

Reviews

Silicone Grease: A Serendipitous Reagent for the Synthesis of Exotic Molecular and Supramolecular Compounds

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A review describing a series of (mostly accidental) intriguing reactions of silicone grease with various highly polar organometallic reagents is presented. The products are unusual and unexpected (sometimes supramolecular) compounds, incorporating various fragments of the parent polysiloxane chain, such as disiloxane or other oligosiloxane units, $(\text{OSiMe}_2)_n\text{O}$ ($n = 2, 3$, etc.), dimethylsilanone Me_2SiO , dimethylsilylene Me_2Si , and other methylsilicon moieties.

1. Introduction

Silicone grease is a dimethylsiloxane polymer, $(\text{Me}_2\text{SiO})_x$, that is routinely used in the laboratory for sealing ground glass joints in glassware used in synthesis, often in the synthesis of air- and moisture-sensitive organometallic compounds. Silicone grease generally is regarded as chemically inert toward most common reagents and solvents, and little consideration usually is given to the possibility that it might become involved in the reactions performed when it is used. It is partially soluble in organic media, and organic solvents with which it comes in contact can extract it into the reaction mixture. No laboratory handbook seems to contain any warning about this possibility. The polar silicon–oxygen bond is known to be reactive toward both alkaline and acidic reagents, and in recent years several cases of serendipitous participation of silicone grease in a number of reactions have been reported. These are unwanted accidents, but the unexpected formation of some interesting, even exotic, compounds suggests that the subject deserves some attention. Indeed, following such incidents, in some cases the silicone grease was deliberately introduced in certain organometallic syntheses, as it proved to be a useful source of Me_2SiO units that were able to insert into various polar bonds. In other cases, the silicone grease provided poly(dimethylsiloxane) fragments with two or more silicon atoms, which were incorporated in the final product.

A number of intriguing examples of reactions in which silicone grease became involved as a reactant have been collected and are presented here. In several cases the products of these reactions are unexpected organometallic supermolecules, made up of two, four, or more self-assembled molecular units.¹ It can be seen from the

following presentation that a remarkable diversity of compounds has been obtained by this technique, suggesting that poly(dimethylsiloxane)s, as silicone grease or in other forms (vide infra), could be attractive candidates for exploration of new reactions. This article does not attempt to speculate about the mechanisms of the reactions presented nor to cover comprehensively the reactivity of polysiloxanes. Thus, when we speak of "dimethylsilanone insertion", this does not imply that monomeric Me_2SiO is involved as an intermediate. Emphasis is only upon silicone grease as a potential (mostly unintended) reagent.

Silicone grease is basically a linear polymer, consisting of chains of alternating dimethylsilylene units and oxygen atoms, $(-\text{SiMe}_2-\text{O}-)_x$, terminated in most cases with Si–OH groups. Other terminal groups also may be possible, e.g., OSiMe_3 units (a very small proportion). The composition of commercial samples may vary slightly depending on the manufacturer, due to various additives used. Silicone greases for use at higher temperature may also contain some MePhSiO units. Therefore, when available, information is given about the origin of the silicone grease product employed in the reactions cited below.

2. Siloxane Chain Cyclization into Silacrown Rings

Alkali metal ion host–guest complexes of organocyclosiloxanes could not be prepared directly from the components. Attempts to use $(\text{Me}_2\text{SiO})_n$ ($n = 7$ and 8) in reactions with Na^+ cations were unsuccessful,² but two such complexes have been isolated from accidental reactions of silicone grease with reactive basic reagents and one has been fully characterized by X-ray diffraction. The crown ligand in each case was tetradecameth-

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(1) Haiduc, I.; Edelman, F. T. *Supramolecular Organometallic Chemistry*; Wiley-VCH: Weinheim, New York, 1999.

(2) Yuzhelevskii, Yu. A.; Pchelintsev, V. V.; Fedoseeva, N. N. *Vysokomol. Soedin.* **1976**, *18B*, 873; *Chem. Abstr.* **1977**, *86*, 73181v.

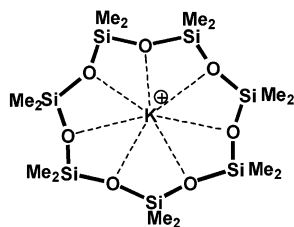


Figure 1. Crown ether type complexation of potassium by $(\text{Me}_2\text{SiO})_7$.

ylcycloheptasiloxane, which complexed a potassium cation, to form the silacrown ether complex $[\text{K}(\text{Me}_2\text{SiO})_7]^+$ (Figure 1). Thus, $[\text{K}(\text{Me}_2\text{SiO})_7]^+(\text{K}^+)_3\{[\text{InH}(\text{CH}_2\text{Bu}^t)_3]^- \}_4$ was obtained on crystallization of $\text{K}^+[\text{InH}(\text{CH}_2\text{Bu}^t)_3]^-$ from heptanes in the presence of adventitious silicone grease.³ In the second example $[\text{K}(\text{Me}_2\text{SiO})_7]^+[\text{K}\{\text{C}(\text{SiMe}_3)_2(\text{SiMe}_2\text{Vi})\}_2]^-$ was formed on attempted metalation of $\text{HC}(\text{SiMe}_3)_2(\text{SiMe}_2\text{Vi})$ with methylpotassium in methylcyclohexane/diethyl ether solvent mixture.⁴ The ring size of the silacrown ring formed probably is determined by a template effect of potassium.

3. Siloxane Chain Fragmentation and Incorporation of Di- and Trisiloxane Units

In the synthesis of barium bis(3,5-dimethylpyrazolate) from barium metal and 3,5-dimethylpyrazole (dmpz) in THF, an accidental reaction with silicone grease produced $[(\text{thf})_6\text{Ba}_6(\text{dmpz})_8(\text{OSiMe}_2)_2\text{O}]_2$, described as a molecule with six barium cations in a plane capped by two siloxane dianions (located above and below the plane) and framed by eight dmpz anions (Figure 2a).⁵ According to the basic concepts of supramolecular chemistry,¹ this in fact is a supermolecule, self-assembled from a hexametallal planar cluster and the disiloxane ligands. The compound was also obtained in a similar reaction using octamethylcyclotetrasiloxane, $(\text{Me}_2\text{SiO})_4$, deliberately introduced into the system.⁵

Silicone grease was attacked by thallium(I) ethoxide in toluene, to form a polymeric disiloxanolate complex, $[\{\text{Tl}_2(\text{OSiMe}_2)_2\text{O}\}_2]_x$, containing Tl_4O_4 cuboidal units, interconnected through double disiloxane bridges (Figure 2b).⁶

N-Trimethylsilyltriethylphosphanimine, $\text{Me}_3\text{Si}-\text{N}=\text{PEt}_3$, reacted with potassium hydride in the presence of silicone grease (Baysilon) in the absence of solvent to form a disiloxane complex which could be extracted with THF and crystallized. X-ray analysis of the product established that it is a centrosymmetric dimer of composition $[\text{K}_4(\text{THF})_3(\text{Me}_3\text{SiNPEt}_2)_2(\text{OSiMe}_2)_2\text{O}]_2$, containing two pentagonal prismatic $\text{K}_4\text{P}_2\text{N}_2\text{O}_2$ units interconnected through disiloxane bridges (Figure 2c).⁷ The formation of this compound was explained in terms

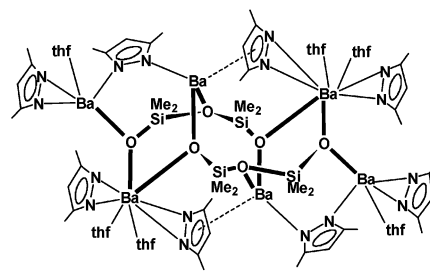
(3) Churchill, M. R.; Lake, C. H.; Chao, S. H. L.; Beachley, O. T., Jr. *J. Chem. Soc., Chem. Commun.* **1993**, 1577.

(4) Eaborn, C.; Hitchcock, P. B.; Izod, K.; Smith, J. D. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2936.

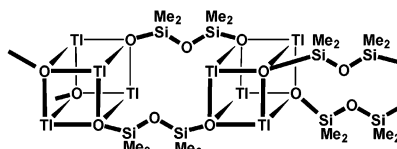
(5) Steiner, A.; Lawson, G. T.; Walford, B.; Leuser, D.; Stalke, D. *J. Chem. Soc., Dalton Trans.* **2001**, 219.

(6) Harvey, S.; Lappert, M. F.; Raston, C. L.; Skelton, B. W.; Srivastava, G.; White, A. H. *J. Chem. Soc., Chem. Commun.* **1988**, 1216.

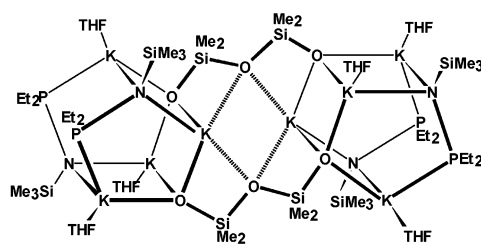
(7) Chitsaz, S.; Neumüller, B.; Dehnicke, K. *Z. Anorg. Allg. Chem.* **2003**, *629*, 592.



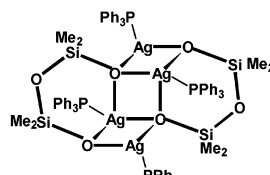
(a) (ref. 5)



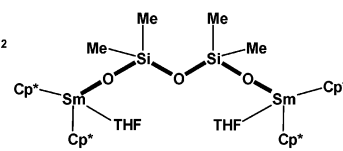
(b) (ref. 6)



(c) (ref. 7)



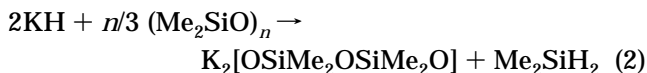
(d) (ref. 8)



(e) (ref. 9)

Figure 2. Structure diagrams of compounds incorporating disiloxane units.

of two simultaneous reactions:

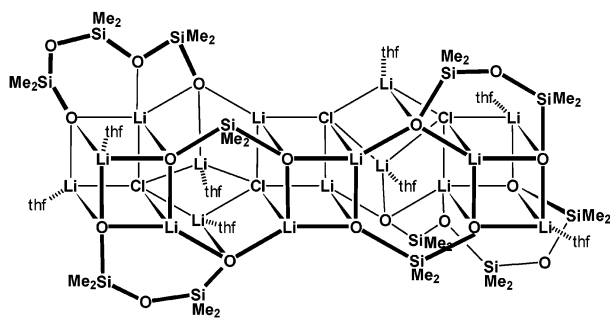


An unusual feature of this structure is the coordination of both terminal and bridging oxygen atoms of the disiloxane units to potassium cations.

The reaction of the tetrameric silver complex $[\text{Ag}(\text{C}_6\text{H}_4\text{CH}_2\text{NMe}_2)_2]_4$ with triphenylphosphine in the presence of adventitious silicone grease resulted in the formation of a tetranuclear silver disiloxane complex, $[(\text{AgPPh}_3)_2(\text{OSiMe}_2)_2\text{O}]_2$, based upon a ladder-like tricyclic core Ag_4O_4 (Figure 2d).⁸

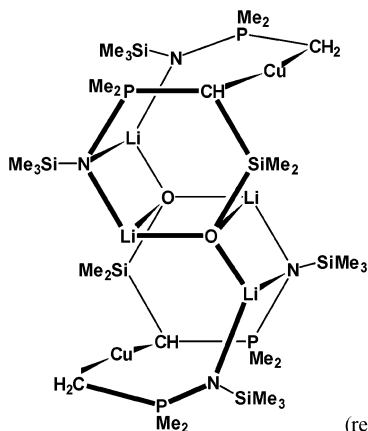
Dimeric bis(pentamethylcyclopentadienyl)samarium hydride, $[(\text{C}_5\text{H}_5)_2\text{SmH}]_2$, dissolved in THF, in the presence of silicone grease (from Dow Corning) said to contain cyclosiloxanes, produced a disiloxane derivative, $[\text{Cp}^*_2\text{Sm}(\text{THF})_2(\text{OSiMe}_2)_2\text{O}]$, in quantitative yield (Figure 2e). The disiloxane could also be prepared deliberately (88% yield) in a reaction of $[(\text{C}_5\text{H}_5)_2\text{SmH}]_2$ with

(8) Edwards, D. A.; Harker, M.; Mahon, M. F.; Molloy, K. C. *J. Chem. Soc., Dalton Trans.* **1997**, 3509.



(ref. 10)

Figure 3. Structure diagram of $[\text{Li}_{16}(\text{OSiMe}_2\text{OSiMe}_2\text{-OSiMe}_2\text{O})_2(\text{OSiMe}_2\text{OSiMe}_2\text{O})_2(\text{OSiMe}_2\text{O})_2\text{Cl}_4]$.



(ref. 11)

Figure 4. Structure diagram of $[\text{Li}\{\text{Me}_3\text{SiNPMe}_2\text{CH}_2\text{-CuCH}(\text{PMe}_2\text{NSiMe}_3)(\text{SiMe}_2\text{OLi})\}]_2$.

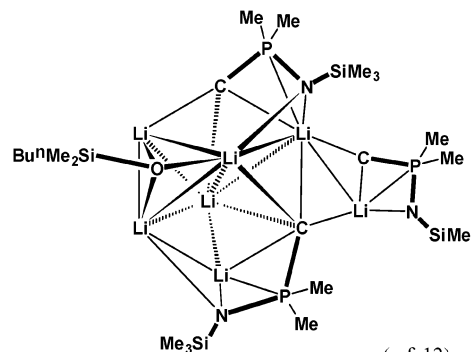
hexamethylcyclotrisiloxane, $(\text{Me}_2\text{SiO})_3$, but could not be obtained directly from silicone grease.⁹

In the reaction between Me_2GaCl with Bu^tAsLi_2 (1:1 molar ratio) a 16-nuclear lithium complex, $[\text{Li}_{16}(\text{OSiMe}_2\text{-OSiMe}_2\text{OSiMe}_2\text{O})_2(\text{OSiMe}_2\text{OSiMe}_2\text{O})_2(\text{OSiMe}_2\text{O})_2\text{Cl}_4]$, incorporating both disiloxane and trisiloxane fragments in addition to OSiMe_2O units (but no organogallium or -arsenic moieties!) was obtained (48% yield) as a result of accidental silicone grease participation.¹⁰ The structure of this compound is a unique condensed system of rings and heterocubane units shown in Figure 3.

4. Dimethylsilanone Insertion into M–X Bonds

Lithiated phosphanimines react with silicone grease by inserting dimethylsilanone units, Me_2SiO , into C–Li bonds. Thus, $[\text{LiCH}_2\text{PMe}_2\text{NSiMe}_3]_4$ reacted with copper(I) chloride in the presence of silicone grease (Baysilon) to form a dimeric complex, $[\text{Li}\{\text{Me}_3\text{SiNPMe}_2\text{CH}_2\text{CuCH}(\text{PMe}_2\text{NSiMe}_3)(\text{SiMe}_2\text{OLi})\}]_2$, as a result of formal dimethylsilanone insertion into a C–Li bond (30% yield based on CuCl). This compound is a dimeric supermolecule built around a ladder made of a central Li_2O_2 planar ring and two fused Li_2NO rings (Figure 4).¹¹

It is assumed that the lithium derivative of the carbodianion $[\text{Li}_2\text{CHPMe}_2\text{NSiMe}_3]$ is formed first as an intermediate which reacts with the polysiloxane. Such a carbodianion has been observed in the reaction of the



(ref. 12)

Figure 5. Structure diagram of the $\text{Li}_7(\text{CHPMe}_2\text{NSiMe}_3)_3\text{-}(\text{OSiMe}_2\text{Bu}^n)$ unit (only half of the dimeric supermolecule is shown for clarity).

silylated phosphanimine $\text{Me}_3\text{P}=\text{N}-\text{SiMe}_3$ with butyllithium and MCl_2 ($\text{M} = \text{Co}, \text{Zn}$) in the presence of silicone grease, leading to the formation of a polynuclear dimeric complex, $[\text{Li}_7(\text{CHPMe}_2\text{NSiMe}_3)_3(\text{OSiMe}_2\text{Bu}^n)]_2$, also as a result of dimethylsilanone insertion.¹² The complex has an intricate structure based upon a Li_{14} cluster. The $\text{Li}_7(\text{CHPMe}_2\text{NSiMe}_3)_3(\text{OSiMe}_2\text{Bu}^n)$ unit is shown in Figure 5, to illustrate the insertion of the $\text{Bu}^n\text{Me}_2\text{SiO}$ moiety. The reaction mechanism is not known, but probably monomeric silanone *as such* is not involved.

Other examples are known, illustrated in Figure 6. A formal dimethylsilanone insertion into a Li–C bond occurs when 1-naphthyllithium comes in contact with silicone grease (Rhône Poulenc) in a pentane solution on long standing at room temperature, to form hexameric $[\text{LiOSiMe}_2\text{Np}]_6$ ($\text{Np} = \text{naphthyl}$). The molecular structure (established by X-ray diffraction) is based upon a distorted Li_6 octahedron, with $\mu^3\text{-OSiMe}_2\text{Np}$ groups centered above six of the eight faces of the octahedron, and contains strong Li–Li bonds (2.47 vs 2.67 Å in the Li_2 molecule) (Figure 6a).¹³

Lithiated 2-amino-6-methylpyridine reacts with silicone grease (deliberately introduced) in diethyl ether at 0 °C to form a tetranuclear complex, $[\text{Li}_4(\text{C}_5\text{H}_3\text{-NMeNHSiMe}_2\text{O})_4]$, in 60% yield, as a result of dimethylsilanone insertion into Li–N bonds. The compound is based on a pseudocubane Li_4O_4 core, each lithium atom being part of a six-membered LiOSiNCN chelate ring (Figure 6b).¹⁴

Insertion of dimethylsilanone units into Li–P bonds occurred when LiPEt_2 was stored in diethyl ether solution for several months at –20 °C, in accidental contact with silicone grease (Dow Corning). The product is a hexagonal prismatic hexamer, $[\text{LiOSiMe}_2\text{PEt}_2]_6$ (Figure 6c).¹⁵

Dimethylsilanone insertion into a Mg–N bond occurred on reaction of $[\text{Mg}(\text{NHC}_6\text{H}_4\text{AsMe}_2\text{-2})(\text{THF})_{1.5}]$ with silicone grease, resulting in the formation of $[\{\text{Mg}_2(\mu^2:\eta^1\text{-NHC}_6\text{H}_4\text{AsMe}_2)_2(\mu^3:\eta^2\text{-OSiMe}_2\text{NC}_6\text{H}_4\text{AsMe}_2)\text{-}$

(11) Neumüller, B.; Müller, A.; Dehnicke, K. *Z. Anorg. Allg. Chem.* **2002**, *628*, 100.

(12) Müller, A.; Neumüller, B.; Dehnicke, K.; Magull, J.; Fenske, D. *Z. Anorg. Allg. Chem.* **1997**, *623*, 1306.

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(14) Jones, C.; Junk, P. C.; Leary, S. G.; Smithies, N. A. *J. Chem. Soc., Dalton Trans.* **2000**, 3186.

(15) Jones, R. A.; Koschmieder, S. U.; Atwood, J. L.; Bott, S. G. *J. Chem. Soc., Chem. Commun.* **1992**, 726.

(9) Evans, W. J.; Ulibarri, T. A.; Ziller, J. W. *Organometallics* **1991**, *10*, 134.

(10) Iravani, E.; Dashti-Mommertz, A.; Neumüller, B. *Z. Anorg. Allg. Chem.* **2003**, *629*, 1136.

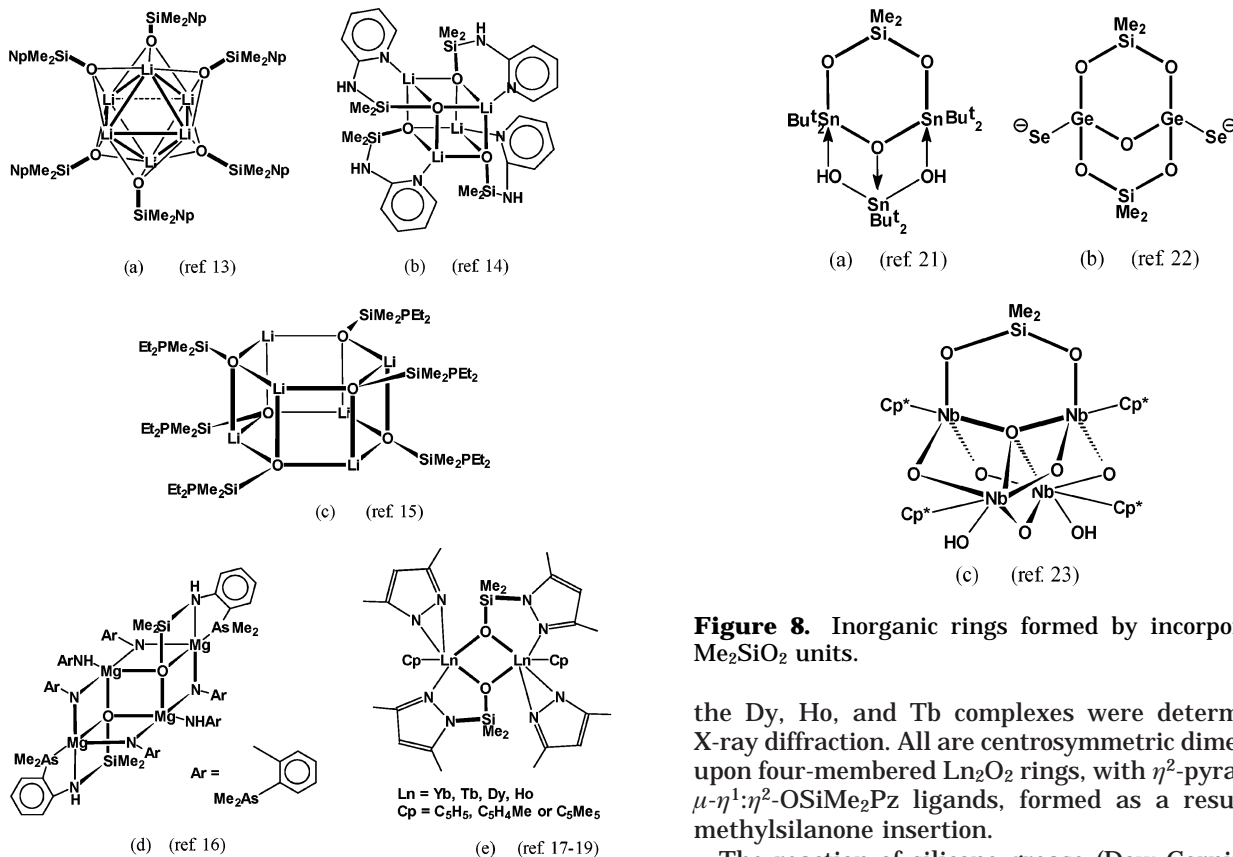


Figure 6. Structure diagrams of compounds formed by insertion of dimethylsilanone.

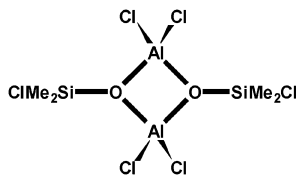


Figure 7. Structure diagram of $[\text{Cl}_2\text{AlOSiMe}_2\text{Cl}]_2$.

(THF) $_2$] (Figure 6d). In this accidental reaction the yield was 16%, but deliberate introduction of silicone grease into the reaction mixture raised the yield to 67% (based on Me_2SiO polymer).¹⁶

Several compounds resulting from dimethylsilanone insertion into lanthanide–nitrogen bonds have been prepared by deliberate use of silicone grease in reactions with pyrazole organolanthanide complexes, after the first observation of such an accidental reaction. Thus, $[(\eta^5\text{-C}_5\text{H}_4\text{Me})\text{Yb}(\text{3,5-Me}_2\text{Pz})_2]$, on recrystallization from a THF solution contaminated with silicone grease, afforded $[(\eta^5\text{-C}_5\text{H}_4\text{Me})\text{Yb}(\text{3,5-Me}_2\text{Pz})(\text{3,5-Me}_2\text{PzSiMe}_2\text{O})]_2$ (26% yield), whose molecular structure (Figure 6e, $\text{Ln} = \text{Yb}$, $\text{Cp} = \text{C}_5\text{H}_4\text{Me}$) was established by X-ray diffraction.¹⁷ Following this observation, high-vacuum silicone grease (made in China) was deliberately used as a reagent in the synthesis of a series of similar lanthanide complexes, with $\text{Ln} = \text{Nd}$, Gd , Dy , Ho , Sm , Tb (yields between 35 and 50%),^{18,19} and the crystal structures of

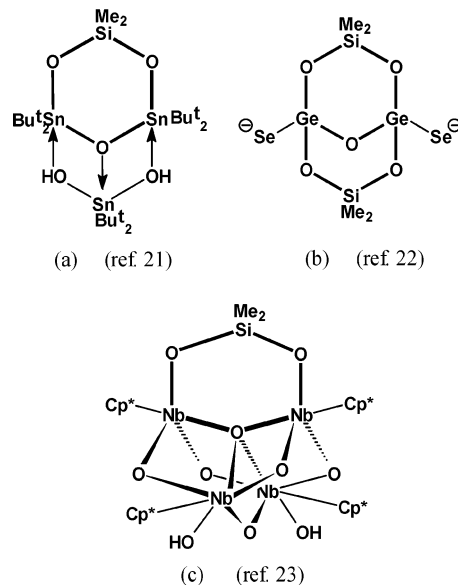


Figure 8. Inorganic rings formed by incorporation of Me_2SiO_2 units.

the Dy, Ho, and Tb complexes were determined by X-ray diffraction. All are centrosymmetric dimers based upon four-membered Ln_2O_2 rings, with η^2 -pyrazole and $\mu\text{-}\eta^1\text{:}\eta^2\text{-OSiMe}_2\text{Pz}$ ligands, formed as a result of dimethylsilanone insertion.

The reaction of silicone grease (Dow Corning) with anhydrous aluminum chloride in 1:1 Al:Si ratio (in hexane at room temperature), which produced $[\text{Cl}_2\text{AlO-SiMe}_2\text{Cl}]_2$ in 84% yield,²⁰ can also be regarded formally as a dimethylsilanone insertion into the Al–Cl bond. The structure (Figure 7) was established by single-crystal X-ray diffraction. This reaction could be useful for the reprocessing (recycling) of silicone polymer wastes. The hydrolysis of $[\text{Cl}_2\text{AlOSiMe}_2\text{Cl}]_2$ on an aluminum surface gave a coating of silicone oil interspersed with hydrated aluminum chloride.²⁰

5. Inorganic Ring Formation through Incorporation of Me_2SiO_2 Units

An attempt to prepare $\text{Bu}^t_2\text{Sn}[\text{Pb}(\text{Mes})_3]_2$ ($\text{Mes} = \text{mesityl}$) by reaction of $\text{Bu}^t_2\text{SnCl}_2$ with LiPbMes_3 resulted in isolation of a tricyclic stannasiloxane, identified by single-crystal X-ray diffraction as a self-assembled supramolecular adduct of $[(\text{Bu}^t_2\text{Sn})_2(\mu\text{-O})(\mu\text{-Me}_2\text{SiO}_2)]$ with $\text{Bu}^t_2\text{Sn}(\text{OH})_2$ (Figure 8a). In the absence of silicone grease the reaction product was $(\text{Bu}^t_2\text{SnO})_3$. In both cases the adventitious presence of oxygen was responsible for the formation of the stannoxane and the silicone grease provided the organosilicon moiety.²¹

A bicyclic anionic system of two fused Ge_2SiO_3 rings was formed (in 19% yield) in the reaction of potassium metal dissolved in liquid ammonia, with [2.2.2]-cryptand and GeSe_2 at low temperature (-77°C),

(19) (a) Zhou, X.; Huang, Z.; Cai, R.; Zhang, L.; Zhang, L.-X. *Organometallics* **1999**, *18*, 4128. (b) Zhou, X.; Huang, Z.; Cai, R.; Zhang, L.; Liu, Y.; Duan, C. *Synth. React. Inorg. Met.-Org. Chem.* **2000**, *30*, 649.

(20) Alexander, M. R.; Mair, F. S.; Pritchard, R. G.; Warren, J. E. *Appl. Organomet. Chem.* **2003**, *17*, 730.

(21) Cervantes-Lee, F.; Sharma, H. K.; Haiduc, I.; Pannell, K. H. *J. Chem. Soc., Dalton Trans.* **1998**, 1.

(16) Cole, M. L.; Jones, C.; Junk, P. C. *New J. Chem.* **2002**, *26*, 89.

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(18) Zhou, X.; Ma, H.; Huang, Z.; Cai, R.; You, X.; Huang, X. J. *Organomet. Chem.* **1997**, *545–546*, 309.

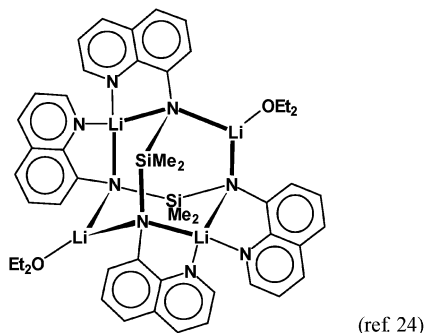


Figure 9. Adamantane structure formed by incorporation of Me_2Si units.

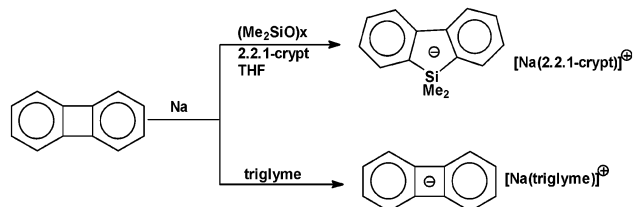


Figure 10. Anion formed by incorporation of a Me_2Si unit.

silicone grease being the source of Me_2SiO_2 units. The crystal structure (Figure 8b) of the resulting $[\text{K}^+(2.2.2\text{-crypt})]_2[\text{Ge}_2(\mu\text{-O})(\mu\text{-Me}_2\text{SiO}_2)_2(\text{Se}^-)_2]$ was established by X-ray diffraction.²²

An intricate polycyclic structure (Figure 8c) was identified by X-ray diffraction, in the compound $[(\eta^5\text{-C}_5\text{Me}_5\text{Nb})_4(\text{OH})_2(\mu\text{-O})_5(\mu_4\text{-O})(\mu\text{-Me}_2\text{SiO}_2)]$, formed during an oxidation reaction of $[\eta^5\text{-C}_5\text{Me}_5\text{Nb}(\mu\text{-Cl})(\mu\text{-O})_3]$ in the presence of adventitious silicone grease.²³ The compound contains a Nb_2SiO_3 ring fused to three Nb_2O_2 rings in an unusual configuration.

6. Incorporation of Dimethylsilylene Groups

During attempted lithiation of 8-aminoquinoline with $n\text{-BuLi}$ in diethyl ether, at 0°C , a red compound of composition $\{[(\text{NC}_9\text{H}_6\text{N})_2\text{SiMe}_2]\text{Li}_2(\text{OEt}_2)\}_2$, with an adamantane skeleton $\text{Li}_4\text{Si}_2\text{N}_4$ (Figure 9), was isolated. The SiMe_2 group originates from silicone grease, and the compound also could be prepared by reaction of $\text{Me}_2\text{Si}(\text{NHC}_9\text{H}_6\text{N})_2$ with n -butyllithium in diethyl ether, in the absence of silicone grease.²⁴

The treatment of biphenylene with sodium metal in THF, in the presence of [2.2.1]-cryptand and silicone grease, resulted in ring expansion with formation of a silafluorene anion. In the absence of silicone grease, biphenylene reacts with sodium metal in triglyme to form just the anion of biphenylene (Figure 10).²⁵

7. Incorporation of Trimethylsiloxy Groups

In some cases, reactions with silicone grease result in incorporation of trimethylsiloxy units, OSiMe_3 , into the final product. It is not clear whether the OSiMe_3

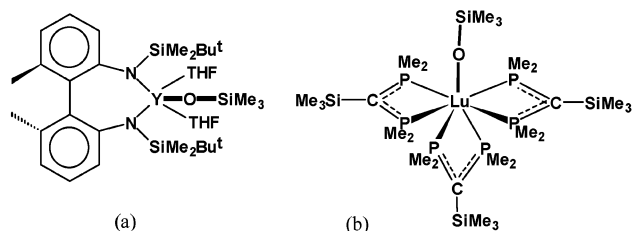
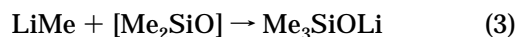


Figure 11. Compounds formed by incorporation of Me_2SiO units.

units are present in the silicone grease (as end groups of the siloxane chains) or, more likely, are formed during the reaction, by attack of methyllithium on silicone grease:



The lithium trimethylsilanolate thus formed may then react with an organometallic halide.

This case is illustrated by the formation of a trimethylsiloxy derivative of an yttrium amido complex in an attempted methylation of the corresponding chloride with methyllithium in the presence of silicone grease (Dow Corning). The compound formed (in 50% yield) by replacement of chlorine with OSiMe_3 groups contains a nearly linear $\text{Y}-\text{O}-\text{Si}$ bond (175.5°) (Figure 11a).²⁶

The reaction of $[\text{Lu}(\text{THF})\{\text{C}(\text{PMe}_2)_2(\text{SiMe}_3)\}_3]$ with methyllithium sometimes gave, in a random way but in good yield, in the presence of silicone grease, the seven-coordinate lutetium compound $[\text{Li}(\text{THF})_4][\text{Lu}(\text{OSiMe}_3)\{\text{C}(\text{PMe}_2)_2(\text{SiMe}_3)\}_3]$, as a result of OSiMe_3 group incorporation (Figure 11b). The usual product of the reaction is the six-coordinate complex $[\text{LuMe}(\text{THF})\{\text{C}(\text{PMe}_2)_2(\text{SiMe}_3)\}_2]$. The $\text{Lu}-\text{O}-\text{Si}$ bond is practically linear (174.4°).²⁷

8. Conclusions and Outlook

It is obvious from the examples cited that the reactions of silicone grease require highly polar compounds, organometallic anions and carbanions being the aggressive, active species. Two practical conclusions emerge from the above presentation:

(a) If incorporation of an organosilicon moiety into the final product in a reaction of polar organometallic reagents is undesirable, care must be exercised about the possible contamination with silicone grease.

(b) Interesting and unpredictable novel compounds, which in most cases cannot be prepared by design, can be obtained by reacting organosiloxanes with polar organometallic reagents.

Certainly, such reactions can be extended to polyorganosiloxanes other than silicone grease (a polymer), in particular to cyclosiloxanes (cyclic oligomers). Indeed, octamethylcyclotetrasiloxane can (sometimes) furnish the same products as the polymeric siloxane, as mentioned above.⁵ In another example cited above,⁹ hexamethylcyclotrisiloxane, $(\text{Me}_2\text{SiO})_3$, was used as a source of siloxane fragments instead of silicone grease, which did not react. The cyclic trimer is known as a very

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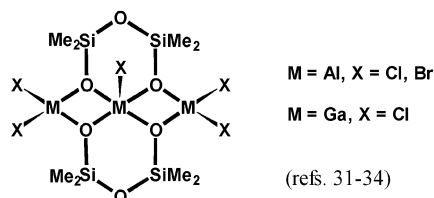


Figure 12. Chemical diagram of tetracyclic $[M_3X_5(OSiMe_2-OSiMe_2O)_2]$.

reactive siloxane, and the strained six-membered ring can easily undergo ring opening and cleavage reactions. The ring strain is caused by the Si–O–Si bond angles of 136° , compared with the higher value of 142.5° in the tetramer.²⁸ Probably, both the tetramer and the linear poly(dimethylsiloxane) polymer are strain free. This suggests that the reactivity of dimethylsiloxanes in reactions of the types cited above could be finely tuned, by deliberately using the readily available trimer or tetramer in addition to, or instead of, the polymeric silicone grease. This idea is well supported by a detailed study of the cleavage of permethylcyclodioxanes $(Me_2SiO)_n$ ($n = 3, 4, \text{ and } 5$) and linear siloxanes $Me_3SiOSiMe_3$ and $Me_3Si(OSiMe_2)_2OSiMe_3$, with dialkylaluminum hydrides R_2AlH ($R = Me, Bu^i, Bu^t$), which gave different products for each siloxane.²⁹ On the other hand, the reaction of $[(Mes^*)AlH(\mu-H)]_2$ with the cyclotrisiloxane $(Me_2SiO)_3$ produced $[(Mes^*)Al(\mu-O)]_4$, without incorporation of organosilicon units.³⁰ The reactions of poly(dimethylsiloxanes), cyclic or linear, with $AlCl_3$, $AlBr_3$, $AlMe_3$, and $GaCl_3$ also gave interesting organometallosiloxanes, e.g., tetracyclic $[M_3X_5(OSiMe_2-OSiMe_2O)_2]$ ($M = Al, Ga; X = Cl, Br$; Figure 12).^{31–34}

In this context it is worth remembering that organocyclodioxanes are well known to be reactive compounds

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and to show a great propensity for redistribution (equilibration) reactions and ring cleavage reactions with numerous reagents, including inorganic and organometallic compounds.³⁵ This article is not intended as a review of such reactions. Perhaps some, especially those with metal reagents, deserve a reinvestigation with modern techniques, to establish the nature of the compounds formed.

It can be anticipated that much interesting new chemistry can be explored using reactions of cyclic and linear polymeric siloxanes with polar organometallic, carbanionic and related reagents. Such chemistry may be relevant for better understanding the structure and behavior of silica-supported organometallic catalysts³⁶ and could enrich the already spectacular chemistry of metallasiloxanes.³⁷ It is also worth mentioning that silicone grease (Dow Corning) has been reported as a powerful catalyst for the polymerization of gaseous diazomethane to give polymethylene.³⁸

Probably other serendipitous reactions of silicone grease have been encountered in various laboratories but were discarded unreported, as undesirable accidents. Possibly, some other published reports may have escaped my attention. I would be grateful to anyone who could provide me with any additional examples.

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Note Added in Proof. Two more references reporting silicone grease reaction products have been identified after this paper was accepted for publication. The two papers describe $[Ph_3P(CH)PPh_3]^+[Me_2In(OSiMe_2O-SiMe_2O)]^-$ (containing a monocyclic anion)³⁹ and $[Co_4(\mu_3-NPEt_3)_2(HNPEt_3)_2(OAc)_2(OSiMe_2OSiMe_2O)_2]$ (based upon a ladder structure and CoO_3Si_2 rings).⁴⁰

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