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Chalcogeno[bis(phosphaalkenyl)] Germanium and Tin Compounds

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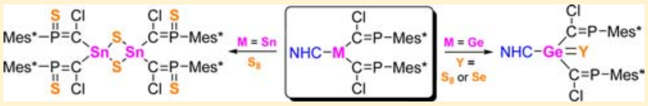
Supporting Information



ABSTRACT: The first diphosphaalkenylstannylene stabilized through complexation with a carbene NHC−Sn[C(Cl)═PMes*]$_2$ **1** (Mes* = 2,4,6-tri-*tert*-butylphenyl; NHC = :C{N(*i*Pr)C(Me)}$_2$) was isolated and fully characterized including single crystal X-ray diffraction analysis. Its reaction with elemental sulfur rapidly gives the cyclic Sn_2S_2 (dithiadistannetanne) derivative **3**, presumably formed by dimerization of a stannathione intermediate. By contrast, its germanium analogue NHC−Ge[C(Cl)═PMes*]$_2$ **7** leads to the corresponding monomeric germathione **4** and germaselenone **5**. The germaselenone was more stable than the germathione and could be structurally characterized. An unusual thermal cyclization reaction of the last one occurs with an excess of selenium to give the Ge_2Se_3 (triselenadigermolane) ring derivative **6**.

INTRODUCTION

Low-valent group 14 compounds have attracted much attention in fundamental chemistry because of their particular structures and high reactivities.[1] Since the discovery of the Arduengo-type carbene in 1991,[2] the rapid development of the chemistry of N-heterocyclic carbenes (NHC), their use in transition metal catalysis[3] and more recently as organocatalysts[4] have increased interest in their higher congeners of group 14 elements.[5]

Among the stabilization strategies of germylenes or stannylenes, the intermolecular coordination has aroused a great interest in the last decades particularly with the use of NHC as stabilizing coligand.[6] In the germanium series, after the isolation of the first carbene-germanium(II) adducts, (NHC−GeI_2[7] and a NHC−heterocyclic germylene[8]), a large variety of transient germanium(II) species has been isolated by employing electron-donating NHC.[9] In contrast, there are few examples of tin analogues. Both carbene−tin complexes NHC−$SnCl_2$ and NHC−$SnAr_2$ (Ar = 2,4,6-*i*$Pr_3C_6H_2$) were prepared and structurally characterized in the same year.[10] Later, a zwitterionic carbene-stannylene adduct was obtained by cleavage of a dibenzotetraazafulvalene by a diaza-stannylene.[11] To the best of our knowledge, there are only two examples of unstable entities stabilized by coordination to NHC: the tin(II) dihydride in the form of the carbene-tungsten bis-adduct NHC−$SnH_2W(CO)_5$[12] and the hypermetallyl stannylenes NHC−Sn[M($SiMe_3$)$_3$]$_2$, (M = Si, Ge, Sn)].[13] One of the most characteristic feature of group 14 divalent derivatives is their high potential as building blocks in organometallic chemistry; for example, their oxidation by elemental chalcogens constitutes an usual and clean route to double bonded species M═E (M = Si, Ge, Sn; E = S, Se, Te).[14] Although numerous germanium and tin compounds with double bond to chalcogens have been isolated using kinetic or thermodynamic stabilization,[15] the examples of M═E stabilized by NHC are rare. To the best of our knowledge, only few derivatives of the type NHC−SiR_2═E (E = O, S, Se, Te) and NHC−GeR_2═O, stable at room temperature, were described.[16]

We have recently reported the synthesis of the bis(phosphaalkenyl)germylene NHC−Ge[C(Cl)═PMes*]$_2$ (Mes* = 2,4,6-tri-*tert*-butylphenyl; NHC = :C{N(*i*Pr)C(Me)}$_2$[17]), the first representative of a new class of germylenes using the phosphaalkenyl −P═C⟨ unit as ligands and the stabilizing coordination properties of the NHC; such a derivative with a C═PMes* moiety is particularly interesting since due to multiple possibilities of reaction or coordination (lone pair on phosphorus, divalent germanium atom and P═C double bonds) it can potentially present an unexpected and rich reactivity which was proved by its reaction with transition-metal complexes.[18]

These results prompted us to investigate the synthesis of its tin analogue NHC−Sn[C(Cl)═PMes*]$_2$ and to explore the reactivity of these new germylene and stannylene with elemental chalcogens; all of which is presented herein.

RESULTS AND DISCUSSION

Synthesis and Structure of the Bis(phosphaalkenyl)tin(II) Compound 1. The addition of NHC−$SnCl_2$ to a freshly prepared solution of Mes*P═C(Li)Cl in THF at low temperature afforded the novel stannylene NHC−Sn[C(Cl)═

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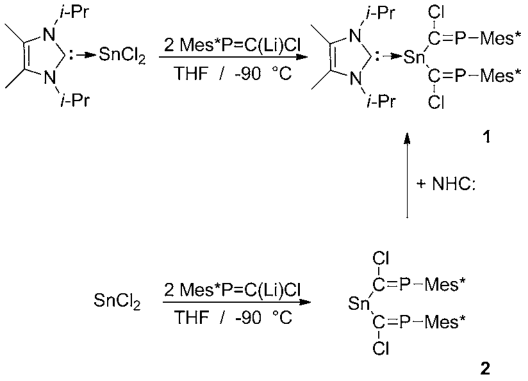
PMes*]$_2$ **1**, which was isolated as a light brown air-sensitive powder in a good yield. In the ^{31}P NMR spectrum, only one signal appeared at 277.4 ppm indicating the formation of one isomer. As previously observed in the case of the germanium analogue,[18] the free disubstituted stannylene **2**, obtained from the dichlorostannylene $SnCl_2$, was not stable and decomposed after some hours in solution. However, it was unambiguously characterized by adding NHC to a freshly prepared solution in THF by formation of its carbene adduct **1** (Scheme 1).

Scheme 1. Synthesis of Compounds 1 and 2



The stannylene **1** is stable up to 60 °C in tetrahydrofuran or in toluene but a rapid decomposition is observed in dichloromethane or in chloroform. It was fully characterized by NMR spectroscopy and single-crystal X-ray structure analysis. The ^{1}H and ^{13}C NMR spectra show typical resonances expected for the carbenic moiety[10a] and for the phosphaalkenyl group.[18] The ^{119}Sn NMR spectrum displays a singlet at −130.8 ppm upfield-shifted compared to that of NHC−$SnCl_2$ (−59.4 ppm)[10a] but in the range of three-coordinate tin(II) derivatives.[13] The X-ray structure analysis shows an *E*/*E* configuration around the P=C double bond and a tricoordinate tin center which exhibits a flattened pyramidal geometry (Figure 1, Table 1). The Sn−$C_{carbene}$ distance (2.316(2) Å) suggests a similar strength as for the donor/acceptor interaction in NHC−$SnCl_2$ (2.290(5) Å)[10a] but weaker than the one in the recently reported coordinative derivative IPr−$SnH_2W(CO)_5$[9h] (2.230(6) Å) (IPr = $(HCNAr')_2C$:, Ar′ = 2,6-*i*$Pr_2C_6H_3$). We should note that the Sn−$C_{carbene}$ distance is longer than the Sn1−C1 and Sn1−C2 bond lengths corresponding to simple covalent bonds.

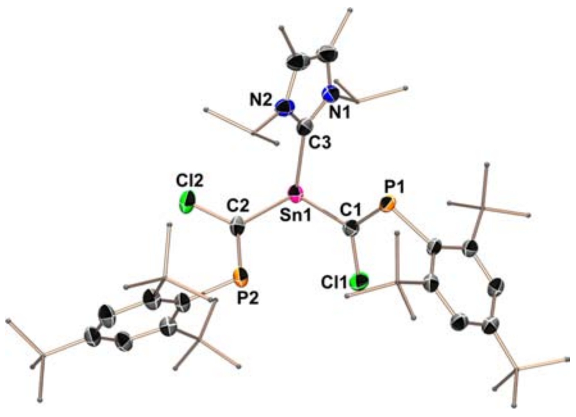


Figure 1. Molecular structure of compound **1** in the solid state (50% probability level for the thermal ellipsoids). For clarity, hydrogen atoms are omitted and methyl/isopropyl/*t*-Bu groups are simplified.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for Compounds 1, 3, 5, and 6

	1	3
Sn1−C1	2.230(2)	2.1384(15)
Sn1−C2	2.239(2)	2.1428(16)
Sn1−$C_{carbene}$	2.316(2)	
Sn1−S1		2.4134(4)
P1−C1	1.674(2)	1.6497(17)
P2−C2	1.672(2)	1.6512(17)
P1−S2		1.9187(6)
P2−S3		1.9350(6)
C1−Sn1−C2	98.24(8)	120.49(6)
C1−Sn1−S1		110.35(5)
C2−Sn1−S1		111.02(4)
	5	**6**
Ge1−C1	1.986(5)	1.945(4)
Ge1−C2	1.972(5)	1.956(4)
Ge2−C3		1.945(4)
Ge2−C4		1.953(4)
Ge1−$C_{carbene}$	2.048(5)	
Ge1−Se1	2.2426(7)	2.3482(6)
Ge1−Se2		2.3584(7)
Ge2−Se1		2.3497(7)
Ge2−Se3		2.3529(6)
Se2−Se3		2.3508(7)
P1−C1	1.673(5)	1.666(4)
P2−C2	1.660(5)	1.655(4)
P3−C3		1.668(4)
P4−C4		1.657(4)
C1−Ge1−C2	109.0(2)	110.52(15)
C3−Ge2−C4		111.70(15)
Se1−Ge1−Se2		108.87(2)
Se1−Ge2−Se3		108.61(2)

Oxidation Reactions with Sulfur and Selenium. The reactivity of the stannylene **1** was studied toward chalcogens and compared to that of the corresponding germylene NHC−Ge[C(Cl)=PMes*]$_2$ **7** previously prepared.[18] Addition of an excess of sulfur to the stannylene **1** led exclusively to the dithiadistannetanne **3** with elimination of the carbene. The four-membered ring is probably obtained by dimerization of the transient stannathione S=Sn[C(Cl)=PMes*]$_2$ and sulfur oxidative addition to the phosphorus atoms.

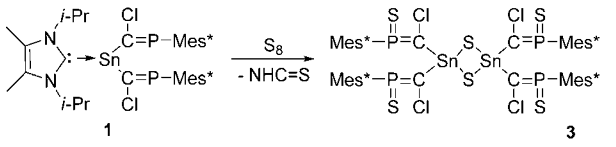
The ^{31}P NMR spectrum of **3** displayed only one signal at 189.2 ppm ($^{2}J_{P-^{117/119}Sn}$ = 258.8/270.6 Hz) showing that the four phosphorus atoms are magnetically equivalent. The low field chemical shift is characteristic of a $\lambda^5\sigma^3$ phosphorus atom; similar chemical shifts have been reported for derivatives with a Mes*P(=S)=CGe moiety.[19] The ^{1}H and ^{13}C NMR data clearly indicate the absence of the carbenic moiety and the perfect symmetry of the molecule. In addition, a triplet of triplet at −95.3 ppm with two coupling constants ($^{2}J_{Sn-P}$ = 270.7 Hz and $^{4}J_{Sn-P}$ = 7.5 Hz) was observed in the ^{119}Sn NMR spectrum in agreement with the formation of such metalloheterocycles.

The structure of **3** was unambiguously determined by single crystal X-ray diffraction analysis (Figure 2). Compound **3** has a dinuclear structure with bridging sulfur atoms in which the tin atom exhibits a distorted tetrahedral geometry. The four-membered ring is planar by symmetry and has an inversion

Table 2. Crystallographic Data for Compounds 1, 3, 5, and 6

	1	3	5	6
formula	$C_{49}H_{78}Cl_2N_2P_2Sn$	$C_{76}H_{116}Cl_4P_4S_6Sn_2.C_7H_8$	$C_{49}H_{78}Cl_2GeN_2P_2Se.1.5(C_7H_8)$	$C_{76}H_{116}Cl_4Ge_2P_4Se_3.2(C_5H_{12})$
mol wt	946.66	1817.24	1117.73	1821.72
temp. (K)	193(2)	193(2)	193(2)	193(2)
λ(Mo Kα) (Å)	0.71073	0.71073	0.71073	0.71073
cryst syst	triclinic	triclinic	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a (Å)	12.8737(2)	12.4775(4)	9.9799(5)	11.6532(17)
b (Å)	15.0045(3)	13.8395(4)	22.0637(12)	19.582(4)
c (Å)	16.0067(3)	14.3456(4)	27.7366(15)	21.979(4)
α (deg)	66.4910(10)	94.8930(10)	87.142(3)	78.469(7)
β (deg)	69.4920(10)	97.332(2)	87.901(2)	89.317(6)
γ (deg)	73.1300(10)	110.1260(10)	82.048(2)	74.700(6)
V (Å^3)	2614.52(8)	2284.64(12)	6038.4(6)	4735.6(14)
Z	2	1	4	2
d_{calcd} (g/cm^3)	1.202	1.321	1.229	1.278
μ (mm^{-1})	0.684	0.910	1.288	2.007
F(000)	1000	946	2364	1900
cryst size (mm)	0.20 × 0.20 × 0.10	0.50 × 0.38 × 0.36	0.38 × 0.06 × 0.04	0.10 × 0.08 × 0.04
θ range (deg.)	5.10 - 28.28	5.10 - 28.28	5.11 - 24.71	5.11 - 24.71
index range h k l	$-17 \leq h \leq 17$	$-16 \leq h \leq 16$	$-11 \leq h \leq 11$	$-13 \leq h \leq 13$
	$-19 \leq k \leq 19$	$-18 \leq k \leq 18$	$-25 \leq k \leq 25$	$-23 \leq k \leq 23$
	$-21 \leq l \leq 21$	$-19 \leq l \leq 19$	$-32 \leq l \leq 32$	$-25 \leq l \leq 25$
no of reflns collected/unique	35801/12828	36008/11261	100435/20176	70423/15831
	R(int) = 0.0441	R(int) = 0.0169	R(int) = 0.1033	R(int) = 0.0616
completeness to θ(%)	98.9	99.2	98.0	98.0
data/restraints/params	12828/0/529	11261/141/546	20176/783/1456	15831/324/1034
goodness-of-fit	1.007	1.049	1.046	1.013
R1, wR2 ($I > 2(\sigma)I$)	0.0360, 0.0813	0.0240, 0.0610	0.0597, 0.1084	0.0391, 0.0825
R1, wR2 (all data)	0.0534, 0.0899	0.0268, 0.0636	0.1285, 0.1282	0.0738, 0.0958
largest diff. peak, hole (eÅ^{-3})	0.651, −0.322	0.888, −0.431	0.576, −0.488	0.682, −0.360

Scheme 2. Synthesis of Dithiadistannetanne 3



center at the midpoint of the ring. The phosphaalkenyl substituents are attached to each tin atom with one above and the other one below the ring and the chlorine and sulfur atoms are situated in a trans position relatively to the P=C double bond. The Sn1−S1 and Sn1−S1′ bond lengths (2.4134(4) and 2.4196(4) Å) are comparable to those previously observed for sulfido-bridged dimers (average 2.41−2.47 Å).[15c,20] By contrast, no reaction occurs at room temperature between **1** and selenium; heating the reaction mixture at 40 °C involved a slow decomposition of stannylene.

In the case of the Ge(II) compound **7**, rapid reactions take place with both sulfur and selenium (Scheme 3). The ^{31}P NMR spectra show the presence of a sole signal at 289.9 ppm for **4** and 291.3 ppm for **5**, slightly downfield shifted in comparison with that of the starting derivative NHC−Ge[C(Cl)=PMes*]$_2$ indicating that no oxidative reaction occurs at the phosphorus atom. This difference of behavior between the tin and germanium compounds could be explained by the larger steric hindrance in the case of the germanium derivatives which prevents both dimerization reactions and oxidation at the phosphorus atom.

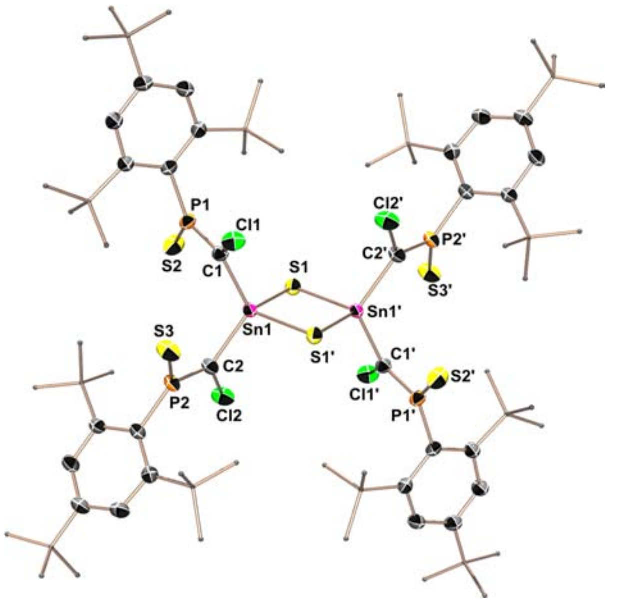
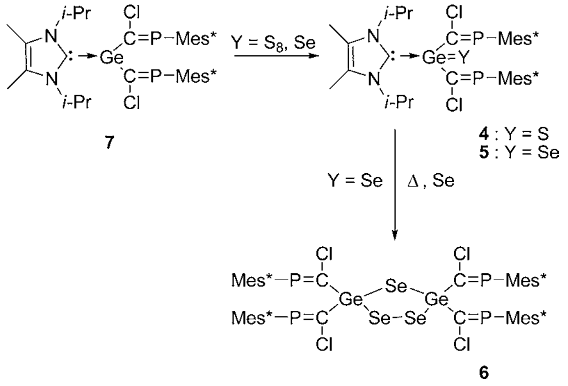


Figure 2. Molecular structure of compound **3** (50% probability level for the thermal ellipsoids). For clarity, hydrogen atoms and cocrystallized solvent (toluene) are omitted and *t*-Bu groups are simplified.

The germathione **4** was characterized by ^{1}H and ^{31}P NMR spectroscopy but decomposed to unidentified products after some hours in solution; contrary to its tin analogue, the head-

Scheme 3. Synthesis of Chalcogeno (S, Se) Germanium Compounds



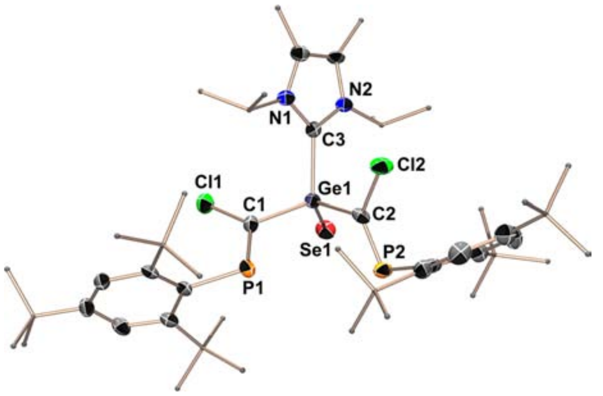


Figure 3. Molecular structure of compound **5** in the solid state (50% probability level for the thermal ellipsoids). For clarity, hydrogen atoms and cocrystallized solvent (toluene) are omitted and methyl/isopropyl/*t*-Bu groups are simplified. The asymmetric unit contains two independent molecules; only one is shown.

to-tail dimer sometimes formed from Ge═S compounds,[21] was never obtained. By contrast, the germaselenone **5** was stable and could be isolated and characterized by NMR spectroscopy and by X-ray diffraction studies (Figure 3). Some germaselenones stabilized owing to extremely bulky groups on the germanium atom or by intramolecular complexation have previously been reported.[15a,b,f,22] In our case, as the steric crowding close to the germanium atom is relatively small, the stabilization is probably due to the complexation by the carbene. The presence of the carbene is proved in the ^{13}C NMR spectrum of **5** by a signal at the expected chemical shift for the carbenic carbon atom (149.94 ppm) coupled with the phosphorus atom (${}^{3}J_{C-P}$ = 10.0 Hz). Although **4** could not be isolated due to its low stability, the fact that its ^{1}H NMR spectrum is very similar to that of **5** unambiguously proves its germathione structure. The ^{77}Se NMR spectrum of **5** displays a singlet at −173.7 ppm that is in the range of the values observed for germaselenones stabilized by intramolecular complexation (−28.7 to −348 ppm).[15f,22b] Figure 3 shows its molecular structure. The asymmetric unit contains two chemically similar but crystallographically different molecules of **5** in which the germanium atom is four-coordinated in a tetrahedral environment. The Ge−Se distance of 2.2426(7) Å is in good agreement with the values reported for Ge═Se bonds (2.199(1) and 2.223(9) Å).[15f,22b] The Ge−C$_{carbene}$ bond (2.048(5) Å) is about the same as that of the starting germylene (2.087(2) Å),[18] whereas the Ge−C(═P) bonds are slightly shorter (1.972(5) and 1.986(5) Å versus 2.011(2) and 2.014(2) Å).[18]

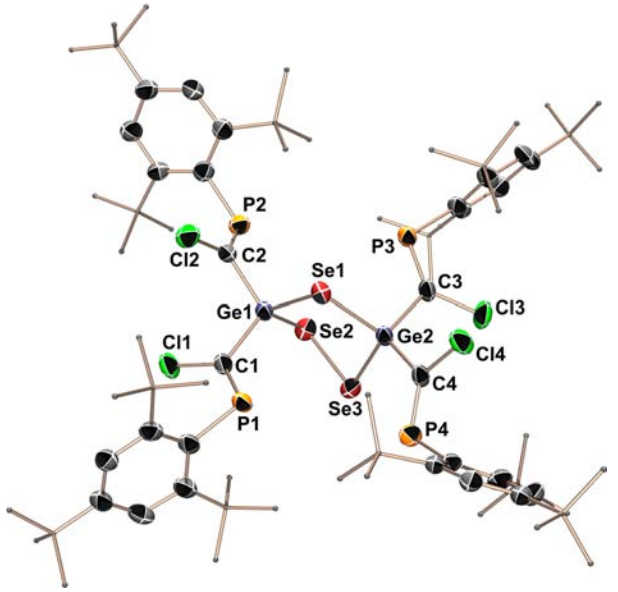


Figure 4. Molecular structure of compound **6** in the solid state (50% probability level for the thermal ellipsoids). For clarity, hydrogen atoms and cocrystallized solvent (pentane) are omitted and *t*-Bu groups are simplified.

Heating the germaselenone NHC−Ge(═Se)[C(Cl)═PMes*]$_2$ **5** at 80 °C in the presence of selenium led to the new five-membered ring derivative **6** containing three selenium and two germanium atoms with elimination of the NHC. This compound is probably formed by an initial head-to-tail dimerization followed by selenium insertion. So far, only two similar heterocycles (tetradentate [Ge$_2$Se$_7$]$^{-4}$ anions) have been reported.[23] Compound **6** was fully characterized and the solid state structure has been determined by single crystal X-ray diffraction studies (Figure 4). As observed for tetraselenagermolanes,[24] compound **6** presents a distorted half-chair conformation in which the two germanium and two selenium atoms (Se1 and Se2) almost lie in the same plane with the third selenium (Se3) at 1.365 Å out of the mean plane. The Ge−Se distances (average 2.35 Å) are slightly shorter than in the [Ge$_2$Se$_7$]$^{-4}$ anions (2.41 Å)[21a] and in a tetraselenagermolane (2.42 Å).[23a,24] Let us note that even with an excess of selenium and under heating, the formation of compounds with a P═Se unit has not been observed, contrary to the case of the tin derivative **1** which reacts with sulfur to form P═S double bonded derivative. The ^{77}Se NMR spectrum reveals the presence of two singlets at −160.4 and −500.0 ppm.

■ CONCLUSION

In summary, the first bis(phosphaalkenyl)tin(II) compound stabilized by intramolecular coordination of N-heterocyclic carbene was isolated and fully characterized, including molecular structure determination by single crystal X-ray diffraction analysis. Its reactivity toward sulfur showed the oxidation of both tin and phosphorus atoms leading to a four-membered Sn$_2$S$_2$ inorganic ring compound, probably by dimerization of a stannathione intermediate. A different behavior was observed for the germylene analogue with the sole oxidation of the germanium center and the formation of doubly bonded Ge═Y (Y = S, Se) compounds. The germaselenone was more stable than the germathione and could be structurally characterized. The slightly larger steric crowding around the Ge═Y than around the Sn═Y double bonds due to shorter M═Y and M−C distances can probably explain the nondimerization of the germathione and the germaselenone. An unusual thermal cyclization reaction of the germaselenone occurs with an excess of selenium to give a $\mathrm{Ge_2Se_3}$ inorganic ring (triselenadigermolane) derivative.

■ EXPERIMENTAL SECTION

General Procedures. All manipulations were performed in a dry and oxygen-free atmosphere of argon by using standard Schlenk-line and glovebox techniques. Solvents were purified with the MBRAUN SBS-800 purification system. NMR spectra were recorded with a Bruker Avance II 300 apparatus: ^{1}H (300.13 MHz), ^{13}C (75.48 MHz), ^{31}P (121.50 MHz), ^{119}Sn (111.92 MHz), and with a Bruker Avance 400: ^{77}Se (76.27 MHz) at 298 K, in $\mathrm{C_6D_6}$. Chemical shifts are expressed in parts per million with residual solvent signals as internal reference (^{1}H and $^{13}\mathrm{C}\{^{1}\mathrm{H}\}$) or with an external reference ($\mathrm{H_3PO_4}$ for ^{31}P, $\mathrm{SnMe_4}$ for ^{119}Sn, and $\mathrm{Me_2Se}$ for ^{77}Se). Melting points were measured in a sealed capillary using the Stuart automatic melting point SMP40 apparatus. The compounds NHC−$\mathrm{SnCl_2}$[10a] and Mes*P═$\mathrm{CCl_2}$[25] were prepared according to literature procedures.

Synthesis. *Compound 1.* A suspension of NHC−$\mathrm{SnCl_2}$ (0.30 g, 0.82 mmol) in THF (3 mL) was added to a solution of Mes*P═C(Li)Cl[25,26] (1.64 mmol) freshly prepared in THF (6 mL) at −90 °C. After 1 h of stirring at low temperature, the solution was allowed to warm up to room temperature and was stirred for an additional one hour. The volatiles were removed under reduced pressure and the residue was extracted with toluene (12 mL). After filtration, the filtrate was evaporated under vacuum to yield **1** as a light brown powder (0.63 g, 82%). Crystallization from a saturated toluene solution at room temperature gave brown crystals suitable for X-ray studies. m.p.: 157 °C (dec). ^{1}H NMR ($\mathrm{C_6D_6}$): δ = 1.19 (d, $^{3}J_{\mathrm{H-H}}$ = 7.0 Hz, 12H, $\mathrm{CH}\mathit{Me}_2$); 1.35 (s, 18H, $\mathrm{C_pCMe_3}$); 1.51 (s, 6H, ═CMe); 1.74 (s, 18H, $\mathrm{C_oCMe_3}$); 1.78 (s, 18H, $\mathrm{C_oCMe_3}$); 5.62 (sept, $^{3}J_{\mathrm{H-H}}$ = 6.8 Hz, 2H, $\mathrm{C}\mathit{H}\mathrm{Me_2}$); 7.64 (s, 4H, $\mathrm{CH_{Ar}}$). ^{13}C NMR ($\mathrm{C_6D_6}$): δ = 10.12 (═C*Me*); 22.16 ($\mathrm{CH}\mathit{Me}_2$); 31.55 ($\mathrm{C_pC}\mathit{Me}_3$); 32.64 and 32.73 ($\mathrm{C_oC}\mathit{Me}_3$); 34.98 ($\mathrm{C_pCMe_3}$); 38.11 and 38.26 ($\mathrm{C_oCMe_3}$); 53.24 ($\mathrm{CHMe_2}$); 121.29 and 121.70 ($\mathrm{C_m}$); 126.20 (NC═); 140.74 (dd, $^{1}J_{\mathrm{C-P}}$ = 83.9 Hz, $^{5}J_{\mathrm{C-P}}$ = 8.5 Hz, $\mathrm{C_iP}$); 149.22 ($\mathrm{C_p}$); 153.46 (d, $^{2}J_{\mathrm{C-P}}$ = 7.3 Hz, $\mathrm{C_o}$); 175.29 (t, $^{3}J_{\mathrm{C-P}}$ = 14.4 Hz, C:); 205.13 (dd, $^{1}J_{\mathrm{C-P}}$ = 108.2 Hz, $^{3}J_{\mathrm{C-P}}$ = 19.2 Hz, C═P). ^{31}P NMR ($\mathrm{C_6D_6}$): δ = 277.4 ($^{2}J_{\mathrm{P-^{117/119}Sn}}$ = 349.1/364.1 Hz). ^{119}Sn NMR ($\mathrm{C_6D_6}$): δ = −130.8 (t, $^{2}J_{\mathrm{Sn-P}}$ = 360.0 Hz). Anal. Calcd for $\mathrm{C_{49}H_{78}Cl_2N_2P_2Sn}$ (946.72): C, 62.16; H, 8.30; N, 2.96%. Found: C, 62.28; H, 8.25; N, 3.50%.

Compound 2. A freshly prepared solution of Mes*P═C(Li)Cl (0.83 mmol) in THF (3 mL) was added to a suspension of $\mathrm{SnCl_2}$ (0.08 g, 0.42 mmol) in THF (2 mL) at −90 °C. The solution was stirred for 15 min and then allowed to warm up to room temperature. The compound **2** was identified by ^{31}P NMR spectrometry (δ = 264.0 ppm). Addition of the carbene NHC directly into the NMR tube led to the formation of compound **1**.

Compound 3. A suspension of $\mathrm{S_8}$ (0.02 g, 0.08 mmol) in toluene (2 mL) was added to a solution of **1** (0.10 g, 0.11 mmol) in toluene (1 mL) at −70 °C. After warming up to room temperature, the orange solution was stirred for 2 h. After filtration and evaporation of the solvent under reduced pressure, derivative **3** was isolated as a yellow powder (0.11 g, 61%). Yellow crystals suitable for X-ray studies were obtained from toluene at −24 °C. m.p.: 180 °C. ^{1}H NMR ($\mathrm{C_6D_6}$): δ = 1.18 (s, 36H, $\mathrm{C_pCMe_3}$); 1.86 (s, 72H, $\mathrm{C_oCMe_3}$); 7.64 (d, $^{4}J_{\mathrm{H-P}}$ = 5.4 Hz, 8H, $\mathrm{CH_{Ar}}$). ^{13}C NMR ($\mathrm{C_6D_6}$): δ = 30.85 ($\mathrm{C_pC}\mathit{Me}_3$); 33.97 ($\mathrm{C_oC}\mathit{Me}_3$); 35.29 ($\mathrm{C_pCMe_3}$); 39.34 ($\mathrm{C_oCMe_3}$); 122.71 (d, $^{1}J_{\mathrm{C-P}}$ = 54.8 Hz, $\mathrm{C_iP}$); 123.96 (d, $^{3}J_{\mathrm{C-P}}$ = 13.4 Hz, $\mathrm{C_m}$); 135.69 (d, $^{1}J_{\mathrm{C-P}}$ = 67.8 Hz, C═P); 154.94 (d, $^{4}J_{\mathrm{C-P}}$ = 3.3 Hz, $\mathrm{C_p}$); 156.23 (d, $^{2}J_{\mathrm{C-P}}$ = 7.4 Hz, $\mathrm{C_o}$). ^{31}P NMR ($\mathrm{C_6D_6}$): δ = 189.2 ($^{2}J_{\mathrm{P-^{117/119}Sn}}$ = 258.8/270.7 Hz). ^{119}Sn NMR ($\mathrm{C_6D_6}$): δ = −95.3 (tt, $^{2}J_{\mathrm{Sn-P}}$ = 270.7 Hz; $^{4}J_{\mathrm{Sn-P}}$ = 7.5 Hz). Anal. Calcd for $\mathrm{C_{76}H_{116}Cl_4P_4S_6Sn_2}$ (1725.25): C, 52.91; H, 6.78%. Found: C, 53.46; H, 7.24%.

Compound 4. A suspension of $\mathrm{S_8}$ (0.03 g, 0.10 mmol) in toluene (2 mL) was added to a solution of germylene **7** (0.15 g, 0.17 mmol) in toluene (2 mL) at −80 °C. The mixture was allowed to warm up to room temperature when the solution became clear brown. The solution was cooled again at low temperature (around −40 °C) and filtered to remove the excess of sulfur. The solvent was evaporated under reduced pressure and **4** was obtained as a red-brown powder (0.13 g, 87%). Derivative **4** is stable in solution only for several hours, decomposing to unidentified products. M.p.: 97−98 °C. ^{1}H NMR ($\mathrm{C_6D_6}$): δ = 1.22 (d, $^{3}J_{\mathrm{H-H}}$ = 6.9 Hz, 12H, $\mathrm{CH}\mathit{Me}_2$); 1.31 (s, 18H, $\mathrm{C_pCMe_3}$); 1.54 (s, 6H, =CMe); 1.71 (s, 18H, $\mathrm{C_oCMe_3}$); 1.76 (s, 18H, $\mathrm{C_oCMe_3}$); 6.50−6.80 (m, 2H, $\mathrm{C}\mathit{H}\mathrm{Me_2}$); 7.62 (d, $^{4}J_{\mathrm{H-P}}$ = 6.3 Hz, 4H, $\mathrm{CH}_{\mathit{Ar}}$). ^{31}P NMR ($\mathrm{C_6D_6}$): δ = 289.9.

Compound 5. A suspension of Se (0.03 g, 0.44 mmol) in toluene (3 mL) was added to a solution of germylene **7** (0.10 g, 0.11 mmol) in toluene (3 mL) at −70 °C. After 30 min of stirring at room temperature, the solution was filtered and the red filtrate was evaporated under low pressure. Derivative **5** was isolated as a orange powder (0.10 g, 96%), and crystallized from toluene at −24 °C. m.p.: 173 °C. ^{1}H NMR ($\mathrm{C_6D_6}$): δ = 1.23 (d, $^{3}J_{\mathrm{H-H}}$ = 6.9 Hz, 12H, $\mathrm{CH}\mathit{Me}_2$); 1.32 (s, 18H, $\mathrm{C_pCMe_3}$); 1.57 (s, 6H, ═CMe); 1.71 (s, 18H, $\mathrm{C_oCMe_3}$); 1.78 (s, 18H, $\mathrm{C_oCMe_3}$); 6.45−6.65 (m, 2H, $\mathrm{C}\mathit{H}\mathrm{Me_2}$); 7.62 (d, $^{4}J_{\mathrm{H-P}}$ = 6.6 Hz, 4H, $\mathrm{CH_{Ar}}$). ^{13}C NMR ($\mathrm{C_6D_6}$): δ = 10.36 (═C*Me*); 22.02 ($\mathrm{CH}\mathit{Me}_2$); 31.41 ($\mathrm{C_pC}\mathit{Me}_3$); 33.25, 33.59 ($\mathrm{C_oC}\mathit{Me}_3$); 34.98 ($\mathrm{C_pCMe_3}$); 38.10 and 38.87 ($\mathrm{C_oCMe_3}$); 51.37 ($\mathrm{CHMe_2}$); 121.48 and 122.74 ($\mathrm{C_m}$); 125.13 (C═); 137.04 (d, $^{1}J_{\mathrm{C-P}}$ = 66.9 Hz, $\mathrm{C_iP}$); 149.94 (t, $^{3}J_{\mathrm{C-P}}$ = 10.0 Hz, C:); 150.11 ($\mathrm{C_p}$); 153.63, 154.98 ($\mathrm{C_o}$); 172.29 (d, $^{1}J_{\mathit{C-P}}$ = 92.0 Hz, C═P). ^{31}P NMR ($\mathrm{C_6D_6}$): δ = 291.3. ^{77}Se NMR ($\mathrm{C_6D_6}$): δ = −173.7. Anal. Calcd for $\mathrm{C_{49}H_{78}Cl_2GeN_2P_2Se}$ (979.61): C, 60.08; H, 8.03; N, 2.86%. Found: C, 60.60; H, 8.18; N, 3.31%.

Compound 6. A suspension of Se (0.05 g, 0.64 mmol) in toluene (2 mL), was added to a solution of **7** (0.14 g, 0.16 mmol) in toluene (4 mL) at −70 °C. The mixture was stirred for 30 min at room temperature; the ^{31}P NMR spectrum showed the complete conversion to derivative **5**. After heating for 2.5 h at 80 °C, the mixture was filtered and the filtrate was completely evaporated under low pressure to yield **6** as a red powder (0.16 g, 59%). Crystals suitable for X-ray studies were obtained from toluene at −24 °C. m.p.: 92 °C. ^{1}H NMR ($\mathrm{C_6D_6}$): δ = 1.28 (s, 36H, $\mathrm{C_pCMe_3}$); 1.60 (s, 36H, $\mathrm{C_oCMe_3}$); 1.62 (s, 36H, $\mathrm{C_oCMe_3}$); 7.59 (d, $^{4}J_{\mathrm{H-P}}$ = 2.7 Hz, 8H, $\mathrm{CH}_{\mathit{Ar}}$). ^{13}C NMR ($\mathrm{C_6D_6}$): δ = 31.30 ($\mathrm{C_pC}\mathit{Me}_3$); 33.16 ($\mathrm{C_oC}\mathit{Me}_3$); 35.05 ($\mathrm{C_pC}\mathit{Me}_3$); 38.04 and 38.08 ($\mathrm{C_oCMe_3}$); 122.35 ($\mathrm{C_m}$); 134.91 (d, $^{1}J_{\mathrm{C-P}}$ = 66.0 Hz, $\mathrm{C_iP}$); 151.18 ($\mathrm{C_p}$); 154.05 and 154.42 ($\mathrm{C_o}$); 163.78 (dd, $^{1}J_{\mathrm{C-P}}$ = 88.6 Hz, $^{5}J_{\mathrm{C-P}}$ = 8.0 Hz, C═P). ^{31}P NMR ($\mathrm{C_6D_6}$): δ = 295.8. ^{77}Se NMR ($\mathrm{C_6D_6}$): δ = −160.4 and −500.0 ppm. Anal. Calcd for $\mathrm{C_{76}H_{116}Cl_4Ge_2P_4Se_3}$ (1677.60): C, 54.41; H, 6.97%. Found: C, 54.94; H, 7.53%.

X-ray Structure Determinations. X-ray data for compounds **1**, **3**, **5**, and **6** were collected at low temperature (193 K) on a Bruker-AXS SMART APEX II diffractometer (compound **1**) and on a Bruker-AXS APEX II Quazar diffractometer using a 30 W air-cooled microfocus source (ImS) with focusing multilayer optics (compounds **3**, **5** and **6**) with graphite-monochromated MoKα radiation (wavelength = 0.71073 Å) by using phi- and omega-scans. The data were integrated with SAINT, and an empirical absorption correction with SADABS was applied.[27] The structures were solved by direct methods, using SHELXS-97[28] and refined using the least-squares method on F^2.[29] All non-H atoms were treated anisotropically. The H atoms were located by difference Fourier maps and refined with a riding model. Crystallographic data are summarized in Table 1.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Crystallographic data in CIF format for compounds **1**, **3**, **5**, and **6**. This material is available free of charge via the Internet at http://pubs.acs.org

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Notes

The authors declare no competing financial interest.

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