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Direct Formation of Ge−C Bonds from GeO_2

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Abstract: Germanium dioxide in the presence of 5% KOH reacted with dimethyl carbonate (DMC) at 250 °C to give $(MeO)_4Ge$. The reaction of GeO_2 and DMC is similar to that reported for SiO_2; however, the rate of reaction for germanium is much higher than that of the corresponding silicon reaction. In a side-by-side experiment using SiO_2 and GeO_2 where the surface area of the silicon dioxide was 2 orders of magnitude higher than that of the GeO_2, the base-catalyzed reaction with DMC was about an order of magnitude higher for the germanium dioxide. When GeO_2 and 5% KOH were reacted with DMC at 350 °C, two products formed: $(MeO)_4Ge$ (70%) and $MeGe(OMe)_3$ (30%). Confirmation of the identity of $MeGe(OMe)_3$ was by GCMS, ^1H and ^{13}C NMR, and comparison to an authentic sample made by reaction of $MeGeCl_3$ with NaOMe. Experiments to determine the mechanism of the direct formation of Ge−C from GeO_2 ruled out participation from CO, H_2, or carbon. The KOH-catalyzed reaction of other metal oxides was explored including B_2O_3, Ga_2O_3, TiO_2, Sb_2O_3, SnO_2, and SnO. Boron reacted to give unknown volatile products. Antimony reacted to give a solid which analyzed as $Sb(OMe)_3$. SnO reacted with DMC to give a mixture that included $(MeO)_4Sn$ and possibly $Me_3Sn(OMe)$.

Introduction

Rochow and Mueller discovered the copper-catalyzed direct reaction of silicon with methyl chloride in the 1940s (eq 1, amounts in weight percent).[1−3]

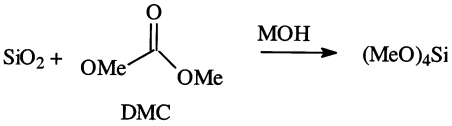
$$
\mathrm{Si} + \mathrm{MeCl} \xrightarrow[250\text{-}300\ ^\circ\mathrm{C}]{\mathrm{Cu} + \text{promoters}}
$$

$$
\begin{array}{ll}
\mathrm{Me_2SiCl_2\ (D)} & (83{-}93\%) \\
\mathrm{MeSiCl_3\ (T)} & (3{-}10\%) \\
\mathrm{Me_4Si\ (S)} & (0.01{-}0.5\%) \\
\mathrm{Me_2SiHCl\ (M2H)} & (0.01{-}0.5\%) \\
\mathrm{MeSiHCl_2\ (MH)} & (0.1{-}5.0\%) \\
\mathrm{Me_3SiCl\ (M)} & (1.0{-}5.0\%) \\
\text{high boilers} & (1.0\text{-}5.0\%)
\end{array}
\tag{1}
$$

The silicon direct process is one of two main catalytic reactions to form silicon−carbon bonds, the other being hydrosilylation (eq 2).[4−6]

$$
\mathrm{R_3SiH} + \mathrm{R'CH{=}CH_2} \xrightarrow{\mathrm{Pt}} \mathrm{R_3SiCH_2CH_2R'} \tag{2}
$$

A direct reaction of silicon dioxide to form molecular species containing Si−C bonds is not known. Recently, Ono et al. reported the direct reaction of silicon dioxide with base and dimethyl carbonate (DMC) to make tetramethoxysilane, eq 3.[7]



(3)

Several related reactions of silicon dioxide to make alkoxysilanes have been reported.[8−13] Subsequent conversion of alkoxysilanes to a Si−C-containing compound can be accomplished by using a sacrificial alklylating agent such as that shown in eq 4.[14,15]

$$
\mathrm{Si(OMe)_4} + \mathrm{MeMgBr} \xrightarrow{\text{ether}} \mathrm{Me_{4-x}Si(OMe)_x} \tag{4}
$$

A three-year effort was recently completed by GE researchers called “Direct Production of Silicones from Sand”.[16] No direct *catalytic* method was found for production of the Si−C bond

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from any compound with four oxygen groups, although a new, unexpected formation of a Si−C bond was found by *stoichiometric* reaction of tetramethoxysilane with sodium hydride.[17]

The chemistry of germanium is similar to that of silicon. A germanium direct process[18−25] and Ge−H[26,27] addition across double bonds are the two catalytic methods for formation of germanium−carbon bonds. Direct catalytic formation of Ge−H bonds has been reported via Ge(II) species.[28] However, a reaction analogous to eq 3 for germanium had not been previously reported. In addition, the only reported method for synthesis of $(MeO)_4Ge$ or $MeGe(OMe)_3$ involves the reaction of MeOH with GeX_4[29] or $MeGeX_3$ (X = halide). Formation of tetramethoxygermane is potentially interesting because of the need for GeO_2 precursors as refractive index modifiers in the fiber-optics industry.[30−33]

Recently, Dupont researchers reported the first direct stannylation of aromatic hydrocarbons, forming new C−Sn bonds.[34] This work employed $(CF_3CO_2)_4Sn$ reacting reversibly with benzene and *p*-xylene to make isolable aryltin compounds. This work received considerable interest owing to the plethora of C−C bond-forming reactions arylstannanes undergo. Nonetheless, direct stannylation of aromatic or alkyl hydrocarbons from tin oxides has not yet been reported.

This report describes (1) the facile base-catalyzed reaction of germanium oxide and DMC toward $(MeO)_4Ge$, (2) a comparison of the reactivity of SiO_2 with that of GeO_2, and (3) the unexpected direct synthesis of $MeGe(OMe)_3$, the first direct reaction from GeO_2 to form molecular Ge−C-containing species.

Results and Discussion

Germanium dioxide with 5% KOH was reacted with DMC in a fixed-bed reactor at 250 °C, resulting in virtually quantitative formation of $(MeO)_4Ge$. As expected, the chemistry of germanium dioxide was similar to that found for reaction with silicon dioxide, eq 3. It was of interest to determine if germanium was more reactive than silicon in the base-catalyzed reaction of the oxide with DMC.

Table 1. PSD and Surface Area of GeO_2 and Two SiO_2

compound	particle size, μM (std dev)	surface area, m^2/g
GeO_2	2.2 (1.3)	2.1
SiO_2 (Minusil)	2.3 (1.3)	2.6
SiO_2 (silica gel)	<1 (0.5)	200

A silicon dioxide source of particle size and surface area roughly equivalent to those of the germanium oxide was used to compare reactivity to that of germanium. Table 1 details the particle size and surface area of the germanium dioxide used in this study and two different silicon dioxides investigated. Equimolar amounts of GeO_2 and SiO_2 (Minusil, α-quartz) were combined with 5% KOH by weight and reacted in the fixed-bed reactor with DMC at 250 °C. Quantitative conversion of all of the GeO_2 in the bed occurred to give $(MeO)_4Ge$. The SiO_2 reacted to produce only a trace of $(MeO)_4Si$. Similarly, Minusil alone was poorly reactive: in the presence of 5% KOH, only trace levels of $(MeO)_4Si$ formed. The comparison of reactivity experiment was repeated, except that silica gel was used in place of Minusil. Silica gel is amorphous and has a high surface area. The amorphous silicon dioxide sources were the most reactive of all the many SiO_2 compounds investigated.[16] Nevertheless, germanium dioxide was much more reactive than silicon dioxide (silica gel), despite the fact that the silicon dioxide used had a surface area 2 orders of magnitude higher than that of the germanium oxide used (Figure 1). All of the GeO_2 in the bed was consumed in less than 2 h, while almost 6 h was needed to react all of the silicon dioxide present in the bed. Both germanium and silicon dioxides were quantitatively consumed to form $M(OMe)_4$ (M = Ge and Si).

The base-catalyzed reaction of germanium dioxide was repeated at higher temperature. When the reaction was performed at 350 °C, a second product was formed in about 25% selectivity with a lower gas chromatographic (GC) retention time than the $Ge(OMe)_4$. Analysis of the new product by gas chromatography/mass spectroscopy (GCMS) was consistent with formation of $MeGe(OMe)_3$.[35] ^1H and ^{13}C NMR analysis of the product mixture from reaction of 5% base and GeO_2 with DMC showed the presence of new peaks in the methyl and methoxide regions. An authentic sample of $MeGe(OMe)_3$ was prepared following the procedure of West et al.,[36] and mass spectroscopic and ^1H and ^{13}C NMR analysis confirmed that the new product was indeed $MeGe(OMe)_3$.[37]

The origin of formation of $(MeO)_4Ge$ from the base-catalyzed reaction with DMC is likely similar to that proposed for the silicon analogue (Scheme 1).[16] Analysis of the gases from the base-catalyzed reactions of both silicon and germanium dioxide with DMC by GCMS showed primarily formation of CO_2. The route in Scheme 1 is further supported by previous work on dissolution of silicon dioxide and base.[38] In addition, the higher reactivity of germanium vs silicon is consistent with the fact that germanium is more electropositive than silicon, and the

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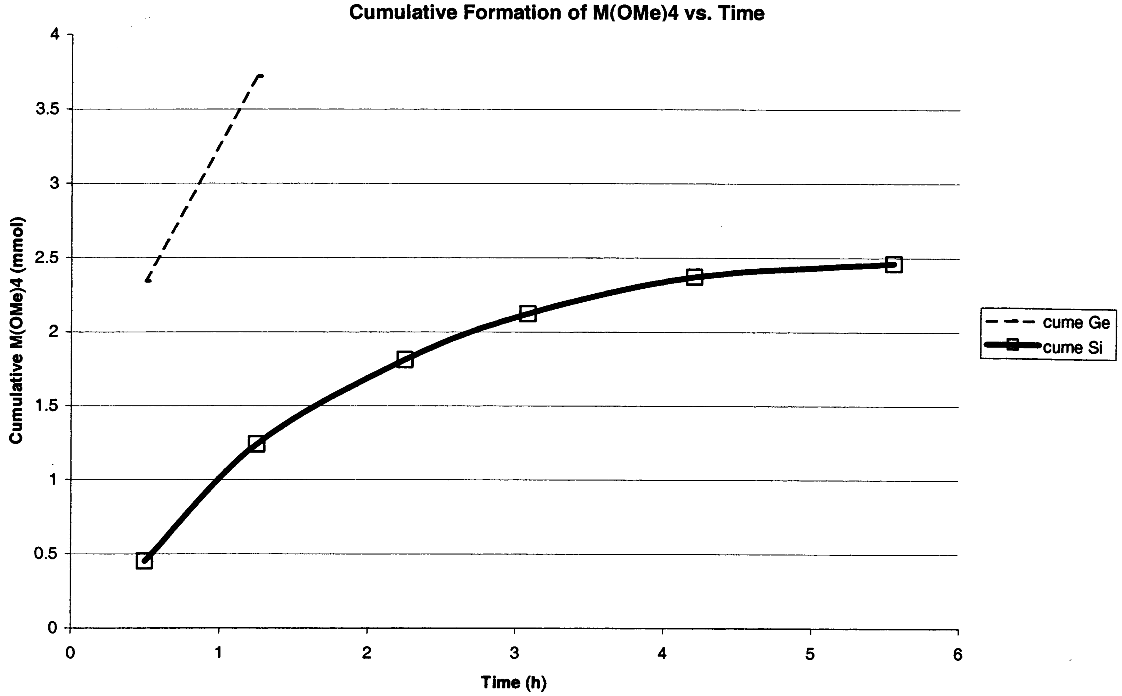
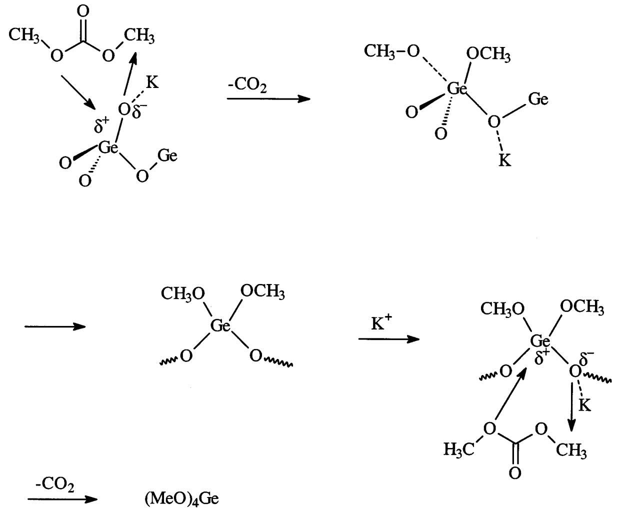


Figure 1. Relative rate of formation of $M(OMe)_4$ vs time (M = Ge and Si, silica gel).

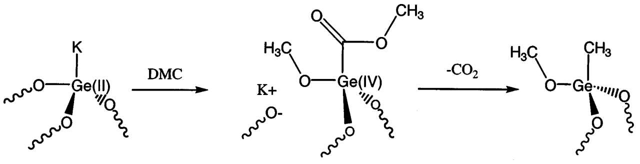
Scheme 1. Possible Scheme for KOH-Catalyzed Formation of $(MeO)_4Ge$ from GeO_2 and DMC



proposed scheme would predict that germanium would be more reactive than silicon. However, there is no clear route for formation of the Ge−C bond. One possibility may be via alkoxycarbonylgermanium intermediates, formed by reaction of DMC with reduced Ge on the surface, which decarboxylate to yield Me−Ge species (Scheme 2). Experiments were conducted to test this hypothesis.

A reviewer is thanked for noting that there remains a continuing debate on the relative electronegativity of group 14 elements.[39] We are persuaded by the calculations of Ghanty and Ghosh[40] and of Datta and Hati[41] and the experimental evidence cited therein, which support the statement that germanium is less electronegative (and thus more electropositive) than silicon. A more meaningful argument on our part would be based upon relative Ge−O/Si−O bond enthalpies (659 vs 800 kJ/mol according to *CRC Handbook of Chemistry and Physics*[42]), where the increased reactivity arises from the relatively weaker Ge−O bonds.

Scheme 2. Possible Scheme for Formation of $MeGe(OMe)_3$ from Reduced Ge Species and DMC



The base-catalyzed reactions of GeO_2 and DMC at 250 °C resulted in an off-white solid residue, while the reactions run at 350 °C, e.g., when Ge−C bond formation occurred, resulted in black bed residues. We ruled out catalytic processes due to the adventitious presence of other elements in the germanium oxide. In addition, XRD of our GeO_2 used revealed the structure to be hexagonal. We considered three possibilities for formation of the Ge−C bond. Carbon monoxide was considered as a possible reducing agent. Formation of CO, and its possible role as an oxygen acceptor, was supported by a reaction between 5% KOH, GeS_2, and DMC at 250 °C. While reaction of germanium disulfide did not result in formation of germanium

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methoxides, GCMS analysis of the gas products from this reaction did show O═C═S. The observation of carbonyl sulfide suggests that if CO can remove S from GeS_2, then possibly CO can remove an oxygen from GeO_2. However, when the base-catalyzed reaction of GeO_2 and DMC was carried out in a gas stream containing 10 vol % CO, no Ge−C bond formation occurred at 250 °C, nor was there observed an increase in Ge−C formation at the typical temperature of 350 °C.

A second possible reducing agent for Ge−C formation was H_2. Like the CO example above, addition of H_2 to the carrier gas stream in the base-catalyzed reaction of GeO_2 with DMC did not result in extra Ge−C bond formation. Finally, we considered that carbon could act as an oxygen acceptor. Carbon deposition from nonproductive DMC decomposition likely occurred via C−H bond breakage.[16] Therefore, base-catalyzed reaction of GeO_2 with DMC was performed in the presence of activated carbon. No additional formation of Ge−C bonds was caused by the presence of activated carbon, and no additional species were formed. Thus, at this point, the mechanism of formation of $MeGe(OMe)_3$ from base-catalyzed reaction of GeO_2 and DMC is not known.

Other Metals. We investigated the reaction of some other metal oxides in a manner similar to that described for GeO_2. When Ga_2O_3, TiO_2, or SnO_2 was used with 5 wt % KOH in place of GeO_2 in the reaction with DMC, no condensed product containing the appropriate metal was obtained, nor was there significant weight loss from the bed. These results suggest that virtually no reaction of these metal oxides with DMC occurred from 250 to 350 °C. B_2O_3 was combined with 5 wt % KOH and then reacted with DMC from 250 to 350 °C. No boron-containing product was condensed. However, the bed lost almost all of its weight. A volatile, noncondensed material was made from this reaction, but its identity is not known at this time.

When Sb_2O_3 was used with 5% KOH and contacted with DMC, a reaction did occur. There were no antimony-containing products in the condensables, but a solid was formed in the heated elbow region that exits the reactor (past the glass frit holding the solids). Thus, some volatile material exited the bed and deposited as a solid on the elbow. The solid, brown, hard material was insoluble in common organic solvents and was not volatile enough to give a mass spectrum. Elemental analysis showed a reasonable match consistent with $Sb(OMe)_3$. In one experiment performed at 350 °C, the bed lost 85% of its weight, consistent with virtually complete conversion of the antimony oxide to volatile products. A likely possibility is that the antimony methoxide formed as a monomer that was volatile enough to escape the reactor but immediately polymerized on the elbow.

Finally, the reaction of SnO (as opposed to SnO_2 as described above) was performed with 5% KOH and DMC. Up to 60% weight loss was noted when the reaction was carried out at 350 °C; less weight loss occurred at lower temperatures. The identity of the main tin-containing product is equivocal. GC analysis showed a relatively clean mixture composed of unreacted DMC, a new peak with slightly higher retention time than that of $(MeO)_4Si$, and the internal standard, cyclooctane. GCMS analysis of the product solution was consistent with formation of $(MeO)_4Sn$. While no library mass spectrum of $(MeO)_4Sn$ was available, a computer-generated pattern closely matched the observed pattern we found. Contradictory evidence was obtained for the tin-based product by NMR. The ^{119}Sn NMR showed primarily one peak at +126 ppm. The literature values of ^{119}Sn NMR for the series $(Me_{4-n}Sn(OMe)_n$ ($n = 0-4$) are consistent with our 126 ppm peak assigned to $Me_3Sn(OMe)$.[43] Furthermore, the ^1H NMR showed two methoxide resonances at 3.30 (major) and 3.26 (minor) ppm. In addition, the ^1H NMR showed a peak at 0.32 ppm with (presumed) ^{Sn-H}J coupling (satellites) of 58 Hz. The 3.26/0.32 ppm peaks are consistent in location, relative intensity, and coupling constant with $Me_3Sn(OMe)$, while the single 3.30 ppm peak could be assigned to $(MeO)_4Sn$, as suggested by the GC/GCMS data.[43−44] It is possible that the $(MeO)_4Sn$ and $Me_3Sn(OMe)$ (if present) coeluted in the GC and thus gave rise to the single peak there and a complicated mixture in the mass spectrum obtained in the GCMS analysis.

Summary. In this report, we describe the facile base-catalyzed reaction of germanium oxide and DMC toward $(MeO)_4Ge$ in high GeO_2 conversion (80%) and selectivity (>98%). A comparison of the reactivity of SiO_2 with that of GeO_2 revealed Ge to be significantly more reactive to base-catalyzed reaction with DMC than Si, despite 2 orders of magnitude difference in their surface areas. Increasing the temperature from 250 to 350 °C resulted in the unexpected direct synthesis of $MeGe(OMe)_3$ with $(MeO)_4Ge$ in a 1:3 ratio, with a very slight drop in overall GeO_2 conversion (72%). This is the first reported direct reaction from GeO_2 to molecular Ge−C-containing species. Apparently, other metal oxides in combination with base will react with DMC to give metal alkoxides. Some evidence exists, at least for tin, that direct metal−carbon bond formation can occur for a metal other than germanium.

Experimental Section

Measurements. GC measurements were made using a Hewlett-Packard model 6890 instrument with a thermal conductivity detector and a 30 m HP 1 column (0.32 mm i.d. and 0.25 μM film thickness). GCMS data were recorded using a JEOL SX 102 high-resolution, double-focusing magnetic sector instrument with a 30 m DB 5 capillary column. NMR spectra were recorded in $CDCl_3$ with TMS as an internal standard on a GE QE-300 instrument, ^1H and ^{13}C NMR at 300.15 and 75.48 MHz, respectively. XRD measurements were performed on a Siemens D500 diffractometer, which utilized a Bragg−Brentano vertical Θ:Θ goniometer. The instrument used a Cu anode tube, (wavelength for Cu Kα1 = 1.54056 Å), and sample was measured at the following parameters:

power generation	instrument setup
kV = 45 mA = 40	2Θ range = 10−90° step size = 0.05° dwell time = 2 s slit size: Siemans D500 = 1°

Particle size measurements (10 replicates) were made as follows. Small samples of powder were removed and placed on a glass slide. A small droplet of dispersion fluid with a refractive index that provided good contrast between the powder and background was applied to a glass cover slip. The cover slip was placed on the powder sample and dispersed using mechanical agitation. The slide was then placed on a transmitted light microscope (Zeiss Photomicroscope III) and observed at sufficient magnification to distinguish the size and shape of the power. The microscope was outfitted with a high-resolution camera (Kodak ES1), which was interfaced to a computer in order to provide a digital

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Table 2. Analysis of Elements in GeO_2, Minusil, and Silica Gel

element	GeO_2, ppm	Minusil, ppm	silica gel, ppm
Al	<10	780	78
B	<20	10	<10
Ba	<10	13	20
Be	<10	<10	<10
Ca	<10	212	783
Cd	<10	<10	<10
Co	<10	<10	<10
Cr	<10	<10	<10
Cu	<10	<10	<10
Fe	<10	290	38
Ga	<10	<10	<10
Mg	<10	36	123
Mn	<10	<10	<10
Mo	<10	<10	<10
Ni	<10	<10	<10
P	<10	51	13
Pb	<10	<10	<10
Sn	<10	<10	<10
Sr	<10	10	<10
Ti	<10	140	112
V	<10	<10	<10
Zn	<10	<10	<10
Zr	<10	23	41
As	<10	<10	<10
Bi	<10	<25	<25
Ge	major	<10	<10
Hf	<10	<10	<10
Hg	<10	<10	<10
In	<10	<10	<10
Nb	<10	<10	<10
Sb	<10	<10	<10
Ta	<10	<25	<25
Te	<10	<25	<25
Th	<10	<25	<25
U	<10	<10	<10
W	<10	<10	<10
Si	75		

XRD analysis showed that all of the GeO_2 was in the hexagonal phase.

image for further analysis. Image analysis software (Clemex Vision) was used to quantify the particle sizes.

Materials. GeO_2 was obtained from Aldrich. Elemental analysis was done by Galbraith. Minusil was obtained from GE Silicones (Waterford, NY), and silica gel was obtained from JT Baker (60−200 mesh). Table 2 gives elemental analysis data for the metal oxides used.

Procedures. Reactions were performed in a fixed-bed reactor as described previously.[45] The reactor was a glass tube (20 cm long; 1 cm i.d.) with a porous glass grid to hold the GeO_2 sample. The reactor was centered vertically in a Nichrome ribbon-wound glass tube (5 cm o.d.). Two pairs of electrodes were fitted to the Nichrome to create two heated zones. The top heating zone was used to preheat the DMC/carrier gas mixture, and the bottom section was for the reactor itself. The Nichrome-wound tube was centered in a quartz glass tube (6.4 cm o.d.) for insulation and safety purposes. The carrier gas stream was regulated by using a mass flow controller (MKS Instruments type 1179A) connected to a four-channel readout device (MKS Instruments type 247D). The DMC was added into the carrier gas stream (typically argon) above the upper heating zone through a septum via motor-driven syringe. The reactor downstream was collected using a water-chilled condenser.

Typical Procedure. The GeO_2 source was stirred in an aqueous solution of KOH. The suspension was heated to dryness, and the solid obtained was further dried overnight at 115 °C. The material was ground and charged into the fixed-bed flow reactor. The solid (typically 1.0 g) was kept at the reaction temperature in the argon stream for 1 h. DMC (typically 20 mmol/h = 1.68 mL/h; a total of 10 mL) was fed into the carrier gas stream (20 mL/min) using a motor-driven syringe. The reaction products downstream were collected in fractions using a water-chilled condenser and analyzed by gas chromatography. Formation of $Ge(OMe)_4$ and $MeGe(OMe)_3$ was confirmed by GCMS and ^1H and ^{13}C NMR. The GeO_2-utilization values were calculated from the collected amounts of $Ge(OMe)_4$ and $MeGe(OMe)_3$. The weight difference in the GeO_2 bed before and after reaction was also determined; however, a black carbon-based deposit rendered a precise weight determination impossible.

The GeO_2/KOH mixture was added to the fixed-bed reactor (1 g) and then heated to 250 °C with DMC injection and the Ar carrier gas. More than 80% of the GeO_2 reacted to make a single product, $Ge(OMe)_4$. The product was confirmed by GC, GCMS, and ^1H and ^{13}C NMR analysis. GC analysis showed a single peak with retention time just below that of the cyclooctane internal standard. GCMS analysis showed that the mass spectrum of the observed peak had a peak envelope centered around 196 amu. Fragments indicated loss of OMe groups. Ge has five naturally occurring isotopes giving rise to the envelope pattern. ^1H NMR showed a single resonance at 3.59 ppm ($CDCl_3$), and ^{13}C NMR showed a single resonance at 53.96 ppm.

The experiment was repeated, except that the temperature was 350 °C. GC analysis showed that $Ge(OMe)_4$ and $MeGe(OMe)_3$ were produced in about a 3:1 ratio. Total GeO_2 conversion was 72%. Confirmation of the formation of $MeGe(OMe)_3$ was accomplished with GCMS (EI) and GCMS (CI, H^+). The latter technique showed the parent ion center around 179 amu. Fragments were observed for $M^+ - CH_3$ and $M^+ - OMe$. ^1H NMR showed the presence of new methoxy resonances at 3.53 ppm and $Ge-CH_3$ methyl resonance at 0.59 ppm, while ^{13}C NMR showed the presence of a new methoxy carbon resonance at 52.01 ppm and a CH_3-Ge methyl resonance at −6.2 ppm; reference ^1H and ^{13}C values for $Ge-CH_3$ were 0.51 and −7.43 ppm, respectively.[31]

Synthesis of $MeGe(OMe)_3$.[36] To a three-necked round-bottom flask equipped with an argon inlet, reflux condenser, and magnetic stir bar was added $MeGeCl_3$ (9.5 g, 49 mmol, Gelest). NaOMe was prepared by slow addition of Na (3.6 g, 156 mmol) to MeOH (35 mL) under Ar. The NaOMe/MeOH solution was slowly added to $MeGeCl_3$, first at 0 °C and then at reflux (2 h), with stirring. A white precipitate was removed by filtration. The MeOH was removed by ambient pressure distillation, and then the product was purified through a short path column at 135 °C at ca. 100 mmHg. About 2.5 g of colorless liquid was collected.

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