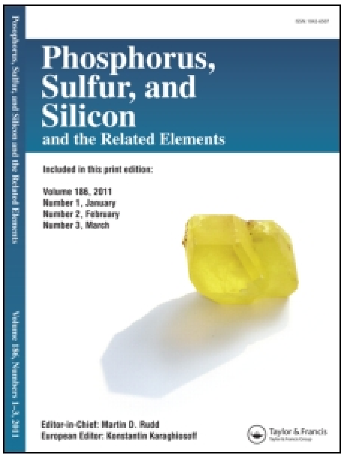

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Syntheses and Crystal Structures of [$ClPh_2Sn\{E(Ph_2SN)_2\}$] (E = CH, N)

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SYNTHESES AND CRYSTAL STRUCTURES OF [$\mathrm{ClPh_2Sn\{E(Ph_2SN)_2\}}$] (E = CH, N)

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Reaction of lithium salts, Li{E(SPh$_2$N)$_2$} (E = CH (1$^-$), N(2$^-$)) with diphenyltin dichloride in THF at –20 °C gave the corresponding tin-complexes [ClPh$_2$Sn{E(Ph$_2$SN)$_2$}] (E = CH (3), N (4)) in good yields. The crystal structures of both compounds were determined by X-ray crystallographic analysis and showed to consist with a monomeric chelate structure that contains a distorted trigonal bipyramidal tin atom with a nitrogen and a chlorine atom in the axial sites. The chelated ligands in 3 and 4 adopt a boat and a twist boat conformation, respectively.

Supplemental materials are available for this article. Go to the publisher's online edition of *Phosphorus, Sulfur, and Silicon and the Related Elements* to view the free supplemental file.

Keyword λ^6-Sulfanenitrile; organotin compounds; sulfonium diketimide analogues; X-ray crystallographic analysis

INTRODUCTION

The coordination chemistry of β-diketiminato ligands (A) has attracted considerable attention.[1] β-Diketiminato ligands have been recognized as useful monoanionic spectator ligands due to their strong binding to metal centers and tenability by variation of backbone substituents. Although there have been significant studies of the effects of varying backbone

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Dedicated to Professor Naomichi Furukawa on the occasion of his 70th birthday.

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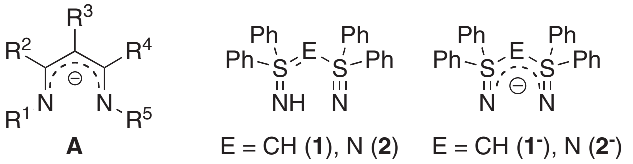
substituents,[2] there have been only limited attempts to alter the backbone itself in order to further modify the coordination sphere around the metal.

Recently we have succeeded in the preparation of a new type of λ^6-sulfanenitrile ligands **1** and **2** incorporating S^{VI}–N donors into the ligand backbone, resulting in sulfonium diketimide analogues.[3,4] The thiazyl nitrogen ($S^{VI}\equiv N$) has a nucleophilic character. For example, triphenyl-λ^6-sulfanenitrile (Ph_3SN) reacts with several electrophiles and $CuCl_2$ to give the corresponding iminosulfonium salts ([Ph_3SNR][X]: R = alkyl, tosyl, acyl, NO_2) and copper complexes ($[CuCl_2\{\mu\text{-}NSPh_3\}]_2$ and $[CuCl_2\{Ph_3SN\}_2]$).[5] Moreover, coordination studies of λ^6-sulfanenitrile with an SN triple bond at both ends, $\{Ph_2S(NPh_2SN)_2\}$, have been performed, which showed that the ligand worked as a bidentate *N,N′* ligand.[6] These results prompted us to explore the possibility that deprotonated **1** and **2** could be utilized as bidentate ligands. In this article, we report the synthesis and the structural characterization of tin–sulfonium diketiminates **3** and **4** (Scheme 1).

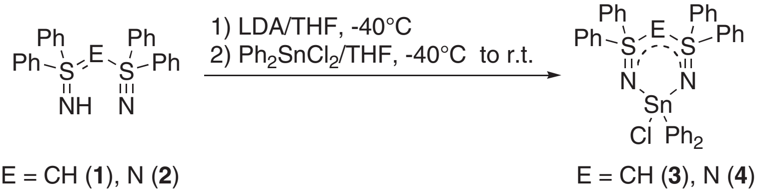


A E = CH (**1**), N (**2**) E = CH (**1**$^-$), N (**2**$^-$)

Scheme 1

RESULTS AND DISCUSSION

The ligands, $\{E(Ph_2SN)(Ph_2SNH)\}$ [E = CH (**1**), N (**2**)] were synthesized by the reaction of fluorodiphenyl-λ^6-sulfanenitrile (FPh_2SN)[7] with α-lithiated methyldiphenyl-λ^6-sulfanenitrile ($MePh_2SN$)[8] and that with sodium salt of diphenylsulfodiimide ($Ph_2S(NH)_2$), respectively.[3,4a] The reaction of lithium salts, $Li\{E(SPh_2N)_2\}$ [E = CH (**1**$^-$), N(**2**$^-$)], prepared by deprotonation of **1** and **2** with lithium diisopropylamide (LDA), with 1.1 molar amounts of diphenyltin dichloride in THF at −20°C, gave the corresponding tin complexes $[ClPh_2Sn\{E(Ph_2SN)_2\}]$ [E = CH (**3**), N (**4**)] in 89% and 93% yields, respectively (Scheme 2). ^1H NMR, IR, and elemental analyses were consistent with the structures **3** and **4**.



E = CH (**1**), N (**2**) E = CH (**3**), N (**4**)

Scheme 2

The crystal structures of the novel tin complexes **3** and **4** were determined by X-ray crystallographic analysis. For comparison, single crystal X-ray determination of protonated ligand $\{CH(Ph_2SNH)_2\}^+ClO_4^-$ (**5**) was also carried out. ORTEP drawings of **3**–**5** are

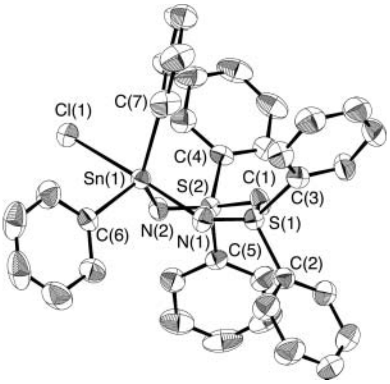


Figure 1 ORTEP drawing of **3** [50% probability thermal ellipsoids; H atoms have been omitted for clarity].

depicted in Figures 1–3. Crystal data for **3**–**5** are given in Table I. Selected bond lengths and angles for **3**–**5** are collected in Table II.

A six-membered metallacycle [Sn(1)—N(1)—S(1)—C(1)—S(2)—N(2)] in **3** is formed by chelation of the two nitrogen atoms of ligand $\{CH(Ph_2SN)_2\}^-$ ($\mathbf{1}^-$) to the tin atom, resulting in a boat conformation (Figure 1). The tin and the central carbon atom (C1) lie outside the quasiplane formed by S_2N_2 of the ring by 0.967 and 0.292 Å, respectively. The bite angle of N(1)—Sn(1)—N(2) [89.54(13)°] is larger than those of tin–β-diketiminates, $[ClMe_2Sn\{HC(Ph_2CNR)_2\}]$ [R = TMS, 81.0(3)°; H, 82.1(1)°].[9] The distance between the central carbon atom (C1) and the tin atom (3.526 Å) is somewhat shorter than the sum of their van der Waals radii (3.85 Å),[10] which is indicative of the presence of the weak interaction. However, this weak interaction may cause the six-membered ring to fold toward the tin atom.[9] The five coordinate tin atom in **3** adopts a distorted trigonal bipyramidal geometry (Figure 1). The equatorial plane is formed by one nitrogen atom of ligand $\mathbf{1}^-$ and two carbon atoms of the phenyl groups (the sum of bond angles for NSnC2 girdle is 359.3°). The chlorine atom and nitrogen atom of ligand $\mathbf{1}^-$ occupy the axial positions, in agreement with the value of the Cl(1)—Sn(1)—N(1) angle of 172.69(9)°. The axial Sn—Cl bond length of 2.676(11) Å is significantly longer than that of $[Ph_2SnCl_2]$

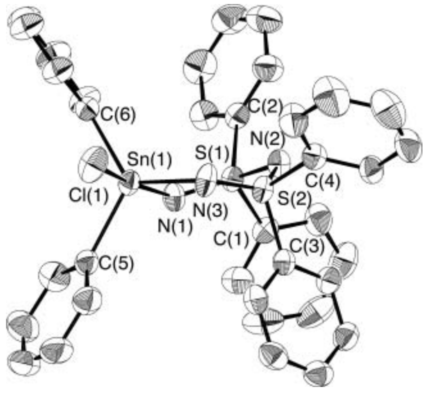


Figure 2 ORTEP drawing of **4** [50% probability thermal ellipsoids; H atoms have been omitted for clarity].

(mean 2.346(2)[11]). The $\{CH(Ph_2SN)_2\}^-$ ($\mathbf{1}^-$) is asymmetically attached to the tin atom, and the axial Sn—N(1) bond (2.175(4) Å) is longer than the equatorial Sn—N(2) bond [2.046(3) Å] and that of [$Ph_2Sn\{t\text{-}Bu_3PN\}_2$] [mean 1.972(6) Å[12]].

The crystal structure of **4** also adopts a monomeric distorted trigonal bipyramidal structure with a tin atom binding to two nitrogen atoms of ligand $\mathbf{2}^-$, two carbon atoms of the phenyl groups, and one chloride. The apical Cl(1)—Sn(1)—N(1) angle is 171.14(5)°, while the equatorial angles (mean 119.97(8)°) correspond to ideal value of 120°. Although the chelated ligand adopts a twist boat conformation, the distance between the central nitrogen atom (N(2)) and the tin atom (3.737 Å) is considerably long (the sum of their van der Waals radii; 3.54 Å[10]). The bite angle of N(1)—Sn(1)—N(2) (88.97(7)°) in **4** is similar to that of **3**. Similarly, the axial Sn—Cl (2.5392(7) Å) and Sn—N(1) (2.2294(17) Å) bond lengths are significantly larger than that of tetracoordinated organotin compounds (e.g., [Ph_2SnCl_2] and [$Ph_2Sn\{t\text{-}Bu_3PN\}_2$]).[11,12]

Comparison with the structure of related derivatives such as protonated ligand $\{E(Ph_2SNH)_2\}^+$ [E = CH (**5**), N (**6**)[4a]] reveals that the terminal S—N bond lengths in the tin complexes **3** and **4** [**3**; mean 1.507(4) Å, **4**; mean 1.4856(18) Å] are slightly shorter than those of the corresponding protonated ligands **5** and **6** [**5**; mean 1.518(4) Å, **6**; mean 1.503(3) Å[4a]], while the internal S—C(1) [mean 1.690(3) Å] and S—N(2) [mean 1.6196(17) Å] bond lengths are close and somewhat large, respectively [**5**; mean 1.686(5) Å, **6**; mean

Table I Crystallographic data for compounds **3**—**5**

.	**3**	**4**	**5**
Formula	$C_{37}H_{31}ClN_2S_2Sn$	$C_{36}H_{30}ClN_3S_2Sn$	$C_{25}H_{23}ClN_2O_4S_2$
Fw	721.90	722.89	515.02
Crystal size (mm)	0.30 × 0.20 × 0.10	0.40 × 0.30 × 0.30	0.40 × 0.30 × 0.20
Temp (K)	296(2)	296(2)	296(2)
λ (Å)	0.71075	0.71075	0.71075
Crystl Syst.	Monoclinic	Triclinic	Orthorhombic
Space group	Pc	P-1	Pna21
a (Å)	8.9534(14)	9.8002(15)	15.3448(14)
b (Å)	11.099(2)	9.9884(13)	10.8930(15)
c (Å)	16.450(2)	17.227(3)	14.614(2)
α (deg)	90.00	95.525(12)	90.00
β (deg)	100.785(2)	101.550(12)	90.00
γ (deg)	90.00	97.509(12)	90.00
V (Å^3)	1605.8(5)	1624.9(4)	2442.8(5)
Z	2	2	4
ρ_c (Mg/m^3)	1.493	1.477	1.400
μ (mm^{-1})	1.038	1.027	0.362
F (000)	732	732	1072
T_{min}/T_{max}	0.7459/0.9033	0.6841/0.7481	0.8686/0.9311
θ range/deg	1.83–27.42	2.53–29.98	2.65–29.99
Reflections collected	14766	9941	3699
Independent reflections	6996	9440	3699
R_{int}	0.0391	0.0368	0.000
Data/restraints/parameters	6996/2/388	9440/0/388	3699/1/319
R_1, wR_2 ($I>2\sigma[I]$)	0.0293, 0.0672	0.0275, 0.0663	0.0403, 0.1059
R_1, wR_2 (all data)	0.0335, 0.0815	0.0485, 0.0725	0.1048, 0.1261
GOF/F^2	1.120	1.020	1.004

Table II Selected bond lengths (Å) and angles (deg) compounds **3**–**5**

3			
Sn(1)–Cl(1)	2.6762(11)	S(1)–C(2)	1.801(4)
Sn(1)–N(1)	2.175(4)	S(1)–C(3)	1.811(4)
Sn(1)–N(2)	2.046(3)	S(2)–N(2)	1.510(3)
Sn(1)–C(5)	2.131(4)	S(2)–C(1)	1.686(3)
Sn(1)–C(6)	2.127(4)	S(2)–C(3)	1.796(4)
S(1)–N(1)	1.504(4)	S(2)–C(4)	1.794(4)
S(1)–C(1)	1.693(3)		
Cl(1)–Sn(1)–N(1)	172.69(9)	N(2)–Sn(1)–C(6)	115.58(15)
Cl(1)–Sn(1)–N(2)	83.17(10)	C(5)–Sn(1)–C(6)	116.25(16)
Cl(1)–Sn(1)–C(5)	88.24(10)	N(1)–S(1)–C(1)	119.46(17)
Cl(1)–Sn(1)–C(6)	90.86(10)	N(2)–S(2)–C(1)	120.53(18)
N(1)–Sn(1)–N(2)	89.54(13)	Sn(1)–N(1)–S(1)	121.31(19)
N(1)–Sn(1)–C(5)	96.66(14)	Sn(1)–N(2)–S(2)	122.00(18)
N(1)–Sn(1)–C(6)	91.82(14)	S(1)–C(1)–S(2)	118.59(19)
N(2)–Sn(1)–C(5)	127.49(15)		
4			
Sn(1)–Cl(1)	2.5392(7)	S(1)–C(1)	1.800(2)
Sn(1)–N(1)	2.2294(17)	S(1)–C(2)	1.799(2)
Sn(1)–N(3)	2.0470(18)	S(2)–N(2)	1.6158(17)
Sn(1)–C(5)	2.151(2)	S(2)–N(3)	1.4901(18)
Sn(1)–C(6)	2.136(2)	S(2)–C(3)	1.789(2)
S(1)–N(1)	1.4810(17)	S(2)–C(4)	1.782(2)
S(1)–N(2)	1.6233(17)		
Cl(1)–Sn(1)–N(1)	171.14(5)	N(3)–Sn(1)–C(6)	117.59(9)
Cl(1)–Sn(1)–N(3)	82.20(5)	C(5)–Sn(1)–C(6)	118.83(8)
Cl(1)–Sn(1)–C(5)	92.62(6)	N(1)–S(1)–N(2)	122.27(9)
Cl(1)–Sn(1)–C(6)	92.14(6)	N(2)–S(2)–N(3)	122.20(10)
N(1)–Sn(1)–N(3)	88.97(7)	Sn(1)–N(1)–S(1)	126.45(10)
N(1)–Sn(1)–C(5)	91.55(8)	S(1)–N(2)–S(2)	112.70(10)
N(1)–Sn(1)–C(6)	92.69(8)	Sn(1)–N(3)–S(2)	126.77(11)
N(3)–Sn(1)–C(5)	123.48(8)		
5			
S(1)–N(1)	1.518(4)	S(2)–N(2)	1.518(4)
S(1)–C(1)	1.689(5)	S(2)–C(1)	1.683(5)
S(1)–C(2)	1.778(4)	S(2)–C(3)	1.7782(4)
S(1)–C(3)	1.788(4)	S(2)–C(4)	1.800(5)
N(1)–S(1)–C(1)	120.8(2)	S(1)–C(1)–S(2)	121.1(3)
N(2)–S(2)–C(1)	120.7(2)		

The atom labeling scheme is shown in Figures 1–3.

1.600(3) Å[4a]]. Although crystals of the free ligand **1** have not yet proved suitable for X-ray crystallographic studies, the crystal structures of **2** have been reported.[4b] The mean values of the terminal and internal S—N bonds in **4** are close to those of the free ligand **2** [terminal; mean 1.486(2) Å, internal: 1.615(2) Å].[4b] Very recently, we have reported that the coordinated S—N bond lengths in $[\mathrm{MCl_2\{Ph_2S(NPh_2SN)_2\}}]$ and $[\mathrm{M\{Ph_2S(NPh_2SN)_2\}_2]Cl_2}$ (M = Co(II), Ni(II), Cu(II)) are similar to those of the free ligand, and the internal S—N bond lengths lie between those of single and double bonds, which indicates that the bond order in the N≡S—N=S=N—S≡N backbone of the free ligand was maintained.[6] These results also indicate as a consequence of the coordination of **1** and **2**.

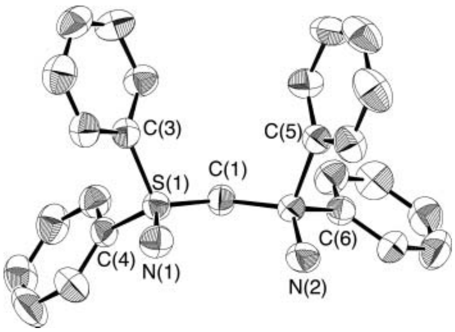


Figure 3 ORTEP drawing of **5** [50% probability thermal ellipsoids; H atoms and perchlorate anions have been omitted for clarity].

EXPERIMENTAL

All NMR spectra were obtained with a Bruker Avance-400S and a JEOL-LNM 400 spectrometer with TMS as the internal standard. IR spectra were recorded on a Jasco FTIR-4200 spectrometer. Melting points were measured on a Yanaco Mp-J3 melting point apparatus. Elemental analyses were carried out at the Chemical Analysis Center of the College of Science and Technology, Nihon University.

All reagents and solvents were obtained commercially and were further purified by general methods when necessary. The free ligands, $\{E(Ph_2SN)(Ph_2SNH)\}$ [E = CH (**1**), N (**2**)], and protonated ligand, $\{CH(Ph_2SNH)\}^+ClO_4^-$ (**5**), were synthesized as described previously.[3,4a]

Preparation of [$ClPh_2Sn\{E(Ph_2SN)_2\}$] [E = CH (3), N (4)]

Lithium diisopropylamide (0.55 mL of 2.0 M solution in heptane/THF/ethylbenzene, 1.1 mmol) was added dropwise at −40°C to a solution of **1** or **2** (1.0 mmol) in THF (25 mL) and stirred for 1 h. A solution of diphenyltin dichloride (378 mg, 1.1 mmol) in THF (5 mL) was then added. The mixture was stirred for 1h at −40°C and then warmed up to room temperature. The solution was evaporated under reduced pressure. The residue was dissolved in dichloromethane, and then insoluble matter was filtered. After the filtrate was evaporated, the residue was purified by crystallization from chloroform-ether.

Data for **3**: Yield 84%; mp 199–200°C (decomp.); ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.78 (brs, 1H), 7.18–7.23 (m, 6H), 7.31 (t, $J = 7.7$ Hz, 8H), 7.42 (t, $J = 7.7$ Hz, 4H), 7.82 (d, $J = 7.7$ Hz, 8H), 8.06–8.08 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 126.3, 127.6 (s, $J_{C\text{-}Sn} = 26.5$ Hz), 128.5 (s, $J_{C\text{-}Sn} = 8.1$ Hz), 128.9, 132.1, 136.7 (s, $J_{C\text{-}Sn} = 28.5$ Hz), 145.4 (s, $J_{C\text{-}Sn} = 351$ Hz); IR (KBr cm^{-1}) 3048, 1475, 1445, 1431, 1310, 1198, 921; Calcd for $C_{37}H_{31}ClN_3S_6Sn$: C, 61.56; H, 4.33; N, 3.88; Found: C, 61.27; H, 4.43; N, 3.90.

Data for **4**: Yield 87%; mp 199–200°C (decomp.); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.13–7.21 (m, 6H), 7.30 (t, $J = 7.6$ Hz, 8H), 7.40 (t, $J = 7.6$ Hz, 4H), 7.84–7.85 (br, 8H), 8.08 (dd, $J_1 = 7.2$ Hz, $J_2 = 2.0$ Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 126.3, 127.5 (s, $J_{C\text{-}Sn} = 45.3$ Hz), 128.5 (s, $J_{C\text{-}Sn} = 9.1$ Hz), 128.8, 132.1, 136.6 (s, $J_{C\text{-}Sn} = 30.9$ Hz), 146.1 (s, $J_{C\text{-}Sn} = 499$ Hz); IR (KBr cm^{-1}) 3050, 1474, 1444, 1423, 1246, 1173, 1068, 952; Calcd for $C_{36}H_{30}ClN_3S_6Sn$: C, 59.81; H, 4.18; N, 5.81; Found: C, 59.43; H, 4.13; N, 5.65.

X-Ray Crystallography

Single crystals were obtained by recrystallization from chloroform–ether (for **3** and **4**) and dichloromethane–ether (for **5**). Diffraction data were collected with a Rigaku RAXIS RAPID imaging plate (for **3**) and a Rigaku AFC7R diffractometer (for **4** and **5**) using graphite monochromated Mo Kα radiation ($\lambda = 0.71075$ Å). The data were corrected for Lorentz and polarization effects, and an empirical absorption correction was applied, which resulted in transmission factors (see Table I). The structures **3–5** were solved by the direct method using SHELXS-97 and were refined using SHELXL-97.[13]

Supplementary Material

X-ray crystallographic files in CIF format for the structure determination of **3–5**. CCDC 711593 to 711595 (for **3–5**, respectively) contain the supplementary crystallographic data for this article. These data can be obtained free of charge at http://www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK (fax: +4 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk). Supplementary data associated with this article also can be found in the online version.

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