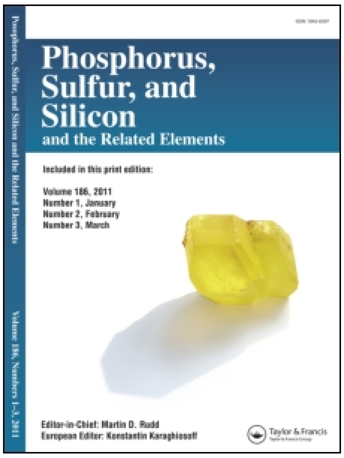


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

BONDING MODE OF TETRAHYDROBORATE ANION TOWARDS ORGANOTINS

N. S. Neelam Jalil[a]; I. Abdulmumin[a]
[a] Department of Chemistry, Ahmadu Bello University, Zaria, Nigeria

To cite this Article Jalil, N. S. Neelam and Abdulmumin, I.(1996) 'BONDING MODE OF TETRAHYDROBORATE ANION TOWARDS ORGANOTINS', Phosphorus, Sulfur, and Silicon and the Related Elements, 118: 1, 1 — 6
To link to this Article: DOI: 10.1080/10426509608038794
URL: http://dx.doi.org/10.1080/10426509608038794

Phosphorus, Sulfur, and Silicon, 1996, Vol. 118, pp. 1–6
Reprints available directly from the publisher
Photocopying permitted by license only

BONDING MODE OF TETRAHYDROBORATE ANION TOWARDS ORGANOTINS

N. S. NEELAM JALIL* and I ABDULMUMIN

Department of Chemistry, Ahmadu Bello University, Zaria, Nigeria

(Received 30 August 1995; Revised 14 May 1996; In final form 14 May 1996)

The interaction of methyltin trichloride, dibutyltin diacetate and tributyltin chloride with an excess of KBH_4 in dry THF results in the formation of novel compounds of the type $CH_3Sn(BH_4)_3$, $(C_4H_9)_2Sn(BH_4)_2$ and $(C_4H_9)_3Sn(BH_4)$. The complexes were characterized by their decomposition points, conductivity measurements, elemental analyses and IR spectroscopic studies. Conductivity measurements show their non-ionic nature and IR predicts tridentate behaviour of tetrahydroborate anion in these complexes.

Keywords: Methyltin trichloride; dibutyltin diacetate; tributyltin chloride; IR; conductivity measurements

INTRODUCTION

In recent years metal tetrahydroborate study has been of renewed interest to inorganic and organometallic chemists due to their manifold utility.[1–4] Several covalent tetrahydroborates with main group elements, transition metals, lanthanides and actinides[4–7] have been reported. Ideally studies of any system of molecules should rest upon a firm structural foundation. For metal tetrahydroborates one of the most significant structural questions concerns the mode by which the BH_4^- group is attached to the metal. Structural studies have shown that the tetrahydroborate anion bonding to metal ions is invariably through hydrogen via three center (M-H-B) bonds of the kind well known for the boron hydrides themselves.[8,9] Geometries having mono,[10] di and tri[5] hydrogen bridge bonds have been observed for mononuclear complexes. In addition, the coordination of the tetrahydroborate anion to a metal ion is usually accompanied by

---

*Corresponding author.

changes in its vibrational spectrum that are characteristic of the mode of attachment.[11] Therefore, vibrational spectroscopy is often used as one of the methods for discerning the gross structural features of M-BH_4 ligation. Although it suffers limitations of overinterpretation, yet it has been found to be of considerable utility since the tautomeric process which permutes bridge and terminal hydrogen in the majority of tetrahydroborate complexes is rapid on the NMR time scale at all accessible temperatures in solution. NMR spectra exhibits a single kind of boron hydride proton rather than the expected resonances for terminal and bridging hydrogens.[12] The mode of coordination of BH_4^- to metal cannot be ascertained unambiguously by X-ray diffraction method because it is not particularly suitable for locating hydrogen near the heavy metal.[5]

Tetrahydroborate anion is reported to bind with some organometals[4,10] but there is no report on its interaction with organotins. In continuation of our studies on some organotins and Group IV metal halides[13] and in the light of the immense importance of the tetrahydroborate anion in diverse fields, we undertook this project to explore the bonding mode of tetrahydroborate anion towards organotins. We report on the synthesis and characterization of the tetrahydroborates of methyltin trichloride, dibutyltin diacetate and tributyltin chloride.

RESULTS AND DISCUSSION

The reactions of methyltin trichloride, dibutyltin diacetate and tributyltin chloride with an excess of KBH_4 in dry THF yields $CH_3Sn(BH_4)_3$, $(C_4H_9)_2Sn(BH_4)_2$ and $(C_4H_9)_3$-$Sn(BH_4)$ according to the following equations.

$$CH_3SnCl_3 + 3KBH_4 \xrightarrow{THF} CH_3Sn(BH_4)_3 + 3KCl \qquad (1)$$

$$(C_4H_9)_2Sn(CH_3COO)_2 + 2KBH_4 \xrightarrow{THF} (C_4H_9)_2Sn(BH_4)_2 + 2CH_3COOK \qquad (2)$$

$$(C_4H_9)_3SnCl + KBH_4 \xrightarrow{THF} (C_4H_9)_3Sn(BH_4) + KCl \qquad (3)$$

In these reactions KBH_4 is taken in excess in order to prevent reduction of the central atom. Table I presents the analytical data which confirm to the composition of the complexes. All the complexes are stable and soluble in DMF and DMSO but insoluble in common organic solvents. The molar conductances of 10^{-3} M solution of the complexes show them to be non-electrolytes in DMF.[14]

TABLE I Analytical Data and Some Physical Constants of the Complexes

Complex	*Colour*	*Dec.P. °C*	*% C Found (Calc.)*	*% H Found (Calc.)*	*% B Found (Calc.)*	*% Sn Found (Calc.)*	*% Yield*	*Molar Conductivity (Ohm^{-1} cm^{-1} mol^{-1})*
$CH_3Sn(BH_4)_3$ $CH_{15}B_3Sn$	White	208– 216	6.70 (6.74)	8.40 (8.42)	18.20 (18.21)	66.63 (66.63)	75	18
$(C_4H_9)_2Sn(BH_4)_2$ $C_8H_{26}B_2Sn$	White	200– 210	36.60 (36.62)	9.90 (9.91)	8.22 (8.24)	45.22 (45.23)	70	20
$(C_4H_9)_3Sn(BH_4)$ $C_{12}H_{31}BSn$	White	192– 202	47.28 (47.31)	10.15 (10.18)	3.53 (3.55)	38.94 (38.96)	70	22

The central focus of this project was to ascertain the mode of binding of the BH_4^- anion to organotins and the effect of the alkyl substituents in the complexes on the bonding. The mode of bonding of the tetrahedral BH_4^- ligand to a metal ion in a metal-tetrahydroborate is a fundamental and structural feature of the complex. IR spectroscopy can provide useful data on the metal-ligand coordination geometry and bonding and it allows a ready distinction to be drawn among the mono, di and tridentate anion in the complexes. The structurally significant bands lie in the range 2600−1000 cm^{-1} and principally involve the stretching and deformation of B–H bonds and some stretching of M–H bonds[5] also. The terminal hydrogen-boron stretch (ν B–H_t) and bridge hydrogen-boron stretch (ν B–H_b) are the two most easily recognised changes which depend on the mode of bonding of the BH_4^- anion (mono, di or tridentate behavior) and are expected to be relatively "pure" i.e. unmixed with other low frequency modes. This involves principally motion of a very light atom bonded to a relatively heavy atom. Similarly because of the large number of intervening bonds (and spatial separation of the groups), it is reasonable to assume that structurally diagnostic vibrations of one BH_4^- group in a complex are not coupled to similar vibrations in another BH_4^- group (or other ligands) in the same complex.

A single band due to ν (B–H_t) in complexes was observed in the range 2565–2570 cm^{-1} which was attributable to tridentate behavior of the BH_4^- ligand.[5,11] Such tridentate behavior has also been observed for the tetrahedral tetrahydroborates of zirconium, tin and hafnium.[5,6] Absence of a doublet in this region ruled out the bidentate behavior of the BH_4^- anion.[15] A doublet at 2150–2275 cm^{-1} in all the complexes was attributed to the B–H_b stretching mode.[5] Distinct absorption had been observed in the IR spectra of the complexes in the range 1230–1390 cm^{-1} which was associated with H_b–B–H_t bending.[16] The other band of significant intensity was in the range 1185–1200 cm^{-1} due to the bridge deformation band. The band at 420–440 cm^{-1} has been assigned to the deformation of the ν Sn(M–H)$_3$B bridges.[16] The effect of alkyl substituents does not seem to have any significant effect on the mode of bonding of the tetraborate anion to tin. However, with the increase in the number of alkyl groups in the molecule the stretching frequencies of B–H_b and Sn–H_b bonds shifted to lower and higher wave numbers, respectively, while ν Sn-H_t stretching frequency remained unchanged. The presence of same central atom in all the complexes ruled out the mass effect as a major cause of changes in the IR frequencies of these bands. This specifically happens when the strength of the M–BH_4 interaction increases[17] and eventually the electron density in B–H_b bonds decrease. Since the orbitals of proper symmetry were available the back donation of electrons, (Sn→H_b-B), also occurred increasing the electron density in Sn–H_b bonds.

Based on the above results we suggest a tetrahedral structure for these newly synthesized complexes. Figure 1 presents the proposed structures of the complexes.

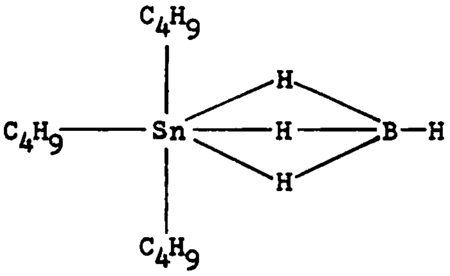
EXPERIMENTAL

Methyltin trichloride (Aldrich), di-*n*-butyltin diacetate and tri-*n*-butyltin chloride (B.D.H.) were used as received. THF and DMF were distilled and dried before use by conventional methods. Decomposition points were recorded on a Gallenkamp melting point apparatus. Elemental analyses for C and H were carried out on a Coleman analyzer. Molar conductances of the complexes were determined at 10^{-3} M concentrations in DMF using a Waynekerr Universal Conductivity Bridge type B-221. Tin, boron and chlorine were estimated gravimetrically.[18] Chloride was not detected. Infrared spectra were recorded in CsBr discs on a Perkin Elmer RB 31000 infrared spectrometer.

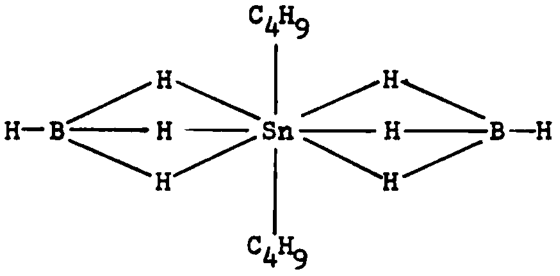
Preparation of the Complexes

All the complexes were prepared by the following general procedure.

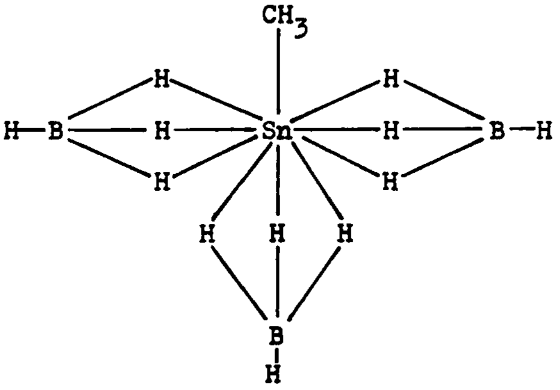
To a 10 mmole of organotin trichloride (2.40 g CH_3SnCl_3, 3.51 g $(C_4H_9)_2Sn(CH_3COO)_2$ and 3.25 g $(C_4H_9)_3SnCl$) in 50 mL THF was added 100 mmole (5.39 g) KBH_4 (excess). The reaction mixture was allowed to stir for ten hours when a white solid crystallized. The solvent was removed under vacuum and the solid was washed with THF three times with 10 mL aliquots each time. It was washed with ether, then dried in an oven at 110°C for six hours and finally in a vacuum dessicator over silica gel for 24 hours. The specific data for the characterization of the complexes is given in Table I.



$(C_4H_9)_3Sn(BH_4)$



$(C_4H_9)_2Sn(BH_4)_2$



$CH_3Sn(BH_4)_3$

FIGURE 1 Proposed Structures of the complexes.

References

[1] G. G. Hlatky and R. H. Crabtree, *Coord. Chem. Rev.*, **65**, 1 (1985).

[2] J. A. Jensen, S. R. Wilson, A. J. Schultz and G. S. Girolami, *J. Am. Chem. Soc.*, **109**, 8094 (1987).

[3] J. Y. Beach and S. H. Bauer, *J. Am. Chem. Soc.*, **62**, 3440 (1940).

[4] J. T. Spencer, *Prog. Inorg. Chem.*, **21**, 145 (1994).

[5] T. J. Marks and J. R. Kolb, *Chem. Rev.*, **77**, 263 (1977).

[6] K. S. Siddiqi, Fathi M. A. M. Aqra, S. A. Shah and S. A. A. Zaidi, *Polyhedron*, **13**, 247 (1994).

[7] J. E. Gozum, S. R. Wilson and G. S. Girolami, *J. Am. Chem. Soc.*, **114**, 9483 (1992).

[8] E. L. Muetterties, "Boron Hydride Chemistry", Academic Press, New York, 1975.

[9] G. A. Olah, K. Wade and R. E. Williams, Eds; "Electron Deficient Boron and Carbon Chemistry", Wiley Interscience, New York, 1990.

[10] J. A. Jensen and G. S. Girolami, *Inorg. Chem.*, **28**, 2107 (1989).

[11] T. J. Marks, W. J. Kennelly, J. R. Kolb and L. A. Shipm, *Inorg. Chem.*, **11**, 2540 (1972).

[12] T. J. Marks and L. A. Shimp, *J. Am. Chem. Soc.*, **94**, 1542 (1972).

[13] N. S. Neelam Jalil, *Synth. React. Inorg. Met.-Org. Chem.*, **20**, 1285 (1990) and references therein.

[14] W. J. Geary, *Coord. Chem. Rev.*, **7**, 81 (1971).

[15] D. A. Coe and J. W. Nibler, *Spectrochim Acta*, **29**, 1789 (1973).

[16] B. E. Smith, H. F. Shurvell and B. D. James, *J. Chem. Soc. Dalton Trans.*, 710 (1978).

[17] T. J. Marks and W. J. Kennelly, *J. Am. Chem. Soc.*, **97**, 1439 (1975).

[18] G. Brauer, "Handbook of Preparative Inorganic Chemistry", 2nd Edn. Vol I, Academic Press, London, 1963, p. 736. J. Bassett, R. C. Danney, C. H. Jeffery and J. Mendham, "Vogel's Textbook of Quantitative Inorganic Analysis", 4th Edn., Longman Inc., New York, 1981, pp. 484 and 494.