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

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1. Experimental procedure for compounds **2** and **3**

[HC{(PPh$_2$=NSiMe$_3$)(PPh$_2$=S)}SnN(SiMe$_3$)$_2$] (2). Toluene (20 mL) was added to a mixture of **1** (0.51 g, 1.01 mmol) and [Sn{N(SiMe$_3$)$_2$}$_2$] (0.88 g, 2.01 mmol) at ambient temperature. The resulting orange mixture was stirred for overnight. Volatiles were removed under reduced pressure. The residue was washed with hexane and then extracted with Et$_2$O. The insoluble precipitate was filtered off, and the orange filtrate was concentrated to yield colorless crystals of **2** (0.37 g, 46.9%). M.p. 130°C; elemental analysis (%) calcd for C$_{34}$H$_{48}$N$_2$P$_2$SSi$_3$Sn: C 52.24, H 6.19, N 3.59; found: C 51.94, H 6.01, N 3.37; ^{1}H NMR (395.9 MHz, C$_6$D$_6$, 25°C): δ = 0.072 (s, 9H, SiMe$_3$), 0.48 (s, 18H, N(SiMe$_3$)$_2$), 3.84 (dd, 1H, PCHP, $^2J_{P-H}$ = 10.9 Hz), 6.89-7.08 (m, 15H, Ph), 7.49-8.22 (m, 5H, Ph); ^{13}C NMR (99.5 MHz, C$_6$D$_6$, 25°C): δ = 3.53 (SiMe$_3$), 7.71 (N(SiMe$_3$)$_2$), 31.5 (d, PCP, J = 55.9 Hz), 129.5-135.5 ppm (m, Ph); ^{31}P NMR (160.3 MHz, C$_6$D$_6$, 25°C): δ = 30.2 (t, $^2J_{Sn-P}$ = 73.7 Hz), 34.7 ppm (t, $^2J_{Sn-P'}$ = 39.0 Hz); ^{119}Sn NMR (147.6 MHz, C$_6$D$_6$, 25°C): δ = -19.3 ppm.

[(PPh$_2$=NSiMe$_3$)(PPh$_2$=S)C=Sn:]$_2$ (3): Toluene (20 mL) was added to a mixture of **1** (0.50 g, 0.99 mmol) and [Sn{N(SiMe$_3$)$_2$}$_2$] (0.89 g, 2.03 mmol) at ambient temperature. The resulting orange mixture was refluxed for overnight. The solvent was removed in *vacu*o. The residue was washed with hexane and then extracted with CH$_2$Cl$_2$. The insoluble precipitate was filtered off, and the orange filtrate was concentrated to yield yellow crystals of **3** (0.74 g, 30.1 %). M.p. 180°C (dec.); elemental analysis (%) calcd for C$_{56}$H$_{58}$N$_2$P$_4$S$_2$Si$_2$Sn$_2$: C 54.21, H 4.72, N 2.26; found: C 54.04, H 4.39, N 2.11; ^{1}H NMR (395.9 MHz, C$_6$D$_6$, 25°C): δ = 0.04 (s, 9H, SiMe$_3$), 6.64-7.12 (m, 15H, Ph), 7.18-7.42 (m, 2H, Ph), 7.86-8.04 (br s, 1H, Ph), 8.28-8.40 ppm (br s, 2H, Ph); ^{13}C NMR (99.5 MHz, C$_6$D$_6$, 25°C): δ = 2.30 (SiMe$_3$), 129.2-134.5 ppm (m, Ph); ^{31}P NMR (161.7 MHz, C$_6$D$_6$, 25°C): δ = 20.5 (d, $^2J_{P-P'}$ = 17.5 Hz), 27.4 ppm (d, $^2J_{P-P'}$ = 17.5 Hz); ^{119}Sn NMR (147.6 MHz, C$_6$D$_6$, 25°C): δ = 132.1 ppm (dd, $^2J_{Sn-P}$ = 177.1 Hz).

X-ray data collection and structural refinement. Intensity data for compounds **2** - **3** were collected using a Bruker Kappa APEX II diffractometer. The crystal of **2** was measured at 103(2)K and that of **3** was measured at 143(2) K. The structures were solved by direct phase determination (SHELXS-97)[1] and refined for all data by full-matrix least squares methods on F^2. All non-hydrogen atoms were subjected to anisotropic refinement and H atoms were generated geometrically and allowed to ride on their respective parent atoms.

2
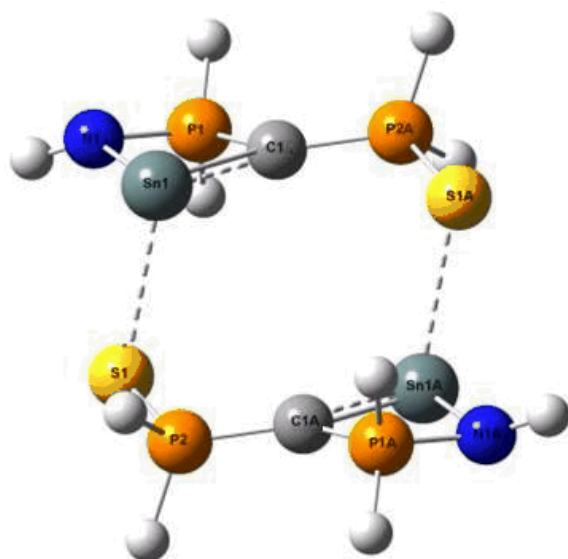
2. **Figure S1**. Simple derivative **3A**

3. **Table S1**. Pertinent bonds and its respective atomic hybridization, contribution (Contr.), occupancy, and Wiberg bond index of compound **3A**

Bond	Atom(1)	Contr. %	Hybrid Type	Atom(2)	Contr. %	Hybrid Type	Occupancy	Wiberg index
Sn(1)-C(1) (σ)	Sn	14.7	$s^{0.25}p^{2.00}$	C	85.3	$sp^{2.00}$	1.91	0.513
Sn(1)-C(1) (π)	Sn	3.1	p	C	96.9	p	1.73	-
P(1)-C(1) (σ)	P	42.0	$sp^{2.05}$	C	58.0	$sp^{2.26}$	1.98	1.105
P(1)-N(1) (σ)	P	32.9	$sp^{2.98}$	N	67.1	$sp^{2.82}$	1.99	0.979
P(2A)-C(1) (σ)	P	41.7	$sp^{1.93}$	C	58.2	$sp^{1.78}$	1.99	1.109
P(2)- S(1) (σ)	P	50.5	$s^{0.94}p^{3.00}$	S	49.5	$s^{0.36}p^{3.00}$	1.98	1.077

4. The optimized geometry at the B3LYP/LanL2DZ(d,p) level and the total energies of **3A**. The C_i symmetry, E= -244.699839 hartree, (including the zero-point-correction).

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Sn      -0.513715    -1.270934    -1.848645
C       -0.035639    -0.862540     2.100928
N        0.895405    -1.070185    -3.533340
P        0.602481    -2.328192     1.473909
P        1.198519     0.546860    -3.330650
S        1.651580    -2.100314    -0.286616
Sn       0.513715     1.270934     1.848645
C        0.035639     0.862540    -2.100928
N       -0.895405     1.070185     3.533340
P       -0.602481     2.328192    -1.473909
P       -1.198519    -0.546860     3.330650
S       -1.651580     2.100314     0.286616
H       -1.622049     1.686472     3.893340
H       -2.583503    -0.799406     3.029255
H       -1.096610    -1.297932     4.553068
H        1.492612    -3.050761     2.334760
H       -0.406914    -3.332695     1.301056
H        1.622049    -1.686472    -3.893340
H        2.583503     0.799406    -3.029255
H        1.096610     1.297932    -4.553068
H       -1.492612     3.050761    -2.334760
H        0.406914     3.332695    -1.301056
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8. The augmented LanL2DZ basis set - LanL2DZ(d,p).

Since the compound **3A** includes heavy main-group element - Sn, the effective core potential basis set have to be adopted in the course of calculation in order to account for the relativistic effect. However, the selected LanL2DZ basis set is short of the d polarization function, which appropriately illuminates the bonding nature of hypervalent systems. Thus, we added the d, p polarization function into the LanL2DZ basis set and denoted as LanL2DZ(d,p) basis set. The augmented LanL2DZ basis set, which combine the efficiency of a core-potential-containing basis set with the accuracy of all-electron basis set such as 6-31+G(d,p), can give substantially more correct optimized structure and electronic properties.

Reference

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