Supplementary data for this paper are available from the IUCr electronic archives (Reference: LN1067). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1999). C55, 363-365

(*Z*)- and (*E*)-1-methylthio-1-triphenylstannyl-2-phenylethene

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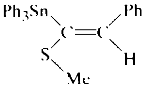
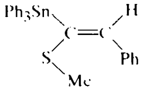
Abstract

The structures of the title compounds, (*Z*)-Ph_3Sn—C(SMe)=CHPh, (I), and (*E*)-Ph_3Sn—C(SMe)=CHPh, (II) {both $[Sn(C_6H_5)_3(C_9H_9S)]$, (1-methylthio-2-phenylethenyl)triphenyltin}, were determined by single-crystal X-ray diffraction at room temperature. Both structures consist of discrete molecules in which the Sn atom is tetrahedrally coordinated by three phenyl groups and one 1-methylthio-2-phenylethenyl group. The planar ethenyl skeleton forms angles of 58.9 (2) and 34.0 (3)° with the 2-phenyl substituent in (I) and (II), respectively, excluding π interactions between them. In *Z*-isomer (I), the methyl substituent on sulfur lies in the plane of the ethenyl group [torsion angle C—S—C=C 3.0 (5)°], but this is not the case in *E*-isomer (II), which reveals a torsion angle C—S—C=C of 156.1 (8)°.

Comment

The hydrometallation of non-symmetrically substituted alkynes can afford four possible isomeric ethenyl metal complexes. Especially in the case of alkynes $R'C{\equiv}CYR_n$ with Lewis basic heteroatom groups (YR_n = NR_2, PR_2, OR, SR; R/R' = alkyl, aryl, H), it might be difficult to predict the regio- and/or stereoselectivity. In the case of the hydrostannylation of PhC≡CSPh by Ph_3SnH, both the non-catalysed and the Pd-catalysed reactions are quite selective and yield one major isomer at about 90–95% in each case. Because the assignment of the isomers by means of NMR spectroscopy (^1H, ^{13}C and ^{119}Sn) is not straightforward, the structures of both isomers were determined by single-crystal X-ray diffraction. The non-catalysed reaction gave (*Z*)-Ph_3Sn—C(SMe)=CHPh, (I), and the Pd-catalysed reaction (*E*)-Ph_3Sn—C(SMe)=CHPh, (II).


(I)


(II)

The molecular structures and numbering schemes are shown in Fig. 1. Both complexes consist of discrete molecules in which the Sn atoms are tetrahedrally coordinated by three phenyl ligands and one 1-methylthio-2-phenylethenyl ligand [C—Sn—C: 106.3 (1)–112.7 (1)° in (I) and 105.6 (3)–110.0 (3)° in (II)]. The three Sn—C_{Ph} bond lengths are similar [(I): 2.131 (4)–2.143 (4), mean value 2.135 Å; (II): 2.135 (8)–2.162 (8), mean value 2.146 Å]. In the case of isomer (I), the Sn—$C_{ethenyl}$ bond seems to be slightly longer [(I): 2.173 (4); (II): 2.148 (7) Å]. There are no significant differences in the Sn—C bond lengths in Ph_3Sn—CH=CH_2 [Sn—C_{Ph} 2.11 (3)–2.17 (4) and Sn—$C_{ethenyl}$ 2.07 (3)–2.15 (3) Å; Theobald & Trimaille, 1984] and (*Z*)-Ph_3Sn—C(CMe_2OH)=CHMe [Sn—C_{Ph} 2.118 (3)–2.129 (3) and Sn—$C_{ethenyl}$ 2.125 (3) Å; Willem *et al.*, 1994].

The ethenyl skeleton (C1–C3, Sn, S) is nearly planar [maximum deviation: 0.064 (3) Å for C2 in (I), and 0.027 (6) Å for C1 in (II)]. As in *trans*-[Pt{(*E*)-C-(SMe)=CHPh}Cl(PPh_3)$_2$] (Steinborn *et al.*, 1998), in *Z*-isomer (I), the methyl substituent on sulfur (C9) also lies in this plane [deviation 0.011 (8) Å; torsion angle C9—S—C1=C2 3.0 (5)°]; this is not the case in *E*-isomer (II) [deviation 0.73 (2) Å; torsion angle C9—S—C1=C2 156.1 (8)°]. Without obvious reason, the angles at the ethenyl C1 and C2 atoms exhibit

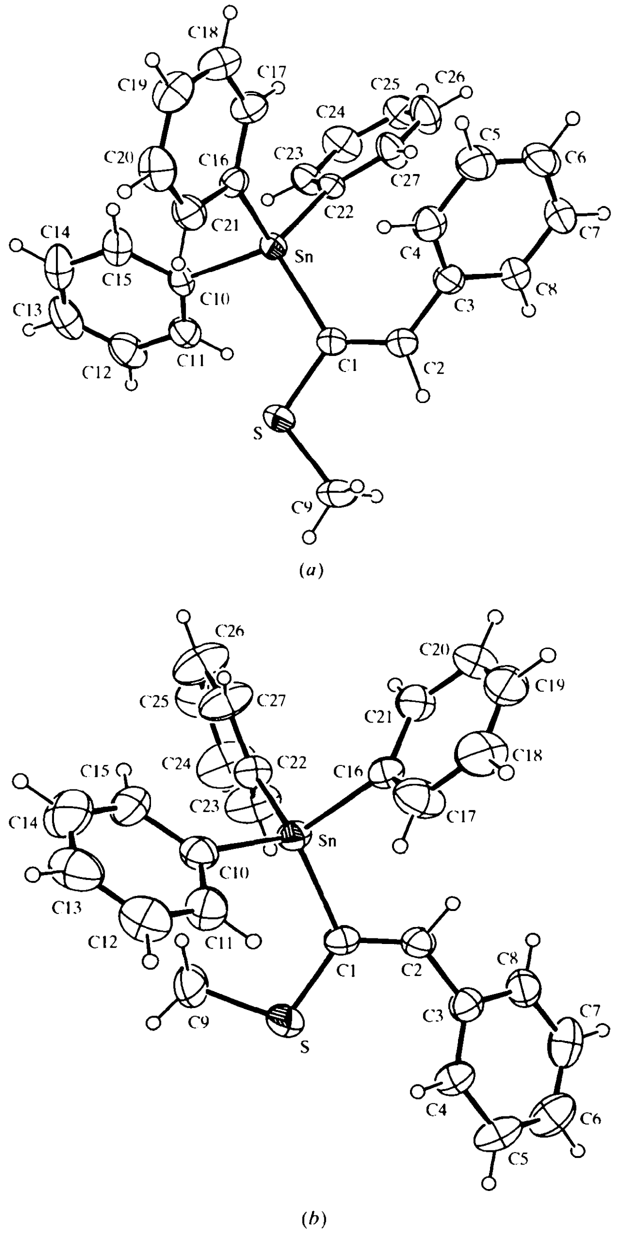


Fig. 1. The molecular structures of (*a*) *Z*-isomer (I) and (*b*) *E*-isomer (II) showing 30% probability displacement ellipsoids. H atoms are shown as circles of an arbitrary radius.

distinct deviations from the ideal angle of 120° expected for sp^2-hybridized C atoms [111.6 (2)–126.6 (4)° for (I) and 117.6 (5)–130.0 (7)° for (II)]. The interplanar angles of 58.9 (2) and 34.0 (3)° between the 2-phenyl substituent (C3–C8) and the ethenyl group in (I) and (II), respectively, exclude π interactions.

The closest C_{Ph}—H···S distance is intermolecular in (I) [C26···S^i 3.594 (7) and H26···S^i 2.79 Å; symmetry code: (i) $1+x$, y, z] and intramolecular in (II) [C4···S 3.125 (10) and H4···S 2.63 Å].

Experimental

(*Z*)-Ph_3Sn—C(SMe)=CHPh, (I), was synthesized by the reaction of stoichiometric amounts of Ph_3SnH and PhC≡CSMe in *n*-hexane at 328 K under anaerobic conditions. After 5 h, the precipitate was filtered, washed with hexane and dried *in vacuo* (yield: 69%; m.p. 379 K). Crystals suitable for X-ray diffraction studies were obtained from chloroform/*n*-pentane solution. (*E*)-Ph_3Sn—C(SMe)=CHPh, (II), was obtained using an analogous reaction in THF at 243 K in the presence of 1 mol% [$Pd(PPh_3)_4$]. After 15 min, the solvent was removed *in vacuo* affording an oily residue (purity: 95%). Crystals (m.p. 341–343 K) suitable for X-ray diffraction studies separated after standing for several weeks at 288 K.

Compound (I) – *Z* isomer

Crystal data

[$Sn(C_6H_5)_3(C_9H_9S)$]
M_r = 499.21
Monoclinic
$P2_1/c$
a = 10.190 (9) Å
b = 19.104 (9) Å
c = 12.808 (9) Å
β = 110.67 (6)°
V = 2333 (3) $Å^3$
Z = 4
D_x = 1.421 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 32 reflections
θ = 5.23–16.73°
μ = 1.195 mm^{-1}
T = 298 (2) K
Block
0.8 × 0.6 × 0.4 mm
Colourless

Data collection

Stoe Stadi-4 four-circle diffractometer
$\omega/2\theta$ scans
Absorption correction: semi-empirical *via* ψ scan (North *et al.*, 1968)
T_{min} = 0.45, T_{max} = 0.62
6742 measured reflections
4101 independent reflections

3750 reflections with $I > 2\sigma(I)$
R_{int} = 0.109
θ_{max} = 25°
$h = -12 \rightarrow 12$
$k = 0 \rightarrow 23$
$l = -15 \rightarrow 15$
1 standard reflection
frequency: 60 min
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.044
$wR(F^2)$ = 0.098
S = 1.160
4100 reflections
289 parameters
Only H-atom U's refined
$w = 1/[\sigma^2(F_o^2) + (0.0414P)^2 + 0.9634P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 1.144 e $Å^{-3}$
$\Delta\rho_{min}$ = −1.402 e $Å^{-3}$
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °) for (I)*

C1—C2	1.331 (5)	C10—Sn	2.143 (4)
C1—S	1.740 (4)	C16—Sn	2.131 (4)
C1—Sn	2.173 (4)	C22—Sn	2.133 (4)
C9—S	1.789 (5)		
C2—C1—S	123.7 (3)	C16—Sn—C10	106.28 (13)
C2—C1—Sn	124.6 (3)	C22—Sn—C10	106.7 (2)
S—C1—Sn	111.6 (2)	C16—Sn—C1	111.34 (13)

C1—C2—C3	126.6 (4)	C22—Sn—C1	112.74 (14)
C1—S—C9	105.1 (2)	C10—Sn—C1	107.9 (2)
C16—Sn—C22	111.57 (14)		

Compound (II) - *E* isomer

Crystal data

$[Sn(C_6H_5)_3(C_9H_9S)]$
$M_r = 499.21$
Triclinic
$P\bar{1}$
$a = 9.5512$ (8) Å
$b = 11.0433$ (8) Å
$c = 12.3793$ (10) Å
$\alpha = 83.380$ (8)°
$\beta = 81.737$ (8)°
$\gamma = 67.018$ (7)°
$V = 1187.1$ (2) Å^3
$Z = 2$
$D_x = 1.397$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 32 reflections
$\theta = 10.0$–$13.5°$
$\mu = 1.174$ mm^{-1}
$T = 293$ (2) K
Prism
0.4 × 0.3 × 0.2 mm
Colourless

Data collection

Stoe Stadi-4 four-circle diffractometer
$\omega/2\theta$ scans
Absorption correction: semi-empirical *via* ψ scan (North *et al.*, 1968)
$T_{\min} = 0.62$, $T_{\max} = 0.79$
3732 measured reflections
3732 independent reflections

3070 reflections with $I > 2\sigma(I)$
$\theta_{\max} = 25°$
$h = -11 \rightarrow 8$
$k = -12 \rightarrow 13$
$l = 0 \rightarrow 14$
1 standard reflection frequency: 60 min intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.051$
$wR(F^2) = 0.189$
$S = 1.239$
3721 reflections
287 parameters
Only H-atom *U*'s refined
$w = 1/[\sigma^2(F_o^2) + (0.1046P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max} = 0.766$ e Å^{-3}
$\Delta\rho_{\min} = -0.841$ e Å^{-3}
Extinction correction: *SHELXL*93
Extinction coefficient: 0.030 (4)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 2. *Selected geometric parameters (Å, °) for (II)*

C1—C2	1.345 (11)	C10—Sn	2.162 (8)
C1—S	1.761 (7)	C16—Sn	2.135 (8)
C1—Sn	2.148 (7)	C22—Sn	2.141 (7)
C9—S	1.769 (10)		
C2—C1—S	120.7 (6)	C16—Sn—C1	108.1 (3)
C2—C1—Sn	117.6 (5)	C22—Sn—C1	110.6 (3)
S—C1—Sn	121.6 (4)	C16—Sn—C10	105.6 (3)
C1—C2—C3	130.0 (7)	C22—Sn—C10	110.9 (3)
C1—S—C9	105.1 (5)	C1—Sn—C10	111.6 (3)
C16—Sn—C22	110.0 (3)		

For both compounds, data collection: *STADI*4 (Stoe & Cie, 1996*a*); cell refinement: *STADI*4; data reduction: *X-RED* (Stoe & Cie, 1996*b*); program(s) used to solve structures: *SHELXS*86 (Sheldrick, 1990); program(s) used to refine structures: *SHELXL*93 (Sheldrick, 1993); molecular graphics: *ORTEP*III (Burnett & Johnson, 1996); software used to prepare material for publication: *SHELXL*93.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA1382). Services for accessing these data are described at the back of the journal.

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A dimeric form of the nickel(II) thiocyanate complex of bis(3-aminopropyl)methylamine

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Abstract

The structure of bis[*N*,*N*-bis(3-aminopropyl)methylamine]-1κ^3N,2κ^3N-di-μ-thiocyanato-1:2κ^2N:*S*;1:2κ^2S:*N*-dithiocyanato-1κN,2κN-dinickel(II), $[Ni_2(NCS)_4(C_7H_{19}N_3)_2]$ or $[Ni_2(\mu\text{-}SCN)_2(medpt)_2(NCS)_2]$, where medpt is bis(3-aminopropyl)methylamine, consists of two crystallographically independent dimer types differing in their orientations. In each dimer, the two Ni^{II} ions are bridged by two SCN$^-$ ligands in an end-to-end fashion. The coordination polyhedra about the Ni^{II} atoms are distorted octahedra consisting of three N atoms of the medpt lig-