

Heavy Ketones, the Heavier Element Congeners of a Ketone

RENJI OKAZAKI*[†] AND NORIHIRO TOKITOH*[‡]

Department of Chemical and Biological Sciences, Faculty of Science, Japan Women's University, Bunkyo-ku, Tokyo 112-8681, Japan, and Institute for Fundamental Research of Organic Chemistry, Kyushu University, Higashi-ku, Fukuoka 812-8581, Japan

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ABSTRACT

In contrast to ketones, one of the most important classes of organic compounds, their heavier element congeners, "heavy ketones", are much less explored because of their extremely high reactivities. This Account reviews the synthesis, reactivities, and structures of stable heavy ketones containing silicon, germanium, and tin as well as those of moderately stable lead analogues. These heavy ketones are kinetically stabilized by taking advantage of bulky substituents, yet they can undergo a variety of reactions due to the intrinsic high reactivity of heavier group 14–16 double bonds. Systematic comparisons for silicon through lead compounds reveal interesting differences in their properties, depending on the elements.

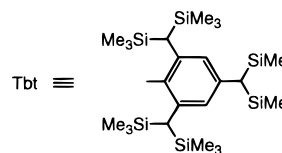
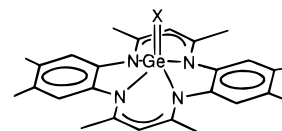
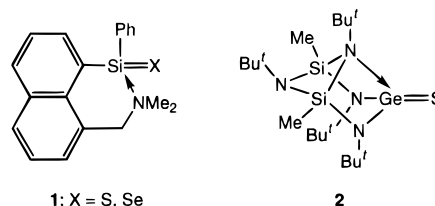
Introduction

The carbonyl group bearing a carbon–oxygen double bond is probably the most important functionality in organic chemistry, and its chemistry is well established. In contrast, the chemistry of compounds having a double bond between heavier group 14 and group 16 elements has been much less explored. It was commonly accepted for many years that compounds having double bonds between such heavier main group elements would not be able to exist as stable species because of their extremely high reactivity in contrast to those of the second row elements ("double-bond rule").¹ After the isolation of the first stable $P=C^2$ and $Si=C^3$, $P=P$,⁴ and $Si=Si$ ⁵ double-bond compounds, however, stable congeners of double-bond

Renji Okazaki, born in Tokyo in 1937, received his Ph.D. with Prof. O. Simamura at the Department of Chemistry, the Graduate School of Science, The University of Tokyo in 1966. He was on the faculty of the department (research associate, associate professor, and full professor) until he moved in 1998 to Japan Women's University, where he is currently full professor. His research interests include the chemistry of main group element compounds ranging from group 13 to 16 and the synthesis of bowl- and capsule-shaped molecules with emphasis on their application to the stabilization of highly reactive functional groups as well as to molecular recognition. He received the Divisional Award (Organic Chemistry) of the Chemical Society of Japan in 1987, the Humboldt Research Award in 1997, and the Award of the Chemical Society of Japan in 1999.

Norihiro Tokitoh, born in 1957, received his Ph.D. at The University of Tokyo in 1985. He became Research Associate at Tsukuba University in 1986, and then Research Associate (1989) and Associate Professor (1994) at The University of Tokyo. He was promoted to Professor of Chemistry at the Institute for Fundamental Research of Organic Chemistry, Kyushu University, in 1998, and moved to the Institute for Chemical Research, Kyoto University in April 2000. His main research fields are organoheteroatom and organometallic chemistry, and his current research interests are focused on the kinetic stabilization of highly reactive low-coordinate compounds of heavier main group elements. He received the Progress Award in Synthetic Organic Chemistry of Japan in 1992, the Progress Award of the Society of Silicon Chemistry in 1996, and the Japan IBM Science Award in 1998.

compounds involving heavier group 14, 15, and 16 elements have been prepared, mainly by taking advantage of kinetic stabilization afforded by bulky substituents.⁶ In some cases, coordination by heteroatoms, such as nitrogen or oxygen, is known to be effective in the stabilization of such double-bond species (thermodynamic stabilization). Several heavier element congeners of a group 14–16 double-bond species which are stabilized by intramolecular nitrogen coordination are known, and examples are shown below (**1**,⁷ **2**,⁸ and **3**⁹).¹⁰ The properties of double



bonds in these thermodynamically stabilized compounds are, however, considerably perturbed by the coordination and hence not suitable for a study on the intrinsic character of the double bonds. We have recently developed a new steric protection group, 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl (abbreviated to Tbt hereafter).¹¹ This ligand has been shown to be very effective for kinetic stabilization of highly reactive species such as doubly bonded compounds of heavier main group elements, including the heavier element congeners of a ketone, which we refer to as "heavy ketones".^{12,13} The use of this effective protecting group is crucial for the isolation of heavy ketones, because they can be kinetically stabilized by only two substituents on group 14 elements. This Account describes the synthesis, structure, and reactivity of heavy ketones.

Synthesis

The high reactivity of heavy ketones $RR'M=X$ obviously results from the fact that its $M-X$ π -bond energy is much smaller than the corresponding $M-X$ σ -bond energy, as one can see from Table 1.¹⁴ It is difficult, therefore, to synthesize heavy ketones $RR'M=X$ by simple elimination

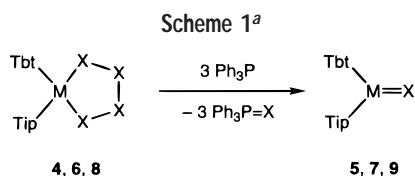
[†] Japan Women's University.

[‡] Kyushu University.

Table 1. Bond Energies (kcal mol⁻¹) and Lengths (Å) for M=X Calculated at the B3LYP/TZ(d,p) Level

H ₂ M=X		X			
		O	S	Se	Te
H ₂ C=X	σ^a	93.6	73.0	65.1	57.5
	π^b	95.3	54.6	43.2	32.0
	d^c	1.200	1.617	1.758	1.949
	Δ^d	15.5	11.9	11.1	10.1
H ₂ Si=X	σ^a	119.7	81.6	73.7	63.2
	π^b	58.5	47.0	40.7	32.9
	d^c	1.514	1.945	2.082	2.288
	Δ^d	8.1	9.4	9.3	8.7
H ₂ Ge=X	σ^a	101.5	74.1	67.8	59.1
	π^b	45.9	41.1	36.3	30.3
	d^c	1.634	2.042	2.174	2.373
	Δ^d	8.6	9.5	9.2	8.6
H ₂ Sn=X	σ^a	94.8	69.3	64.3	56.4
	π^b	32.8	33.5	30.6	26.3
	d^c	1.802	2.222	2.346	2.543
	Δ^d	7.6	8.9	8.5	8.1
H ₂ Pb=X	σ^a	80.9	60.9	57.0	50.3
	π^b	29.0	30.0	27.8	24.4
	d^c	1.853	2.273	2.394	2.590
	Δ^d	8.5	9.2	8.9	8.1

^a σ -bond energy. ^b π -bond energy. ^c Length of an M=X double bond. ^d Percent reduction in a bond length defined as [(single bond length - double bond length)/single bond length] \times 100.



^a **4, 5:** M = Si, X = S. **6, 7:** M = Ge, X = S. **8, 9:** M = Ge, X = Se.

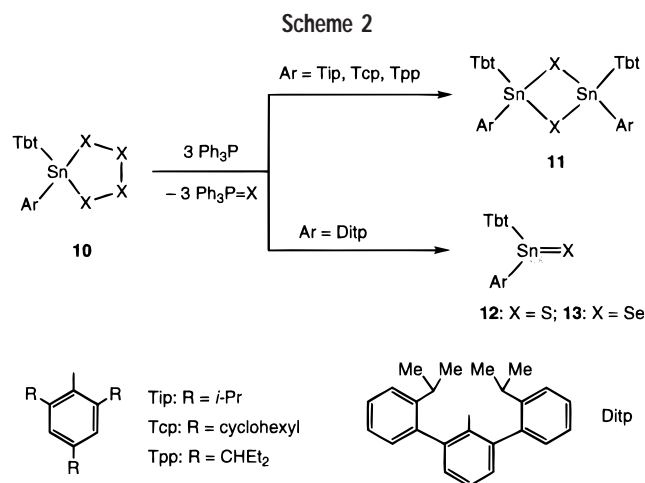
of HYZ from a precursor (or intermediate) RR'M(XH)(YZ), which is a commonly used method for the synthesis of ketones.

We have developed three approaches for the synthesis of heavy ketones: (1) retrocycloaddition of 1,2,4-trichalcogenadimetallolanes,¹⁵ (2) chalcogenation of divalent group 14 element compounds, and (3) dechalcogenation of 1,2,3,4-tetrachalcogenometallolanes with trivalent phosphorus reagents. Among these, the last approach proved to be most useful for the isolation of pure specimens of heavy ketones, although the second one is also sometimes quite successful.

Dechalcogenation of Tetrachalcogenometallolanes.

Treatment of Tbt- and 2,4,6-triisopropylphenyl (Tip)-substituted tetrathiasilolane **4** with 3 molar equiv of triphenylphosphine in hexane at room temperature resulted in the formation of silanethione **5** (Scheme 1) as yellow crystals which are very stable in the absence of water and oxygen, even up to the melting point (185–187 °C).^{14,16}

When a similar desulfurization was carried out for Tbt- and 2,4,6-trimethylphenyl (mesityl, Mes)-substituted tetrathiasilolane Tbt(Mes)Si₄ at -78 °C, a yellow solution of silanethione Tbt(Mes)Si=S was obtained, the formation of which was evidenced by quenching with the same trapping reagents as in the case of the Tip-substituted silanethione **5** (vide infra, Scheme 6). However, it was impossible to isolate Tbt(Mes)Si=S because of its ready head-to-tail dimerization, which gave the corresponding

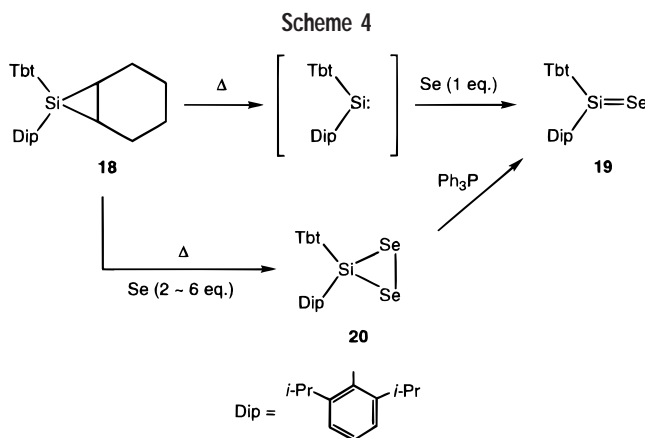
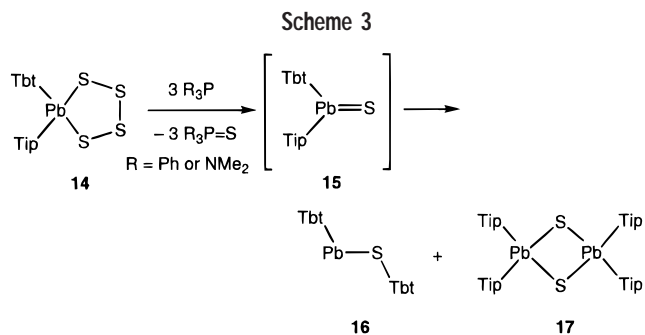


1,3,2,4-dithiadisiletane derivative at room temperature, indicating the importance of steric protection in the isolation of a monomeric silanethione.

This dechalcogenation methodology was also successful in the synthesis of stable germanethione and germaneselone.¹⁷ Dechalcogenation of Tbt- and Tip-substituted tetrathia- and tetraselenagermolane, **6** and **8**, with triphenylphosphine afforded the expected germanethione **7** (orange-yellow crystals) and germaneselone **9** (red crystals) in quantitative yields, respectively (Scheme 1). Germanethione **7** is thermally very stable; heating of its hexane solution in a sealed tube at 160 °C for 3 days resulted in a complete recovery of **7**. This is in sharp contrast with the extremely high instability of dimethylgermanethione (Me₂Ge=S), which is reportedly stable only below 40 K.¹⁸

The combination of Tbt and Tip substituents was found to be insufficient for the stabilization of stannanethione and stannaneselone. It cannot prevent the dimerization of the Sn=X (X = S, Se) bond with even higher reactivity than the corresponding Si and Ge analogues, because the bond lengths around the Sn atom become longer and hence the steric protection by the substituents becomes less effective than the Si and Ge cases. Thus, desulfurization by triphenylphosphine of Tbt- and Tip-substituted tetrathia-stannolane **10** (Ar = Tip, X = S) and tetraselena-stannolane **10** (Ar = Tip, X = Se) gave **11**, dimerized products of intermediary stannanethione¹⁹ and stannaneselone.²⁰ The use of even bulkier substituents Tcp or Tpp instead of Tip also resulted in the formation of the dimer **11**, but the combination of Tbt and Ditp, a terphenyl ligand with two isopropyl groups, led to the isolation of stable stannanethione **12**¹⁹ and stannaneselone **13**²⁰ as red crystals (Scheme 2).

Desulfurization of Tbt- and Tip-substituted tetrathia-plumbolane **14** with hexamethylphosphorous triamide at -78 °C gave plumbanethione **15**, as evidenced by a trapping experiment giving cycloadducts as in the cases of the lighter heavy ketones (see Scheme 6),²¹ but the same reaction at 50 °C using hexamethylphosphorous triamide or triphenylphosphine afforded plumbylene **16** and 1,3,2,4-dithiaplumbetane **17** instead of the dimer of plumbanethione **15** (Scheme 3).²² The mechanism for the formation

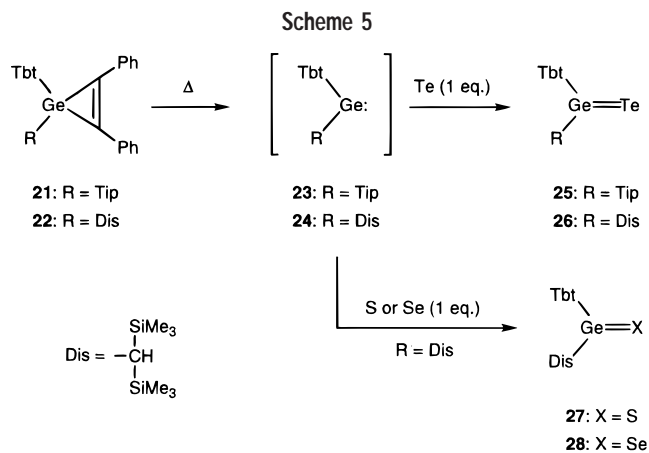


of **16** and **17** involving intermediary plumbylenes Tbt-Pb-STip and Tip-Pb-STbt formed by a 1,2-aryl migration is proposed.²²

Chalcogenation of Divalent Group 14 Element Compounds. The dechalcogenation of tetrachalcogenametallolanes is an excellent synthetic approach to heavy ketones, but tetrachalcogenametallolanes are not always available. In such cases, the chalcogenation of divalent species is a method of choice.

Although tetrathiasilolane **4** can be synthesized by the reaction of elemental sulfur with silylene Tbt(Tip)Si prepared by reduction of dibromide Tbt(Tip)SiBr₂ with lithium naphthalenide,¹⁴ a similar reaction with selenium did not afford the corresponding tetraselenide. However, the reaction of Tbt(Dip)Si (Dip = 2,6-diisopropylphenyl), generated by thermolysis of silirane **18**, with 1 equiv of selenium gave silaneselone **19** as a red solid.²² The thermolysis of **18** in the presence of excess (2–6 equiv) selenium produced diselenasilirane **20**, the deselenation of which with triphenylphosphine gave also **19** (Scheme 4).²³

In contrast to tetrachalcogenagermolanes **6** and **8** which can be easily prepared,^{17c} a cyclic polytelluride, an expected precursor of a germanetellone, could not be obtained by similar methods. Since we found that germirenes **21** and **22** are excellent precursors of germylenes Tbt(Tip)Ge **23** and Tbt(Dis)Ge **24** (Dis = bis(trimethylsilyl)methyl, or disil), respectively,²⁴ they were allowed to react with 1 equiv of tellurium to give germanetellones **25** and **26** as stable green crystals (Scheme 5).²⁵ Germanethione **27** and germaneselone **28**, bearing an alkyl substituent, Dis, were similarly synthesized by the reaction of **22** with 1 molar equiv of sulfur and selenium, respectively.^{17c}



Structural and Spectroscopic Properties

X-ray Crystallographic Analysis. The most important structural feature of a carbonyl compound is its trigonal planar geometry, which results from the sp²-hybridized carbon. Since it has been revealed experimentally as well as theoretically that the heavier element analogues of an alkene, i.e., disilene,^{6a,b} digermene,^{6a} distannene,^{6a} and diplumbene,²⁶ have a trans-bent structure, in contrast to an alkene with a planar geometry, it is quite interesting to study the structural features of heavy ketones. Fortunately, most of the heavy ketones synthesized in the present study have provided single crystals suitable for X-ray structural analysis. The results for silanethione **5**, germanethione **7**, germaneselones **9** and **28**, germanetellones **25** and **26**, and stannaneselone **13** are summarized in Table 2, and the ORTEP drawing of **25** is shown in Figure 1. All heavy ketones examined have an almost completely trigonal planar geometry and a distinct double-bond nature, as judged by $\Sigma\angle M$ and Δ_{obs} , respectively (for the definition of $\Sigma\angle M$ and Δ_{obs} , see Table 2). The observed double-bond lengths and Δ_{obs} values are in good agreement with calculated values for H₂M=X listed in Table 1.¹⁴ These findings clearly indicate that heavy ketones have structural features similar to those of a ketone, although their double-bond character is lower than that of the corresponding carbon homologues, as judged from their Δ_{obs} (Table 2) as well as Δ (Table 1) values.

It should be noted that all the M=X bond lengths observed here are significantly shorter than those reported for the corresponding double-bond compounds stabilized by intramolecular coordination of heteroatoms, e.g., Si=S (2.013(3) Å for **1**), Ge=S (2.063(3) Å for **2**; 2.110(2) Å for **3**), Ge=Se (2.247(1) Å for **3**), Ge=Te (2.446(1) Å for **3**), and Sn=Se (2.39 Å for **3**). This indicates that compounds **1–3** are electronically perturbed by heteroatom substituents.

NMR Spectra. As in the case of ¹³C NMR, the low-field chemical shifts are characteristic of sp²-hybridized nuclei also in the heavy ketones. For example, the ²⁹Si chemical shifts of silanethione **5** and silaneselone **19** are 167 and 174 ppm, respectively. In contrast, the ²⁹Si NMR signals of Corriu's compounds **1** (X = S) and **1** (X = Se) appear at 22.3 and 29.4 ppm, respectively,⁷ indicating the high sp³ nature of the silicon centers in **1**. Similarly, our stannaneselone **12** and stannaneselone **13** have ¹¹⁷Sn chemical

Table 2. Structural Parameters of Heavy Ketones Tbt(R)M=X

R M X compound	Tip Si S 5	Tip Ge S 7	Tip Ge Se 9	Dis Ge Se 28	Tip Ge Te 25	Dis Ge Te 26	Ditp Sn Se 13
M–X (Å)	1.948(4)	2.049(3)	2.180(2)	2.173(3)	2.398(1)	2.384(2)	2.375(3)
Δ_{obs} (%) ^a	9	9	9	8	9	8	9
$\Sigma\angle M$ (deg) ^b	359.9	359.4	359.3	360.0	359.5	360.0	359.9

^a The bond shortening (%) compared to the corresponding single bonds. ^b Summation of the bond angles around M atom.

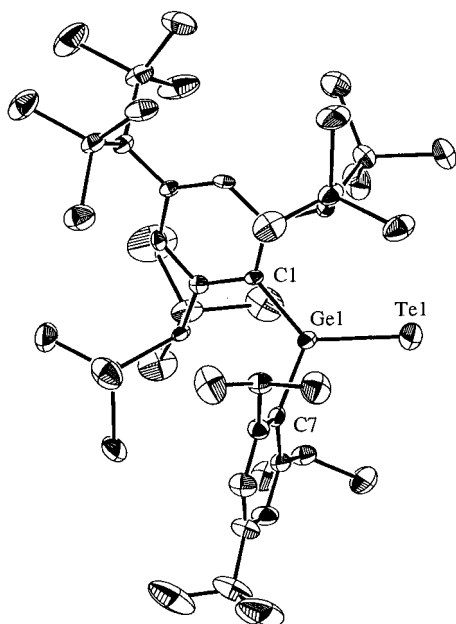


FIGURE 1. ORTEP drawing of germanetellone Tbt(Tip)Ge=Te (**25**) with thermal ellipsoid plot (30% probability).

shifts of 531 and 440 ppm, respectively, while Parkin's compounds **3** resonate at a much higher field, i.e., –303 ppm (**3**: M = Sn, X = S) and –444 ppm (**3**: M = Sn, X = Se).^{9b} This clearly shows that the thermodynamically stabilized tin–chalcogen double bonds in **3** (M = Sn; X = S, Se) are electronically perturbed to a great extent. Such information is not available for germanium-containing heavy ketones because of the difficulty in observing Ge NMR, but the low-field resonating ⁷⁷Se and ¹²⁵Te NMR chemical shifts of germaneselonas [**9** (941 ppm) and **28** (872 ppm)]^{16c} and germanetellones [**25** (1143 ppm) and **26** (1009 ppm)]²⁴ are in keeping with the sp² hybridization of these elements.

UV–Vis Spectra. All heavy ketones prepared in the present study are colored compounds and show characteristic visible absorptions listed in Table 3.

It is known that the n– π^* absorptions of a series of R₂C=X (X = O, S, Se, Te) compounds undergo a systematic red shift on going down the periodic table.²⁷ A similar tendency is observed also for the Si, Ge, and Sn series of Tbt(R)Si=X (X = S, Se), Tbt(R)Ge=X (X = S, Se, Te), and Tbt(R)Sn=X (X = S, Se). In contrast, one can see a very interesting trend in the absorption maxima of two series Tbt(R)M=S and Tbt(R)M=Se (M = C, Si, Ge, Sn). In both series the λ_{max} values are greatly blue-shifted on going from carbon to silicon congeners, whereas λ_{max} values of silicon, germanium, and tin congeners are red-shifted with

Table 3. Electronic Spectra (n– π^*) of Doubly Bonded Compounds between Group 14 Elements and Chalcogens

	observed ($\lambda_{\text{max}}/\text{nm}$) ^a		calcd ⁱ	
	X = S	X = Se	$\lambda_{\text{max}}/\text{nm}$	$\Delta\epsilon_{\text{n}\pi^*}/\text{eV}^k$
TbtCH=X	587 ^b	792 ^c	H ₂ C=S	460 10.81
Tbt(R)Si=X	396 ^d	456 ^e	H ₂ Si=S	352 10.27
Tbt(R)Ge=X ^f	450 ^g	519 ^g	H ₂ Ge=S	367 9.87
Tbt(R)Sn=X	473 ^h	531 ⁱ	H ₂ Sn=S	381 9.22
			H ₂ Pb=S	373 9.11

^a In hexane. ^b Reference 27a. ^c Reference 27b. ^d R = Tip. Reference 13. ^e In THF. R = Dip. ^f X = Te: λ_{max} 640 nm. Reference 24. ^g Reference 16c. ^h R = Tip. Reference 29. ⁱ R = Ditp. Reference 20. ^j CIS/TZ(d,p)//B3LYP/TZ(d,p). ^k $\epsilon_{\text{LUMO}(\pi^*)} - \epsilon_{\text{HOMO}(\text{n})}$.

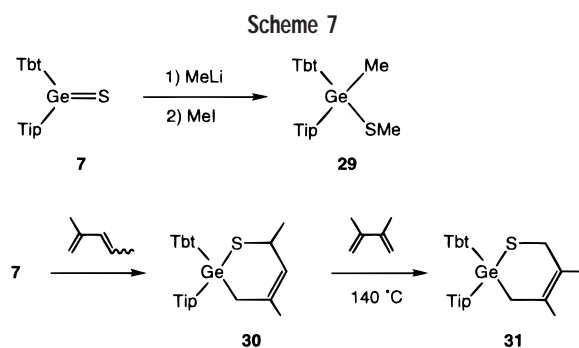
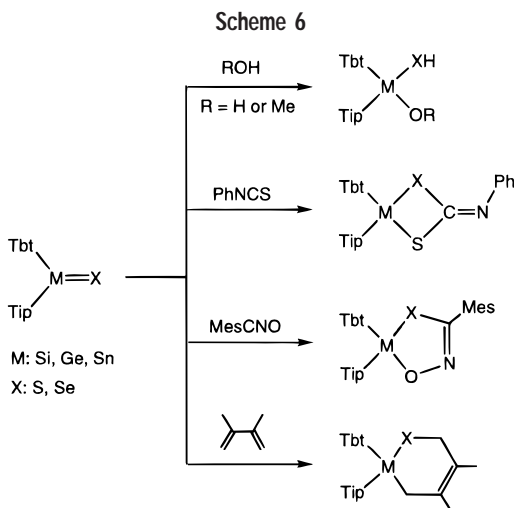
increasing atomic number of the group 14 elements. This trend is also found in calculated values for H₂M=S (M = C, Si, Ge, Sn). Since calculated $\Delta\epsilon_{\text{n}\pi^*}$ values increase continuously from H₂Sn=S to H₂C=S, a long-wavelength absorption for H₂C=S (and hence for TbtCH=S^{28a}) most likely results from a large repulsion integral ($J_{\text{n}\pi^*}$) for the carbon–sulfur double bond as in the case of H₂C=O vs H₂Si=O.²⁹

Raman Spectra. The stretching vibrations of the M=X bond were measured from Raman spectra for silanethione **5** (724 cm^{–1}), germanethiones **7** (521 cm^{–1}) and **27** (512 cm^{–1}), and germanetellones **9** (381 cm^{–1}) and **28** (386 cm^{–1}). These values are in good accordance with those calculated for H₂M=X compounds (723, 553, and 387 cm^{–1}, respectively).¹⁴ It is noteworthy that the observed value of Tbt(Tip)Ge=S **7** is very close to that observed by IR spectroscopy for Me₂Ge=S (518 cm^{–1}) in an argon matrix at 17–18 K,¹⁸ indicating similarity in the bond nature of both germanethiones despite the great difference in the size and nature of the substituents.

Reactions

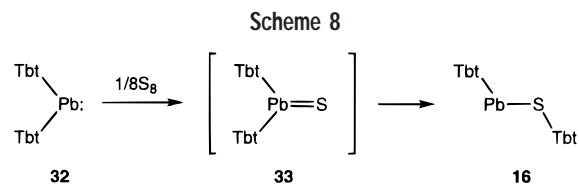
The most important feature in the reactivity of a carbonyl functionality is reversibility in reactions across its carbon–oxygen double bond (addition–elimination mechanism via a tetracoordinate intermediate), as is observed, for example, in reactions with water and alcohols. The energetic basis of this reversibility is the fact that the σ and π bond energies of the C=O bond are almost similar (Table 1). In contrast, an addition reaction involving a heavy ketone is highly exothermic and hence essentially irreversible because of its much smaller π bond energy than the corresponding σ bond energy.

All heavy ketones synthesized in the present study react with water and methanol almost instantaneously to give tetracoordinate adducts (Scheme 6).^{14,17c,30} They also



undergo cycloadditions with unsaturated systems such as phenyl isothiocyanate, mesitronitrile oxide, and 2,3-dimethyl-1,3-butadiene to give the corresponding [2 + 2], [2 + 3], and [2 + 4] cycloadducts, respectively. The former two reactions proceed at room temperature, while the reaction with the diene takes place at higher temperature with the lighter homologues requiring more severe conditions.

Reaction of **7** with methyllithium followed by alkylation with methyl iodide gives a germophilic product **29**. The [2 + 4]cycloaddition of **7** with 2-methyl-1,3-pentadiene affords **30** regioselectively. When a hexane solution of **30** is heated at 140 °C in a sealed tube in the presence of excess 2,3-dimethyl-1,3-butadiene, a dimethylbutadiene adduct **31** is obtained in a high yield, indicating that the Diels–Alder reaction of germanethione **7** with a diene is reversible and hence a diene adduct such as **30** or **31** can be a good precursor of germanethione **7**.^{17c} As mentioned earlier, heavy ketones of silicon, germanium, and tin isolated in this study are thermally stable, no change being observed upon heating of their solutions. In contrast, a plumbanethione behaves differently. When stable plumbylene Tbt_2Pb **32**³¹ was sulfurized by 1 molar equiv of elemental sulfur at 50 °C, the heteroleptic plumbylene **16** was obtained (Scheme 8)³² instead of plumbanethione $\text{Tbt}_2\text{Pb}=\text{S}$ **33**, which is an expected product in view of the reactivity observed for divalent species of silicon, germanium, and tin (vide supra). The formation of **16** is most reasonably explained in terms of 1,2-migration of Tbt group in the intermediate plumbanethione **33**, and this observation is supporting evidence for the 1,2-aryl migra-



tion in plumbanethione **15** proposed in the reaction shown in Scheme 3. This unique 1,2-aryl migration in a plumbanethione is in keeping with a theoretical calculation which reveals that plumbylene $\text{HPb}(\text{SH})$ is about 39 kcal mol⁻¹ more stable than plumbanethione $\text{H}_2\text{Pb}=\text{S}$.³³

Conclusion and Outlook

The present study has shown that heavy ketones are capable of existence as stable species if their highly reactive $\text{M}=\text{X}$ bond is adequately protected toward dimerization by bulky substituents (kinetic stabilization). Although the structural features of their $\text{M}=\text{X}$ bonds ($\text{M} = \text{Si}, \text{Ge}, \text{Sn}$), such as trigonal planar geometry and bond shortening compared to the corresponding $\text{M}-\text{X}$ single bonds, are similar to those of ketones, heavy ketones have much higher reactivity because of their weak π -bonds. The present systematic study on heavy ketones containing silicon through lead has revealed that, unlike lighter congeners, a heavy ketone containing lead, $\text{R}_2\text{Pb}=\text{X}$, is unique in that it is less stable than its isomeric plumbylene $\text{RPb}-\text{XR}$. While tellurium-containing heavy ketones such as **25** and **26** can be isolated as quite stable species, no stable heavy ketone containing oxygen has been isolated so far, although we have found that gemanone $\text{Tbt}(\text{Tip})\text{-Ge}=\text{O}$ is stable in solution at room temperature.³⁴ The synthesis of oxygen-containing heavy ketones, especially that bearing a $\text{Si}=\text{O}$ bond, remains to be achieved in the future.

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