

before a fuller understanding of the different intermediates in the two processes will emerge. The ability of the bifunctional reagents **2** to be coaxed to react with the highly polarized heteroatom unsaturation of an aldehyde, even in preference to cycloaddition to an electron-deficient double bond, agrees with the theoretical description of a TMM-PdL₂ species.¹²

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(12) Control experiments demonstrates no carbonyl addition in the absence of Pd(0) catalysts with these silicon or tin conjunctive reagents. The silicon reagent can also cycloadd to aldehydes under these conditions but the yields are inferior, many cases fail, and much more drastic conditions are required. We attribute the differences to the ability of i vs. ii, which form as a result



of trapping the initial carbonyl-TMM-PdL₂ adduct by TMSOAc or R₃SnOAc, to cyclize. In the former case, products derived from i can be isolated, but we have not been able to detect the products derived from ii which suggests its suggests its cyclization must be efficient. Alternatively, R₃SnOAc may be sufficiently unreactive that **2** cyclizes directly and ii never forms. **Note Added in Proof:** 1,3-Diyl trapping by benzaldehyde has recently been reported. Little, R. D.; Bode, H.; Stone, K. J.; Wallquist, O.; Dannecker, R. *J. Org. Chem.* 1985, 50, 2400.

First Examples of Polynuclear, Sulfur-Containing, Zirconium Compounds. The Synthesis and Structural Characterization of the Trinuclear Zr₃S₃(S-*t*-Bu)₂(BH₄)₄(THF)₂ and the Hexanuclear Zr₆S₆(S-*t*-Bu)₄(BH₄)₈(THF)₂ Clusters

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Recent interest in Zirconium chemistry derives to a considerable extent from the demonstrated importance of certain low-valent Zr compounds in CO activation and reduction.¹ The rarity of soluble polynuclear Zr clusters and the potential importance of such molecules in small-molecule activation prompted us to examine the methodology for the synthesis of such species. We have focused our attention on Zr-S clusters, with the anticipation that once obtained such molecules will be thermodynamically unstable relative to O, N, or halide ligands and consequently well suited as synthons for future studies. Furthermore, reduction of polynuclear Zr-S clusters or their derivatives may well lead to low-valent Zr clusters with unusual catalytic properties.

The coordination chemistry of Zirconium with sulfur ligands is limited to that of the octahedral dithiolene, (Zr(L)₃)³⁻, complexes,² the eight-coordinate dithiocarbamate complexes,³ Zr-(R₂Dtc)₄, and the pentagonal-bipyramidal (Cp)Zr(Me₂Dtc)₃ complex.⁴ To our knowledge aliphatic thiolate complexes of Zr are virtually unknown, and only a brief report on the synthesis of the blue Zr(SPh)₄ complex has appeared in the literature.⁵ In this paper we report on the synthesis of two new Zr clusters that

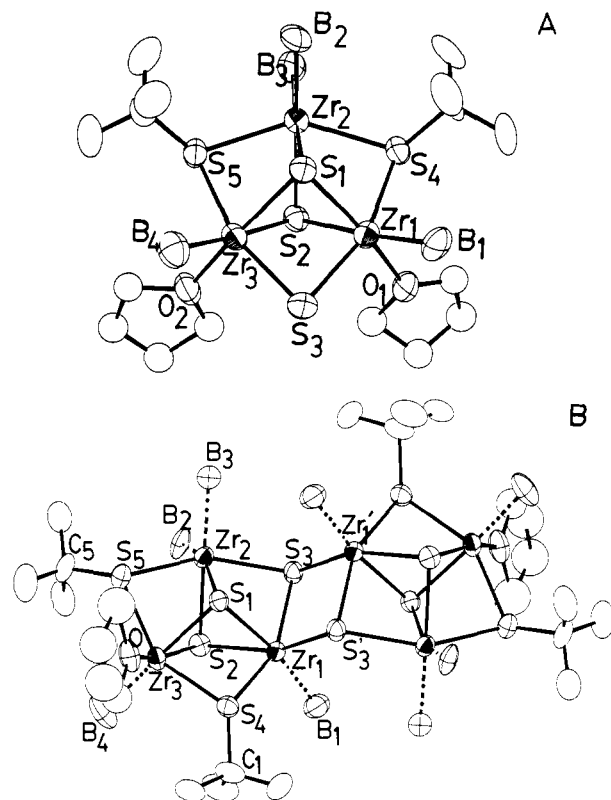
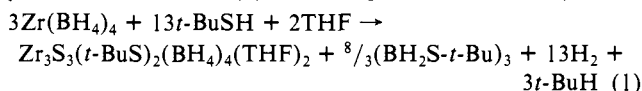


Figure 1. Structure and labeling of Zr₃S₃(S-*t*-Bu)₂(BH₄)₄(THF)₂ (A) and Zr₆S₆(S-*t*-Bu)₄(BH₄)₈(THF)₂ (B). Thermal ellipsoids as drawn by ORTEP (Johnson, C. K. ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, TN, 1965) represent the 40% probability surfaces. In A and B above only the B atoms of the BH₄⁻ ligands are drawn.

contain BH₄⁻, *t*-BuS⁻, S²⁻, and THF ligands.

The trinuclear Zr₃S₃(*t*-BuS)₂(BH₄)₄(THF)₂ cluster, I, is obtained from the reaction between Zr(BH₄)₄ and *t*-BuSH, in 70% yield (based on Zr(BH₄)₄), according to the stoichiometry. This



reaction (eq 1) proceeds in THF at ambient temperature with a steady evolution of H₂ for about 30 min and goes to completion when the pale yellow solution is further heated to ~50 °C for 4–6 h. Crystals of I are obtained following dilution with diethyl ether and *n*-hexane and cooling to -20 °C.⁶ After the isolation of I from solution, the very soluble (BH₂S-*t*-Bu)₃ byproduct is obtained in 90% yield (based on eq 1) by concentrating the filtrate to near dryness. The structure of this cyclic thioborane has been determined.⁷

A concentrated solution of I in CD₂Cl₂ upon standing for ca. 24 h at ambient temperature deposited yellow crystals of a compound (II) with a powder diffraction pattern different than that of I. The single-crystal X-ray structures of I and II were determined⁸ and reveal the trimeric nature of I and the hexameric

(6) Anal. Calcd for C₁₆H₅₀B₄O₂S₅Zr₃: C, 25.66; H, 6.68; B, 5.88; S, 21.39; Zr, 36.09. Found: C, 26.69; H, 7.31; B, 5.87; S, 19.10; Zr, 35.33. Infrared spectra (KBr, cm⁻¹): ν(B-H), 2527 (s), 2465 (s), 2414 (s); ν(B-H_b), 2182 (s), 2111 (s), 2050 (sh), 1986 (s); δ(Zr-H-B) 1232 (vs); μ(C-S) 838 (vs).

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(8) Crystal and refinement data for Zr₃S₃(*t*-BuS)₂(BH₄)₄(THF)₂ (I): *a* = 11.545 (3) Å, *b* = 16.481 (4) Å, *c* = 18.118 (4) Å, β = 91.123 (2)°; space group P2₁/c, Z = 4; *d*_{calcd} = 1.45 g/cm³; μ = 11.4 cm⁻¹, 2θ_{max} = 40 (Mo K_α, 0.710 69 Å); Unique Reflections 3248, used in refinement 2169 (*F*_o² > 3σ(*F*_o²)); parameters 235; final *R* = 0.06. Crystal and refinement data for Zr₆S₆(*t*-BuS)₄(BH₄)₈(THF)₂: *a* = 12.443 (1) Å, *b* = 15.197 (2) Å, *c* = 18.365 (2) Å, β = 70.214 (7)°; space group P2₁/c, Z = 2; *d*_{calcd} = 1.55 g/cm³; μ = 12.5 cm⁻¹; 2θ_{max} = 45 (Mo, K_α, 0.710 69 Å); unique reflections 4275; used in refinement 3102 (*F*_o² > 3σ(*F*_o²)); parameters 278; final *R* = 0.04.

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Table I. Interatomic Distances (Å) and Angles (deg) in the $Zr_3S_3(S-t-Bu)_2(BH_4)_4(THF)_2$ (I), $Zr_6S_6(S-t-Bu)_4(BH_4)_8(THF)_2$ (II), and $[Mo_3S_2Cl_9]^{3-}$ 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 _f	2.594 (6, 18) ^f	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 _g -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 ^m	2.344 (3, 8) ⁿ	2.29 (3, 2) ^o	
Zr-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 $Zr_3(\mu_3-S)_2(\mu_2-S)_3$ core as a structural feature. The latter roughly has a hexagonal-bipyramidal structure where two μ_2 -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 study⁹ and an electron-diffraction study¹⁰ 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 $(MeCp)_2Hf(BH_4)_2$ complex¹¹ 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.

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Supplementary Material Available: Listings of structure factors and positional and thermal parameters for $Zr_3S_3(S-t-Bu)_2(BH_4)_4(THF)_2$ and $Zr_6S_6(S-t-Bu)_4(BH_4)_8(THF)_2$ (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 characterized⁵ 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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