

# Correspondence

## Tin-119 Mossbauer Spectrum of 3-Stanna-1,2-dicarba-closo-dodecaborane(11)

Sir:

We previously reported the preparation and characterization of 3-Sn-1,2-B<sub>9</sub>C<sub>2</sub>H<sub>11</sub>,<sup>1</sup> a molecule analogous to dicyclopentadienyltin(II)<sup>2</sup> in the respect that carbametallic boranes are similar to metallocenes in general.<sup>3</sup> The evidence presented for the original characterization of 3-Sn-1,2-B<sub>9</sub>C<sub>2</sub>H<sub>11</sub> (derived mainly from vapor phase and solution measurements) was consistent with a nominally icosahedral structure with a "bare" tin atom at one vertex of the deltahedron,<sup>4,5</sup> *i.e.*, a molecule in which 26 electrons can be assigned to the framework bonding<sup>5</sup> such that tin is formally divalent with an exodeltahedral lone pair. Thus, although carbenoid character is maintained in the proposed structure, the tin is not "sandwiched" between two rings, a salient difference from other metallocenes.

The <sup>119</sup>Sn Mossbauer resonance of pure, solid 3-Sn-1,2-B<sub>9</sub>C<sub>2</sub>H<sub>11</sub> was run at 77°K vs. a <sup>119m</sup>SnO<sub>2</sub> source and displayed resonance ( $\delta$  4.67 ± 0.04;  $\Delta E_Q$  = 3.83 ± 0.04 mm/sec) substantially above that of  $\beta$ -tin,<sup>6</sup> on this basis we confirm the valence state as tin(II).<sup>6</sup> The degree of the isomer shift and the magnitude of the quadrupole splitting are intriguingly large. Among the few data available for comparison,

(1) R. W. Rudolph, R. L. Voorhees, and R. E. Cochoy, *J. Amer. Chem. Soc.*, **92**, 3351, (1970). The nomenclature used here differs from that of the original report but conforms with that suggested by IUPAC, *Pure Appl. Chem.*, **30**, 681 (1972).

(2) E. O. Fischer and H. Grubert, *Z. Naturforsch. B*, **11**, 423 (1956); L. D. Dave, D. F. Evans, and G. Wilkinson, *J. Chem. Soc.*, 3684 (1959).

(3) M. F. Hawthorne, *Accounts Chem. Res.*, **1**, 281 (1968).

(4) A deltahedron is a polyhedron with triangular faces.

(5) R. W. Rudolph and W. R. Pretzer, *Inorg. Chem.*, **11**, 1974 (1972); K. Wade, *Chem. Commun.*, 792 (1971).

(6) The isomer shift of  $\beta$ -Sn (*ca.* 2.65 mm/sec with respect to SnO<sub>2</sub> at ambient temperature) is taken as the dividing line between the two valences, all tin(IV) compounds falling below and all tin(II) compounds above; see, D. E. Fenton and J. J. Zuckerman, *Inorg. Chem.*, **8**, 1771 (1969).

we find no other Sn(II) compounds to have such a positive isomer shift relative to SnO<sub>2</sub>;<sup>7</sup> the quadrupole splitting is also atypical of previously observed values for Sn(II).<sup>7</sup> However, the proposed structure of 3-Sn-1,2-B<sub>9</sub>C<sub>2</sub>H<sub>11</sub> predictably would give rise to a marked asymmetry in the distribution of charge about the tin atom and on this basis the observed quadrupole splitting is satisfying.

It has been suggested that a higher isomer shift is indicative of more 5s<sup>2</sup> character for tin(II),<sup>8</sup> in this vein a comparison of the values for 3-Sn-1,2-B<sub>9</sub>C<sub>2</sub>H<sub>11</sub> and Sn( $\pi$ -C<sub>5</sub>H<sub>5</sub>)<sub>2</sub> (4.67 and 3.74 mm/sec,<sup>9</sup> respectively) would indicate less directional character for the lone-pair electrons of the former. Correspondingly, we have not observed complex formation between 3-Sn-1,2-B<sub>9</sub>C<sub>2</sub>H<sub>11</sub> and Lewis acids like BF<sub>3</sub> under conditions where ( $\pi$ -C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Sn·BF<sub>3</sub> has recently been reported.<sup>9</sup> Moreover, in agreement with previous characterization of the stannacarborane in solution and in the vapor state, the Mossbauer spectrum showed that it has no tendency to polymerize to the Sn(IV) state as observed for Sn( $\pi$ -C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>.<sup>9</sup>

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**Registry No.** 3-Sn-1,2-B<sub>9</sub>C<sub>2</sub>H<sub>11</sub>, 27082-69-5.

(7) For examples see R. V. Parish, *Progr. Inorg. Chem.*, **15**, 101 (1972).

(8) J. D. Donaldson and B. J. Senior, *J. Chem. Soc. A*, 1796 (1966).

(9) P. G. Harrison and J. J. Zuckerman, *J. Amer. Chem. Soc.*, **92**, 2577 (1970).

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