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INSERTION REACTIONS OF CALCIUM ATOM INTO Si-Cl AND Ge-Cl BONDS

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Calcium atom is inserted into Si-Cl and Ge-Cl bonds of organosilylchlorides and organogermylchlorides to give the corresponding organosilylcalcium chlorides and organogermylcalcium chlorides, respectively.

Activation of group 4B element-halogen bonds, especially Si-Cl bond, by typical metals (M) have received considerable interest in reaction intermediates and in organic synthesis.$^{1)}$ However, there is no definite report on preparation of Si-M-Cl compounds in spite of many efforts. Recently, we have reported on preparation of arylcalcium halides, which are unobtainable in solutions, by use of calcium metal vapor.$^{2)}$ So, we tried to activate Si-Cl and Ge-Cl bonds by calcium metal vapor and succeeded to prepare the first examples of organosilylcalcium chlorides (1) and organogermylcalcium chlorides (2).

A typical reaction is as follows. The apparatus was similar to that described by Timms, Green, and other workers.$^{3)}$ Calcium metal (granule, 99% pure, 0.5 g, 12.5 mmol) was vaporized at a temperature of ca. 900 °C using a filament of tungsten in vacuo (ca. 5×10^{-2} Torr) at a rate of ca. 20 mg min^{-1}. During the vaporization of calcium metal, triethylchlorosilane (9.3 g, 62.5 mmol) was introduced as vapor, into reaction vessel. Triethylsilylcalcium chloride prepared from calcium metal vapor and excess of triethylchlorosilane vapor condensed on the wall of the reaction vessel which was cooled to 77 K with liquid nitrogen. The color of triethylsilylcalcium chloride (1a) thus prepared is deep blue. The reaction vessel was warmed to 0 °C and then bromobenzene (9.4 g, 60.0 mmol) was introduced. The reaction vessel was removed from vacuum line and allowed to warm under argon to room temperature and left to stand for 1 h. After hydrolysis of the reaction mixture with water, the organic layer was extracted with ether.$^{4)}$

Solvent-free 1 and 2 are very reactive solides and decompose very rapidly in an atomosphere. Hydrolysis of 1 and 2 gave the corresponding reduction products, hydrosilanes and hydrogermanes, respectively. Reactions of 1a with various substrates, especially organic halides, were examined. The product from the reaction of 1a with excess of bromobenzene or chlorobenzene was phenyltriethylsilane, formed in 24% and 5% yields, respectively. With fluorobenzene, 1a gave a small quantity of phenyltriethylsilane. Alkyl halides also gave substitution products.

In the reaction of dichlorosilane or dichlorogermane, two Si-Cl or two Ge-Cl bonds could not be activated by calcium metal vapor at the same time. These results are summarized in Table 1.

In general, the yields of 1 and 2 as shown in Table 1 are low. The low yields of 1 and 2 may be due to the following reasons: (1) The yields of 1 and 2 were based on the amount of consumed calcium metal, assuming that all calcium metal except for that remaining in the crucible reacted with organosilylchlorides and organogermylchlorides. Unreacted calcium metal may be also condensed on the wall of the reaction vessel. (2) Disilanes and digermanes probably from the reactions of 1 and 2 with organosilylchlorides and organogermylchlorides were formed in 3-6% yields. Taking into consideration of above facts, the yields of 1 and 2 as shown in Table 1 may be underestimated.

Magnesium atom was not inserted into Si-Cl and G-Cl bonds of organosilylchlorides and organogermylchlorides effectively by our procedure.

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Table 1. Reactions of Silylcalcium Chlorides and Germylcalcium Chlorides with Various Substrates[a)]

Compound	Substrate	Product (Yield/%)
Me_3SiCl	PhBr	$PhSiMe_3$ (16.0)
Et_3SiCl	H_2O	Et_3SiH (27.0)
	PhBr	$PhSiEt_3$ (24.0), Et_3SiH (3.0)
	PhCl	$PhSiEt_3$ (5.0), Et_3SiH (10.0)
	PhF	$PhSiEt_3$ (trace), Et_3SiH (15.0)
	n-BuI	n-$BuSiEt_3$ (26.1)
	n-BuBr	n-$BuSiEt_3$ (26.0), Et_3SiH (1.1)
$PhMe_2SiCl$	H_2O	$PhMe_2SiH$ (44.5)
Me_2SiCl_2	PhBr	$PhMe_2SiCl$ (13.7)
Et_3GeCl	H_2O	Et_3GeH (26.4)
Et_2GeCl_2	H_2O	$Et_2Ge(H)Cl$ (6.2)

a) An average of at least 2 determinations. Based on the consumed calcium metal. Reactions were performed at room temperature for 1 h.

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4) Co-condensation of calcium metal vapor and then excess of triethylchlorosilane vapor leads to the formation of 1a in 5-10% yields. The reactions of calcium metal with organic substartes in the reaction vessel are negligible.

$(Et_3Si)_2Ca\cdot CaCl_2$ is undeniable as the structure of 1a.

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