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Catalytic Synthesis of Cyclic and Linear Germoxanes Mediated by an Iron Complex

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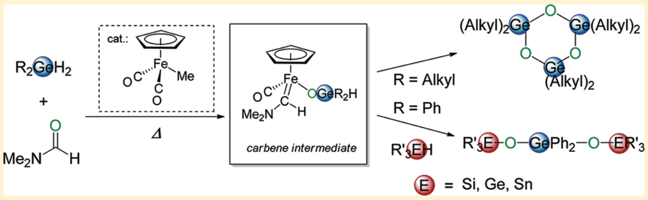
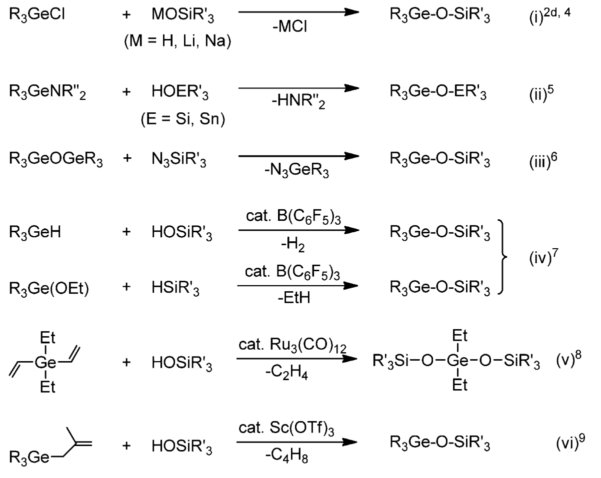
Ⓢ *Supporting Information*

ABSTRACT: Six-membered cyclic germoxanes $(R_2GeO)_3$ were selectively prepared via the thermal reaction of $(alkyl)_2GeH_2$ in dimethylformamide (DMF). Linear metallagermoxanes with an E−O−Ge−O−E backbone (E = Si, Ge, Sn) were prepared by the reaction of Ph_2GeH_2 with R_3EH in DMF. Their cyclic and linear germoxane formations were achieved using an iron catalyst, $(\eta^5\text{-}C_5H_5)Fe(CO)_2Me$. An iron carbene complex was proposed to be an intermediate in the catalytic reaction.



Polysiloxanes with a $(-Si-O-)_n$ backbone have been widely used in chemical synthesis because of their stability toward water and air as well as their insulation and heatproof properties. The germanium analogues, cyclic and linear poly- and oligogermoxanes and their derivatives with Ge−O−E fragments (E = Si, Ge, Sn), have recently attracted considerable attention owing to their high refractive index, low dielectric constant, and biocompatible properties.[1] The most common method for the formation of (poly)germoxanes is the hydrolysis of germyl halides. However, the hydrolysis of R_2GeCl_2, for example, gives various types of germoxanes such as cyclic oligomers and linear oligomers/polymers. In addition, the selectivity and dispersity of these compounds have not yet been controlled. To construct an unsymmetrical Ge−O−E fragment, hydrolysis of a mixture of R_3GeCl and R_3ECl and dehydration of a mixture of R_3GeOH and R_3EOH can be employed; however, the desired product $R_3Ge-O-ER_3$ is always contaminated by homocondensation products such as $R_3Ge-O-GeR_3$ and $R_3E-O-ER_3$ because of the lack of selectivity.[2,3] Selective formation of compounds with a Ge−O−E fragment has been achieved by condensation of germanium chloride with silanol (silanolate) (Scheme 1i),[2d,4] germamine with silanol or stannanol (Scheme 1ii),[5] and germoxane with silyl azides (Scheme 1iii).[6] However, these processes have drawbacks: the removal of corrosive or explosive byproducts produced stoichiometrically is necessary, and the use of germanium, silicon, and tin substrates result in these methods being unstable toward moisture. To the best of our knowledge, there are only three reports of catalytic methods for Ge−O−Si bond formation. One is based on $B(C_6F_5)_3$-catalyzed dehydrogenative coupling of hydrogermanes with silanols and dealkylative coupling of alkoxygermanes with hydrosilanes (Scheme 1iv).[7] Another is based on Ru-catalyzed de-ethylene coupling of vinylgermane with silanol (Scheme 1v).[8] The last process is scandium-catalyzed deisobutene coupling of allylgermane with silanol (Scheme 1vi).[9] However, the catalytic formation of Ge−O−Ge and Ge−O−Sn bonds has not been reported to date.[10]

Scheme 1. Reported Methods for Preparation of an Unsymmetrical Ge−O−E Fragment



Several reactions of hydrosilanes with amides such as dimethylformamide (DMF) in the presence of catalyst of iron complexes[11] and other transition-metal complexes[12] have been reported to form disiloxanes.[13] In these reactions, the oxygen atom in the produced siloxane stems from amide, and the amide is finally reduced to amine. Although some reaction mechanisms have been proposed, there is little experimental evidence supporting such a reaction mechanism.

Herein, we report the first example of catalytic and selective synthesis of cyclic germoxanes and linear germoxanes with an E−O−Ge−O−E backbone (E = Si, Ge, Sn). In addition, we show

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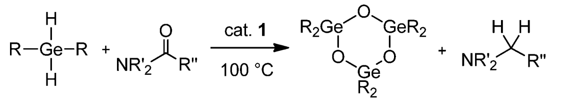
an unprecedented reaction mechanism involving an iron carbene complex that could be isolated and characterized by X-ray analysis.

The reaction of an iron methyl complex, $CpFe(CO)_2Me$ (**1**; Cp = η^5-C_5H_5), with an excess of tertiary germanes R_3GeH (R = Et, Ph) in DMF gave no coupling products. This is in complete contrast to the formation of $R_3Si-O-SiR_3$ in the reaction of **1** with R_3SiH in DMF.[11a,b] In contrast, a treatment of Et_2GeH_2 with a catalytic amount of **1** in DMF produced 1,1,3,3,5,5-hexaethylcyclotrigermoxane in an excellent yield (Table 1, entry 1). The product was identified on the basis of ^1H and ^{13}C NMR and high-resolution mass spectra. The same cyclization reaction occurred using other amides as solvents but the conversion yields decreased (entries 2–4). No coupling products were obtained in the absence of amide (entry 5), indicating that amide serves as an oxygen supplier in this reaction. The cyclization reaction can even be achieved by reducing the amount of catalyst **1** from 5 to 0.1 mol % (entries 1, 6–8). The TON of 380 in entry 8 is the highest value shown by an iron catalyst in amide reduction reactions.[11] This cyclization reaction was effective for other secondary germanes, such as $^nBu_2GeH_2$, $^cHex_2GeH_2$, and $(PhCH_2)_2GeH_2$ (entries 9–11); however, interestingly, it was not effective for Ph_2GeH_2 (entry 12). This unreactivity of Ph_2GeH_2 appears to occur for electrical reasons, because the sterically more bulky cyclohexyl-substituted germane ($^cHex_2GeH_2$) gave the corresponding product in excellent yield under the same conditions (entry 10).

Table 1. Catalytic Synthesis of Germoxane by an Iron Complex[a]

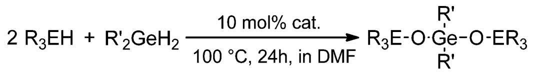


entry	R	R′	R″	time/h	cat.[b] /mol %	yield[c] /% (TON)
1	Et	Me	H	6	5	>99 (20)
2	Et	Me	Me	6	5	70 (14)
3	Et	Bu	H	6	5	56 (11)
4	Et	Ph	H	6	5	23 (5)
5	Et	none		6	5	NR[d]
6	Et	Me	H	24	1	>99 (99)
7	Et	Me	H	48	0.5	84 (168)
8	Et	Me	H	48	0.1	38 (380)
9	^{n}Bu	Me	H	24	1	>99 (99)
10	^{c}Hex	Me	H	24	1	>99 (99)
11	CH_2Ph	Me	H	24	1	27 (27)
12	Ph	Me	H	24	1	NR

[a] Reaction conditions: 100 °C, sealed glass tube, $[R_2GeH_2]/[amide]$ = 1/10. [b] On the basis of the $[R_2GeH_2]$:[**1**] ratio. [c] Isolated yield of the cyclic germoxane. [d] NR = no reaction.

In general, the reaction of Et_2GeH_2 with R_3EH (E = Si, Ge, Sn) in DMF yields the cross coupling product $R_3E-O-GeEt_2-O-ER_3$ and homocoupling products such as $(Et_2GeO)_3$ and $R_3E-O-ER_3$, whereas the reaction of Ph_2GeH_2 with R_3EH may prevent the formation of $(Ph_2GeO)_3$. Therefore, it is possible that Ph_2GeH_2 is an appropriate starting material for selective metallagermoxane formation. We examined the reaction of Ph_2GeH_2 with hydrosilane, hydrogermane, and hydrostannane in DMF with an iron catalyst. The results are shown in Table 2. The treatment of Ph_2GeH_2 with 2 equiv of Et_3SiH in DMF in the presence of **1** (10 mol %) at 100 °C led to complete consumption of Ph_2GeH_2 and Et_3SiH after 24 h, and disilagermoxane, $Et_3Si-O-GePh_2-O-SiEt_3$, was obtained as a single product in 88% isolated yield (entry 1).

Table 2. Synthesis of Linear Sila-, Germa-, and Stannagermoxanes[a]



cat. : $CpFe(CO)_2Me$ (**1**), (η^5-C_5Me_5)$Fe(CO)_2Me$ (**2**), $Fe(CO)_5$ (**3**), $[CpFe(CO)_2]_2$ (**4**)

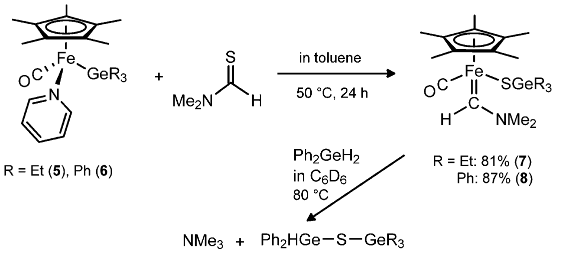
entry	E	R_3	R′	cat.	yield[b] /%
1	Si	Et_3	Ph	**1**	88
2	Si	Et_3	Ph	**2**	TR[c]
3	Si	Et_3	Ph	**3**	TR[c]
4	Si	Et_3	Ph	**4**	38
5[d]	Si	$Me_2{}^tBu$	Ph	**1**	67
6	Si	Me_2Ph	Ph	**1**	TR[c,e]
7	Si	Ph_3	Ph	**1**	TR[c,e]
8	Ge	Et_3	Ph	**1**	42
9	Ge	$^nBu_3$	Ph	**1**	54
10	Sn	$^nBu_3$	Ph	**1**	35
11	Si	Et_3	Et	**1**	38[f]
12	Si	Et_3	Bu	**1**	28[f]

[a] Reaction conditions: 100 °C, 24 h, sealed glass tube, $[R_2GeH_2]/[R_3SiH]/[amide]/[1]$ = 10/20/50/1. [b] Isolated yield. [c] TR = trace amount of silagermoxane and a nearly quantitative yield of disiloxane were isolated. [d] 48 h. [e] When other hydrosilanes, such as R_3SiH (R_3 = $MePh_2$, $(^nHex)_3$, $(^cHex)_3$, $(OEt)_3$, $Me_2(CH{=}CH_2)$) were used, the corresponding disiloxanes were mainly obtained. [f] Cyclogermoxane was also formed.

This is the first example of the selective formation of a compound with a Si–O–Ge–O–Si backbone. The catalytic activity of this reaction was examined for the following iron complexes: $Cp^*Fe(CO)_2Me$ (**2**; Cp* = η^5-C_5Me_5), $Fe(CO)_5$ (**3**), and $[CpFe(CO)_2]_2$ (**4**). In the cases of **2** and **3**, $Et_3Si-O-SiEt_3$ was the main product (entries 2 and 3). Complex **4** gave the cross-coupling product in 38% yield with the formation of disiloxane (entry 4). Thus, complex **1** among these iron complexes showed the best catalytic activity toward the cross-coupling reaction. The reaction of $^tBuMe_2SiH$ formed the corresponding disilagermoxane (entry 5). The reactions of $PhMe_2SiH$ and Ph_3SiH produced only a trace amount of disilagermoxane and yielded the corresponding disiloxanes as the main products (entries 6 and 7). Both silanes have reportedly been converted into disiloxanes by **1** in DMF.[11a] This cross-coupling reaction could be applied to the coupling of tertiary germane (R_3GeH) or stannane (R_3SnH) with Ph_2GeH_2 (entries 8–10). The use of secondary germanes other than Ph_2GeH_2 caused formation of the corresponding disilagermoxanes, but cyclic germoxanes were also obtained (entries 11 and 12).

As described above, $CpFe(CO)_2Me$ (**1**) has been shown to be a good catalyst precursor for reactions in which R_2GeH_2 (R = Et, ^{n}Bu, ^{c}Hex, CH_2Ph) and DMF are converted into cyclic germoxane and NMe_3, and Ph_2GeH_2, DMF, and R_3EH (E = Si, Ge, Sn) are converted into $R_3E-O-GePh_2-O-ER_3$ and NMe_3. In these reactions, the essence is dehydrogenative oxygenation of an E–H portion by amide catalyzed by an iron complex to construct an E–O–E framework and NMe_3. It should be noted that there are two interesting aspects to these reactions. One is selective E–O–E bond formation,[11a,b] and the other is amide reduction to amine via the E–H bond.[11c,d,e,12] However, the role of an iron complex in the catalytic cycle remains to be determined. To elucidate this role, we attempted several related experiments, and found that stoichiometric reactions of germyl complexes, $Cp^*Fe(CO)(py)(GeR_3)$ (R = Et (**5**), Ph (**6**)), with *N*,*N*-dimethylthioformamide corresponding to the thio derivative of DMF provided some information regarding the catalytic reaction mechanism (Scheme 2).

Scheme 2. Formation of Iron−Carbene Complexes (7, 8) and Their Reactivity



The reaction led to the isolation of carbene complexes, $Cp^*Fe(CO)(CHNMe_2)(SGeR_3)$ (R = Et (**7**), Ph (**8**)). X-ray analysis was conducted, as single crystals of **8** were obtained. The molecular structure of **8** is depicted in Figure 1. Complex **8** adopts a three-legged piano-stool geometry in which the iron center bears one Cp*, one carbonyl, one thiogermoxy group, and one amino-substituted carbene ligand. The Fe1−C3 bond distance (1.883 Å) is shorter than that of a typical Fe═C bond in a Fischer-type carbene ligand.[14] The bond length between the nitrogen atom N1 and the carbene carbon atom C3 (1.300 Å) is also shorter than that of a typical N−C single bond (1.47 Å). The sum of angles around N1 is 360.0°, which is consistent with the sp^2 hybridization of N1. These results indicate that the nitrogen lone pair is delocalized in the carbene carbon plane.

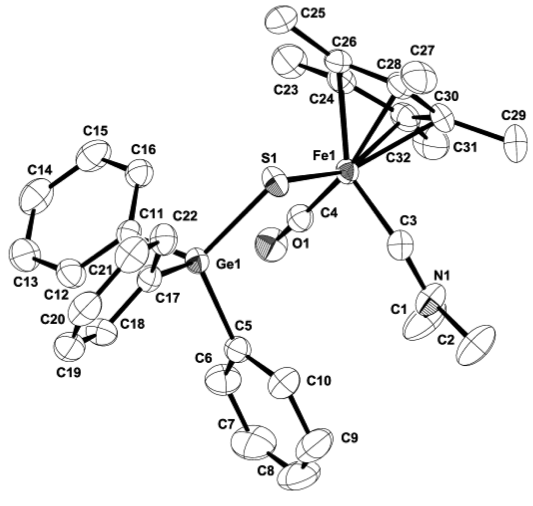


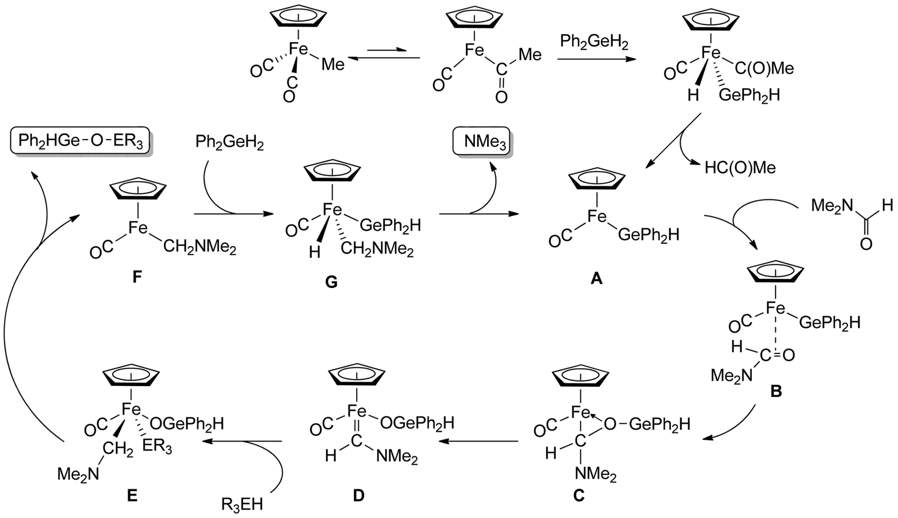
Figure 1. ORTEP drawing of **8**.

If the carbene complex bearing a $SGeR_3$ ligand is an intermediate, reaction of the isolated complexes with Ph_2GeH_2 would form NMe_3 and $Ph_2HGe{-}S{-}GeR_3$. Thermal reactions of **7** and **8** with Ph_2GeH_2 in C_6D_6 were performed, and the generation of NMe_3 was confirmed by ^1H NMR (a singlet at 2.05 ppm) analysis of both complexes, while formations of $Ph_2HGe{-}S{-}GeEt_3$ and $Ph_2HGe{-}S{-}GePh_3$ were confirmed by GC-MS for **7** and **8**, respectively (Scheme 2). These results indicate that the carbene complexes **7** and **8** are the intermediates in the reduction of dimethylthioformamide by hydrogermane to give amine and thiogermoxane and that it is highly likely that an analogous carbene complex is formed in the catalytic reaction of formamide.

A part of the catalytic cycle proposed in the reaction of Ph_2GeH_2 with R_3EH in DMF promoted by $CpFe(CO)_2Me$ (**1**) to give $R_3E{-}O{-}GePh_2{-}O{-}ER_3$ is shown in Scheme 3. $CpFe(CO)_2Me$ reacts with Ph_2GeH_2 to generate an actual catalyst, the 16e species $CpFe(CO)(GePh_2H)$ (**A**), via CO insertion into the Fe−Me bond, oxidative addition of a Ge−H bond of Ph_2GeH_2, and reductive elimination of MeC(O)H (the formation was confirmed by ^1H NMR, with a quintet signal at 9.23 ppm and a doublet signal at 2.34 ppm in C_6D_6).[15] Next, amide coordinates to the active species in an η^2 fashion using the C═O π electrons to give **B**, followed by germyl migration to the oxygen atom to generate **C**. A similar silyl migration to nitrile nitrogen in a transition-metal coordination sphere has been proposed for the reaction of $CpFe(CO)_2Me$ with R_3SiH and RCN[16] and for reactions of $CpFe(CO)_2Me$ and $CpMo(CO)_3Me$ with R_3SiH and R_2NCN.[17] Dissociation of the oxygen in **C** from the iron and subsequent C−O oxidative addition of the ligand to Fe forms the Fischer-type carbene complex **D**. The analogous iron complex with thiogermoxy and carbene ligands has been isolated and characterized as mentioned above. If E−H bond addition of R_3EH to the Fe═C double bond occurs, complex **E** will be formed. A similar addition of silane to a carbene complex has been proposed.[18] Reductive elimination of $R_3E{-}O{-}GePh_2H$ from **E** gives **F**. Pannell and co-workers proposed a similar complex **F** as an intermediate in the formation of disiloxane by **1**.[11b] Although a stepwise mechanism is proposed in the progression from **D** to **F**, a concerted mechanism cannot be ruled out. Oxidative addition of a Ge−H bond in Ph_2GeH_2 toward **F** results in the formation of **G**. Subsequent reductive elimination of H and CH_2NMe_2 ligands yields NMe_3 with regeneration of **A**. $R_3E{-}O{-}GePh_2H$ formed in this cycle can be involved in the catalytic cycle in place of Ph_2GeH_2 to finally give $R_3R{-}O{-}GePh_2{-}O{-}ER_3$. In the reaction of $CpFe(CO)_2Me$ with $(alkyl)_2GeH_2$ and DMF where R_3EH does not exist, a complex corresponding to **D** reacts with $(alkyl)_2GeH_2$ to give $(alkyl)_2HGe{-}O{-}Ge(alkyl)_2H$. This compound is subsequently involved in the catalytic cycle to finally give the six-membered cyclic germoxane.

In summary, $CpFe(CO)_2Me$ was found to be a good precursor for dehydrogenative oxygenation of $(alkyl)_2GeH_2$ in the reaction with DMF to form six-membered cyclic germoxanes. The iron complex also works as a precursor of selective preparation of the E−O−Ge−O−E backbone (E = Si, Ge, Sn) in the reaction of Ph_2GeH_2 with R_3EH in DMF. This is the first example of the selective preparation of compounds in which five group 14 elements and oxygen are used and in which the elements are arrayed linearly and alternately. The catalytic cycle including an iron carbene complex was proposed on the basis of the isolation and characterization of the iron carbene complex bearing the thiogermoxyl ligand prepared in the reaction of an iron germyl complex with thioformamide. The findings presented here will open a new field of material chemistry of E−O−E′ compounds (E, E′ = Si, Ge, Sn) that has not yet been

Scheme 3. Proposed Catalytic Cycle



thoroughly explored and will have a strong impact on well-investigated silicon chemistry.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Text giving detailed experimental procedures and the characterization data for the products and a CIF file giving crystallographic data for **8**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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