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Heavier Ketones

Chemical Tricks To Stabilize Silanones and Their Heavier Homologues with E=O Bonds (E = Si–Pb): From Elusive Species to Isolable Building Blocks

*Yun Xiong, Shenglai Yao, and Matthias Driess**

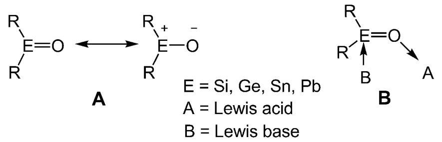
carbonyl compounds · germanium · main group elements · multiple bonds · silicon

Dedicated to Prof. Heinrich Nöth on the occasion of his 85th birthday

In contrast to the well-established chemistry of ketones ($R_2C{=}O$), the reactivity of the elusive heavier congeners $R_2E{=}O$ (E = Si, Ge, Sn, Pb) is far less explored because of the high polarity of the E=O bonds and hence their tendency to oligomerize with no activation barrier. Very recently, great advances have been achieved in the synthesis of isolable compounds with E=O bonds, including the investigation of donor-stabilized isolable silanones and the first stable "genuine" germanone. These compounds show drastically different reactivities compared to ketones and represent versatile building blocks in silicon–oxygen and germanium–oxygen chemistry. This and other exciting achievements are described in this Minireview.

1. Introduction

Ketones ($R_2C{=}O$), because of their carbonyl group, represent one of the most important building blocks in organic synthesis, and are produced on massive scales in industry for solvents, polymer precursors, and pharmaceuticals. Their remarkable stability with respect to oligomerization is due to the relatively small polarity of the carbonyl group (electronegativity on the Pauling scale: carbon 2.5, oxygen 3.5) and the almost same strength of the C=O σ and π bonds. In contrast, the drastically smaller electronegativities of Si (1.7), Ge (2.0), Sn (1.7), and Pb (1.6) combined with the intrinsically weaker π bonds result in greater polarities of the respective E=O bonds (E = Si–Pb). Therefore, unlike carbonyl groups, such E=O moieties with their large zwitterionic character ($>E^{\delta+}\text{-}O^{\delta-}$; **A**) are unstable and readily undergo head-to-tail oligomerization reactions even at very low temperatures.[1] In other words, the synthesis of stable heavier congeners of ketones is a challenge. This was already recognized as early as the end of the 19th century, when Friedel and later on Kipping and co-workers attempted to synthesize an isolable silanone ($R_2Si{=}O$). They were facing the extraordinary high reactivity of the Si=O bond, which prevented the isolation of a monomeric silanone but led to the seminal discovery of the polysiloxanes $(R_2SiO)_n$, one of the most important organic–inorganic hybrid polymers.[2] The polysiloxanes were given the name "silicones" by Kipping in 1901 to describe them by analogy of their formula (R_2SiO) to ketones (R_2CO). Monomeric molecules containing silicon–oxygen double bonds were later named silanones. Nevertheless, the early attempts to prepare an isolable silanone compound remained as "Kipping's dream" to silicon chemists.



E = Si, Ge, Sn, Pb
A = Lewis acid
B = Lewis base

The first evidence for the existence of E=O species (E = Si, Ge) was reported in 1969, when elusive silanones[3,4] and germanones[5] were successfully trapped and spectroscopically characterized by applying extreme experimental conditions. At liquid nitrogen temperatures (−196 °C) in an inert matrix, reactive Si=O and Ge=O species could be prevented from oligomerizing and could be identified by means of IR spectroscopy through their diagnostic stretching vibrations (Si=O: $\tilde{\nu} = 1150\text{–}1300\ \text{cm}^{-1}$;[3,4] Ge=O: $\tilde{\nu} = 860\text{–}1000\ \text{cm}^{-1}$).[5]

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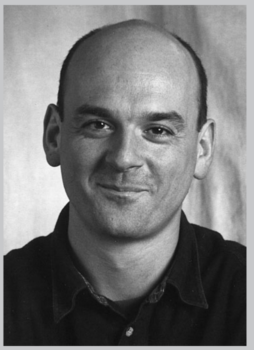
[*] Dr. Y. Xiong, Dr. S. Yao, Prof. Dr. M. Driess
Department of Chemistry: Metallorganics and Inorganic Materials, Technische Universität Berlin
Strasse des 17. Juni 135, 10623 Berlin (Germany)
E-mail: matthias.driess@tu-berlin.de

Further investigations of gas-phase species by mass spectrometry and chemiluminescence emission studies have provided evidence for the existence of the silicon analogue of formaldehyde ($H_2Si{=}O$).[6] The preparation, photoluminescence properties, and reactivity of Si=O-containing species stabilized on the surface of activated silica[7] have been studied both theoretically and experimentally in surface chemistry.[8] Furthermore, it has been proposed that the origin of the room-temperature photoluminescence of electrochemically etched porous silicon wafers is attributed to the presence of terminal Si=O moieties acting as chromophors.[9] Additionally, the development of new synthetic methods in molecular chemistry in the late 1980s enabled further investigations on elusive E=O species (E = Si, Ge) as transient intermediates in solutions.[10]

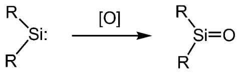
The last three decades have witnessed tremendous progress in the realization of stable compounds bearing multiple bonds between third-row and second-row elements by taking advantage of kinetic and thermodynamic stabilization.[1d] The successful synthesis of the first isolable compounds with Si=E bonds (E = Si, C) reported in 1981 by the research groups of West and Brook opened a new fascinating chapter in doubly bonded silicon compounds.[11] In addition, the availability of isolable metallylenes (silylenes, germylenes, stannylenes, and plumbylenes),[12,13] paved the way to stable multiply bonded silicon–chalcogen compounds.[14–17] However, in nearly all cases, the attempted synthesis of a heavier ketone with a E=O bond, through oxygenation of the respective divalent centers of the metallylenes, failed. Only very recently, Tamao, Matsuo, and co-workers used the sterically demanding substituent Eind (Eind = 1,1,3,3,5,5,7,7-octaethyl-*s*-hydrindacen-4-yl) to successfully synthesize the first isolable genuine germanone $(Eind)_2Ge{=}O$.[18] The synthesis of a stable silanone and analogous E=O (E = Sn, Pb) containing species is still a challenge. Fortunately, by applying the very successful concept of Lewis acid/base stabilization in main group chemistry,[19] we succeeded recently in the synthesis of stable silanone and germanone complexes with a E=O moiety (E = Si, Ge; **B**) to explore the chemistry of the E=O bonds at ambient temperature.[20] Based on the same synthetic strategy, quite recently the research groups of Roesky and Ueno isolated several new donor-supported silanones.[21] In this Minireview we highlight recent striking progress in the synthesis, characterization, and reactivity of isolable silanone complexes, their heavier congeners, and related systems with E=O bonds, which paved the way to unexpected novel molecular building blocks and functional groups in heavier Group 14 element chemistry.

Yun Xiong was born in Hubei Province (P.R. China). She studied Chemistry at Hubei Normal College (1983–1987, BSc) and Yunnan University (1987–1990, MSc). She then worked at the Wuhan University of Science and Technology as a chemistry lecturer (1990–1993) and then at the Hua-Zhong Normal University as a lecturer (1994–1998) and an associate professor of chemistry (1999–2000). In 2000 she moved to Germany and completed her PhD at the Johannes Gutenberg University of Mainz under the supervision of Karl W. Klinkhammer. In 2006 she joined the group of Matthias Driess at the TU Berlin.

Shenglai Yao was born in Guangxi (P.R. China). From 1984 to 2000 he studied chemistry (1984–1988, BSc, 1997–2000, MSc) and worked as Research Officer (1988–1997) at the Hua-Zhong Normal University, Wuhan City, Hubei Province (P.R. China). From 2000 to 2005 he carried out PhD research under the supervision of Karl W. Klinkhammer at the Johannes Gutenberg University of Mainz, Germany. He then joined the research group of Matthias Driess at the Technische Universität Berlin and now works as a senior researcher in the group.



Matthias Driess was born in Eisenach (Germany). He studied Chemistry and Philosophy at the University of Heidelberg. His PhD was gained in the field of boron-phosphorus chemistry from the University of Heidelberg in 1988. He then worked for one year as a postdoctoral fellow at the University of Wisconsin at Madison (USA) with Robert West. He returned to the University of Heidelberg and finished his Habilitation in 1993. In 1996 he became full professor of Inorganic Chemistry at the University of Bochum before moving to the Department of Chemistry (Metallorganic Chemistry and Inorganic Materials) of the TU Berlin in 2004.

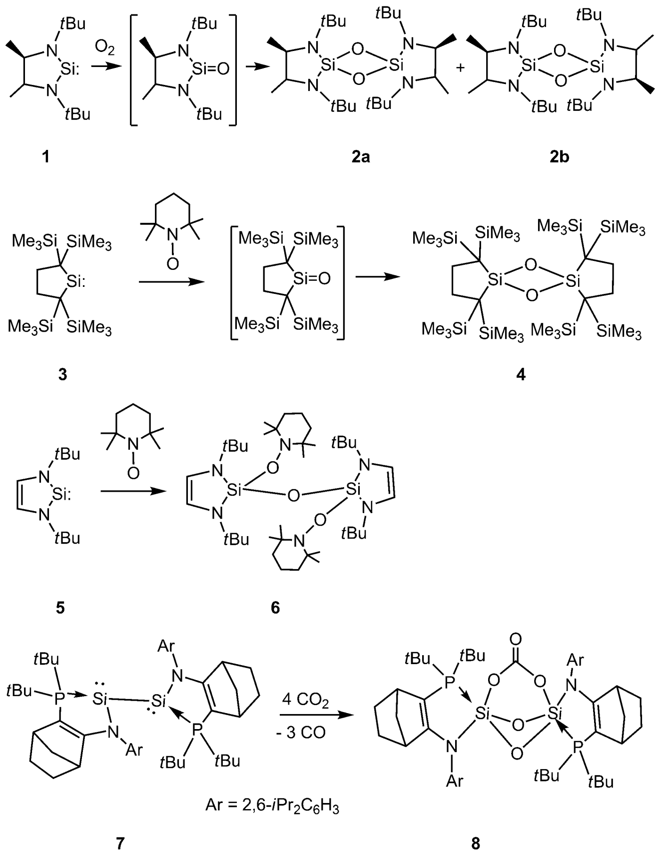


Scheme 1. Direct oxygenation of silylene to silanone.

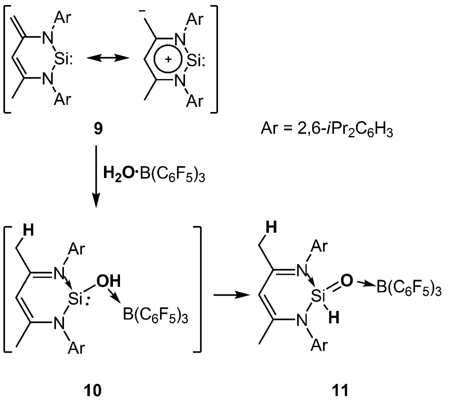
2. Silanones

Recently, the direct oxygenation of stable N-heterocyclic and carbocyclic silylenes to generate isolable silanones was investigated (Scheme 1). In these investigations, CO_2, N_2O, Me_3NO, or 2,2,6,6-tetramethylpiperidinyloxyl (TEMPO), in special cases even O_2, were employed as gentle oxygenation reagents. The oxidation products, however, depend both on the nature of the silylenes and the oxidants. It turned out that the oxidation of silylenes bearing relatively small protecting substituents furnishes Si_2O_2 dimers (formally through head-to-tail [2+2] cycloaddition of the hypothetical Si=O species). For example, the reaction of silylene **1** with dioxygen at −78 °C yielded the pair of dimers **2a** and **2b** (Scheme 2).[22] Similarly, dimer **4** was obtained from the reaction of silylene **3** with TEMPO.[23] In contrast, silylene **5** reacted with TEMPO to afford an isolable siloxysilane **6**.[24] In addition, the bis(silylene) **7** reacted with carbon dioxide to give the remarkable bicyclic disiloxanyl carbonate **8**.[25]

The bulky substituted, zwitterionic N-heterocyclic silylene **9** (Scheme 3) developed by us does not react with N_2O and



Scheme 2. Formation of cyclic siloxanes by oxygenation of stable silylenes.



Scheme 3. Zwitterionic nature of **9** and formation of the Si=O complex **11**.

CO_2.[26a] However, **9** is capable of activating dioxygen at low temperatures, but only results in unidentified insoluble products. An alternative oxidation of **9** with TEMPO afforded merely a 1:2 addition product with a Si(TEMPO)$_2$ moiety.[26b] Interestingly, the introduction of Lewis bases and/or acids, which can stabilize the desired Si=O subunit, into the oxidation processes enabled several isolable silanone complexes to be obtained from some stable silylene precursors.

2.1. Donor- and Acceptor-Stabilized Si=O

The zwitterionic nature of **9** allowed its reaction with the water–borane complex $H_2O{\cdot}B(C_6F_5)_3$ to furnish the first donor–acceptor-stabilized sila-aldehyde derivative **11** (Scheme 3), presumably via the 1,4-addition intermediate **10**.[27a] Remarkably, the oxygen atom of the Si=O subunit in **11** stems from water. As a consequence of the ylide-like nature of the Si=O bond, the concurrent presence of both the intramolecular N donor and Lewis acid acceptor ($B(C_6F_5)_3$) in **11** causes substantial stabilization of the Si=O subunit. The Si–O bond of 155.2(2) pm in **11** is slightly longer than the value of 153.7 pm calculated for the parent system $H_2N(H)Si{=}O$ (Figure 1).[27a,b]

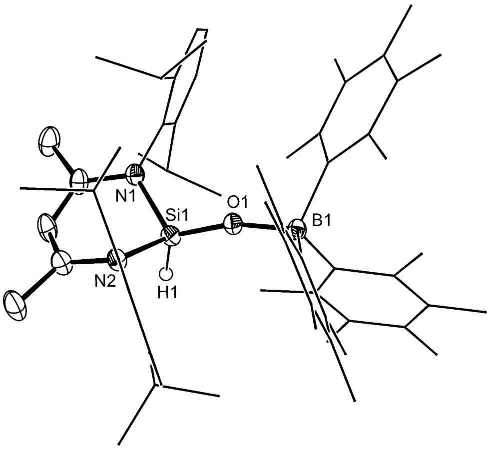


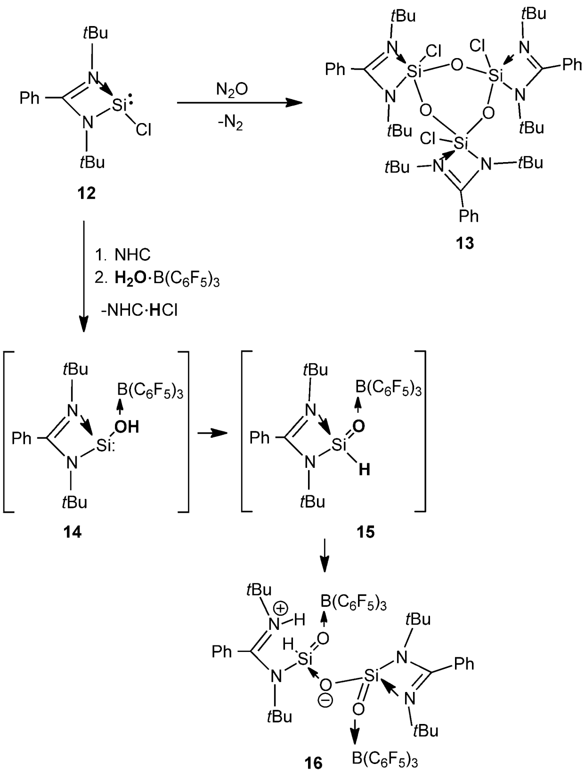
Figure 1. Molecular structure of the sila-aldehyde derivative **11**, with thermal ellipsoids set at 50%.

Roesky and co-workers carried out the oxidation of chlorosilylene **12**[28a] with N_2O and obtained the Si_3O_3 trimer **13**[28b] instead of the expected silanone (Scheme 4). Nevertheless, the reaction of **12** with $H_2O{\cdot}B(C_6F_5)_3$ and the N-heterocyclic carbene (NHC) 1,3-bis(2,6-diisopropylphenyl)imidazole-2-ylidene) furnished a borane-stabilized silicon analogue of acid anhydride **16**,[21a] possibly via intermediates **14** and **15**. In the molecular structure of **16**, the lengths of the formal Si=O bonds (153.9(2) and 158.0(2) pm) differ because of steric congestion and the electronic influence of the strong Lewis acid $B(C_6F_5)_3$.

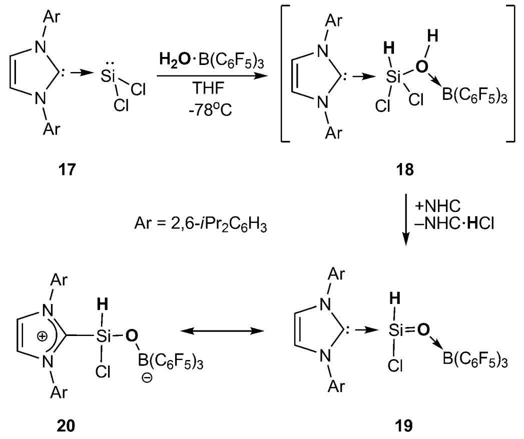
Analogously, the reaction of dichlorosilylene complex **17**[28c] with $H_2O{\cdot}B(C_6F_5)_3$ led to a stable silaformyl chloride **19** via the addition intermediate **18** (Scheme 5).[21b] Complex **19** features a formal Si=O bond with a length of 156.8(15) pm and was presumed to contain a contribution from the resonance structure **20**.

2.2. A Donor-Stabilized Silanoic Silyl Ester

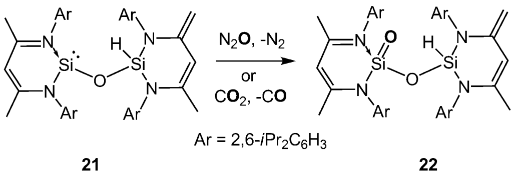
Direct oxygenation of the Si^{II} center of the siloxysilylene **21**, derived from **9** and water,[27a] by N_2O or CO_2 yielded **22** with release of N_2 or CO, respectively (Scheme 6).[29a] Complex **22** represents an intramolecular donor-stabilized silanoic



Scheme 4. The silicon analogue of acid anhydride **16**.



Scheme 5. Formation of a silaformyl chloride derivative.



Scheme 6. Formation of the donor-stabilized silanoic silyl ester **22**.

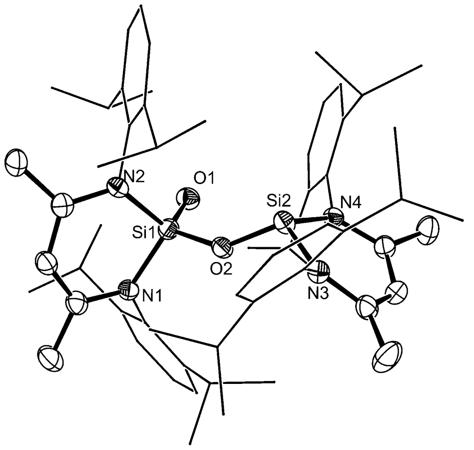
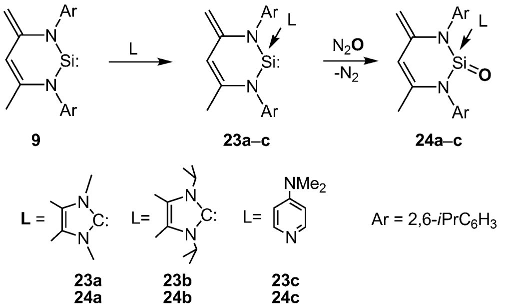


Figure 2. Molecular structure of the silanoic silyl ester **22**, with thermal ellipsoids set at 50%.

silyl ester featuring a terminal Si=O subunit. The length of the Si=O bond is 157.9(3) pm, and thus significantly smaller than the respective Si–O single bonds in **22** (162.9(2), 162.6(2) pm; Figure 2). Although the substantial contribution from a zwitterionic $Si^{+}-O^{-}$ resonance structure was confirmed by ^{29}Si solid-state NMR and theoretical investigations and the silicon center in **22** is tetrahedrally coordinated, the terminal Si=O moiety still shows significant π character.[29b]

2.3. Donor-Stabilized Silanones

When a strong Lewis base such as an N-heterocyclic carbene (NHC) or 4-dimethylaminopyridine (DMAP) is introduced into silylene **9**, the nucleophilicity of the silicon(II) center increases significantly (**23a–c**; Scheme 7), which enables, on release of N_2, facile activation by N_2O and formation of the donor-substituted silanones (sila-ureas) **24a–c**.[30–32] The structures of **24a–c** are notable for their remarkably short Si1–O1 bonds of 154.1(2) pm for **24a**, 152.7(2) and 153.4(2) pm for **24b**, and 1.545(2) pm for **24c** (Figure 3).



Scheme 7. Formation of donor-substituted silanones **24a–c**.

Selective oxygenation reactions of the Si^{II} centers in **23a** and **23b** could be achieved by using dioxygen, which led to the isolable dioxasilirane adducts **25a** and **25b**, respectively (Scheme 8). Interestingly, **25b** underwent an internal oxygen atom transfer in solution at room temperature to give the cyclic urea stabilized silanone (sila-urea) complex **26**.[33]

Complex **26** exhibits a short Si1–O1 double bond of 153.2(2) ppm and a long Si1–O2 dative bond of 172.7(2) pm (Figure 4, left). The coordinative interaction of the C=O→Si=O moieties in **26** was supported by the calculated NRT bond

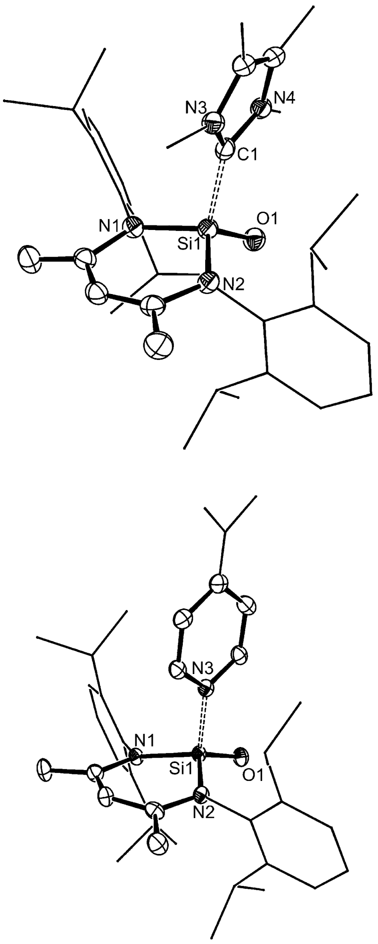


Figure 3. Molecular structures of **24a** (top) and **24c** (bottom), with thermal ellipsoids set at 50%.

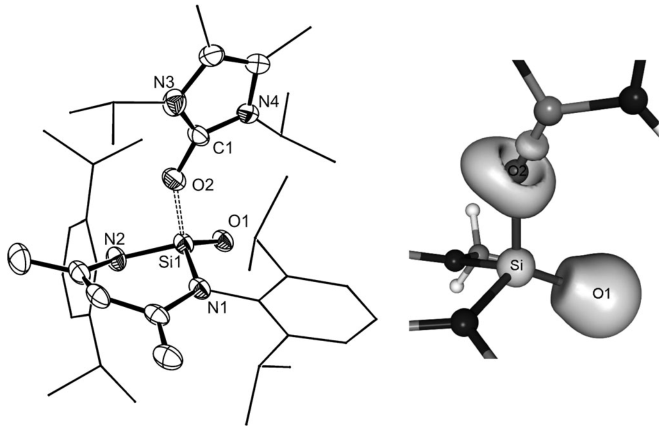
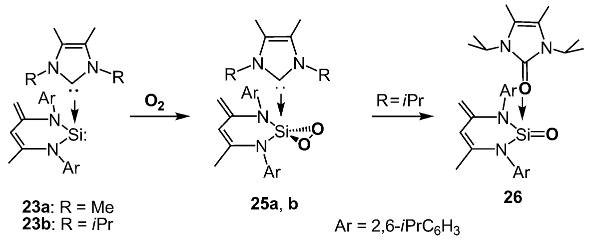
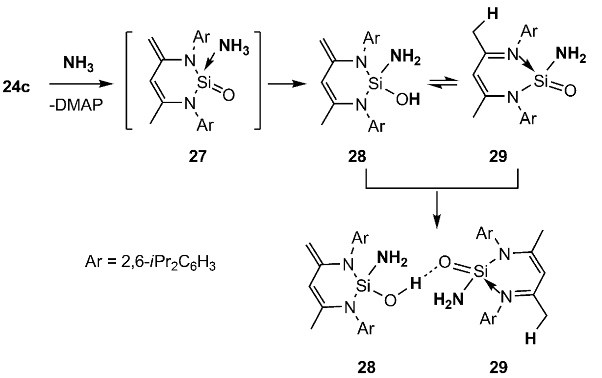


Figure 4. Molecular structure of **26** (left; with thermal ellipsoids set at 50%) and ELF representation of a model compound (right, ELF surface).



Scheme 8. Formation of the cyclourea-stabilized silanone **26**.



Scheme 9. Reaction of the DMAP-stabilized silanone **24c** with ammonia.

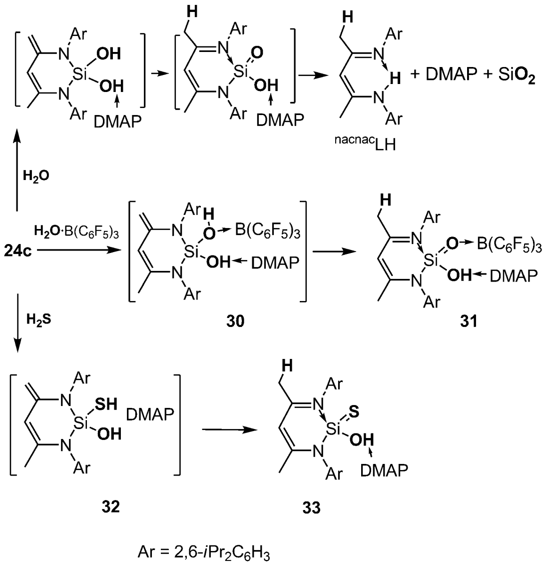
orders (NRT = natural resonance theory), the Wiberg bond indices, and plots of the electron localization function (ELF) of a model compound (Figure 4, right). A partial multiple-bonding character of the Si=O moiety was also suggested by the calculations.

2.4. Donor-Stabilized Silanoic Amides

Although both NHC-stabilized silanones **24a**,**b** are inert towards ammonia, the DMAP-coordinated complex **24c** reacts readily with ammonia under N-H activation[32] (Scheme 9). A possible reason for this is the weaker coordination of DMAP than NHC to the Si center and thus the formation of intermediate **27** with release of DMAP. Finally, the addition reaction of ammonia to the Si=O bond leads to the sila-hemiaminal **28**. In accordance with DFT calculations, the latter readily tautomerizes to furnish the silanoic amide derivative **29**. Compounds **28** and **29** were observed in equilibrium in solution and can be isolated by cocrystallization. The crystals consist of pairs of **28** and **29** interconnected by Si−OH⋯O=Si hydrogen bonds between the OH groups of **28** and the Si=O group of **29**. Compound **29**, with a Si2−O2 bond length of 154.5(2) pm, represents a unique donor-stabilized silicon analogue of carboxylic amide.[32]

2.5. A Donor–Acceptor-Stabilized Silanoic Acid and Related Analogues

The remarkable reactivity of the Si=O subunit in **24c** enabled access to the first complexes of silicon analogues of carboxylic acids. While the reaction of **24c** with H_2O leads to the "free" protonated β-diketiminate ligand LH, DMAP, and SiO_2 (Scheme 10), the conversion of **24c** with $H_2O{\cdot}B(C_6F_5)_3$ gave an isolable silanoic acid complex **31** via intermediate **30**.[34a] In contrast to the reaction with H_2O, exposure of **24c** to

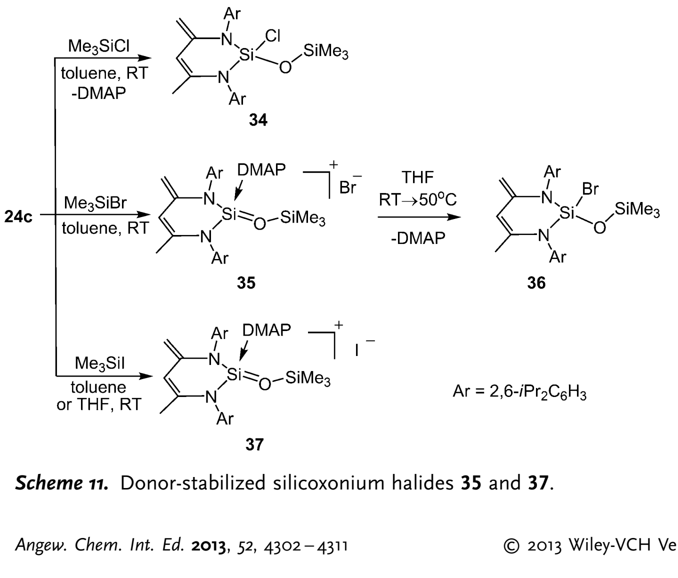


Scheme 10. The silanoic acid complex **31** and its thio analogue **33**.

H_2S gas affords the stable complex **33**, a silathiocarboxylic adduct.[34a] The hydroxysilanethiol **32** is proposed to be formed as the initial intermediate, which subsequently isomerizes through a 1,5-proton shift from the SH group to the exocyclic methylene group to afford **33** as the final product. It should be mentioned that Roesky and co-workers were able to synthesize germanium analogues of carboxylic acids LGe(=X)OH (X = S, Se) by direct reaction of the hydroxogermylene LGeOH (L = HC[C(Me)N(Ar)]$_2$, Ar = 2,6-iPr$_2$C$_6$H$_3$) with equivalent amounts of elemental sulfur or selenium.[34b,c]

2.6. Donor-Stabilized Silicoxonium Halides

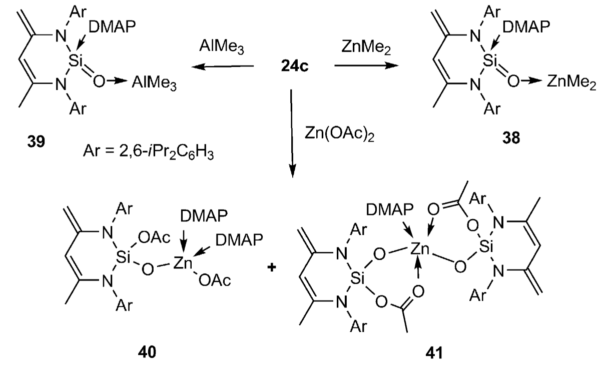
The high reactivity of the Si=O bond could also be used to tame silicoxonium systems. This could be achieved by reaction of the DMAP-stabilized silanone **24c** with trimethylsilyl halides (Scheme 11).[35] The reaction of **24c** with Me_3SiCl afforded the addition product **34**. In comparison, the formation of Si–Br and Si–I bonds is less favored and the addition of Me_3SiBr and Me_3SiI to **24c** led to saltlike precipitates of **35** and **37**, respectively, with a donor-stabilized silicoxonium cation. Compound **35** is stable in the solid state; however, in THF solution at room temperature it slowly converted into **36**. In contrast, the ion pair **37** even survived in boiling THF. Both **35** and **37** have relatively long Si–O bonds (158.3 pm) for a resonance-stabilized Si=O system.



Scheme 11. Donor-stabilized silicoxonium halides **35** and **37**.

2.7. Donor Si=O→Metal Complexes

Complexes of the Si=O subunit to metals were unknown until recently. As a consequence of the lone pair of electrons at the oxygen atom of the Si=O moiety, **24c** can form a stable metal complex with $ZnMe_2$ and $AlMe_3$ to yield **38** and **39**, respectively (Scheme 12).[36] The Si–O bonds in **38** (154.8(1) pm; Figure 5) and **39** (154.7(2) pm) are significantly shorter than those of the borane-stabilized adducts **11** (155.2(2) pm) and **19** (156.8(15) pm). In contrast, the Si=O bond in **24c** undergoes an addition reaction with zinc acetate to give the addition products **40** and **41** (Scheme 12).[36]



Scheme 12. Reactivity of **24c** toward $AlMe_3$, $ZnMe_2$, and $Zn(OAc)_2$.

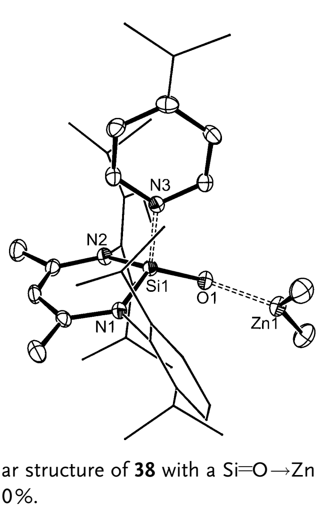
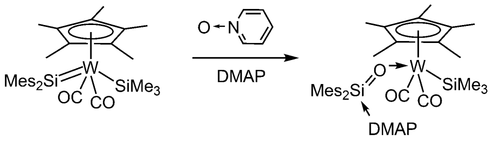


Figure 5. Molecular structure of **38** with a Si=O→Zn moiety. Thermal ellipsoids set at 50%.



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Scheme 13. Formation of a silanone/transition-metal complex **42**. Mes = 2,4,6-$Me_3C_6H_2$.

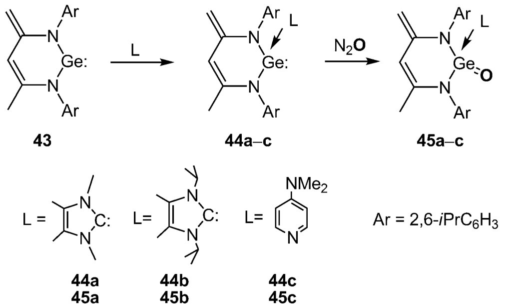
Very recently, Ueno and co-workers isolated the genuine silanone/transition-metal complex **42** (Scheme 13) by oxidation of a transition-metal complex with pyridine-*N*-oxide in the presence of the auxiliary ligand DMAP. This silanone features a DMAP-stabilized Si=O moiety coordinated to tungsten with a Si–O bond length of 155.8(4) pm.[21c]

3. Germanones

Similar to the development of chemical tricks to tame silanones, the synthesis of stable germanones with a Ge=O subunit experienced a long journey. In 1978 the first transient dialkylgermanones were reported.[37] During the last two decades several germylenes with dicoordinated germanium centers have been synthesized and probed for their applicability in the synthesis of germanones. Akin to the silicon analogues, the quest for germanones usually ended up with oligomerization of the desired Ge=O species. Moreover, in 1995 Tokitoh et al. employed bulky protecting groups to generate the diarylgermanone (Tbt)(Tip)Ge=O (Tbt = 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl, Tip = 2,4,6-triisopropylphenyl) which is only moderately stable in solution at room temperature and undergoes intramolecular cyclization to form a benzogermacyclobutene.[38a] Similarly, in 1996 Jutzi et al. examined the oxygenation of bis(2,4,6-tri-*tert*-butylphenyl)germylene with Me_3NO. The desired germanone, however, rearranges very rapidly through a C–H insertion process to give a germaindanol.[38b] On the other hand, in 2001 Schmidbaur and co-workers described the oxidation of bis-[2,6-(1-naphthyl)phenyl]germylene with N_2O. The expected germanone could only be identified by mass spectrometry.[39] In the last case, the supporting ligand is probably not bulky enough to prevent the Ge=O moiety from undergoing head-to-tail oligomerization or rearrangement.

3.1. Donor-Stabilized Germanones

In 2006 we reported the synthesis of the zwitterionic N-heterocyclic germylene (NHGe:) **43** (Scheme 14).[13d] Similar to its silicon analogue **9**, compound **43** does not react with N_2O or CO_2 at room temperature. However, when a donor ligand NHC[40a] or DMAP[40b] is coordinated to the divalent germanium atom, the nucleophilicity of the Ge^{II} center in the complexes **44a–c** becomes so strong that it can be easily oxidized by N_2O to give the isolable donor-stabilized germanones **45a–c**.



Scheme 14. Donor-stabilized germanones **45a–c**.

Interestingly, the Ge–O bond length of 164.6(2) pm in the DMAP-stabilized germanone **45c** is slightly shorter than those observed in the NHC-supported **45a,b** (167.2(3) pm for **45a**; 167.0(2), 166.4(2) pm for **45b** (Figure 6). This indicates that the Ge=O moiety in **45c** is less disrupted than those in **45a,b**. In contrast to silanone complex **24c**, which forms an adduct with a Si=O→$AlMe_3$ moiety, **45c** reacts with $AlMe_3$ to afford the addition product **46** (Scheme 15).

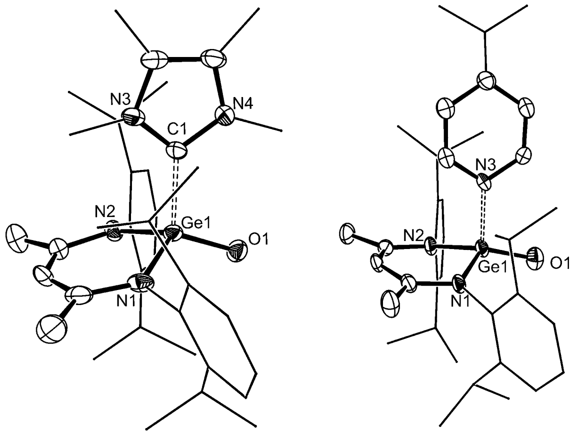
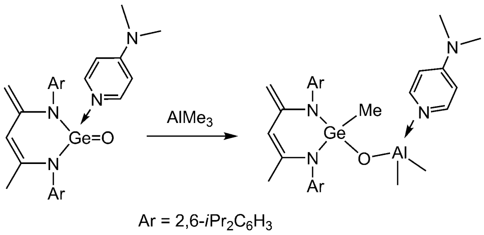


Figure 6. DMAP-stabilized germanones **45a** (left) and **45c** (right). Thermal ellipsoids set at 50%.

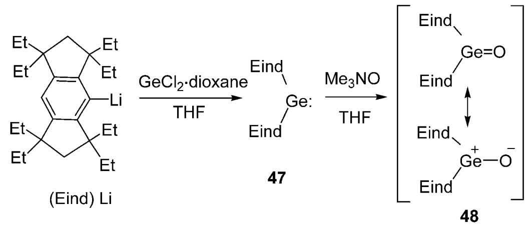


45c **46**

Scheme 15. Addition reaction of **45c** to $AlMe_3$.

3.2. A "Genuine" Germanone

In 2012 Tamao, Matsuo, and co-workers eventually isolated the first germanone **48** bearing a three-coordinate germanium atom. Germanone **48** resulted from oxidation of



Scheme 16. From germylene **47** to genuine germanone **48**.

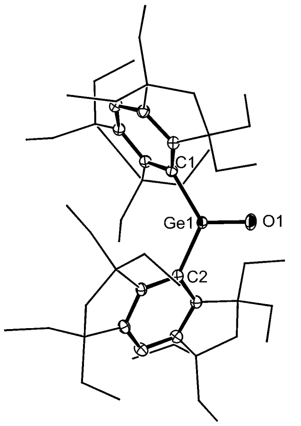
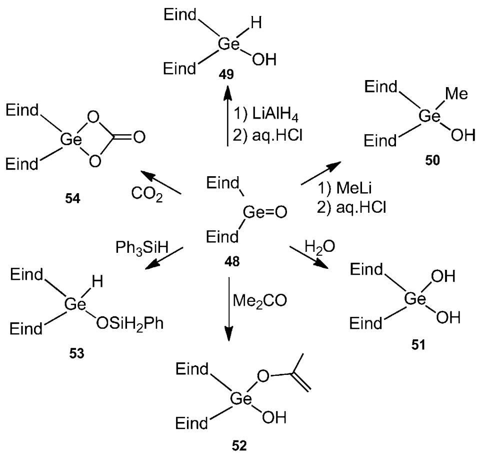
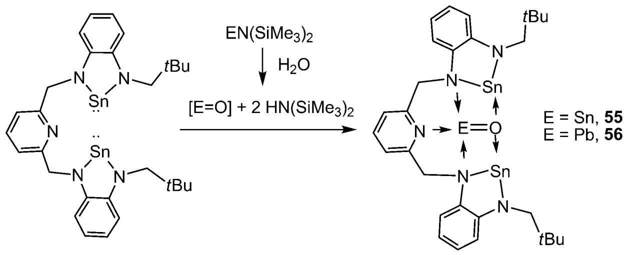


Figure 7. Molecular structure of the genuine germanone **48**, with thermal ellipsoids set at 50%.

the sterically congested germylene (Eind)$_2$Ge: **47** with trimethylamine *N*-oxide (Scheme 16).[18] Interestingly, the Ge=O bond length of 164.68(5) pm in **48** (Figure 7) is nearly identical to that in **45c**, thus reflecting the fact that the Ge=O bond possesses an intrinsically high ylide-like character similar to the Si=O bond. As expected, **48** can be reduced by $LiAlH_4$ to yield compound **49**. It can also undergo addition reactions with diverse substrates to furnish the addition products **50**–**54** (Scheme 17).[18]



Scheme 17. Reactivity of the germanone **48**.



Scheme 18. Species with Sn=O and Pb=O subunits.

4. Stannanones and Plumbanones

Compared with silanones and germanones, investigations on stable stannanones and plumbanones have been scarcely reported to date.[41] Up to now, the only related isolable molecular complexes are the divalent species **55** and **56** bearing a formal E=O subunit (E = Sn, Pb; Scheme 18).[41c] Similar to the donor- and acceptor-stabilized silanones mentioned above, **55** and **56** each features a formal E=O unit with the metal atom (tin or lead) and the oxygen atom stabilized by Lewis bases and acids, respectively. The metal center in each compound is four coordinate and the oxygen atom is three coordinate. Thus, the relative long Sn=O bond of 211.4(2) pm in **55** and the long Pb=O bond of 215.8(7) and 217.7(6) pm in **56** are indicative of little E=O (E = Sn, Pb) multiple-bond character.

5. Summary and outlook

The most recent progress on how to tame elusive compounds featuring E=O bonds (E = Si, Ge, Sn, and Pb) has been highlighted in this Minireview.[42] The generation of a series of silanone complexes supported by N-heterocyclic carbenes, pyridine donors, or intramolecular N-donor stabilization, and of the first stable "genuine" germanone with a Ge=O subunit are the most noteworthy synthetic developments in the field of heavier ketone analogues. This has brought to light that the reactivities of Si=O and Ge=O bonds are remarkably different from that of the carbonyl group. In particular, the selective addition of ammonia to these compounds and their ability to undergo E=O→metal coordination are unique. The structural and spectroscopic data obtained on these new species and their reactivities have greatly enriched our knowledge on the chemistry of heavier ketones. Although the syntheses of three-coordinate silanones, stannanones, and plumbanones have not yet been successful, exciting developments in the chemistry of these compounds may be anticipated in the near future by applying old and new chemical tricks.

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