, 67.22; H, 4.56.

3-(2-Cyanoethoxy)propenyl thiocyanate (isolated by bulb-to-bulb distillation): n^{20}_D 1.5106; IR (liquid film) 3050, 2920, 2875, 2250, 2155, 2100, 1627, 1475, 1448, 1408, 1356, 1325, 1285, 1255, 1220, 1113, 1055, 938 cm^{-1}; ^{1}H NMR 2.63 (t, J = 6 Hz, 2 H), 3.22 (t, J = 6 Hz, 2 H), 4.15 (t, J = 2 Hz, 2 H), 6.22 (t, J = 2 Hz, 2 H); MS, m/e (%) 168 (M$^+$, 1.7), 110 (100), 98 (34), 57 (57), 54 (39). Anal. Calcd for $C_7H_8N_2OS$: C, 49.98; H, 4.79. Found: C, 50.13; H, 4.79.

10-Methoxycarbonyl-1-decenyl thiocyanate (isolated by column chromatography on silica gel, benzene): n^{20}_D 1.4851; IR (liquid film) 3040, 2925, 2850, 2155, 2100, 1738, 1458, 1432, 1358, 1244, 1196, 1170, 945 cm^{-1}; ^{1}H NMR 1.15–1.7 (m, 12 H), 2.1–2.35 (m, 4 H), 3.61 (s, 3 H), 5.82 (d, J = 15 Hz, 1 H), 6.15 (dt, J = 15 and 7 Hz, 1 H); MS, m/e (%) 255 (M$^+$, 34), 224 (52), 112 (85), 100 (58), 99 (100), 87 (48). Anal. Calcd for $C_{13}H_{21}NO_2S$: C, 61.14; H, 8.29. Found: C, 60.98; H, 8.51.

1-Butyl-1-hexenyl thiocyanate (isolated by bulb-to-bulb distillation): n^{20}_D 1.4368; IR (liquid film) 2960, 2930, 2875, 2860, 2155, 2080, 1615, 1465, 1379, 936, 858 cm^{-1}; ^{1}H NMR 0.8–1.1 (m, 6 H), 1.1–1.7 (m, 8 H), 1.9–2.3 (m, 2 H), 2.40 (t, J = 7 Hz, 1 H), 6.15 (dt, J = 15 and 7 Hz, 1 H); MS, m/e (%) 197 (M$^+$, 44), 99 (59), 98 (100), 95 (54), 83 (57), 55 (77). Anal. Calcd for $C_{11}H_{19}NS$: C, 66.95; H, 9.70. Found: C, 66.83; H, 9.61.

Phenyl thiocyanate (isolated by bulb-to-bulb distillation): n^{20}_D 1.5685; IR (liquid film) 3060, 2145, 1580, 1475, 1440, 1325, 1085, 1067, 1040, 998, 905, 739, 685 cm^{-1}; ^{1}H NMR 7.3–7.6 (m); MS, m/e (%) 135 (M$^+$, 100), 112 (14), 111 (25), 84 (11), 79 (26).

Reaction of (E)-1-Hexenylpentafluorosilicate with Copper(II) Acetate–KSeCN. A mixture of (E)-1-hexenylpentafluorosilicate (289 mg, 1.0 mmol), copper(II) acetate (361 mg, 2.0 mmol), KSeCN (582 mg, 4.0 mmol), and dry DMF (10 mL) was stirred at room temperature for 6 h. GLC analysis of the reaction mixture showed that (E,E)-bis(1-hexenyl) selenide was produced in 58% yield. After addition of benzene the mixture was filtered. The filtrate was washed with brine and water and dried over Na_2SO_4. After evaporation of the solvent the product was isolated by bulb-to-bulb distillation: n^{25}_D 1.5047; IR (liquid film) 3010, 2955, 2920, 2870, 2850, 1740, 1610, 1462, 1435, 1377, 1225, 945, 923 cm^{-1}; ^{1}H NMR 0.92 (t, J = 6 Hz, 6 H), 1.1–1.6 (m, 8 H), 1.9–2.3 (m, 4 H), 5.91 [dt, J = 15 (d), and 6 Hz (t), 2 H], 6.20 (d, J = 15 Hz, 2 H); MS, m/e (%) 248 (18), 247 (14), 246 (100), 244 (48), 243 (18), 242 (19). Anal. Calcd for $C_{12}H_{22}Se$: C, 58.76; H, 9.04. Found: C, 58.89; H, 9.01.

Reaction of Octenylpentafluorosilicate with Copper(II) Acetate in DMF. A mixture of octenylpentafluorosilicate (312 mg, 1 mmol), copper(II) acetate (364 mg, 2 mmol), and dry DMF (5 mL) was stirred at room temperature for 20 h. GLC analysis of the reaction mixture showed that 1-octenyl acetate was formed in 31% yield. After hydrolysis followed by extraction with pentane, the pentane layer was evaporated. The residue was flash distilled and subjected to preparative GLC to purify the product. (E)-1-octenyl acetate: IR (liquid film) 3080, 3025, 2960, 2925, 2855,

1760, 1675, 1655, 1468, 1370, 1223, 1105, 936, 908 cm^{-1}; ^{1}H NMR 0.90 (t, 3 H), 1.30 (br s, 8 H), 1.75–2.0 (m, 2 H), 2.04 (s, 3 H), 5.26 (dt, J = 12 and 7 Hz, 1 H), 6.97 (dt, J = 12 and 1 Hz, 1 H); MS, m/e (%) 170 (M$^+$, 69), 110 (100). Anal. Calcd for $C_{10}H_{18}O_2$: C, 70.55; H, 10.66. Found: C, 70.35; H, 10.76.

Reaction of Alkenylpentafluorosilicates with Copper(II) Acetate in the Presence of an Alcohol. Titration of Copper(I) Species in the Reaction of Octenylpentafluorosilicate with Copper(II) Acetate. A mixture of (*E*)-1-octenylpentafluorosilicate (0.306 g, 0.979 mmol), anhydrous copper(II) acetate (0.365 g, 2.01 mmol), and dry methanol (10 mL) was stirred under nitrogen at room temperature for 2 h. Acetonitrile (20 mL), through which dry nitrogen had been bubbled, was added; this resulted in separation into white precipitates and a green supernatant liquid. An aliquot (20.00 mL) of the liquid layer was titrated as described for the titration of copper(I) chloride, and this showed that 0.992 mmol of a copper(I) species was formed. GLC analysis of the reaction mixture showed that the amount of methyl octenyl ether was 0.356 mmol (36.4% yield). Several repeated experiments, changing the ratio of reactants and/or the reaction time, showed similar results.

General Procedure. A mixture of an alkenylpentafluorosilicate (3.0 mmol), copper(II) acetate (138 mg, 0.75 mmol), and an alcohol (10 mL) was stirred in an open flask at room temperature for 21 h. The color of the reaction mixture gradually changed from green to blue. After addition of ether, the mixture was filtered. The filtrate was washed with brine and dried over $MgSO_4$. After evaporation of the solvent, the product was isolated by distillation, preparative GLC, or column chromatography. Spectral data and elemental analyses of the products are given below.

(*E*)-1-Methoxy-1-octene (isolated by bulb-to-bulb distillation): n^{20}_D 1.4299; IR (liquid film) 3060, 3000, 2955, 2920, 2850, 1663, 1656, 1462, 1375, 1207, 1162, 1130, 933 cm^{-1}; ^{1}H NMR 0.90 (t, 3 H), 1.30 (br s, 8 H), 1.75–2.05 (m, 2 H), 3.44 (s, 3 H), 4.59 (dt, J = 13 and 7 Hz, 1 H), 6.18 (d, J = 13 Hz, 1 H); MS, m/e (%) 142 (M$^+$, 15), 71 (100). Anal. Calcd for $C_9H_{18}O$: C, 76.00; H, 12.76. Found: C, 75.91; H, 13.00.

(*E*)-1-Ethoxy-1-octene (isolated by preparative GLC): n^{20}_D 1.4311; IR (liquid film) 3050, 2955, 2920, 2845, 1662, 1653, 1475, 1463, 1438, 1390, 1377, 1193, 1169, 1130, 933 cm^{-1}; ^{1}H NMR 0.90 (t, 3 H), 1.25 (t, J = 7 Hz, 3 H), 1.30 (br s, 8 H), 1.70–2.10 (m, 2 H), 3.62 (q, J = 7 Hz, 2 H), 4.58 (dt, J = 13 and 7 Hz, 1 H), 6.09 (d, J = 13 Hz, 1 H); MS, m/e (%) 156 (M$^+$, 28), 85 (100). Anal. Calcd for $C_{10}H_{20}O$: C, 76.86; H, 12.90. Found: C, 76.69; H, 13.07.

(*E*)-1-Isopropoxy-1-octene (isolated by preparative GLC): IR (liquid film) 3060, 2995, 2975, 2945, 2875, 1770, 1680, 1660, 1470, 1387, 1376, 1340, 1198, 1168, 1142, 930 cm^{-1}; ^{1}H NMR 0.90 (t, 3 H), 1.15 (d, J = 7 Hz, 6 H), 1.30 (br s, 8 H), 1.70–2.0 (m, 2 H), 3.97 (septet, J = 7 Hz, 1 H), 4.69 dt, J = 13 and 7 Hz), 5.94 (d, J = 13 Hz, 1 H); MS, m/e (%) 170 (M$^+$, 45), 55 (100). Anal. calcd for $C_{11}H_{22}O$: C, 77.58; H, 13.02. Found: C, 77.42; H, 13.27.

(*E*)-1-Allyloxy-1-octene (isolated by bulb-to-bulb distillation): n^{20}_D 1.4462; IR (liquid film) 3055, 2960, 2925, 2855, 1675, 1658, 1460, 1425, 1380, 1195, 1168, 1126, 995, 930 cm^{-1}; ^{1}H NMR 0.90 (t, 3 H), 1.31 (br s, 8 H), 1.70–2.15 (m, 2 H), 4.12 (dt, J = 5 and 1.5 Hz, 2 H), 4.67 (dt, J = 13 and 8 Hz, 1 H), 5.05–5.35 (m, 2 H), 5.7–6.05 (m, 1 H), 6.14 (d, J = 13 Hz, 1 H); MS, m/e (%) 168 (M$^+$, 8), 85 (100). Anal. Calcd for $C_{11}H_{20}O$: C, 78.51; H, 11.98. Found: C, 78.74; H, 12.16.

(*E*)-1-[(*E*)-2-Butenyloxy]-1-octene (isolated by column chromatography on silica gel, pentane): n^{20}_D 1.4492; IR (liquid film) 3080, 3050, 2980, 2950, 2877, 1770, 1683, 1663, 1470, 1385, 1227, 1203, 1172, 1134, 976, 940, 930 cm^{-1}; ^{1}H NMR 0.90 (t, 3 H), 1.27 (br s, 8 H), 1.72 (br d, J = 5 Hz, 3 H), 1.8–2.1 (m, 2 H), 4.01 (br d, J = 5 Hz, 2 H), 4.61 (dt, J = 13 and 7 Hz, 1 H), 5.3–5.85 (m, 2 H), 6.10 (d, J = 13 Hz, 1 H); MS, m/e (%) 182 (M$^+$, 10), 71 (100). Anal. Calcd for $C_{12}H_{22}O$: C, 79.06; H, 12.16. Found: C, 78.95; H, 12.27.

(*E*)-1-(2-Methyl-2-propenyloxy)-1-octene (isolated by column chromatography on silica gel, pentane): n^{20}_D 1.4476; IR (liquid film) 3050, 2950, 2915, 2850, 1675, 1653, 1452, 1376, 1197, 1162, 1135, 932, 920, 902 cm^{-1}; ^{1}H NMR 0.90 (t, 3 H), 1.31 (br s, 8 H), 1.75 (s, 3 H), 1.8–2.15 (m, 2 H), 4.00 (s, 3 H), 4.68 (dt, J = 13 and 7 Hz, 1 H), 4.89 (br d, J = 8 Hz, 2 H), 6.11 (d, J = 13 Hz, 1 H); MS, m/e (%) 182 (M$^+$, 7), 53 (100). Anal. Calcd for $C_{12}H_{22}O$: C, 79.06; H, 12.16. Found: C, 78.88; H, 12.26.

(*E*)-1-Methoxy-2-phenylethene [isolated by column chromatography on silica gel, pentane/benzene (3:1)]: n^{20}_D 1.5642; IR (liquid film) 3070, 3025, 2955, 2930, 2830, 1660, 1645, 1604, 1576, 1490, 1460, 1448, 1433, 1341, 1330, 1313, 1238, 1190, 1153, 1126, 1075, 1032, 1000, 935, 868, 818, 753, 697, 650 cm^{-1}; ^{1}H NMR 3.63 (s, 3 H), 5.69 (d, J = 13 Hz, 1 H), 6.94 (d, J = 13 Hz, 1 H), 7.11 (s, 5 H); MS, m/e (%) 134 (M$^+$, 100), 119 (14), 91 (52).

(*E*)-5-Methoxy-5-decene (bulb-to-bulb distillation gave a mixture of (*Z*)-5-decene (n^{20}_D 1.4327) and (*E*)-5-methoxy-5-decene, the yields of which were 18% and 52%, respectively; isolated by preparative GLC): n^{20}_D 1.4368; IR (liquid film) 3070, 2965, 2930, 2865, 1668, 1466, 1380, 1237, 1209, 1200, 1180, 1115 cm^{-1}; ^{1}H NMR 0.90 (t, J = 7 Hz, 6 H), 1.1–1.6 (m, 8 H), 1.8–2.2 (m, 4 H), 3.40 (s, 3 H), 4.21 (t, J = 7 Hz, 1 H); MS, m/e (%) 170 (M$^+$, 28), 72 (100). Anal. Calcd for $C_{11}H_{22}O$: C, 77.58; H, 13.02. Found: C, 77.48; H, 13.32.

(*E*)-1-Methoxy-10-(methoxycarbonyl)-1-decene (isolated by column chromatography on silica gel, benzene): n^{20}_D 1.4509; IR (liquid film) 3055, 3000, 2925, 2850, 1745, 1675, 1657, 1460, 1436, 1360, 1205, 1175, 1130, 935 cm^{-1}; ^{1}H NMR 1.38 (br s, 10 H), 1.45–1.7 (m, 2 H), 1.7–2.0 (m, 2 H), 2.20 (t, J = 7 Hz, 2 H), 3.42 (s, 3 H), 3.59 (s, 3 H), 4.56 (dt, J = 13 and 7 Hz, 1 H), 6.17 (d, J = 13 Hz, 1 H). Anal. Calcd for $C_{13}H_{24}O_3$: C, 68.38; H, 10.59. Found: C, 68.27; H, 10.81.

(*E*)-1-Methoxy-6-cyano-4-oxahex-1-ene [isolated by column chromatography on silica gel, pentane/ether (1:4)]: n^{20}_D 1.4519; IR (liquid film) 3070, 3010, 2935, 2870, 2255, 1655, 1460, 1450, 1412, 1365, 1327, 1215, 1175, 1113, 1095, 1000, 945, 918 cm^{-1}; ^{1}H NMR 2.48 (t, J = 6 Hz, 2 H), 3.56 (s and t, J = 6 Hz, 5 H), 3.71 (d, J = 7 Hz, 2 H), 4.78 (dt, J = 13 and 7 Hz, 1 H), 6.48 (d, J = 13 Hz, 1 H); MS, m/e (%) 141 (M$^+$, 8), 140 (12), 54 (100). Anal. Calcd for $C_7H_{11}NO_2$: C, 59.56; H, 7.85. Found: C, 59.46; H, 7.80.

Reaction of (*E*)-Octenylpentafluorosilicate with CH_3OD in the Presence of Copper(II) Acetate. A mixture of (*E*)-octenylpentafluorosilicate (312 mg, 1 mmol), copper(II) acetate (46 mg), and CH_3OD (3 mL) was stirred at room temperature for 21 h. Usual workup and distillation gave 64.5 mg of (*E*)-1-methoxyoctene: ^{1}H NMR and MS, m/e (%) 142 (M$^+$, 25.5), 143 (M$^+$ + 1, 2.5); spectral data correspond to the nondeuterated product, $C_6H_{13}CH{=}CHOCH_3$.

Reaction of Alkenylpentafluorosilicates with Copper(II) Acetate in the Presence of Water. The following preparation of octanal is representative of the procedure for the reaction of the alkenylsilicates with copper(II) acetate in the presence of water. A mixture of 1-octenylpentafluorosilicate (1.575 g, 5.0 mmol), copper(II) acetate (114 mg, 0.63 mmol), deionized water (500 μL, 28 mmol), and acetonitrile (15 mL) was stirred in an open flask at room temperature for 2 days. After addition of ether, the mixture was filtered. The filtrate was washed with water and dried over Na_2SO_4. After evaporation of the solvent, bulb-to-bulb distillation of the residue gave 295 mg (46% yield) of octanal. The product was identified by comparison of its spectral data with those of an authentic material.

10-(Methoxycarbonyl)decanal was prepared in a similar fashion: n^{20}_D 1.4450; IR (neat) 2920, 2845, 2715, 1735, 1460, 1433, 1360, 1252, 1190, 1168, 1100 cm^{-1}; ^{1}H NMR 1.32 (br s, 10 H), 1.4–1.75 (m, 4 H), 2.22 (t, J = 7 Hz, 2 H), 2.35 (t, J = 7 Hz, 2 H), 3.62 (s, 3 H), 9.64 (t, J = 1 Hz, 1 H).

Acknowledgment. We thank the Ministry of Education for Grants-in-Aid for Scientific Research (143022, 203518, 265253, 303523), and the Yamada Science Foundation, Shin-etsu Chemical Co., Ltd., and the Kurata Foundation (K.T.) for support of this work. We also acknowledge Dr. Takashi Kawamura, Department of Hydrocarbon Chemistry, Kyoto University, for measuring the ESR spectra concerning the spin trapping.

Registry No. Octylpentafluorosilicate, 65599-39-5; (11-(methoxycarbonyl)decyl)pentafluorosilicate, 65599-43-1; (5-oxyhexyl)pentafluorosilicate, 79618-86-3; (11-bromoundecyl)pentafluorosilicate, 79618-87-4; (2-(3-cyclohexenyl)ethyl)pentafluorosilicate, 65599-41-9; (3-(2-propenyloxy)propyl)pentafluorosilicate, 79618-88-5; 5-hexenylpentafluorosilicate, 79618-89-6; cyclohexylpentafluoro-

silicate, 65599-42-0; ((*E*)-2-phenylethenyl)pentafluorosilicate, 68901-41-7; (*E*)-1-hexenylpentafluorosilicate, 68732-24-1; 5-(5-decenyl)pentafluorosilicate, 70995-87-8; phenylpentafluorosilicate, 66712-45-6; dodecylpentafluorosilicate, 65599-40-8; (*exo*)-2-norbornylpentafluorosilicate, 74380-89-5; (*endo*)-2-norbornylpentafluorosilicate, 74410-83-6; (*E*)-octenylpentafluorosilicate, 70995-82-3; ((*E*)-10-(methoxycarbonyl)-1-decenyl)pentafluorosilicate, 70995-86-7; ((*E*)-3-(2-cyanoethoxy)propenyl)pentafluorosilicate, 74463-90-4; (*Z*)-5-decen-5-ylpentafluorosilicate, 70995-87-8; octyl bromide, 111-83-1; octyl chloride, 111-85-3; methyl 11-chloroundecanoate, 17696-12-7; 6-chloro-2-hexanone, 10226-30-9; 1-bromo-11-chloroundecane, 30295-21-7; 4-(2-chloroethyl)cyclohexene, 63540-00-1; 3-(3-bromopropoxy)prop-1-ene, 15424-07-4; 6-bromo-1-hexene, 2695-47-8; chlorocyclohexane, 542-18-7; (*E*)-1-chloro-2-phenylethene, 4110-77-4; (*E*)-1-bromo-2-phenylethene, 588-72-7; (*E*)-1-bromo-1-hexene, 13154-13-7; (*E*)-5-chloro-5-decene, 10124-72-8; (*E*)-5-bromo-5-decene, 72612-74-9; chlorobenzene, 108-90-7; bromobenzene, 108-86-1; dodecyl chloride, 112-52-7; cyclohexyl bromide, 108-85-0; *exo*-2-norbornyl bromide, 2534-77-2; *endo*-2-norbornyl bromide, 13237-87-1; 2-dodecanone, 6175-49-1; 3-octylcyclohexanone, 57242-85-0; methyl 14-oxopentadecanoate, 54889-71-3; (*E*)-1-octenyl thiocyanate, 74458-26-7; (*E*)-2-phenylethenyl thiocyanate, 61807-26-9; (*E*)-10-(methoxycarbonyl)-1-decenyl thiocyanate, 74458-28-9; (*E*)-3-(2-cyanoethoxy)propenyl thiocyanate, 74458-27-8; (*E*)-5-thiocyanato-5-decene, 74458-29-0; phenyl thiocyanate, 103-72-0; 1-octenyl ethyl ether, 30989-68-5; (*E*)-1-methoxy-1-octene, 62427-06-9; (*E*)-1-isopropoxy-1-octene, 77149-61-2; (*E*)-1-*tert*-butoxy-1-octene, 79618-58-9; (*E*)-1-(allyloxy)-1-octene, 77149-62-3; (*E*)-1-[(*E*)-2-butenyloxy]-1-octene, 79618-59-0; (*E*)-1-(2-methyl-2-propenyloxy)-1-octene, 77149-64-5; (*E*)-1-methoxy-2-phenylethene, 4110-75-2; (*E*)-1-methoxy-10-(methoxycarbonyl)-1-decene, 77149-65-6; (*E*)-1-methoxy-6-cyano-4-oxahex-1-ene, 77149-66-7; (*E*)-5-methoxy-5-decene, 77149-67-8; octanal, 124-13-0; 10-(methoxycarbonyl)decanal, 1931-65-3; copper(II) chloride, 7447-39-4; copper(II) bromide, 7789-45-9; copper(II) acetate, 142-71-2; copper(I) chloride, 7758-89-6; copper(I) iodide, 7681-65-4; copper(II) thiocyanate, 15192-76-4; 3-buten-2-one, 78-94-4; 2-cyclohexenone, 930-68-7; (*E*)-1-ethoxy-1-octene, 77149-60-1; methanol, 67-56-1; ethanol, 64-17-5; 2-propanol, 67-63-0; 2-methyl-2-propanol, 75-65-0; 2-propen-1-ol, 107-18-6; (*E*)-2-buten-1-ol, 504-61-0; 2-methyl-2-propen-1-ol, 513-42-8.

Poly(phenylene oxide) Catalyst Supports Containing (Cyclopentadiene)metal Complexes

L. Verdet and J. K. Stille*

Colorado State University, Fort Collins, Colorado 80523

Received September 15, 1981

Poly(2,6-dimethyl-1,4-phenylene oxide) containing cyclopentadienyl ligands attached to the benzyl carbons was prepared by the reaction of cyclopentadienylsodium with polymer that had been brominated at the benzyl position. Cross-linking took place during the reaction through the cyclopentadiene group. The reaction of 2-norbornen-7-one with poly(2,6-diphenyl-1,4-phenylene oxide) lithiated at the 3-position gave the norbornen-7-ol derivative which was converted to the polymer-attached 7-chloronorbornene. Cyclopentadiene ligands were generated via a retro Diels–Alder reaction of the anion produced from the 7-chloronorbornene. These polymers were converted to polymer-bound cyclopentadienyldicarbonylcobalt, cyclopentadienyldicarbonylrhodium, and titanocene catalysts. The cobalt and rhodium complexes were effective hydroformylation catalysts while the immobilized titanocene hydrogenated cyclohexene 10–70 times faster than the homogeneous analogue.

Introduction

Because there are many advantages to be gained by binding homogeneous catalysts to solid supports, the chemistry of homogeneous catalysts attached to polymers has been the subject of considerable research activity.[1] Cross-linked polystyrene has been the favorite polymer support, primarily because it is available commercially in various bead sizes with varying degrees of cross-link density.

Polystyrene beads, however, are mechanically, chemically, and thermally unstable.[2,3] For example, macroporous styrene–divinylbenzene resins will slough off polymer, particularly in a solvent that swells the bead. In addition, the reduction of carbon monoxide to hydrocarbons (Fischer–Tropsch), the reduction of carbon monoxide to methanol, and the hydroformylation of olefins in which water is used as the hydrogen source (water gas shift) are reactions that require temperatures higher than those usually necessary in homogeneous catalysis and are above or near the ceiling temperature of polystyrene ($T_c \approx 150$ °C). Further, polystyrene has poor chemical stability and will not endure a number of catalytic processes such as oxidation or photochemical reactions.

Poly(phenylene oxides) are a class of thermally stable engineering plastics.[4] Although the *thermooxidative* stability of the 2,6-dimethyl-substituted polymer is lower than other thermally stable polymers, its thermal stability under a nonoxidizing atmosphere is good;[5] however, the 2,6-diphenyl polymer has excellent thermal and oxidative stability. Consequently, we have explored the attachment of cyclopentadiene ligands to poly(2,6-dimethyl-1,4-phenylene oxide) and poly(2,6-diphenyl-1,4-phenylene oxide), the conversion of these cyclopentadiene sites to η^5-cyclopentadiene complexes with cobalt, rhodium, and titanium, and some of the catalytic reactions of these polymer-supported complexes.

Results and Discussion

Preparation of Poly(phenylene oxide)-Attached Cyclopentadiene Ligands. Cyclopentadiene has been chemically bonded to polystyrene either by the reaction of cyclopentadienyl sodium with chloromethylated polystyrene or by the reaction of cyclopentenone with lithiated

(1) Pittman, C. U. In "Polymer Supported Reactions in Organic Synthesis"; Hodge, P., Sherrington, D. C., Eds.; Wiley: New York, 1980; Chapter 5.
(2) Sherrington, D. C., ref 1, Chapter 1.
(3) International Workshop on Heterophase Attached Homogeneous Catalysis, Grenoble, France, 1977. CNRS and NSF.
(4) Arnold, C. *Macromol. Rev.* **1979**, *14*, 265.
(5) Jachowicz, J.; Kryszewski, M.; Sobol, A. *Polymer* **1979**, *20*, 995.

0276-7333/82/2301-0380$01.25/0 © 1982 American Chemical Society