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Review

Serendipitous reactions involving a silicone grease

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The manuscript is dedicated to Professor Ionel Haiduc on the occasion of his 78th birthday.

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ABSTRACT

This review describes serendipitous reactions of silicone grease that were published after 2003 when the previous review had appeared. The products unexpectedly obtained generally contain Me_2SiO units that arise by degradation of silicone grease, some of which have cage-like structures and are difficult to prepare by well-planned synthetic approach.

1. Introduction

Silicone grease is translucent with pasty texture, hydrophobic, extremely low volatile, odorless, nonflammable, not dangerous to human health based on the safety data sheet available, and consists principally of polydimethylsiloxane (>80%), dimethylcyclosiloxane (<1%, various ring sizes) and hydroxy-terminated dimethylsiloxane (*ca.* 5–10%) [1], which is therefore generally recognized as a dimethyldisiloxane polymer, $(Me_2SiO)_n$. Silicone grease is commonly used to seal joints of glassware for manipulating air- and moisture-sensitive compounds or to keep the system under vacuum because of its less reactive nature resulting from strong silicon—oxygen bonds, even though certain strong acids or bases are not compatible because of the decomposition of the polymer to afford fragments with low molecular weights, which contain $Me_3Si[OSi(Me)_2]_xOSiMe_3$, as determined by mass spectrometry and IR spectra [2]. On the other hand, the selective cleavage of silicon—oxygen bonds, which is of current interest in terms of the conversion of abundant silicates to organosilicon compounds [3], requires alkaline- or metal-mediated conditions [4], fluoride catalysts [5] or enzymes [6]. With this in mind, it appears to be unnecessary to consider the possibility that silicon grease is involved in a reaction to afford a compound with siloxane frameworks, and the ^1H NMR spectrum of the reaction mixtures often contains a singlet signal due to the unreacted silicone grease, which is soluble in common organic solvents [7]. However, such unexpected or undesirable reactions take place to introduce Me_2SiO units derived from silicone grease, and a comprehensive review

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was already published in 2004 [8]. This review focuses on the reactions involving silicone grease in the last decade.

2. Involvement of silicone grease with group 2 compounds

The Grignard reagents are strong bases that are not compatible with silicone grease. After silicone grease was dissolved in a diethyl ether solution of phenylmagnesium bromide at 277 K, the reaction mixture was left with hexane for 5 months to afford colorless air-sensitive crystals. The X-ray diffraction analysis revealed that the product is $[Mg_2Br_2(PhMe_2OSi)_2(Et_2O)_2]$ **1**, which was formed through the degradation of a silicone grease (Chart 1) [9].

Reaction of $(Ph_4P)_2[Be_2Cl_6]$ with silicone grease or $(Me_2SiO)_3$ in dichloromethane afforded tetramethyl-trioxosilanato complex $(Ph_4P)_2[Be_4Cl_6(OSiMe_2OSiMe_2O)_2]$ **2** as colorless and moisture sensitive crystals. In the molecular structure of **2**, the four beryllium atoms are bridged by the terminal oxygen atoms of the $(OSiMe_2OSiMe_2O)^{2-}$ ligands to construct Be_2O_2 four-membered rings (Chart 2) [10].

In the reaction of HOdbp (2,6-dibenzylphenol) with strontium metal in the presence of a catalytic amount of mercury at 180 °C to prepare $Sr(Odbp)_2$, a few small diamond-shaped crystals of a strontium phenolate-siloxane cluster-like complex, $[Sr_9(Odbp)_8(O_2SiMe_2)_4(OH)_2(THF)_6(OH_2)_2]\cdot 6THF$ **3** were obtained after leaving a crude product containing $Sr(Odbp)_2$ with silicone grease to seal ground glass joints in THF for several weeks (Chart 3) [11].

3. Involvement of silicone grease with group 13 compounds

When carbodiphosphorane $Ph_3P{=}C{=}PPh_3$ was treated with $InMe_3$ in THF, the corresponding Lewis acid–base adduct, $Me_3In[C(PPh_3)_2]$, was formed in 90% yield. However, during attempt to crystallize the product from a mixture of THF and pentane in the presence of silicone grease, a few crystals of $[HC(PPh_3)_2][Me_2In(OSiMe_2OSiMe_2O)]$ **4** were also obtained and its molecular structure was finally established by X-ray diffraction analysis (Chart 4) [12].

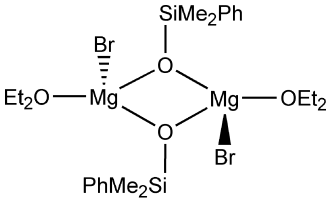

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Chart 1. Adduct of silicone grease and phenylmagnesium bromide.

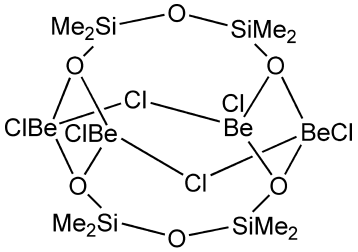

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Chart 2. Cage compound **2** formed from silicone grease and $(Ph_4P)_2[Be_2Cl_6]$.

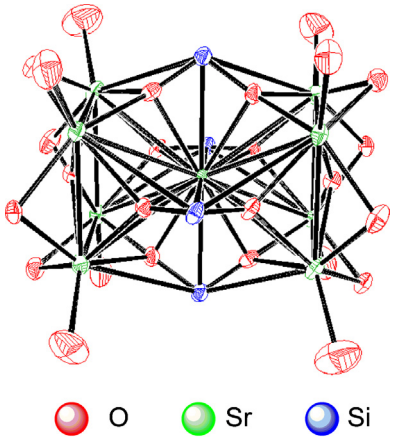


Chart 3. Central framework of nonnuclear Sr complex **3**.

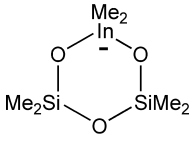
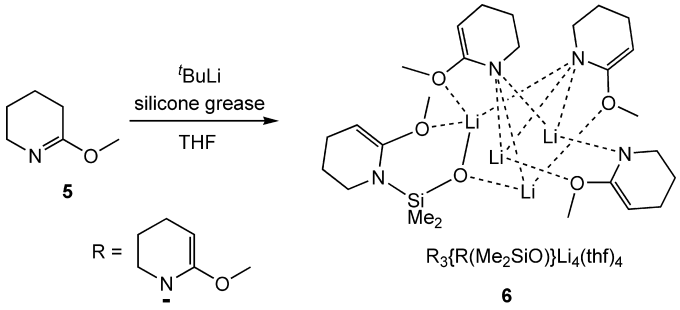


Chart 4. An anionic moiety of compound **4**.

4. Involvement of silicone grease with group 14 compounds

Treatment of a THF solution of *o*-methylvalerolactim ether **5** with *t*-BuLi resulted in the formation of a bright yellow solution, and removal of volatile substances afforded a viscous yellow oil. Recrystallization of the crude product from hexane provided colorless prismatic crystals. The crystals were identified as lithiated aza-enolate derivative $R_3\{R(Me_2SiO)\}Li_4(thf)_4$ **6** (35% yield), ($R = C_6H_{10}NO$) by X-ray diffraction analysis (Scheme 1) [13]. Incorporation of a Me_2SiO moiety is reasonably interpreted by involvement of Me_2SiO^- anion, generated through decomposition of silicone grease. However, attempts to reproduce the results by deliberate addition of silicone grease into the reaction mixture were not successful.

During an attempt to obtain a cyclic selenium cation, $Se_6Ph_2^{2+}$ from $Se_4(AsF_6)_2$, $Li[Al\{OC(CF_3)_3\}_4]$ (2 equiv.) and Se_2Ph_2 in the presence of silicone grease, colorless crystals of $LiD_6[Al\{OC(CF_3)_3\}_4]$ (D_n = *cyclic*-$(Me_2SiO)_n$) **7a** were unexpectedly isolated and characterized by X-ray diffraction analysis (Chart 5) [14]. The lithium atom situated in the center of the ring is coordinated by four oxygen atoms, and the compound can be regarded as a pseudo sila-crown ether, where each of the oxygen atoms is bonded to two dimethylsilylene units. The compound **7a** was alternatively prepared by the reaction of D_6 with $Li[Al\{OC(CF_3)_3\}_4]$ in 95% yield (Scheme 2). Using D_5 instead of D_6 provided the



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Scheme 1. Involvement of silicone grease in the reaction of valerolactim ether **5**.