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The Reaction of Calcium Atoms with Group 4B Catenates, $Me_3E\text{-}E'Me_2R$ (E, E'=Si, Ge, Sn; R=Me, Cl)

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Synopsis. Calcium atoms are thought to be inserted into E–E′ bonds of group 4B catenates, $Me_3E\text{–}E'Me_2R$ (E, E′=Si, Ge, Sn; R=Me, Cl) to give the corresponding $Me_3E\text{–}Ca\text{–}E'Me_2R$ compounds.

The activation of metal-metal bonds of group 4B catenates by metals and metal complexes has received considerable attention in a variety of synthetic organic procedures and catalytic processes.[1–7] In this activation, the oxidation addition of metals or metal complexes into metal–metal bonds of group 4B catenates is generally thought to be the most important process. However, there has been no definite report on insertion reactions of the metal–metal bonds of group 4B catenates by metals.

On the other hand, the study of metal–vapor reactions is of considerable interest in organometallic chemistry since by these methods it is possible to synthesize organometallic compounds which would be difficult, if not impossible, to prepare by other methods, and to study their reactive intermediates.[8]

In this report, we first describe the insertion reactions of metal–metal bonds of group 4B catenates by calcium atoms.

Results and Discussion

Calcium atoms were generated by evaporation from a tungsten filament using essentially the same apparatus and conditions as have been described in the literature (ca. 900 °C and 5×10^{-3} Torr, 1 Torr=133.322 Pa).[9–11] Calcium metal was evaporated at a rate of ca. 20 mg min^{-1}, while an excess of the group 4B catenate compound was co-condensed on the walls of a quartz reaction flask containing a crucible and a perforated inlet tube through which the group 4B catenate compound was admitted. The reaction flask was immersed in liquid nitrogen during calcium evaporation. The color of the co-condensation product of calcium atoms-group 4B catenate compound vapor at 77 K is deep blue, probably due to a weak σ complex.[12] After the calcium evaporation and admission of the group 4B catenate was completed, the reaction flask was warmed to room temperature. The co-condensation product of calcium atoms-group 4B catenate compound vapor turns black. Then, an excess of the organic substrate was admitted as vapor and the reaction flask was left to stand for 1 h. After removing the reaction flask from the vacuum line, the reaction mixture was slowly hydrolyzed with water. The organic layer was extracted with ether.

All products were identified by comparing their GC-MASS and retention times on GLC with those of authentic samples. The results are summarized in Table 1.

Group 4B element-centered anions react with organic halides to give the corresponding substitution products; unreacted anions are converted to the hydrides by hydrolysis.[13]

As shown in Tbale 1, the reaction products of calcium atoms/hexamethyldisilane ($Me_3SiSiMe_3$) and pentamethylchlorodisilane ($Me_3SiSiMe_2Cl$) vapors when treated with phenyl bromide or hydrolyzed gave hexamethylsiloxane. Blank experiments of $Me_3SiSiMe_3$ and $Me_3SiSiMe_2Cl$ in the absence of calcium metal were carried out under identical conditions to give no hexamethylsiloxane ($M_3SiOSiMe_3$). The compound $Me_3SiOSiMe_3$ is probably formed by the insertion of Si–Si bonds by calcium atoms to give Si–Ca–Si followed by hydrolysis in a basic medium.[14] Silylcalcium compounds, thus formed,may be inactive toward phenyl bromide under these conditions.[10]

The reaction products of calcium atoms/(trimethylgermyl)trimethylsilane vapor when treated with phenyl bromide gave phenyltrimethylgermane ($PhGeMe_3$), as expected, besides $Me_3SiOSiMe_3$.

The reaction products of calcium atoms/hexamethyldigermane vapor with phenyl bromide afforded trimethylgermane (Me_3GeH) and $PhGeMe_3$ (Table 1). The formations of $PhGeMe_3$ and Me_3GeH provide strong evidence of the insertion of a Ge–Ge bond of $Me_3GeGeMe_3$ by calcium atoms.

Table 1. Reactions of Calcium Atoms/Group 4B Catenate Compound Vapors with Substrates[a)]

Compound	Substrate	Product (Yield/%)[b)]
$Me_3SiSiMe_3$	H_2O or $PhBr/H_2O$	$Me_3SiOSiMe_3$ (5.0)
$Me_3SiSiMe_2Cl$	H_2O	$Me_3SiOSiMe_3$ (15.0)
$Me_3SiGeMe_3$	$PhBr/H_2O$	$Me_3SiOSiMe_3$ (1.0) $PhGeMe_3$ (trace)
$Me_3GeGeMe_3$	$PhBr/H_2O$	$PhGeMe_3$ (6.0) Me_3GeH (0.5)
$Me_3SiSnMe_3$	$PhBr/H_2O$	$Me_3SiOSiMe_3$ (36.0) $PhSnMe_3$ (2.0) Me_3SnH (42.0) $Me_3SnSnMe_3$ (8.0) Me_3SnOH (10.0)

a) Reactions were performed at room temperature for 1 h. b) Yields of products were based on the calcium metals consumed.

The reaction products of calcium atoms/(trimethylsilyl)trimethylstannane vapor when treated with phenyl bromide afforded $Me_3SiOSiMe_3$, phenyltrimethylstannane ($PhSnMe_3$), trimethylstannane (Me_3SnH), hexamethyldistannane ($Me_3SnSnMe_3$), and trimethylstannol (Me_3SnOH) shown in Table 1. A blank experiment of $Me_3SiSnMe_3$ in the absence of calcium metal was carried out under identical conditions. $Me_3SiOSiMe_3$, $Me_3SnSnMe_3$, and Me_3SnOH were produced in the ratio of 1:1:2. Taking the experimental results into consideration, most of the $Me_3SiOSiMe_3$, $PhSnMe_3$, and Me_3SnH may be derived from the insertion of a Si–Sn bond by a calcium atom.

The degree of insertion of metal–metal bonds of group 4B catenates by calcium atoms increased in the order Si–Si<Ge–Ge<Si–Sn in accord with the metal–metal bond dissociation energy.

The yields of the products shown in Table 1 are very low. The yields of these products were determined on the basis of the amount of calcium metal consumed on the assumption that all of the vaporized calcium metal completely reacted with the substrate.

Experimental

GLC analyses were performed on a Shimazu GC-6A and 8A gas chromatograph with 2 m 20% SE-30 and 2 m 30% Apiezon L columns. GC-MASS spectra were obtained with a JEOL JMS-DX 303 mass spectrometer. NMR spectra were obtained with a Varian FT-80A spectrometer using $CDCl_3$ as the solvent and TMS as the internal standard.

Materials. Calcium metal (granule, 99% pure, Wako chemicals) was commercially available. $Me_3SiGeMe_3$,15) $Me_3GeGeMe_3$,16) $Me_3SiSnMe_3$,17) $PhGeMe_3$,18) Me_3GeH,19) $PhSnMe_3$,20) Me_3SnH,21) $Me_3SnSnMe_3$,22) and Me_3SnOH23) were prepared as described in the cited references.

Reactions of Calcium Atoms/Group 4B Catenate Compound Vapors with Substrate. As a typical example, the reaction of calcium atoms/hexamethyldigermane vapor with phenyl bromide is described. Calcium metal (500 mg, 12.5 mmol) was vaporized at a temperature of ca. 900 °C using a filament of tungsten in vacuo (ca. 5×10^{-3} Torr), at a rate of ca. 20 mg min^{-1}. During the vaporization of calcium metal, digermane (12 g, 51.3 mmol) was introduced into the quartz reaction flask as vapor. Calcium atoms/digermane vapor condensed on the walls of the reaction vessel, which was cooled to 77 K with liquid nitrogen. The initial product at 77 K was a deep blue. The reaction vessel was warmed to room temperature and an excess of phenyl bromide was then admitted as vapor. The reaction vessel was left to stand for 1 h. After removing the reaction vessel from a vacuum line, the reaction mixture was slowly hydrolyzed with water. The organic layer was extracted with ether. The products were identified by comparing their GC-MASS and retention times on GLC with those of authentic samples. The yields of the products were determined by an internal-standard method.

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