Synthesis and characterization of a tin(II) bis(phosphinoyl)methanediide complex: a stannavinylidene derivative†

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The reaction of [$CH_2(PPh_2{=}NSiMe_3)(PPh_2{=}S)$] (1) with two equivalents of [$Sn\{N(SiMe_3)_2\}_2$] in refluxing toluene afforded novel tin(II) bis(phosphinoyl)methanediide complex 3. The structure of compound 3 has been determined by X-ray crystallography and DFT calculations. The topological analysis of the electron densities of compound 3 was performed.

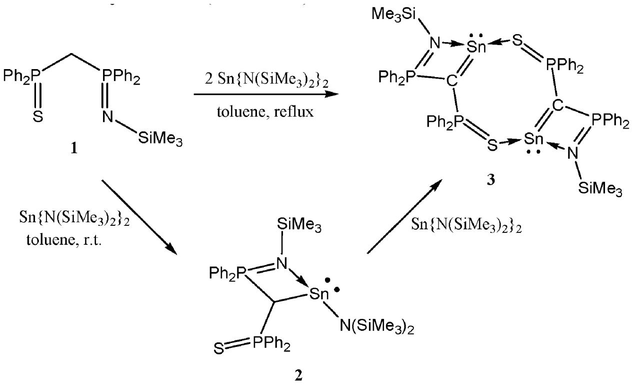
Compounds containing a double bond between carbon and heavier group 14 elements ($>M{=}C<$; M = Si, Ge, Sn) have attracted much attention in the past 20 years, and have been the focus of several reviews.[1] It was found that the thermal stability of the M=C bond is intrinsically low, and it can undergo oligomerization readily. Nevertheless, stable silenes ($>Si{=}C<$),[2] germenes ($>Ge{=}C<$)[3] and stannenes ($>Sn{=}C<$)[4] can be synthesized by incorporating sterically hindered substituents at both carbon and heavier group 14 elements. In contrast, stable heavier group 14 vinylidene analogues ($:M{=}C<$) are scarcely known. Because of lacking bulky substituents at the low-coordinate metal(II) center, they are expected to oligomerize more readily. Until now, only one example of a bisgermavinylidene [$(Me_3SiN{=}PPh_2)_2C{=}Ge{\rightarrow}Ge{=}C(PPh_2{=}NSiMe_3)_2$] containing a weak Ge–Ge interaction has been reported and structurally characterized.[5] The existence of the monomeric germavinylidene intermediate "{$(Me_3SiN{=}PPh_2)_2C{=}Ge:$}" in solution has been demonstrated by the trapping reactions of bisgermavinylidene with various transition metal complexes.[6]

In this communication, we report the synthesis and characterization of a novel tin(II) bis(phosphinoyl)methanediide complex, which is regarded as a stannavinylidene ($:Sn{=}C<$) derivative.

The reaction of [$CH_2(PPh_2{=}NSiMe_3)(PPh_2{=}S)$] (**1**)[7] with two equivalents of [$Sn\{N(SiMe_3)_2\}_2$] in refluxing toluene afforded compound **3** (Scheme 1).[8] Similar reaction of **1** with two equivalents of [$Sn\{N(SiMe_3)_2\}_2$] in toluene at room temperature gave [$HC\{(PPh_2{=}NSiMe_3)(PPh_2{=}S)\}SnN(SiMe_3)_2$] (**2**) together with a small amount of **3**. It is suggested that compound **2** was dehydroaminated by [$Sn\{N(SiMe_3)_2\}_2$] in refluxing toluene to form **3**. In contrast, the reaction of [$CH_2(PPh_2{=}NSiMe_3)_2$] with [$Sn\{N(SiMe_3)_2\}_2$] afforded the 1,3-distannacyclobutane [$Sn\{\mu_2\text{-}C(PPh_2{=}NSiMe_3)_2\}]_2$.[5]

Compounds **2** and **3** were isolated as highly air- and moisture-sensitive colorless and yellow crystalline solids, respectively. Compound **2** is soluble in Et_2O and toluene, while compound **3** is soluble in CH_2Cl_2 and THF only. They have been characterized by NMR spectroscopy and X-ray crystallography. The ^1H NMR spectra of **2** and **3** display resonances for the $SiMe_3$ and phenyl protons. It is noteworthy that the ^{13}C NMR signal for the carbenic carbon in **3** is not observed. Similarly, there is no ^{13}C NMR resonance for the carbenic carbon in the bisgermavinylidene.[5] The ^{31}P NMR signals of **3** [δ 20.5, 27.4 ppm (d, $^2J_{P\text{–}P'}$ = 17.5 Hz)] show an upfield shift compared with those of **2** [δ 30.2 (t, $^2J_{Sn\text{–}P}$ = 73.7 Hz), 34.7 ppm (t, $^2J_{Sn\text{–}P'}$ = 39.0 Hz)]. Comparing the ^{119}Sn NMR signal of **3** [δ 132.1 ppm (dd, $^2J_{Sn\text{–}P}$ = 177.1 Hz)] with that of **2** (δ −19.3 ppm), the 1,3-distannacyclobutane in [2-{$Sn\{C(i\text{-}Pr_2P{=}NSiMe_3)\}$}-6-{$Sn\{CH(i\text{-}Pr_2P{=}NSiMe_3)\}Cl$}-$C_5H_3N$]$_2$ (δ −10.96 ppm)[9] and the 6-stannapentafulvene [$(Tbt)(Mes)Sn{=}CR_2$] (Tbt = 2,4,6-{$CH(SiMe_3)_2$}$_3C_6H_2$, Mes = 2,4,6-$Me_3C_6H_2$, CR_2 = fluorenylidene) (δ 270 ppm),[4d] it is suggested that compound **3** exists as a tin(II) bis(phosphinoyl)methanediide complex and does not undergo oligomerization in solution.

The molecular structure of **2** is shown in Fig. 1.[10] In the asymmetric unit, there are two independent molecules with slightly different bond distances and angles. Only one of them is discussed here for clarity. The methanide ligand is bonded in a *C*,*N*′-chelate fashion to the tin center and displays a trigonal pyramidal geometry. The thiophosphinoyl group of the ligand remains uncoordinated. The sum of the bond angles



Scheme 1 Synthesis of **2** and **3**.

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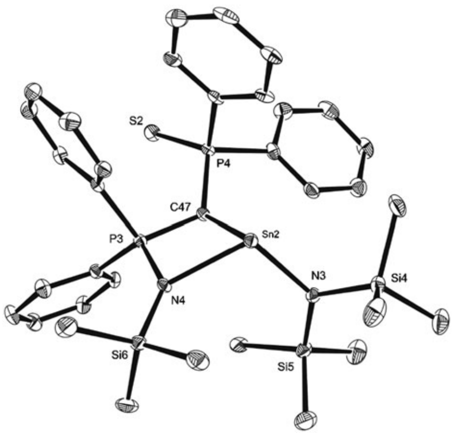


Fig. 1 Molecular structure of **2**. One of two independent molecules in the asymmetric unit is shown. Hydrogen atoms and solvent atoms are omitted for clarity. Selected bond distances (Å) and angles (°): Sn(2)–C(47) 2.384(4), Sn(2)–N(3) 2.152(4), Sn(2)–N(4) 2.275(3), P(3)–C(47) 1.776(4), P(4)–C(47) 1.780(4), P(3)–N(4) 1.612(3), P(4)–S(2) 1.960(2); C(47)–Sn(2)–N(3) 98.8(1), N(3)–Sn(2)–N(4) 106.6(1), C(47)–Sn(2)–N(4) 67.8(1), Sn(2)–N(4)–P(3) 96.0(2), N(4)–P(3)–C(47) 100.2(2), P(3)–C(47)–P(4) 123.4(2).

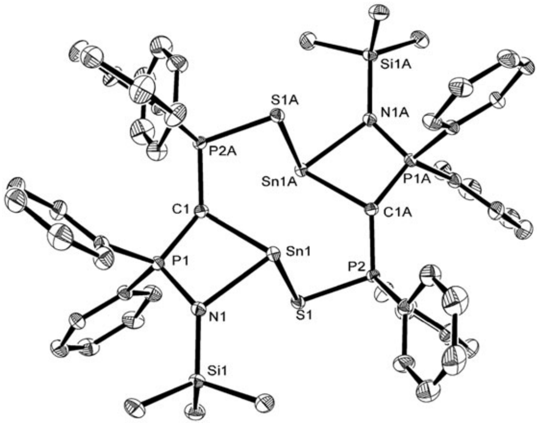
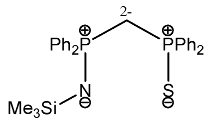


Fig. 2 Molecular structure of **3**. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (°): Sn(1)–C(1) 2.2094(9), Sn(1)–N(1) 2.2554(8), Sn(1)–S(1) 2.6926(2), P(1)–N(1) 1.6158(8), C(1)–P(1) 1.7071(9), C(1)–P(2A) 1.6870(9), P(2)–S(1) 2.0390(3); C(1)–Sn(1)–S(1) 96.34(2), N(1)–Sn(1)–S(1) 91.12(2), C(1)–Sn(1)–N(1) 70.62(3), Sn(1)–N(1)–P(1) 94.15(3), N(1)–P(1)–C(1) 101.89(4), P(1)–C(1)–P(2A) 137.44(5), Sn(1)–C(1)–P(2A) 119.62(5), Sn(1)–C(1)–P(1) 93.26(4).

at the tin center is 273.3°, which is significantly smaller than that of 337.7° in the tetra-coordinated stannylene $[Sn\{N(SiMe_3)C(Ph)C(SiMe_3)(C_5H_4N\text{-}2)\}_2]$.[11] This geometry is consistent with a stereoactive lone pair at the tin center. The Sn(2)–C(47) (2.384(4) Å), Sn(2)–N(3) (2.152(4) Å) and Sn(2)–N(4) (2.275(3) Å) bonds in **2** are comparable with those of $[\{C_5H_4N\text{-}2\text{-}C(SiMe_3)_2\}Sn\{N(SiMe_3)_2\}]$ (Sn–C: 2.356(8) Å, $Sn–N_{amide}$: 2.144(5) Å, $Sn–N_{pyridine}$: 2.299(5) Å), respectively.[12]

The molecular structure of **3** is shown in Fig. 2.[10] It is symmetric and comprised of two "$(PPh_2{=}NSiMe_3)(PPh_2{=}S)CSn$:" moieties bonded together in a head-to-head manner. The tin atom Sn(1) is bonded to the methanediide carbon atom C(1), one nitrogen and one sulfur atom of each ligand. Therefore, the geometry around the tin atom is trigonal pyramidal. The sum of the bond angles at the tin atom is 258.08°, which is comparable with that of **2** (273.3°). This geometry is consistent with a stereoactive lone pair at the tin center. The C(1)–Sn(1) bond (2.2094(9) Å) in **3** is significantly shorter than that of **2** (2.384(4) Å) and the 1,3-distannacyclobutane $[Sn\{\mu^2\text{-}C(PPh_2{=}NSiMe_3)_2\}]_2$ (average 2.322 Å).[5] This demonstrates some double bond character in the C(1)–Sn(1) bond. The C(1)–Sn(1) bond is longer than that of the stannaethene $[\{(Me_3Si)_2CH\}_2Sn{=}C\{(B\mathit{t}\text{-}Bu)_2C(SiMe_3)_2\}]$ (2.025(4) Å)[4a] and the 6-stannapentafulvene $[(Tbt)(Mes)Sn{=}CR_2]$ (2.016(5) Å)[4d] due to the lower oxidation state of the tin atom in **3**. The Sn(1)–N(1) bond (2.2554(8) Å) in **3** is comparable with that of **2** (2.275(3) Å), while it is longer than the terminal Sn–N σ-bond in $[{:}Sn\{N(SiMe_3)_2\}_2]$ (2.096(1) Å).[13] The Sn(1)–S(1) bond (2.6926(2) Å) is longer than the terminal Sn–S σ-bond in $[{:}Sn(SAr)_2]$ (Ar = C_6H_2-2,4,6-*t*-Bu_3) (2.435(1) Å),[14] but it is comparable with that of the aryltin(II) dithiocarboxylate $[{:}Sn(Ar)\{S_2CAr\}]$ (average 2.659 Å).[15]

In order to understand the bonding nature in **3**, a simple derivative $[{:}Sn{=}C(PH_2{=}NH)(PH_2{=}S)]_2$ (**3A**) (Fig. S1, ESI†) was investigated by means of quantum chemical calculations. The calculations were performed by the density functional theory (DFT)[16] B3LYP[17] as implemented in the Gaussian 03 program.[18] To account for the relativistic effect on the tin atoms and hypervalent bonds, one augmented LanL2DZ basis set with the d, p polarization functions (denoted as LanL2DZ(d,p))[19] is adopted in the calculation. Compound **3A** was fully optimized with C_i symmetry and confirmed as a stable molecular structure. The calculated structural parameters (Å, °) (Sn(1)–C(1): 2.217, Sn(1)–N(1): 2.205, P(1)–C(1): 1.722, P(1)–N(1): 1.658, P(2A)–C(1): 1.717, P(2)–S(1): 2.062, Sn(1)–S(1): 2.796; C(1)–Sn(1)–N(1): 70.6, Sn(1)–N(1)–P(1): 96.4, N(1)–P(1)–C(1): 98.2) are in good agreement with the crystallographic data. Each "$(PH_2{=}NH)(PH_2{=}S)CSn$:" moiety in compound **3A** almost locates at the same plane which is slightly different from the X-ray structure of **3**. The natural bond orbital (NBO)[20] analysis shows that the Sn(1) atom is almost non-hybridized (Table S1, ESI†). The Sn(1)–C(1) σ bond is formed by p-rich hybrids on the tin atom ($s^{0.25}p^{2.00}$) and $sp^{2.00}$ hybrids on the carbon atom. The Sn(1)–C(1) π bond is formed by pure p orbitals on both atoms. The electron density of the Sn(1)–C(1) σ and π bonds are mostly occupied by the C(1) atom (85.3% electron density of σ bond and 96.9% electron density of π bond). Thus, the NBO bond order by the natural-resonance-theory (NRT)[21] analysis shows that the Sn(1)–C(1) bond is highly polar (19.5% covalent character, 82.0% ionic character). The lone pair electrons at the tin center are high in s-character with some directionality ($sp^{0.18}$, occupancy: 1.98). It is suggested that the Sn(1)–C(1) bond has a >C=Sn: skeleton. The reactive Sn(1)–C(1) bond is stabilized by the lone pair of electrons on the N(1) and S(1) atoms. The Wiberg bond index (WBI)[22] of the P–C (1.105, 1.109), P–N (0.979) and P–S bonds (1.077) shows that the charge distributions on the ligand backbone are consistent with a resonance structure **A** (Fig. 3), which is an extreme case. One lone pair of electrons on the N(1) atom form p–π conjugation with the π orbital of the Sn(1)–C(1) bond (second-order perturbation stabilizing



A

Fig. 3 The charge distributions on the ligand backbone **A**.

energy: 6.65 kcal mol^{-1}), while another lone pair of electrons donates strongly to the vacant p-rich hybrids ($sp^{23.23}$ (95.9% p-character), occupancy: 0.22) of the Sn(1) atom (second order perturbation stabilizing energy: 80.05 kcal mol^{-1}). One lone pair of electrons on the S(1) atom delocalize to the π* orbital of the Sn(1)–C(1) bond (second-order perturbation stabilizing energy: 42.07 kcal mol^{-1}).

The topological analysis of the electron densities of compound **3** according to Bader's quantum theory of atoms in molecules (QTAIM) was performed.[23] Compound **3** is optimized at the B3LYP[17] level with the cc-pVTZ-PP basis set[24] for Sn and the 6-31G(d) basis set for other atoms. The Laplacian of electron density $\nabla^2\rho$ and the total energy density H at the (3,−1) bond critical point (BCP) show that the Sn–C bonds in **3**, [:Sn(CH_3)H] and [:Sn=CH_2] are polar and covalent (Table 1). The bond nature of the Sn–C bond in **3** is in between that of the :Sn–C bond in [:Sn(CH_3)H] and that of the :Sn=C bond in [:Sn=CH_2]. As there may be substantive π-electron delocalization along the Sn–C bond in compound **3**, it is unsurprising to find that the Sn–C bonds in compound **3** may have little double bond character compared with the :Sn=C bond in [:Sn=CH_2].

In conclusion, the first example of a tin(II) bis(phosphinoyl)-methanediide compound **3**, has been synthesized successfully by the reaction of **1** with two equivalents of [Sn{N($SiMe_3$)$_2$}$_2$] in refluxing toluene. It is suggested that the reaction proceeded through the intermediate compound **2**, which was further dehydroaminated by [Sn{N($SiMe_3$)$_2$}$_2$] to form **3**. X-Ray crystallography shows that the Sn–C bond in compound **3** has some double character. DFT calculations show that the Sn–C bond in **3** has a >C=Sn: skeleton which is stabilized by the lone pair of electrons on the nitrogen and sulfur donors. Topological analysis of the electron densities shows that the Sn–C bond in **3** is polar and covalent and its bond nature is between a single and double bond.

Table 1 Theoretical topological features at the BCP of **3**, [:SnH(CH_3)] and [:Sn=CH_2][a]

Bond	ρ	$\nabla^2\rho$	G	H	$\lvert V\rvert$
3					
Sn(1)–C(1)	0.57	3.24	0.42	−0.20	0.62
C(1)–P(1)	1.22	2.22	1.36	−1.21	2.57
P(1)–N(1)	1.23	14.88	2.02	−0.98	3.00
C(1)–P(2A)	1.24	3.25	1.43	−1.20	2.63
P(2)–S(1)	0.97	−5.58	0.25	−0.64	0.89
Sn(1)–N(1)	0.44	4.50	0.39	−0.08	0.47
Sn(1)–S(1)	0.30	1.36	0.15	−0.06	0.21
[:SnH(CH_3)]					
Sn–C	0.64	2.85	0.44	−0.24	0.67
[:Sn=CH_2]					
Sn–C	0.87	6.52	0.87	−0.41	1.28

[a] Units: ρ (e Å^{-3}); $\nabla^2\rho$ (e Å^{-5}); H, G, $\lvert V\rvert$ (hartree Å^{-3}).

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