Table I. Interatomic Distances (Å) and Angles (deg) in the $Zr_3S_3(S\text{-}t\text{-}Bu)_2(BH_4)_4(THF)_2$ (I), $Zr_6S_6(S\text{-}t\text{-}Bu)_4(BH_4)_8(THF)_2$ (II), and $[Mo_3S_2Cl_9]^{3-\,a}$ Complexes

	I	II	$(Mo_3S_2Cl_9)^{3-}$
M-M	3.47 (3, 12)^{b,c}	3.483 (3, 14)^d	2.62 (3, 4)^e
M-S_b^f	2.594 (6, 18)^g	2.594 (6, 23)^h	2.375 (6, 18)^i
M-M-M	60.0 (3, 30)^j	60.0 (3, 4)^k	60.0 (3, 1.4)^l
M-S_b-M	84.1 (6, 2.0)	84.4 (6, 6)	66.9 (6, 9)
Zr_2-S-t-Bu	2.632 (2, 2)	2.596 (2, 3)	
$Zr_{1,3}$-S-t-Bu	2.650 (2, 4)	2.645 (2, 12)	
Zr-B_t^m	2.344 (3, 8)^n	2.29 (3, 2)^o	
Zr-B_b^p	2.53 (1, 2)	2.512 (1, 12)	
Zr-O	2.240 (2, 9)	2.295 (1, 6)	

^a From ref 12. ^b Range: 3.278 (2)–3.574 (2) Å. ^c In parenthesis the first entry represents the number of independent distances or angles averaged out; the second entry represents the larger of the standard deviations for an individual value estimated from the inverse matrix or of the standard deviation $\sigma = [\sum_{i=1}^{N}(x_i - \bar{x})^2/N(N-1)]^{1/2}$. ^d Range: 3.468 (1)–3.507 (1) Å. ^e Range: 2.556 (1)–2.653 (1) Å. ^f μ_3-Bridging sulfide. ^g Range: 2.554 (4)–2.634 (4) Å. ^h Range: 2.529 (2)–2.648 (2) Å. ^i Range: 2.318 (3)–2.428 (3) Å. ^j Range: 54.70 (2)–62.80 (2)°. ^k Range: 59.60 (5)–60.70 (5)°. ^l Range: 57.7 (1)–61.4 (1)°. ^m Tridentate BH_4^- ligand. ^n Range: 2.331 (20)–2.353 (22) Å. ^o Range: 2.276 (11)–2.325 (11) Å. ^p Bidentate BH_4^- ligand.

nature of II (Figure 1A,B). The latter apparently forms as a result of the dissociation of a THF molecule from I followed by dimerization. A repetition of this process very likely can account for the formation of intractable polymers by either refluxing THF solutions of I and II or by dissolving the clusters in benzene.

The structures of I and II (Figure 1A,B) are closely related and both contain the $Zr_3(\mu_3\text{-}S)_2(\mu_2\text{-}S)_3$ core as a structural feature. The latter roughly has a hexagonal-bipyramidal structure where two $\mu_2\text{-}t$-Bu thiolates and a μ_2-sulfide ligand bridge the Zr atoms in the equatorial plane and two μ_3-sulfido ligands serve as "capping" ligands on the axial positions. The core can be described also as the result of the cofacial fusion of three "octahedrally" coordinated Zr units (viewing the BH_4^- anions as monodentate ligands).

The molecular fragments obtained by the fusion of the Zr_2 and Zr_3 "octahedra" are identical in both structures. There is a difference, however, in the relative orientation of the Zr_1 "octahedron" which is reversed in the two structures (Figure 1A,B).

The Zr–B distances (Table I) show that in both structures three of the BH_4^- anions (B_1, B_3, B_4) serve as tridentate ligands and one (B_2) is bidentate. The Zr–B distances with the *tridentate* BH_4^- ligands at 2.344 (8) and 2.29 (2) Å respectively for I and II are very similar to the one known for $Zr(BH_4)_4$. In the latter complex, a low-temperature X-ray study[9] and an electron-diffraction study[10] show the Zr–B distances at 2.34 and 2.308 (3) Å, respectively. The Zr–B distance with the *bidentate* BH_4^- ligands in I and II at 2.53 (2) and 2.512 (12) Å, respectively, are quite similar to the Hf–B distance in the $(MeCp)_2Hf(BH_4)_2$ complex[11] at 2.553 (6) Å. In this complex the BH_4^- ligands serve as bidentate chelates.

Coordinated by either tetrahydrofuran or BH_4^- as terminal ligands the Zr_1 and Zr_3 atoms in I and II are eight-coordinate. A common and unusual feature in both I and II is the presence of the nine-coordinate Zr_2 that contains both bidentate and tridentate BH_4^- terminal ligands. Although there exist numerous complexes that contain either bidentate or tridentate BH_4^- ligands,[7] I and II represent the first examples of complexes where the BH_4^- ligands display both modes of coordination.

The basic core structure of the $Zr_3(S_{ax})_2$ units in I and II is geometrically similar but metrically different than the $Mo_3(S_{ax})_2$ unit in the $(Mo_3S_2Cl_9)^{3-}$ trianion.[12] In the latter, M–M bonding

results in Mo–Mo distances nearly 1 Å shorter than the Zr–Zr distances in I or II (Table I). The remarkable flexibility of the S^{2-} capping ligands in accommodating the widely different Mo_3 and Zr_3 triangular units in these clusters is illustrated in the M–S_b–M angles that vary from very acute (66.9°) in the Mo cluster to rather oblique values (84.1° and 84.4°) in I and II.

The extreme reactivity of I and II toward solvolysis and their reduction properties presently are under investigation.

Supplementary Material Available: Listings of structure factors and positional and thermal parameters for $Zr_3S_3(S\text{-}t\text{-}Bu)_2$-$(BH_4)_4(THF)_2$ and $Zr_6S_6(S\text{-}t\text{-}Bu)_4(BH_4)_8(THF)_2$ (31 pages). Ordering information is given on any current masthead page.

A Compound with a Tin–Phosphorus Double Bond: The First Stable Stannaphosphene

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There has been much interest in compounds having a double bond between two main-group atoms and particularly in groups 14 and 15 where remarkable results have been reported in the last few years.[1]

Metallaphosphenes (>M=P—, M group 14) have long been speculated to be reactive intermediates but could only be characterized by trapping reactions (M = Si,[2] Ge,[3] Sn[4]). Very recently, owing to bulky substituents on metal and phosphorus, the first stable silaphosphene (>Si=P—) has been characterized[5] and the first stable germaphosphene (>Ge=P—) has been isolated.[6]

In the present paper we describe the synthesis of 2,2-[bis(trimethylsilyl)methyl]-1-(2,4,6-tri-*tert*-butylphenyl)stannaphosphene 1, the first stable compound containing a tin–phosphorus double bond. The highly air-sensitive stannaphosphene 1 has not been obtained in pure form because of its high reactivity but has been unambiguously characterized by its physicochemical data and the first aspects of its chemical reactivity.

Following our synthesis of a germaphosphene,[6] it appeared that a convenient route to 1 might be the dehydrofluorination of the (fluorostannyl)phosphine 2[7,8] by *tert*-butyllithium. Compound

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(7) 2: white crystals, mp 145–147 °C; ^{1}H NMR (C_6D_6) δ 0.20 (br s, 18 H, Me_3Si), 0.37 (s, 18 H, Me_3Si),[8] 1.33 (s, 9 H, *p-t-*Bu), 1.70 (s, 18 H, *o-t-*Bu), 5.32 (dd, 1 H, $^1J_{PH}$ = 205.9, $^2J_{FH}$ = 6.0 Hz, PH), 7.53 (d, 2 H, $^4J_{PH}$ = 3.0 Hz, Ar H); ^{31}P NMR (C_6D_6) δ −110.6 ($^1J_{PH}$ = 205.9, $^2J_{PF}$ = 5.9, $^1J_{P-117_{Sn}}$ = 1150, $^1J_{P-119_{Sn}}$ = 1203 Hz); ^{119}Sn{^{1}H} NMR (C_6D_6) δ +126.3 (reference Me_4Sn), (dd, $^1J_{P-119_{Sn}}$ = 1203, $^1J_{Sn-F}$ = 2715 Hz); ^{19}F NMR (C_6D_6) (reference CF_3COOH) δ −104.6. Anal. Calcd for $C_{32}H_{68}FPSi_4Sn$: C, 52.37; H, 9.34; F, 2.59. Found: C, 52.48; H, 9.39; F, 2.68.

(8) Compounds of the type $[(Me_3Si)_2CH]_2Sn(X)Y$ show generally two Me_3Si NMR signals which are attributed to the tetrahedral tin center as a result of which there are two magnetically distinct sets of Me_3Si environments: Cotton, J. D.; Davidson, P. J.; Lappert, M. F. *J. Chem. Soc., Dalton Trans.* 1976, 2275–2286.
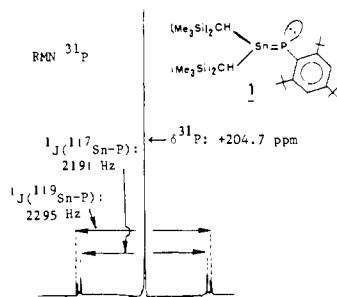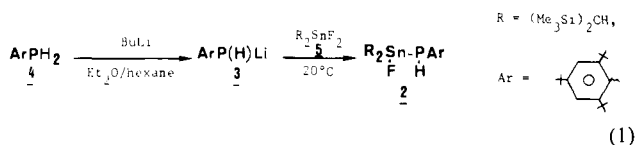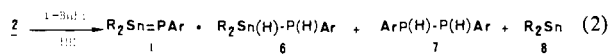
Figure 1.

2 was synthesized by addition of the lithiophosphine 3 (prepared by reacting *n*-butyllithium (1.6 M in hexane) with (2,4,6-*tert*-butylphenyl)phosphine (4) in diethyl ether) to bis[bis(trimethylsilyl)methyl]difluorotin (5)[9,10] (eq 1).

(1)

Addition of 1 equiv of *t*-BuLi to 2 in THF solution was performed at −50 °C. On warming to room temperature a red color developed; after centrifugation of lithium fluoride and removal of solvents under vacuum, we obtained an air-sensitive red crystalline crude material. NMR analysis showed the formation of stannaphosphene 1 as the major product (relative percentage 70%); as minor products we have characterized the secondary phosphine 6[11] (20%), the disecondary diphosphine 7[12] (5%), and the stannylene 8[13] (5%). The probably radical process leading to 6–8 is not yet completely elucidated and its study is now under investigation (eq 2).

(2)

The stannaphosphene structure of 1 was unambiguously determined by ^{1}H, ^{31}P, ^{119}Sn NMR (see Figure 1) and by mass spectroscopy. ^{1}H NMR data (solvent C_6D_6) are as follows: δ 0.25 (s, 18 H, Me$_3$Si), 0.38 (s, 18 H, Me$_3$Si), 1.43 (s, 9 H, p-*t*-Bu), 1.78 (s, 18 H, o-*t*-Bu), 7.43 (d, 2H, $^4J_{PH}$ = 2.5 Hz, ArH). The ^{31}P NMR chemical shift of 1 (+204.7 ppm/H$_3$PO$_4$) falls in the range of the known silaphosphene[5] (+136.0 ppm) and germaphosphene[6] (+175.4 ppm). More significant is the coupling constant between phosphorus and tin: $^1J_{P-^{117}Sn}$ = 2191 Hz, $^1J_{P-^{119}Sn}$ = 2295 Hz. These values, much larger than for single-bonded tin–phosphorus compounds (e.g., 1150 and 1203 Hz respectively in 2), can be attributed to a π-bond between tin and phosphorus. A similar effect has been observed in the coupling constants $^1J_{P-^{29}Si}$ in silaphosphene[5] and $^1J_{PP}$ in diphosphenes.[1] The ^{119}Sn chemical shift, falling at very low field (+658.3 ppm/Me$_4$Sn)[14] is the first

NMR data for tricoordinate, p–π hybridized tin.[15,16] The electronic spectrum of 1 (THF, pentane) exhibits peaks at λ$_{max}$ 460 (n → π*) and 350 nm (π → π*). Mass spectrum presents a parent peak at m/e 714 (^{120}Sn); experimental peak patterns were assigned after comparison with calculated theoretical peak patterns. Thermal stability of 1 is rather good; it persits for a week at room temperature.

The structure of 1 was corroborated by its chemical behavior. Reactivity of 1 is very high toward compounds with active hydrogens, e.g., methanol and hydrogen chloride, which add to the tin–phosphorus double bond; these highly regiospecific reactions, performed at room temperature in pentane, confirm the expected polarity of the Sn=P bond with tin as the more positive partner leading respectively to the secondary phosphines 9[17] and 10[18] in nearly quantitative yields. Reduction of 1 by LiAlH$_4$ affords 6[11] (eq 3).

(3)
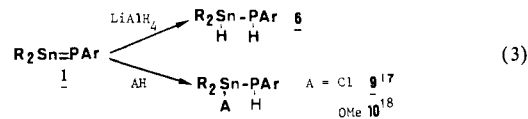
Chemical and physicochemical aspects of the tin–phosphorus double bond of 1 are under active investigation.

(15) Until now, only one compound, the distannene [(Me$_3$Si)$_2$CH]$_2$Sn=Sn[CH(SiMe$_3$)$_2$]$_2$ has been reported to have a tin–tin double bond in the solid phase.[16] But in solution this compound gives the two stannylenes [(Me$_3$Si)$_2$CH]$_2$Sn.[13]

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(17) 9 has been prepared independently from [(Me$_3$Si)$_2$CH]$_2$SnCl$_2$ and 3: white crystals, mp 158 °C; ^{1}H NMR (C_6D_6) δ 0.23 (br s, 36 H, Me$_3$Si), 1.23 (s, 9 H, p-*t*-Bu), 1.60 (s, 18 H, o-*t*-Bu), 7.37 (d, 2 H, $^4J_{PH}$ = 2.2 Hz, Ar H); ^{31}P NMR (C_6D_6) δ −100.3, $^1J_{PH}$ = 195.3, $^1J_{P-^{117}Sn}$ = 1253.1, $^1J_{P-^{119}Sn}$ = 1297.2 Hz. Anal. Calcd for C$_{32}$H$_{68}$ClPSiSn: C, 51.22; H, 9.13; Cl, 4.72. Found: C, 50.88; H, 9.02; Cl, 4.88.

(18) 10 has been prepared independently by reaction between 2 and MeOLi at 90 °C in a sealed tube: ^{1}H NMR (C_6D_6) δ 0.27 (br s, 36 H, Me$_3$Si), 1.30 (s, 9 H, p-*t*-Bu), 1.68 (s, 18 H, o-*t*-Bu), 3.87 (s, 3 H, OMe), 7.53 (d, 2 H, Ar H, $^4J_{PH}$ = 2.2 Hz); ^{31}P (C_6D_6) δ −116.0, $^1J_{PH}$ = 205.3, $^1J_{P-^{117}Sn}$ = 1053.0, $^1J_{P-^{119}Sn}$ = 1103.0 Hz; mass spectroscopy (desorption) 746 (^{120}Sn, M).

Novel Structure of the Complex between Carboxypeptidase A and a Ketonic Substrate Analogue

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As part of a continuing series of high-resolution X-ray crystallographic studies of the interaction of inhibitors with the zinc metalloprotease carboxypeptidase A$_\alpha$ (CPA),[1,2] we report the structure of the complex between CPA and the substrate analogue

(9) 5 has been prepared by fluorination of [(Me$_3$Si)$_2$CH]$_2$SnCl$_2$[10] with KF/EtOH/H$_2$O at 40 °C for 2 h and recrystallized from pentane to afford white needles: mp 113–116 °C; ^{1}H NMR (C_6D_6) δ 0.25 (s, 18 H, Me$_3$Si); ^{119}Sn{^{1}H} NMR (C_6D_6) δ −18.1 (t, $^1J_{SnF}$ = 3042 Hz); ^{19}F NMR (C_6D_6) δ −86.3. Anal. Calcd for C$_{14}$H$_{38}$F$_2$Si$_4$Sn: C, 35.36; H, 8.06; F, 7.99. Found: C, 35.45; H, 8.11; F, 8.05.

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(11) 6 has been prepared in an independent synthesis by reduction of 9 with LiAlH$_4$ in Et$_2$O: ^{1}H NMR (C_6D_6) δ 0.30 (br s, 36 H, Me$_3$Si), 1.33 (s, 9 H, p-*t*-Bu), 1.73 (s, 18 H, o-*t*-Bu), 7.47 (d, 2 H, Ar H, $^4J_{PH}$ = 2.5 Hz); ^{31}P (C_6D_6) δ −129.7, $^1J_{PH}$ = 201.7, $^2J_{PH}$ = 12.0, $^1J_{P-^{117}Sn}$ = 755.9, $^1J_{P-^{119}Sn}$ = 791.2 Hz; IR ν(PH) 2383, ν(SnH) 1826 cm^{-1}. Anal. Calcd for C$_{32}$H$_{69}$PSiSn: C, 53.68; H, 9.71. Found: C, 53.89; H, 9.98.

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