ORGANOMETALLICS

Volume 11, Number 9, September 1992

Communications

Synthesis and Crystal Structure of a Novel Tin(IV) Bent-Sandwich Complex

Lei Jia, Hongming Zhang, and Narayan S. Hosmane*

Department of Chemistry, Southern Methodist University, Dallas, Texas 75275

Received May 18, 1992

Summary: The redox reaction between *closo*-1-Sn-2-($SiMe_3$)-3-(Me)-2,3-$C_2B_4H_4$ (2) and $TiCl_4$ in a molar ratio of 1:1 in a solvent mixture of dry benzene (95%) and THF (5%) at 25 °C produces, in 73% yield, a previously unknown tin(IV) π-complex, 1,1′-*commo*-Sn[2-($SiMe_3$)-3-(Me)-2,3-$C_2B_4H_4$]$_2$ (1), which exhibits an unusual bent-sandwich geometry as confirmed by a single-crystal X-ray diffraction study. The (ring centroid 1)–Sn–(ring centroid 2) angle of 142.5° in 1 is similar to the corresponding angles in (η^5-C_5H_5)$_2$Sn^{II} (145.8°) and (η^5-C_5Me_5)$_2$Sn^{II} (144.1°), and thus the bent geometry of 1 resembles those of the stannocene derivatives despite the formal 4+ oxidation sate of the central tin atom.

The first known sandwiched tin species was stannocene, in which the divalent tin is sandwiched by two monoanionic cyclopentadienide ligands.[1] Since then, a number of C-substituted stannocene derivatives has been made and structurally characterized.[2] Because of the steric bulk, decaphenylstannocene is a parallel-sandwich species and has been the exception to the bent-sandwich geometries, exhibited by all known stannocenes and closely related derivatives that contain 14 interstitial electrons.[3] On the other hand, the tin(II)–carborane complexes are all half-sandwich (closo) species with a "bare" tin occupying one of the vertices of either a pentagonal bipyramid or an icosahedron.[4] To date, none of the ligand systems in organometallic chemistry could produce a sandwiched (commo) tin(IV) complex. We report herein the synthesis and crystal structure of the first bis(carborane)tin(IV) sandwich complex, 1,1′-*commo*-Sn[2-($SiMe_3$)-3-(Me)-2,3-$C_2B_4H_4$]$_2$ (1), which exhibits an unusual bent-sandwich geometry despite the absence of a lone pair of electrons on the metal.

Since the reaction between the [2-($SiMe_3$)-3-(R)-2,3-$C_2B_4H_4$]$^{2-}$ (R = $SiMe_3$, Me, H) dianion and $SnCl_4$ results exclusively in a reductive insertion of the metal, yielding the corresponding *closo*-Sn(II)–carborane complexes, a new synthetic strategy for the preparation of tin(IV) sandwich was warranted.[5] As part of this investigation, *closo*-1-Sn-2-($SiMe_3$)-3-(Me)-2,3-$C_2B_4H_4$ (2)[6] was reacted at 25 °C

---

[1] Atwood, J. L.; Hunter, W. E.; Cowley, A. H.; Jones, R. A.; Stewart, C. A. *J. Chem. Soc., Chem. Commun.* **1981**, 925.

[2] (a) Jutzi, P.; Kohl, F.; Hofmann, P.; Krüger, C.; Tsay, Y. H. *Chem. Ber.* **1980**, *113*, 757. (b) Cowley, A. H.; Jutzi, P.; Kohl, F. X.; Lasch, J. G.; Norman, N. C.; Schlüter, E. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 616. (c) Almlöf, J.; Fernholt, L.; Faegri, K.; Haaland, A.; Schilling, B. R.; Seip, R.; Taugbol, K. *Acta Chem. Scand., Ser. A* **1983**, *A37*, 131. (d) Cowley, A. H.; Lasch, J. G.; Norman, N. C.; Stewart, C. A.; Wright, T. C. *Organometallics* **1983**, *2*, 1691. (e) Wadepohl, H.; Pritzkow, H.; Siebert, W. *Organometallics* **1983**, *2*, 1899. (f) Schmid, G.; Zaika, D.; Boese, R. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 602.

[3] Heeg, M. J.; Janiak, C.; Zuckerman, J. J. *J. Am. Chem. Soc.* **1984**, *106*, 4259.

[4] (a) Hosmane, N. S.; Maguire, J. A. In *Advances in Boron and the Boranes*; Molecular Structure and Energetics 5; Liebman, J. F., Greenberg, A., Williams, R. E., Eds.; VCH: New York, 1988; pp 297–327. (b) Hosmane, N. S.; Maguire, J. A. *Adv. Organomet. Chem.* **1990**, *30*, 99–150. (c) Hosmane, N. S.; Maguire, J. A. In *Electron Deficient Boron and Carbon Clusters*; Olah, G. A.; Wade, K., Williams, R. E., Eds.; Wiley: New York, 1991; pp 215–235. (d) For insertion of Sn(II) into polyhedral borane cages to produce the corresponding anionic closo species, see also: Chapman, R. W.; Kester, J. G.; Folting, K.; Streib, W. E.; Todd, L. J. *Inorg. Chem.* **1992**, *31*, 979 and references therein.

[5] For reductive insertion of tin, see: Islam, M. S.; Siriwardane, U.; Hosmane, N. S.; Maguire, J. A.; de Meester, P.; Chu, S. S. C. *Organometallics* **1987**, *6*, 1936. However, a recent report shows that *closo*-1-Al(Et)-2,3-(Me)$_2$-2,3-$C_2B_9H_9$ reacts with Me_2SnCl_2 or Me_3SnCl to give 1-Sn(Me)$_2$-2,3-(Me)$_2$-2,3-$C_2B_9H_9$, whose crystal structure has not been determined to date (Jutzi, P.; Galow, P. *J. Organomet. Chem.* **1987**, *319*, 139).

[6] For synthesis, see, Hosmane, N. S.; Sirmokadam, N. N.; Herber, R. H. *Organometallics* **1984**, *3*, 1665. For the X-ray stucture, see: Cowley, A. H.; Galow, P.; Hosmane, N. S.; Jutzi, P.; Norman, N. C. *J. Chem. Soc., Chem. Commun.* **1984**, 1564.

0276-7333/92/2311-2957$03.00/0

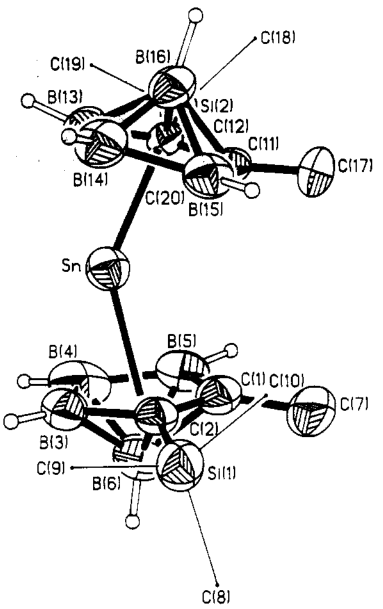

Figure 1. Perspective view of 1 with thermal ellipsoids drawn at the 50% probability level showing the atom-numbering scheme. The thermal ellipsoids of the silyl-C atoms are replaced by the smallest circles of arbitrary radii, and H atoms other than those on the cage atoms are omitted for clarity. Pertinent bond lengths (Å) and angles (deg) include the following: Sn–C(1) = 2.719 (6), Sn–C(2) = 2.716 (5), Sn–B(3) = 2.429 (8), Sn–B(4) = 2.234 (9), Sn–B(5) = 2.421 (8), Sn–C(11) = 2.675 (6), Sn–C(12) = 2.721 (6), Sn–B(13) = 2.425 (7), Sn–B(14) = 2.234 (7), Sn–B(15) = 2.388 (7), Sn–Cnt(1) = 2.105, Sn–Cnt(2) = 2.087, C(1)–C(2) = 1.453 (8), C(11)–C(12) = 1.478 (7); Cnt(1)–Sn–Cnt(2) = 142.5.

with $TiCl_4$ in a molar ratio of 1:1 in a solvent mixture of dry benzene and THF to produce in 73% yield a previously unknown *commo*-stannacarborane complex (1), as shown in eq 1.[7]

$$\underset{\mathbf{2}}{2\ 1\text{-}Sn^{II}\text{-}2\text{-}(SiMe_3)\text{-}3\text{-}(Me)\text{-}2,3\text{-}C_2B_4H_4} + 2TiCl_4 \xrightarrow[\text{THF/benzene}]{25\ °C} 2TiCl_3(THF)_3 + SnCl_2 + \underset{\mathbf{1}}{1,1'\text{-}Sn^{IV}[2\text{-}(SiMe_3)\text{-}3\text{-}(Me)\text{-}2,3\text{-}C_2B_4H_4]_2} \quad (1)$$

The extreme air and moisture sensitivity made it impossible to obtain reproducible microanalytical data for the same sample of 1. The electron-impact (EI) mass spectrum of 1 exhibited a grouping with the major cutoff at m/z 440 corresponding to the parent ion, $[^{120}Sn^{28}Si_2(^{12}CH_3)_8{}^{12}C_4{}^{11}B_8H_8]^+$. Except for the slight differences in the chemical shifts, the ^1H, ^{11}B, and ^{13}C NMR spectra as well as the IR spectra[8] of 1 are all similar to those observed for the corresponding *commo*-sila- and *commo*-germacarboranes that are all parallel slipped sandwich complexes.[9] However, the significant downfield shift of the ^{119}Sn resonances (−139.21 ppm) when compared to that in the *closo*-stannacarborane precursor 2 is an indication of the presence of a *commo*-tin–carborane complex.[8] Nevertheless, the foregoing spectral data do not permit a distinction to be made between bent and parallel sandwich geometries of the complex. Therefore, the X-ray analysis of 1 was undertaken.[10]

The most interesting structural feature of 1 is its bent-sandwich geometry (Figure 1). It has been generally understood that the presence of a lone pair of electrons, halide atoms, or coordinated solvent molecules on the central metal atom would be responsible for the bent-sandwich structures of π-organometallic complexes.[11] Since the distance between the highest residual peak (0.35 e/Å^3)[10] and the *commo*-Sn is only 0.918 Å, which is not a bonding distance of any kind (the Sn–H distances in Me_3SnH and Me_2SnH_2 are 1.71 (7) and 1.68 (2) Å, respectively),[12] the presence of hydride ligands on the tin metal is most unlikely. This is further confirmed by the absence of Sn–H couplings in the proton-coupled ^{119}Sn NMR spectrum of 1.[8] Because of the dinegative charge on each carborane ligand, and the located H's on the cage framework being exclusively the $B–H_{terminal}$ ones,[10] the formal oxidation state of tin in the neutral complex 1 is considered to be 4+ and, therefore, no lone pair of electrons or the hydride ligands are on the metal. The crystal packing diagram (not shown) reveals that the closest intermolecular contact within the unit cell of 1 (Sn···B(13)($-x$, $-y$, $-z$) = 4.019 Å, Sn···B(14)($-x$, $-y$, $-z$) = 4.021 Å, and Sn···Sn($-x$, $-y$, $-z$) = 4.962 Å) exceeds the sum of their van der Waals radii and hence there is no significant influence of the packing forces on the geometry of the complex. However, it is important to note that the solid-state

---

[7] A 3.4-mmol (0.95-g) sample of 2 in a 20-mL mixture of dry benzene (95%) and dry THF (5%) was allowed to react with 3.6 mmol (0.68 g) of pure $TiCl_4$ in vacuo at 0 °C for 4 h and then at 25 °C for 24 h, during which time the solution turned to pale blue with the formation of precipitate at the bottom of the flask. At this point, the mixture was filtered through a frit in vacuo and the solid on the frit was washed with a minimum quantity of dry n-hexane to collect a pale yellow filtrate. The solvents were then removed from the filtrate to collect a slightly brown solid, which was sublimed in vacuo at 75 °C to obtain an off-white solid, identified as 1, in 73% yield (mp 74.3 °C; extremely sensitive to air and moisture and soluble in most of the organic solvents). A small quantity of the brown residue, which remained in the flask after sublimation, was discarded because of its insolubility. To the blue-white solid on the frit was added 15 mL of a solvent mixture of dry n-hexane (70%) and dry THF (30%), the resulting turbid solution was filtered through a frit in vacuo, and the white solid on the frit was washed with n-hexane and dried to collect 0.32 g (1.68 mmol) of $SnCl_2$ (identified by its ^{119}Sn NMR spectrum and melting point). After removal of solvents from the filtrate in vacuo, 1.19 g (3.21 mmol) of a blue crystalline solid, identified as the reduced titanium product $TiCl_3(THF)_3$ (Manzer, L. E. *Inorg. Synth.* 1982, *21*, 135. Thiele, K. H.; Schäfer, W. *Z. Anorg. Allg. Chem.* 1970, *381*, 205), was isolated. The X-ray analysis confirms this identification.

[8] Spectroscopic data: ^1H NMR (C_6D_6, external Me_4Si) δ 2.35 [s (br), 3 H, C_{cage}–Me], 0.25 [s (br), 9 H, $SiMe_3$]; ^{11}B NMR (C_6D_6, external $BF_3{\cdot}OEt_2$) δ 10.59 [br, ill-defined peak, 4 B, basal BH, $^1J(^{11}B–^1H)$ unresolved], 5.04 [d, 2 B, basal BH, $^1J(^{11}B–^1H) \approx 120$ Hz], −40.66 [d, 2 B, apical BH, $^1J(^{11}B–^1H) = 179.99$ Hz]; ^{13}C NMR (C_6D_6, external Me_4Si) δ 136.38 [s (v br), cage carbons (SiCB)], 131.41 [s (v br), cage carbons (CCB)], 22.48 [q, C_{cage}–Me, $^1J(^{13}C–^1H) = 129.1$ Hz], 0.37 [q, $SiMe_3$, $^1J(^{13}C–^1H) = 119.5$ Hz]; ^{119}Sn NMR (C_6D_6, external TMT) δ −139.21 [s (v br), cage Sn]; IR (cm^{-1}; C_6D_6 vs C_6D_6) 2930 (vs, br), 2880 (sh), 2850 (sh) [ν(C–H)], 2540 (vvs), 2245 (vs) [ν(BH)], 1610 (w, br), 1480 (m, br), 1400 (m, br) [$\delta(CH)_{asym}$], 1390 (sh), 1370 (sh), 1340 (vs), 1250 (vs) [$\delta(CH)_{sym}$], 1215 (m, s), 1155 (w, br), 1050 (m, s), 1005 (w, br), 965 (w, br), 900 (sh), 835 (vs, br), 810 (sh) [ρ(CH)], 750 (s), 685 (m), 620 (m), 487 (vs, br), 408 (w, s), 370 (m).

[9] Siriwardane, U.; Islam, M. S.; West, T. A.; Hosmane, N. S.; Maguire, J. A.; Cowley, A. H. *J. Am. Chem. Soc.* 1987, *109*, 4600. Islam, M. S.; Siriwardane, U.; Hosmane, N. S.; Maguire, J. A.; de Meester, P.; Chu, S. S. C. *Organometallics* 1987, *6*, 1936.

[10] Crystal data: $C_{12}H_{32}B_8Si_2Sn$, fw 437.7, colorless needle, orthorhombic, *Pbca*, $a = 14.923$ (2) Å, $b = 16.995$ (3) Å, $c = 18.365$ (3) Å, $V = 4658$ (1) Å^3, $Z = 8$, $D_{calcd} = 1.248$ g/cm^3, $\mu = 1.194$ mm^{-1}. Of 3244 data collected on a Siemens R3m/V diffractometer (Mo Kα, $2\theta = 3.5–44.0°$, at −43 °C) 2866 reflections were independent and 2001 were observed [$I > 3.0\sigma(I)$]. Data were corrected for Lorentz, polarization, and absorption effects. The structure was solved by heavy-atom methods using SHELXTL-PLUS (Sheldrick, G. M. Structure Determination Software Program Package; Siemens Analytical X-ray Instruments, Inc., Madison, WI, 1990). All non-H atoms were refined anisotropically. Cage H atoms were located on difference Fourier maps, and methyl H atoms were calculated. The final refinement of 1 converged at $R = 0.034$, $R_w = 0.044$, and GOF = 1.34 for observed reflections. The maximum and minimum residual electron densities are 0.35 and −0.28 e/Å^3.

[11] *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, U.K., 1982. *Comprehensive Coordination Chemistry*; Wilkinson, G., Gillard, R. D., McCleverty, J. A., Eds.; Pergamon: New York, 1987. *Dictionary of Organometallic Compounds*; Macintyre, J. E., Ed.; Chapman & Hall: New York, 1984, and Suppl. Vol. 1–5 (1985–1989).

[12] Beagley, B.; McAloon, K.; Freeman, J. M. *Acta Crystallogr., Sect. B* 1974, *30*, 444.

Organometallics 1992, *11*, 2959–2961

structure of 1 may not be the ground-state geometry of the molecule, even though no specific intermolecular contacts are found in the crystal lattice. Similar molecules such as $(\eta^5\text{-}Me_5C_5)_2Si$ have very shallow bending potentials and, therefore, exist as independent linear and bent forms in the same lattice.[13]

Although the tin atom adopts an essentially η^5-bonding posture with respect to each of the C_2B_3 faces with the Sn–centroid distances of 2.105 and 2.087 Å, the average Sn–C distances (2.708 (6) Å) are significantly longer than the average Sn–B distances (2.355 (8) Å), thus making the metal slipped toward the three boron atoms with concomitant tightening of the C–C bond (1.453 (8) and 1.478 (7) Å in 1 vs 1.494 (7) Å in 2) on the C_2B_3 face in each ligand. Such slip distortions of the metallacarborane cages have been observed previously.[4] The (ring centroid 1)–Sn–(ring centroid 2) angle of 142.5° in 1 is comparable to the corresponding angles in $(\eta^5\text{-}C_5H_5)_2Sn^{II}$ (145.8°)[1] and $(\eta^5\text{-}C_5Me_5)_2Sn^{II}$ (144.1°),[2a] and thus the bent geometry of 1 resembles those of the stannocene derivatives despite the 2– charge on each carborane ligand. Nonetheless, compound 1 represents the first tin(IV) sandwich complex ever to be reported.

The results of this investigation suggest that a number of novel complexes containing higher oxidation states, that are not normally produced by conventional synthetic approaches, can be synthesized by oxidizing the metal in the complex with an oxidizing metal reagent stronger than the complexed metal itself. We are currently exploiting this synthetic strategy in the preparation of hitherto unexplored carborane sandwich complexes of main-group elements and early transition metals.

Acknowledgment. This work was supported by grants from the National Science Foundation (CHE-9100048), the Robert A. Welch Foundation (N-1016), and the donors of the Petroleum Research Fund, administered by the American Chemical Society.

Supplementary Material Available: Tables of positional and thermal parameters, bond distances, and bond angles (5 pages). Ordering information is given on any current masthead page.

OM9202736

---

[13] Jutzi, P.; Kanne, D.; Krüger, C. *Angew. Chem., Int. Ed. Engl.* 1986, *25*, 164.

$Ru_5(CO)_{15}B(AuPPh_3)$: A Novel Boride Cluster Formed by the Degradation of $Ru_6(CO)_{17}B(AuPPh_3)$

Catherine E. Housecroft,*,[†] Dorn M. Matthews,[†] and Arnold L. Rheingold*,[‡]

University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, U.K., and Department of Chemistry, University of Delaware, Newark, Delaware 19716

Received June 1, 1992

Summary: Under a pressure of CO (55 atm), $Ru_6(CO)_{17}B(AuPPh_3)$ extrudes one ruthenium vertex and forms $Ru_5(CO)_{15}B(AuPPh_3)$ (2) as the only product. Crystallographic characterization of 2 confirms the presence of a square-pyramidal Ru_5 core with an interstitial boron atom lying 0.375 Å below the square face. 2 is the first structurally elucidated example of a boride cluster built upon an M_5B core.

The emerging area of discrete molecular boride clusters has provided examples of boron atoms encapsulated within hexametallic cages; structurally characterized clusters are octahedral $(HRu_6(CO)_{17}B,$[1,2] $[Fe_4Rh_2(CO)_{16}B]^-$,[3] and $H_2Fe_3Rh_3(CO)_{15}B$[3]) and trigonal prismatic ($[H_2Ru_6(CO)_{18}B]^-$).[4] During the reaction to form $[Fe_4Rh_2(CO)_{16}B]^-$, Fehlner has observed the formation of an intermediate species proposed to possess an Fe_4RhB core.[3] Pentanuclear species are well exemplified for molecular transition-metal carbonyl carbides[5-8] and nitrides.[5,9,10] Our own work in

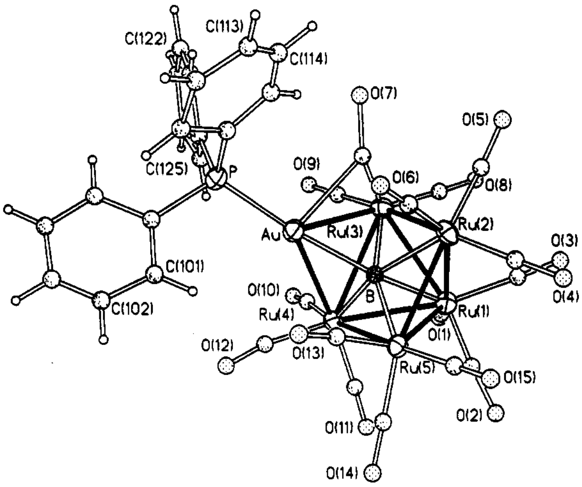

Figure 1. Molecular structure of $Ru_5(CO)_{15}B(AuPPh_3)$ (2).

[†] University Chemical Laboratory.

[‡] University of Delaware.

[1] Hong, F.-E.; Coffy, T. J.; McCarthy, D. A.; Shore, S. G. *Inorg. Chem.* 1989, *28*, 3284.

[2] Draper, S. M.; Housecroft, C. E.; Keep, A. K.; Matthews, D. M.; Song, X.; Rheingold, A. L. *J. Organomet. Chem.* 1992, *423*, 241.

[3] Bandyopadhyay, A. K.; Khattar, R.; Puga, J.; Fehlner, T. P.; Rheingold, A. L. *Inorg. Chem.* 1992, *31*, 465.

[4] Housecroft, C. E.; Matthews, D. M.; Rheingold, A. L.; Song, X. *J. Chem. Soc., Chem. Commun.* 1992, 842.

[5] Gourdon, A.; Jeannin, Y. *J. Organomet. Chem.* 1985, *290*, 199.

[6] Johnson, B. F. G.; Lewis, J.; Nelson, W. J. H.; Nicholls, J. N.; Puga, J.; Raithby, P. R.; Rosales, M. J.; McPartlin, M.; Clegg, W. *J. Chem. Soc., Dalton Trans.* 1983, 277.