

Icosahedra with Slipped Vertices. The Influence of Electron Donation on the Geometry of a Stannadecaborane (Stannacarborane)[†]

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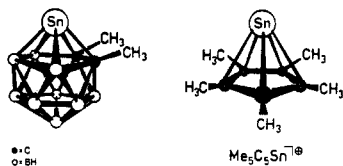
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The syntheses and spectroscopic properties of the adducts of 2,3-dimethyl-1-stanna-2,3-dicarbaborane (1) with 2,2'-bipyridine (bpy) (2), *o*-phenanthroline (*o*-phen) (3), *N,N,N',N'*-tetramethylethylenediamine (TMEDA) (4), pyridine (py) (5), tetrahydrofuran (THF) (6 and 7), and triphenylphosphine (Ph₃P) (8) are reported. The structures of 2 and 7 were determined by X-ray crystallography. Both compounds crystallize in the *P*₂₁/*c* space group (No. 14) with *Z* = 4. For 2, *a* = 12.503 (3) Å, *b* = 10.502 (2) Å, *c* = 18.627 (6) Å, and β = 94.87 (2)°, while for 7, *a* = 10.303 (3) Å, *b* = 10.340 (3) Å, *c* = 14.597 (3) Å, and β = 92.69 (2)°. The major effect of Lewis base complexation is to move the apical Sn atom from an η⁵-bonding in 1 to an η³-borallyl-type bonding in 2 and 7. NMR data have been obtained for 1, 4-8, and related molecules.

Introduction

Although the dicarbollide ligands^{1a} of the type [7,8-*R*₂-7,8-C₂B₉H₉]²⁻ are best known in the context of transition-metal chemistry,^{1b} several such complexes of the main-group elements have, in fact, been isolated (Scheme I).²⁻⁷ The available structural data indicate that the C₂B₃ face of the dicarbollide ligand binds the main-group fragments in an essentially η⁵-fashion, although, as in the case of transition-metal dicarbollides, the binding is somewhat asymmetric. Qualitatively, the interrelationships between main-group and transition-metal fragments can be understood on the basis of the isolobal principle,⁸ e.g., Sn ↔ (η⁵-C₅H₅)Co ↔ (Ph₃P)₂Pt. Further use of this principle highlights the relationship between cyclopentadienides and the C₂B₃ face of dicarbollide ligands.⁹ Similarities between 2,3-Me₂-1-Sn-2,3-C₂B₉H₉ (1) and



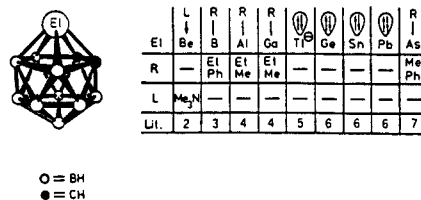
[(η⁵-Me₅C₅)Sn]⁺ thus became apparent.^{10,11} Given the Lewis acidity of the latter,¹² it was anticipated that 1 would behave in a similar fashion. This question is probed in the present work by treatment of 1 with mono- and bidentate Lewis bases.¹³ Particular emphasis is placed on the structural consequences of electron donation to the tin center.

Results and Discussion

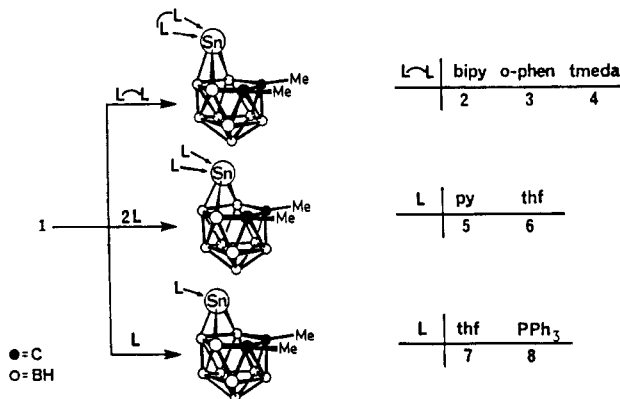
Synthetic Aspects. The stannacarborane 2,3-Me₂-1-Sn-2,3-C₂B₉H₉ (1) was synthesized in 75% yield by treatment of SnCl₂ with Na₂[7,8-Me₂-7,8-C₂B₉H₉] in a manner similar to that described by Rudolph et al.⁶ for the

[†]The compounds described in this paper are named according to the IUPAC convention. In this system, carborane becomes carborane; e.g., the name stannadecaborane refers to the Sn-C₂B₁₀ core.

Scheme I



Scheme II



synthesis of the group 14 metallacarboranes 1,2,3-EiC₂B₉H₁₁. Compound 1 is an air-sensitive, colorless waxy

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- (2) Popp, G.; Hawthorne, M. F. *J. Am. Chem. Soc.* 1968, 90, 6553.
- (3) Hawthorne, M. F.; Wegner, P. A. *J. Am. Chem. Soc.* 1968, 90, 896.
- (4) Young, D. A. T.; Wiersema, R. J.; Hawthorne, M. F. *J. Am. Chem. Soc.* 1971, 93, 5687. See also: Young, D. A. T.; Willey, G. R.; Hawthorne, M. F.; Reis, A. H., Jr.; Churchill, M. R. *Ibid.* 1970, 92, 663.
- (5) Spencer, J. L.; Green, M.; Stone, F. G. A. *J. Chem. Soc., Chem. Commun.* 1972, 1178.
- (6) (a) Rudolph, R. W.; Voorhees, R. L.; Cochoy, R. E. *J. Am. Chem. Soc.* 1970, 92, 3351. (b) Rudolph, R. W.; Chowdhry, V. *Inorg. Chem.* 1974, 13, 248.
- (7) Smith, H. D.; Hawthorne, M. F. *Inorg. Chem.* 1974, 13, 2312.

Table I. Yields, Decomposition Temperatures (Decomp), Solid-State UV/Vis Absorption, and Elemental Analytical Data for Compounds 1-8

compounds ^a	yield, ^b %	decomp, °C	λ , nm ^c	mol formula (M_r)	anal. found (calcd)		
					C	H	N
2,3-Me ₂ -1-Sn-2,3-C ₂ B ₉ H ₉ (1)	75	190	278	C ₄ H ₁₆ B ₉ Sn (279.15)	17.19 (17.21)	5.42 (5.42)	
1-bpy-2,3-Me ₂ -1-Sn-2,3-C ₂ B ₉ H ₉ (2)	70	234	314 (355)	C ₁₄ H ₂₃ B ₉ N ₂ Sn (435.34)	39.05 (38.63)	5.27 (5.33)	6.62 (6.44)
1- <i>o</i> -phen-2,3-Me ₂ -1-Sn-2,3-C ₂ B ₉ H ₉ (3)	42	295	300 400	C ₁₆ H ₂₃ B ₉ N ₂ Sn (459.36)	40.95 (41.84)	5.22 (5.05)	5.90 (6.10)
1-TMEDA-2,3-Me ₂ -1-Sn-2,3-C ₂ B ₉ H ₉ (4)	56	247	280	C ₁₀ H ₃₁ B ₉ N ₂ Sn (395.36)	30.72 (30.38)	8.34 (7.90)	6.82 (7.08)
1,1-(py) ₂ -2,3-Me ₂ -1-Sn-2,3-C ₂ B ₉ H ₉ (5)	54	190	275	C ₁₄ H ₂₅ B ₉ N ₂ Sn (437.36)	38.01 (38.45)	5.78 (5.76)	5.83 (6.41)
1-THF-2,3-Me ₂ -1-Sn-2,3-C ₂ B ₉ H ₉ (6)	65	138		C ₈ H ₂₃ B ₉ OSn (351.26)	27.35 (27.36)	6.64 (6.60)	
1-Ph ₃ P-2,3-Me ₂ -1-Sn-2,3-C ₂ B ₉ H ₉ (7)	66	192	300 (340)	C ₂₂ H ₃₀ B ₉ P ₃ Sn (541.45)	48.22 (48.80)	5.89 (5.58)	

^a Abbreviations: bpy, 2,2'-bipyridine; *o*-phen, *o*-phenanthroline, TMEDA, *N,N,N',N'*-tetramethylenediamine; py, pyridine; THF, tetrahydrofuran; Ph₃P, triphenylphosphine. ^b After recrystallization. ^c Main absorption (shoulder).

Table II. ¹H NMR Spectral Data^a (in ppm) for Compounds 1, 4, 5, 7, and 8

1	2.16 (s, 6 H, CMe), 1.69 (in C ₆ D ₆)
4	1.80 (s, 6 H, CMe), 2.64 [2.18] (s, 12 H, NMe), 2.78 [2.33] (s, 4 H, CH ₂)
5	1.88 (s, 6 H, CMe), 7.48 [7.14] (m, 4 H, py), 7.89 [7.55] (t, 2 H, py), 8.66 [8.51] (d, 4 H, py)
7	2.07 (s, 6 H, CMe), 1.98 [1.81] (m, 4 H, THF), 4.00 [3.71] (m, 4 H, THF)
8	2.01 (s, 6 H, CMe), 7.44 [7.00-7.50] (br, 15 H, phenyl)

^a All spectra recorded in CDCl₃ solution unless otherwise stated; resonances of terminal protons of the carborane cage omitted for clarity. Data for uncomplexed Lewis bases are given in brackets.

solid that was identified on the basis of elemental analysis and spectroscopic characteristics (Tables I-IV). Unfortunately, it was not possible to obtain crystals of 1 suitable for X-ray diffraction experiments. However, the location of the Sn on the C₂B₃ face of 1 is presumed to be very similar to that in Sn(Me₃Si)(Me)C₂B₄H₄.

Metallacarborane 1 is unreactive toward the electrophiles CF₃SO₃Me, MeI, SiCl₄, and SnCl₄. However, like 1-Sn-2,3-C₂B₉H₁₁, 1 is degraded by treatment with gaseous HCl (or methanolic KOH).⁶ Treatment of 1 with 2,2'-bipyridine (bpy), *o*-phenanthroline (*o*-phen), *N,N,N',N'*-tetramethylenediamine (TMEDA), pyridine (py), tetrahydrofuran (THF), triphenylphosphine, and acridine (acr) resulted in air-sensitive solid adducts 2-8 as summarized in Scheme II. Product identification is based on elemental analyses (Table I) and spectroscopic data (Tables II-IV). The structures of 2 and 7 were established by X-ray crystallography (vide infra). The bidentate ligands bpy, *o*-phen, and TMEDA form 1:1 complexes with 1 (2-4). A complex of 2:1 stoichiometry (5) was isolated from the reaction of pyridine with 1. The other monodentate lig-

(8) (a) Elian, M.; Chen, M. M. L.; Mingos, D. M. P.; Hoffmann, R. *Inorg. Chem.* **1976**, *15*, 1148. (b) Hoffmann, R. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 711. (c) Stone, F. G. A. *Ibid.* **1984**, *23*, 89.

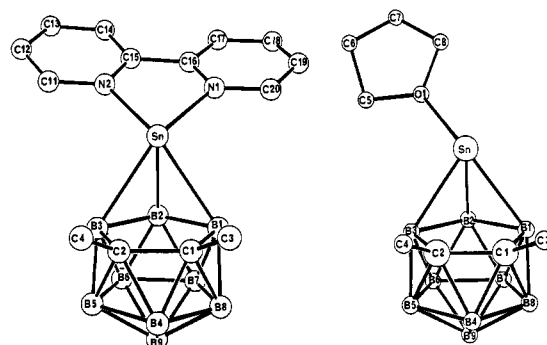
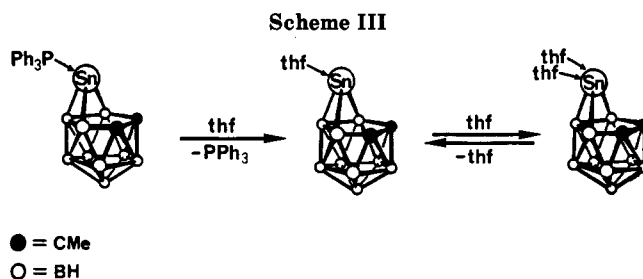
(9) Note, however, calculations by Brown et al. (Brown, D. A.; Fanning, M. O.; Fitzpatrick, N. J. *Inorg. Chem.* **1978**, *6*, 1620) which indicate that rehybridization of the atoms on the open face of the *nido*-carborane dianion results in primarily σ -bonding to the apical atom. This contrasts with the predominantly π -interactions of the cyclopentadienide ligand.

(10) It has been pointed out that the resemblance between anions of the type, [7,8-R₂-7,8-C₂B₉H₉]²⁻ and [Me₅C₅]⁻ is closer than that with [C₆H₅]⁻.

(11) For the synthesis and structure of [(^η-Me₅C₅)Sn]⁺, see: (a) Jutzi, P.; Kohl, F.; Krüger, C. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 59. (b) Jutzi, P.; Kohl, F.; Hoffmann, P.; Krüger, C.; Tsay, Y.-H. *Chem. Ber.* **1980**, *113*, 757. (c) Kohl, F. X.; Jutzi, P. *Ibid.* **1981**, *114*, 488.

(12) (a) Jutzi, P.; Kohl, C.; Krüger, C.; Wolmershäuser, G.; Hoffmann, P.; Stauffert, P. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 70. (b) Kohl, F. X.; Schlüter, E.; Jutzi, P.; Krüger, C.; Wolmershäuser, G.; Hoffmann, P.; Stauffert, P. *Chem. Ber.* **1984**, *117*, 1178.

(13) For a preliminary account of this work, see: Cowley, A. H.; Galow, P.; Hosmane, N. S.; Jutzi, P.; Norman, N. C. *J. Chem. Soc., Chem. Commun.* **1984**, 1564. See also: Hosmane, N. S.; de Meester, P.; Maldar, N. N.; Potts, S. B.; Chu, S. S. C.; Herber, R. H. *Organometallics* **1986**, *5*, 772.

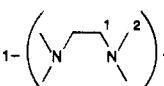
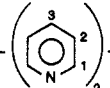
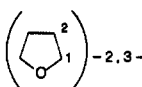
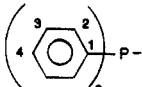
**Figure 1.** Views of 1-(2,2'-bpy)-2,3-Me₂-1-Sn-2,3-C₂B₉H₉ (2) and 1-THF-2,3-Me₂-1-Sn-2,3-C₂B₉H₉ (7).

ands, THF and Ph₃P, form 1:1 complexes, 7 and 8. Interestingly, the 1:1 THF complex 7 will add a second molecule of THF in solution forming what is believed to be the 2:1 complex 6. However, the latter is not isolable because of the facile loss of THF in vacuo, and its identification is based on ¹¹B NMR data. We have not undertaken a comprehensive series of base-competition experiments; however, it is clear from Scheme III that THF is a superior donor toward Sn than Ph₃P.

X-ray Crystal Structures of 2 and 7. The structural consequences of two- and four-electron donation to the apical Sn atom of 1 were investigated by X-ray crystallographic studies of 2 and 7. The solid-state structures of these molecules are illustrated in Figures 1 and 2. Pertinent crystallographic data are assembled in Table V, and listings of atomic positional parameters, bond lengths, and bond angles appear in Tables VI-XI. The solid-state structure of 7 consists of an ordered array of molecules with no short intermolecular contacts. Compound 2 crystallizes with one molecule of THF per stannadecaborane/bpy unit. There are no short intermolecular contacts between 7 and the THF molecule. Inferentially, the solvent molecules are held in the lattice rather weakly, and problems were encountered with crystal decay during data collection. As a consequence, the quality of the X-ray structure of 2 is inferior to that of 7.

The most significant structural feature is that the Sn atoms in 2 and 7 are displaced from the center of the

Table III. $^{13}\text{C}\{^1\text{H}\}$ NMR Spectral Data^a (in ppm) for Compounds 1, 4, 5, 7, and 8

compounds	carbollide		ligand		
	C	Me	C ¹	C ²	C ³
2,3-Me ₂ -1-Sn-2,3-C ₂ B ₉ H ₉ 1	68.6, 69.4 ^b	28.8, 26.5 ^b			
1-()-2,3-Me ₂ -1-Sn-2,3-C ₂ B ₉ H ₉ 4	64.7	26.2	57.3 [57.6]	46.5 [45.7]	
1,1-()-2,3-Me ₂ -1-Sn-2,3-C ₂ B ₉ H ₉ 5	65.4	25.9	147.4 [149.8]	128.1 [126.6]	139.1 [135.7]
1-()-2,3-Me ₂ -1-Sn-2,3-C ₂ B ₉ H ₉ 7	68.0	26.7	68.5 [68.0]	25.5 [26.0]	
1-()P-2,3-Me ₂ -1-Sn-2,3-C ₂ B ₉ H ₉ 8	58.4	21.7	132.4 [137.2]	133.6 [139.9]	129.8 [128.4]

^aSpectra recorded in CDCl₃ except otherwise stated; the value for the resonances of the carbollide C atoms might be inexact (± 0.5 ppm) because of quadrupole relaxation with ¹¹B and ¹⁰B nuclei. Data for uncomplexed Lewis bases given in brackets. ^bIn C₆D₆. ^cC⁴ resonance not observed.

Table IV. ¹¹B Spectral Data^a for Compounds 1, 4, 5, 7, 8, 10, and Related Carbaborane Species

compd	δ (J_{BH} , $J_{\text{BHbridging}}$, Hz)	rel int
1 (in C ₆ H ₆)	-21.9 (142), -23.9 (160), -26.5 (137), -30.4 (149)	4:2:2:1
4 (in CHCl ₃)	-25.0 (167), -28.8, -30.2, -32.5 (120), -43.3 (139)	1:4:2:1:1
5 (in CH ₂ Cl ₂)	-24.8 (160), -28.7 (133), -31.4 (122), -42.8 (140)	1:6:1:1
6 (in THF)	-23.8 (170), -26.5 (153), -27.5, -28.8 (110), -39.6 (144)	1:2:2:3:1
7 (in CHCl ₃)	-23.3, -24.8 (140), -28.1 (129.7), -35.4 (134)	1:5:2:1
8 (in CHCl ₃)	-24.0 (147), -25.7 (155), -29.3 (125), -34.6 (136)	4:2:2:1
10 (in MeCN/CHCl ₃)	-24.0 (161), -26.8, -27.5, -38.0 (163)	1:4:3:1
11 (in C ₆ H ₆)	-23.6 (150), -26.6 (170), -27.9 (144), -28.6 (159)	2:2:4:2
12 (in C ₆ H ₆)	-21.6 (170), -25.2 (164), -28.6 (152), -29.8 (109)	4:2:2:1
13 (in C ₆ H ₆)	-27.3 (138), -36.7 (132), -53.0 (144), -55.1 (157)	3:4:1:1
14 (in C ₆ H ₆)	-11.8 (161), -26.5 (151), -28.3 (171), -34.5 (149), -43.0 (141,49)	2:2:1:1:3

^a δ relative to B(OMe)₃, positive shifts downfield; all resonances are doublets; coupling constants not determined for overlapping resonances.

C(1)C(2)B(1)B(2)B(3) face by 0.62 and 0.42 Å, respectively. The Sn...C(1) and Sn...C(2) distances exceed the sum of covalent radii for Sn and C; hence the bonding of Sn is exclusively to boron atoms B(1), B(2), and B(3). As such, 2 and 7 can be regarded as η^3 -borallyl complexes. A similar distortion from η^5 toward η^3 or η^3 -bonding is observed when the analogous cation [(Me₅C₅)Sn]⁺ is treated with bpy.¹² In this case the Sn atom is displaced 0.49 Å from the center of the Me₅C₅ ring.

Note that the THF ligand in 7 occupies only one of the two possible coordination sites at Sn. The angle between the mirror plane of the dicarbollide moiety and the Sn-

Table V. Crystal and Intensity Collection Data for Compounds 2 and 7

	2	7
formula	C ₁₄ H ₂₃ B ₉ N ₂ Sn·C ₄ H ₈ O	C ₈ H ₂₃ B ₉ OSn
fw	433.82	354.29
cryst system	monoclinic	monoclinic
space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> /Å	12.502 (3)	10.303 (3)
<i>b</i> /Å	10.502 (2)	10.340 (3)
<i>c</i> /Å	18.627 (6)	14.597 (3)
β /deg	94.87 (2)	92.69 (2)
<i>U</i> /Å ³	2437 (1)	1553 (1)
<i>Z</i>	4	4
ρ (calcd)/g cm ⁻³	1.182	1.515
μ (Mo K α)/cm ⁻¹	10.5	16.3
λ (Mo K α)/Å	0.71069	0.71069
cryst size/mm	0.35 × 0.3 × 0.45	0.4 × 0.35 × 0.3
ω -scan angle/deg	0.8 + 0.35 tan θ	0.8 + 0.35 tan θ
2 θ limits/deg	2.0 < 2 θ < 40.0	3.0 < 2 θ < 49.0
total unique measd data	2286	2430
no. of data obsd	1438	1859
data omission	<i>I</i> > 2.0 σ (<i>I</i>)	<i>I</i> > 2.0 σ (<i>I</i>)
no. of variables	209	228
<i>R</i> ^a	0.0767	0.0449
<i>R</i> _w ^b	0.0936	0.0539

$$^a R = (\sum ||F_o| - |F_c||) / \sum |F_o|^2. \quad ^b R_w = [\sum w(|F_o| - |F_c|)^2 / \sum |F_o|^2]^{1/2}.$$

N(2) bond of 2 is 34.0° while the corresponding angle to the Sn-O(1) bond of 7 is 28.2°. This indicates that the THF ligand is bent more toward the mirror plane of the carbaborane cage. The steric requirements of the monodentate ligand are of obvious importance in determining whether a 1:1 or 2:1 complex is formed.

The B(4)-B(5)-B(6)-B(7)-B(8) pentagons of 2 and 7 are planar within experimental error. However, slight folding of the C₂B₃ face along the B(1)-B(3) axis occurs in both molecules as indicated by the fact that the angles between the B(1)-C(1)-C(2)-B(3) and B(1)-B(2)-B(3) planes are 2.8° and 4.1° in 2 and 7, respectively. The ring folding is presumably a consequence of the electron donation promoted "slippage" of the Sn atom to an η^3 -bonding posture.

Table VI. Bond Lengths (Å) for Compound 2^a

atom 1	atom 2	dist	atom 1	atom 2	dist	atom 1	atom 2	dist
Sn1	N1	2.412 (14)	C2	B5	1.75 (3)	B7	B9	1.78 (4)
Sn1	N2	2.374 (15)	B1	B2	1.80 (3)	B8	B9	1.83 (4)
Sn1	B1	2.56 (2)	B1	B7	1.77 (3)	C11	C12	1.34 (3)
Sn1	B2	2.35 (3)	B1	B8	1.81 (4)	C12	C13	1.45 (3)
Sn1	B3	2.55 (2)	B2	B3	1.81 (4)	C13	C14	1.40 (3)
N1	C16	1.32 (2)	B2	B6	1.75 (3)	C14	C15	1.38 (3)
N1	C20	1.36 (2)	B2	B7	1.81 (3)	C15	C16	1.49 (3)
N2	C11	1.37 (3)	B3	B5	1.74 (4)	C16	C17	1.43 (3)
N2	C15	1.35 (3)	B3	B6	1.80 (4)	C17	C18	1.42 (3)
C1	C2	1.60 (3)	B4	B5	1.85 (3)	C18	C19	1.34 (3)
C1	C3	1.52 (3)	B4	B8	1.74 (4)	C19	C20	1.41 (3)
C1	B1	1.71 (3)	B4	B9	1.81 (4)	O01	C01	1.45 (3)
C1	B4	1.72 (3)	B5	B6	1.81 (4)	O01	C02	1.42 (2)
C1	B8	1.78 (3)	B5	B9	1.86 (4)	C01	C04	1.52 (3)
C2	C4	1.43 (3)	B6	B7	1.79 (3)	C02	C03	1.55 (3)
C2	B3	1.66 (3)	B6	B9	1.84 (4)	C03	C04	1.46 (3)
C2	B4	1.78 (3)	B7	B8	1.76 (4)			

^aNumbers in parentheses are estimated standard deviations in the least significant digits.

Table VII. Bond Angles (deg) for Compound 2^a

atom 1	atom 2	atom 3	angle	atom 1	atom 2	atom 3	angle	atom 1	atom 2	atom 3	angle
N1	Sn1	N2	68.1 (5)	B6	B2	B7	61 (1)	B2	B7	B9	110 (2)
N1	Sn1	B1	89.1 (6)	C2	B3	B2	108 (2)	B6	B7	B8	111 (2)
N1	Sn1	B2	88.3 (7)	C2	B3	B5	62 (1)	B6	B7	B9	62 (1)
N1	Sn1	B3	128.4 (7)	C2	B3	B6	108 (2)	B8	B7	B9	62 (1)
N2	Sn1	B1	130.1 (6)	B2	B3	B5	109 (2)	C1	B8	B1	57 (1)
N2	Sn1	B2	90.9 (7)	B2	B3	B6	58 (1)	C1	B8	B4	58 (1)
N2	Sn1	B3	92.2 (7)	B5	B3	B6	61 (1)	C1	B8	B7	102 (2)
B1	Sn1	B2	42.8 (8)	C1	B4	C2	54 (1)	C1	B8	B9	104 (2)
B1	Sn1	B3	67.4 (8)	C1	B4	B5	102 (2)	B1	B8	B4	106 (2)
B2	Sn1	B3	43.1 (9)	C1	B4	B8	62 (1)	B1	B8	B7	60 (1)
C16	N1	C20	122 (2)	C1	B4	B9	107 (2)	B1	B8	B9	107 (2)
C11	N2	C15	121 (2)	C2	B4	B5	58 (1)	B4	B8	B7	107 (2)
C2	C1	C3	120 (2)	C2	B4	B8	106 (2)	B4	B8	B9	61 (1)
C2	C1	B1	113 (2)	C2	B4	B9	106 (2)	B7	B8	B9	59 (1)
C2	C1	B4	65 (1)	B5	B4	B8	110 (2)	B4	B9	B5	60 (1)
C2	C1	B8	113 (2)	B5	B4	B9	61 (1)	B4	B9	B6	106 (2)
C3	C1	B1	118 (2)	B8	B4	B9	62 (2)	B4	B9	B7	104 (2)
C3	C1	B4	116 (2)	C2	B5	B3	57 (1)	B4	B9	B8	57 (1)
C3	C1	B8	115 (2)	C2	B5	B4	59 (1)	B5	B9	B6	59 (1)
B1	C1	B4	113 (2)	C2	B5	B6	105 (2)	B5	B9	B7	105 (2)
B1	C1	B8	63 (1)	C2	B5	B9	106 (2)	B5	B9	B8	106 (2)
B4	C1	B8	60 (1)	B3	B5	B4	106 (2)	B6	B9	B7	59 (1)
C1	C2	C4	122 (2)	B3	B5	B6	61 (1)	B6	B9	B8	106 (2)
C1	C2	B3	110 (2)	B3	B5	B9	109 (2)	B7	B9	B8	58 (1)
C1	C2	B4	61 (1)	B4	B5	B6	106 (2)	N2	C11	C12	120 (2)
C1	C2	B5	111 (2)	B4	B5	B9	59 (1)	C11	C12	C13	119 (2)
C4	C2	B3	120 (2)	B6	B5	B9	60 (1)	C12	C13	C14	120 (2)
C4	C2	B4	118 (2)	B2	B6	B3	61 (1)	C13	C14	C15	117 (2)
C4	C2	B5	118 (2)	B2	B6	B5	109 (2)	N2	C15	C14	123 (2)
C3	C2	B4	112 (2)	B2	B6	B7	61 (1)	N2	C15	C16	115 (2)
B3	C2	B5	61 (1)	B2	B6	B9	110 (2)	C14	C15	C16	122 (2)
B4	C2	B5	63 (1)	B3	B6	B5	58 (1)	N1	C16	C15	118 (2)
C1	B1	B2	105 (2)	B3	B6	B7	107 (2)	N1	C16	C17	121 (2)
C1	B1	B7	104 (2)	B3	B6	B9	107 (2)	C15	C16	C17	121 (2)
C1	B1	B8	61 (1)	B5	B6	B7	107 (2)	C16	C17	C18	117 (2)
B2	B1	B7	61 (1)	B5	B6	B9	61 (1)	C17	C18	C19	119 (2)
B2	B1	B8	109 (2)	B7	B6	B9	59 (1)	C18	C19	C20	122 (2)
B7	B1	B8	59 (1)	B1	B7	B2	60 (1)	N1	C20	C19	118 (2)
B1	B2	B3	103 (2)	B1	B7	B6	107 (2)	C01	O01	C02	117 (2)
B1	B2	B6	108 (2)	B1	B7	B8	62 (1)	O01	C01	C04	101 (2)
B1	B2	B7	59 (1)	B1	B7	B9	111 (2)	O01	C02	C03	100 (2)
B3	B2	B6	61 (1)	B2	B7	B6	58 (1)	C02	C03	C04	108 (2)
B3	B2	B7	106 (2)	B2	B7	B8	111 (2)	C01	C04	C03	109 (2)

^aNumbers in parentheses are estimated standard deviations in the least significant digits.

Similar distortions have been observed in electron-rich transition-metal dicarbollide complexes.¹⁴

The differences in coplanarity between the B₅ pentagonal plane and the two hexagonal planes of the bpy ligand

in 2 are 25.3° and 19.8°. The corresponding values in the bpy complex of [(Me₅C₅)Sn]⁺ are 14.8° and 13.4°.¹² This may imply a stronger interaction between the (bpy)Sn and B(1)-B(2)-B(3) moieties in 2 than in [(Me₅C₅)Sn·bpy]⁺. A similar explanation has been advanced by Grimes,¹⁵

(14) (a) Mingos, D. M. P.; Forsyth, M. J.; Welch, A. J. *J. Chem. Soc., Dalton Trans.* 1978, 1363. (b) Colquhoun, H. M.; Greenhough, T. J.; Wallbridge, M. G. H. *J. Chem. Soc., Dalton Trans.* 1985, 761.

(15) Grimes, R. N.; Rademaker, W. J.; Demiston, M. L.; Bryan, R. R.; Green, P. T. *J. Am. Chem. Soc.* 1972, 94, 1985.

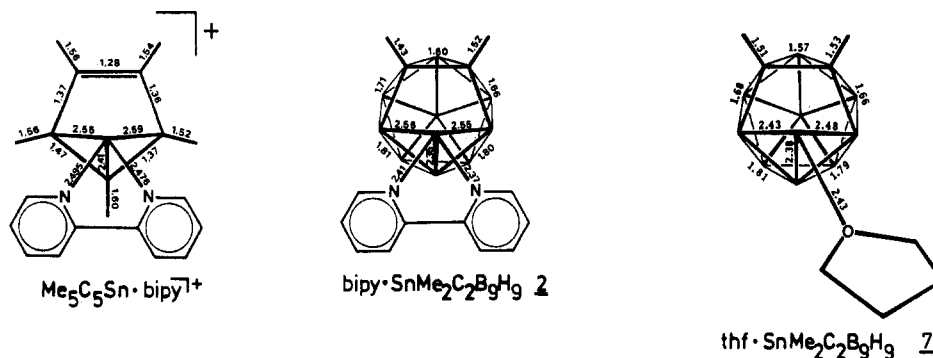


Figure 2. Comparison of the structures of $[(\text{Me}_5\text{C}_5)\text{Sn}(2,2'\text{-bpy})]^+$, 1-(2,2'-bpy)-2,3-Me₂-1-Sn-2,3-C₂B₉H₉ (2), and 1-THF-2,3-Me₂-1-Sn-2,3-C₂B₉H₉ (7).

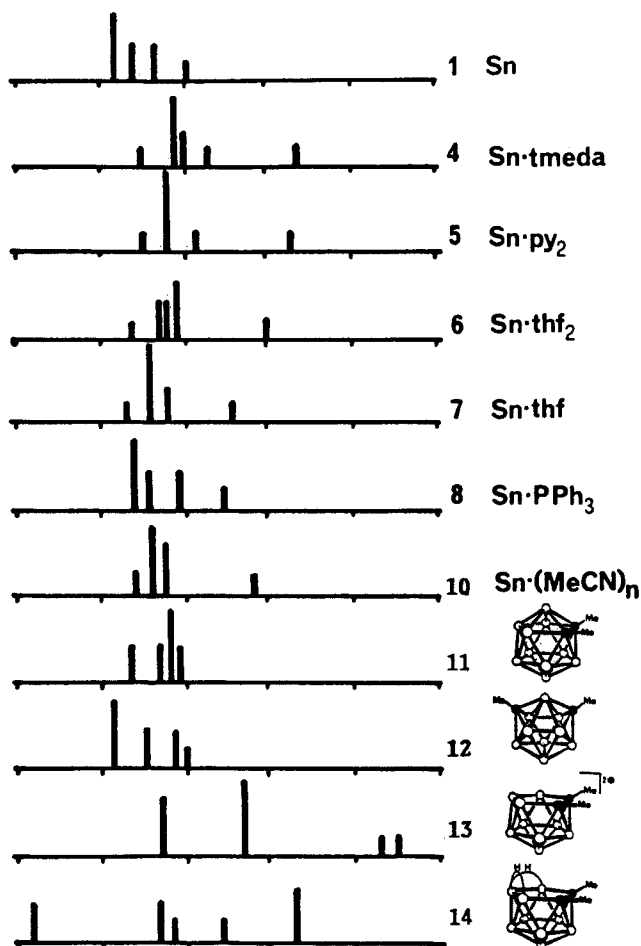


Figure 3. Proton-decoupled ¹¹B NMR line spectra for compounds 1, 4-8, and 10 and some related carborane species, 11-14 (apical fragments only).

Eisenstein,¹⁶ and co-workers to explain the unexpected structure of the metallacarborane 1-Me-1-Ga-2,3-C₂B₉H₉. We also note that the average Sn-N bond length in 2 (2.39 Å) is shorter than that in (bpy)[Me₅C₅Sn]⁺ (2.48 Å).¹²

Spectroscopic Data. The EI mass spectra of complexes 2, 3, 5, and 8 were recorded. However, these spectra were not particularly informative because of dissociation into 1 and the free Lewis bases (which were responsible for the 100% peaks in each case).

Several of the complexes are intensely colored. Thus, 2 and 3 are orange, and 8 is yellow. Pertinent solid-state electronic spectral data are listed in Table I. As in the case of the bpy complex of $[(\text{Me}_5\text{C}_5)\text{Sn}]^+$, the color can be at-

Table VIII. Positional Parameters and Their Estimated Standard Deviations for Compound 2

atom	x	y	z	B, Å ²
Sn1	0.4766 (1)	0.0744 (1)	0.09321 (7)	2.84 (3)
N1	0.545 (1)	0.245 (1)	0.0236 (7)	2.7 (4)
N2	0.656 (1)	0.127 (1)	0.1341 (8)	3.1 (4)
C1	0.255 (2)	0.054 (2)	0.119 (1)	3.5 (5)
C2	0.319 (1)	-0.013 (2)	0.1862 (9)	3.2 (5)
C3	0.206 (2)	-0.026 (2)	0.057 (1)	4.4 (6)
C4	0.333 (2)	-0.148 (2)	0.190 (1)	3.3 (5)
B1	0.303 (2)	0.201 (2)	0.100 (1)	3.0 (6)
B2	0.411 (2)	0.229 (2)	0.169 (1)	3.5 (7)
B3	0.417 (2)	0.083 (3)	0.220 (1)	4.1 (6)
B4	0.189 (2)	0.051 (3)	0.196 (1)	4.7 (7)
B5	0.301 (2)	0.069 (3)	0.266 (1)	3.5 (6)
B6	0.356 (2)	0.225 (2)	0.252 (1)	2.7 (6)
B7	0.278 (2)	0.294 (2)	0.177 (1)	3.0 (6)
B8	0.178 (2)	0.187 (2)	0.143 (1)	4.6 (7)
B9	0.210 (2)	0.203 (2)	0.240 (1)	4.4 (7)
C11	0.708 (2)	0.054 (2)	0.187 (1)	4.0 (5)*
C12	0.814 (2)	0.071 (2)	0.205 (1)	4.8 (5)*
C13	0.867 (2)	0.178 (2)	0.175 (1)	5.2 (6)*
C14	0.813 (2)	0.253 (2)	0.121 (1)	4.7 (5)*
C15	0.707 (2)	0.223 (2)	0.102 (1)	3.1 (5)*
C16	0.643 (2)	0.288 (2)	0.042 (1)	2.8 (4)*
C17	0.686 (2)	0.393 (2)	0.006 (1)	4.1 (5)*
C18	0.622 (2)	0.444 (2)	-0.054 (1)	4.4 (5)*
C19	0.527 (2)	0.391 (2)	-0.074 (1)	3.5 (5)*
C20	0.484 (2)	0.291 (2)	-0.034 (1)	3.3 (5)*
O01	0.916 (1)	0.524 (1)	0.0768 (7)	4.0*
C01	0.877 (2)	0.643 (2)	0.046 (1)	4.0*
C02	1.005 (2)	0.528 (2)	0.129 (1)	4.0*
C03	1.055 (2)	0.657 (2)	0.109 (1)	4.0*
C04	0.973 (2)	0.729 (2)	0.066 (1)	4.0*

* Atoms with an asterisk were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter refined as $(\frac{4}{3})[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos \gamma)B(1,2) + ac(\cos \beta)B(1,3) + bc(\cos \alpha)B(2,3)]$.

tributed to $\eta \rightarrow \pi^*$ transitions.¹²

Proton NMR data for complexes 4, 5, 7, and 8 have been summarized in Table II along with pertinent data for 1 and the free Lewis bases. As expected, the resonances of the Lewis bases experience downfield shifts upon complexation. Note that downfield shifts are also observed for the C-Me groups of the carborane cage. Unfortunately, 2, 3, and 9 were not sufficiently soluble to permit the acquisition of ¹H NMR data.

¹³C NMR spectroscopy reveals that the cage carbon atoms of 4, 5, 7, and 8 are deshielded upon complexation. The C-methyl carbons show a similar trend but to a lesser degree. The differences in the ¹³C chemical shifts of the free and complexed Lewis bases are also small. Note, though, that both increased and decreased shielding are observed for the Lewis base carbon atoms.

It is, however, the ¹¹B NMR spectra that are the most informative from a structural standpoint. Pertinent data

Table IX. Bond Lengths (Å) for Compound 7^a

atom 1	atom 2	dist	atom 1	atom 2	dist	atom 1	atom 2	dist
Sn	O1	2.430 (2)	C1	B5	1.720 (5)	B2	B3	1.791 (5)
Sn	C1	2.653 (3)	C2	C3	2.660 (5)	B2	B6	1.765 (6)
Sn	C2	2.699 (3)	C2	C4	1.527 (5)	B2	B7	1.740 (5)
Sn	B1	2.425 (4)	C2	B1	2.687 (5)	B3	B7	1.774 (6)
Sn	B2	2.375 (4)	C2	B3	1.661 (5)	B3	B8	1.776 (5)
Sn	B3	2.479 (4)	C2	B4	1.713 (5)	B4	B5	1.769 (6)
O1	C5	1.436 (5)	C2	B8	1.694 (5)	B4	B8	1.732 (6)
O1	C6	2.326 (5)	C5	C6	1.520 (6)	B4	B9	1.765 (6)
O1	C7	2.319 (5)	C5	C7	2.358 (6)	B5	B6	1.778 (6)
O1	C8	1.444 (4)	C5	C8	2.393 (6)	B5	B9	1.778 (5)
C1	C2	1.575 (4)	C6	C7	1.442 (7)	B6	B7	1.788 (6)
C1	C3	1.505 (5)	C6	C8	2.366 (6)	B6	B9	1.771 (6)
C1	C4	2.687 (6)	C7	C8	1.500 (6)	B7	B8	1.783 (6)
C1	B1	1.681 (5)	B1	B2	1.811 (5)	B7	B9	1.791 (6)
C1	B3	2.678 (5)	B1	B5	1.766 (5)	B8	B9	1.763 (6)
C1	B4	1.735 (5)	B1	B6	1.766 (6)			

^aNumbers in parentheses are estimated standard deviations in the least significant digits.

for 1 and the soluble stannacarborane complexes are presented in Table IV together with comparable data for some related systems. Note that 1 and *closo*-carboranes such as 1,2-Me₂-1,2-C₂B₁₀H₁₀ (11) and 2,3-Me₂-2,3-C₂B₉H₉ (12) exhibit ¹¹B NMR resonances within a rather narrow range (~10 ppm) while for *nido*-carboranes such as [7,8-Me₂-7,8-C₂B₉H₉]²⁻ (13) or the protonated species 7,8-Me₂-7,8-C₂B₉H₁₁ (14), the range is much broader (~25 ppm). The conspicuous effect of Lewis base complexation to 1 is the appearance of a high-field resonance corresponding to one boron atom. Since the "slippage" of the Sn atom is likely to have the most significant impact on the electron density at B(2), the high field peaks for 4–8 and 11 are ascribed to this boron atom. Note that there is a correlation between the stoichiometry of the complex and the coordination chemical shift, Δδ (defined as the difference in ¹¹B chemical shift between B(2) in the complex and the highest field resonance of 1). Thus, for the 1:1 complexes 7 and 8, Δδ = 4.2 and 5.0 ppm, respectively, while for the 2:1 complexes 4 and 5, Δδ = 12.4 and 14.3 ppm, respectively. In this context, the value of Δδ = 9.2 ppm for 6 seems reasonable for a 2:1 complex. Finally, an acetonitrile complex, 1-(MeCN)_n-2,3-Me₂-1-Sn-2,3-C₂B₉H₉ (10), can be detected in solution. However, in this case Δδ = 7.6 ppm; hence it is not clear whether n = 1 or 2. The ¹H NMR spectra of 10 are indicative of a rapid exchange of free and complexed MeCN. Attempts to isolate 10 were not successful due to the lability of this complex.

Conclusions

The observation of a *closo* structure for 1 is in accord with the rules discussed by Wade,¹⁷ Williams,¹⁸ and Rudolph.¹⁹ Moreover, the use of these guidelines predicts some degree of cage opening upon additional electron donation to a vertex atom. Examples of this phenomenon have so far been confined to transition-metal species with the sole exception of 1,1-Et₂-1-Al-2,3-C₂B₉H₁₂.²⁰ However, comparisons with the latter, which possesses a *nido* structure, are somewhat complicated by the existence of Al–H–B bridges.

The isolobal analogy between 1 and [(Me₅C₅)Sn]⁺ is borne out in the present work. Like 1, [(Me₅C₅)Sn]⁺ possesses an electrophilic Sn atom and forms complexes with py, bpy, and various azines.¹² Furthermore, the structures of 2 and the bpy complex of [(Me₅C₅)Sn]⁺ are

remarkably similar.

Experimental Section

General Considerations. All manipulations were carried out under an atmosphere of dry dinitrogen by using standard Schlenk techniques. All solvents and reagents were appropriately dried and purified. All decomposition temperatures are uncorrected and were determined with a Büchi 510 capillary melting point apparatus. Elemental analyses were carried out by Mikroanalytisches Laboratorium Beller, Göttingen, FRG, or the analytical laboratory of the Universität Bielefeld, Bielefeld, FRG.

Spectroscopic Measurements. Solid-state UV/vis spectra were obtained on a Beckmann Acta M IV spectrophotometer. ¹H (300.1-MHz), ¹¹B (96.3-MHz), and ¹³C{¹H} (75.4-MHz) Fourier transform NMR spectra were recorded on a Bruker AM 300 spectrometer. Mass spectra were measured on a Varian 311 A spectrometer operating at an ionizing voltage of 70 eV.

Preparation of 2,3-Dimethyl-1-stanna-2,3-dicarbododecaborane (1) was prepared by using the approach of Rudolph and co-workers.⁶ Attempted purification by sublimation failed due to decomposition at 190 °C.

Preparation of 1-(2,2'-Bipyridine)-2,3-dimethyl-1-stanna-2,3-dicarbododecaborane (2). A solution of 2,2'-bipyridine (0.40 g, 2.50 mmol) in benzene (30 mL) was added to a solution of 1 (0.59 g, 2.00 mmol) in benzene (100 mL). The resulting yellow suspension was stirred for 24 h, after which time the shining yellow microcrystalline precipitate was filtered, washed twice with 20-mL portions of *n*-hexane, and dried in vacuo. The crude product was recrystallized from THF (250 mL). Crystals of 2 formed upon cooling the solution to –30 °C for about 30 days; yield 0.67 g (75%).

Preparation of 1-(*o*-Phenanthroline)-2,3-dimethyl-1-stanna-2,3-dicarbododecaborane (3). A solution of *o*-phenanthroline (0.083 g, 0.46 mmol) in benzene (15 mL) was added to a solution of 1 (0.13 g, 0.46 mmol) in benzene (10 mL) to give a yellow precipitate of 3 that was washed with *n*-hexane and dried in vacuo; yield 0.09 g (42%).

Preparation of 1-(*N,N,N',N'*-Tetramethylethylenediamine)-2,3-dimethyl-1-stanna-2,3-dicarbododecaborane (4). With use of the procedure described for the preparation of 3, *N,N,N',N'*-tetramethylethylenediamine (0.35 g, 3.00 mmol) was added to a solution of 1 (0.44 g, 1.58 mmol) in benzene (30 mL). The yield of 4 was 0.48 g (80%).

Preparation of 1,1-Bis(pyridine)-2,3-dimethyl-1-stanna-2,3-dicarbododecaborane (5). Pyridine (0.25 mL, 3.00 mmol) was added dropwise to a solution of 1 (0.30 g, 1.30 mmol) in benzene (50 mL). The solution turned slightly yellow, and within 12 h colorless solid 5 precipitated. Crude 5 was washed twice with 10 mL portions of benzene, and recrystallized from dichloromethane (25 mL). The yield of 5 was 0.31 g (54%).

Preparation of 1-(Tetrahydrofuran)-2,3-dimethyl-1-stanna-2,3-dicarbododecaborane (7). Tetrahydrofuran (0.50 g, 7.00 mmol) was added to a solution of 1 (0.75 g, 2.69 mmol) in benzene (50 mL) resulting in the formation of a colorless precipitate. The reaction mixture was stirred for 24 h before removal of the solvent in vacuo. Recrystallization of the crude material from toluene

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Table X. Bond Angles (deg) for Compound 7^a

atom 1	atom 2	atom 3	angle	atom 1	atom 2	atom 3	angle	atom 1	atom 2	atom 3	angle
O1	Sn	C1	129.63 (9)	Sn	C2	B3	64.2 (2)	C1	B3	B2	75.0 (2)
O1	Sn	C2	152.9 (1)	Sn	C2	B4	130.4 (2)	C1	B3	B7	90.7 (2)
O1	Sn	B1	93.5 (1)	Sn	C2	B8	124.6 (2)	C1	B3	B8	71.8 (2)
O1	Sn	B2	87.4 (1)	C1	C2	C3	29.5 (2)	C2	B3	B2	108.0 (3)
O1	Sn	B3	124.6 (1)	C1	C2	C4	120.0 (3)	C2	B3	B7	105.9 (3)
C1	Sn	C2	34.22 (9)	C1	C2	B1	35.7 (2)	C2	B3	B8	58.9 (2)
C1	Sn	B1	38.3 (1)	C1	C2	B3	111.7 (3)	B2	B3	B7	58.4 (2)
C1	Sn	B2	67.7 (1)	C1	C2	B4	63.5 (2)	B2	B3	B8	108.1 (3)
C1	Sn	B3	62.8 (1)	C1	C2	B8	112.1 (3)	B7	B3	B8	60.3 (2)
C2	Sn	B1	63.0 (1)	C3	C2	C4	90.5 (3)	C1	B4	C2	54.4 (2)
C2	Sn	B2	66.5 (1)	C3	C2	B1	63.1 (1)	C1	B4	B5	58.8 (2)
C2	Sn	B3	37.1 (1)	C3	C2	B3	136.0 (2)	C1	B4	B8	103.0 (3)
B1	Sn	B2	44.3 (1)	C1	C3	C2	31.0 (2)	C1	B4	B9	104.5 (3)
B1	Sn	B3	69.5 (1)	C1	C4	C2	30.5 (2)	C2	B4	B5	102.8 (3)
B2	Sn	B3	43.2 (1)	O1	C5	C6	103.7 (3)	C2	B4	B8	58.9 (2)
Sn	O1	C5	121.4 (2)	O1	C5	C7	70.6 (2)	C2	B4	B9	104.5 (3)
Sn	O1	C6	146.0 (2)	O1	C5	C8	33.9 (2)	B5	B4	B8	108.3 (3)
Sn	O1	C7	153.9 (2)	C6	C5	C7	36.1 (3)	B5	B4	B9	60.4 (2)
Sn	O1	C8	120.2 (2)	C6	C5	C8	70.4 (3)	B8	B4	B9	60.5 (2)
C5	O1	C6	39.4 (2)	C7	C5	C8	36.8 (2)	C1	B5	B1	57.6 (2)
C5	O1	C7	73.6 (2)	O1	C6	C5	36.9 (2)	C1	B5	B4	59.6 (2)
C5	O1	C8	112.4 (3)	O1	C6	C7	71.6 (3)	C1	B5	B6	104.0 (3)
C6	O1	C7	36.2 (2)	O1	C6	C8	35.8 (1)	C1	B5	B9	104.6 (3)
C6	O1	C8	73.6 (2)	C5	C6	C7	105.5 (4)	B1	B5	B4	107.8 (3)
C7	O1	C8	38.9 (2)	C5	C6	C8	72.3 (3)	B1	B5	B6	59.8 (2)
Sn	C1	C2	74.5 (2)	C7	C6	C8	37.3 (2)	B1	B5	B9	107.2 (3)
Sn	C1	C3	105.5 (2)	O1	C7	C5	35.8 (1)	B4	B5	B6	107.8 (3)
Sn	C1	C4	79.9 (1)	O1	C7	C6	72.2 (3)	B4	B5	B9	59.7 (2)
Sn	C1	B1	63.5 (2)	O1	C7	C8	37.2 (2)	B6	B5	B9	59.7 (2)
Sn	C1	B3	55.4 (1)	C5	C7	C6	38.4 (2)	B1	B6	B2	61.7 (2)
Sn	C1	B4	132.0 (2)	C5	C7	C8	72.8 (2)	B1	B6	B5	59.8 (2)
Sn	C1	B5	123.5 (2)	C6	C7	C8	107.0 (4)	B1	B6	B7	106.6 (3)
C2	C1	C3	119.5 (3)	O1	C8	C5	33.7 (2)	B1	B6	B9	107.5 (3)
C2	C1	C4	29.5 (2)	O1	C8	C6	70.6 (2)	B2	B6	B5	110.4 (3)
C2	C1	B1	111.2 (3)	O1	C8	C7	103.9 (3)	B2	B6	B7	58.7 (2)
C2	C1	B3	35.2 (2)	C5	C8	C6	37.2 (2)	B2	B6	B9	108.9 (3)
C2	C1	B4	62.1 (2)	C5	C8	C7	70.4 (3)	B5	B6	B7	108.0 (3)
C2	C1	B5	111.3 (3)	C6	C8	C7	35.7 (2)	B5	B6	B9	60.1 (2)
C3	C1	C4	90.0 (3)	Sn	B1	C1	78.2 (2)	B7	B6	B9	60.4 (2)
C3	C1	B1	122.7 (3)	Sn	B1	C2	63.5 (1)	B2	B7	B3	61.3 (2)
C3	C1	B3	147.0 (3)	Sn	B1	B2	66.4 (2)	B2	B7	B6	60.0 (2)
C3	C1	B4	112.8 (3)	Sn	B1	B5	134.9 (3)	B2	B7	B8	110.1 (3)
C3	C1	B5	116.4 (3)	Sn	B1	B6	124.2 (3)	B2	B7	B9	109.2 (3)
C4	C1	B1	135.3 (2)	C1	B1	C2	33.1 (2)	B3	B7	B6	106.5 (3)
C4	C1	B3	61.9 (2)	C1	B1	B2	107.1 (3)	B3	B7	B8	59.9 (2)
C4	C1	B4	72.5 (2)	C1	B1	B5	59.8 (2)	B3	B7	B9	106.8 (3)
C4	C1	B5	132.8 (2)	C1	B1	B6	106.2 (3)	B6	B7	B8	106.3 (3)
B1	C1	B3	76.0 (2)	C2	B1	B2	74.0 (2)	B6	B7	B9	59.3 (2)
B1	C1	B4	113.4 (3)	C2	B1	B5	72.0 (2)	B8	B7	B9	59.1 (2)
B1	C1	B5	62.5 (2)	C2	B1	B6	89.9 (2)	C2	B8	B3	57.1 (2)
B3	C1	B4	76.9 (2)	B2	B1	B5	108.9 (3)	C2	B8	B4	60.0 (2)
B3	C1	B5	96.2 (2)	B2	B1	B6	59.1 (2)	C2	B8	B7	104.1 (3)
B4	C1	B5	61.6 (2)	B5	B1	B6	60.5 (2)	C2	B8	B9	105.4 (3)
C3	C2	B4	72.7 (2)	Sn	B2	B1	69.3 (2)	B3	B8	B4	108.2 (3)
C3	C2	B8	132.6 (2)	Sn	B2	B3	71.5 (2)	B3	B5	B7	59.8 (2)
C4	C2	B1	147.5 (3)	Sn	B2	B6	127.1 (2)	B3	B8	B9	107.9 (3)
C4	C2	B3	119.9 (3)	Sn	B2	B7	129.8 (3)	B4	B8	B7	109.6 (3)
C4	C2	B4	114.3 (3)	B1	B2	B3	101.8 (3)	B4	B8	B9	60.7 (2)
C4	C2	B8	116.5 (3)	B1	B2	B6	59.2 (2)	B7	B8	B9	60.7 (2)
B1	C2	B3	76.0 (2)	B1	B2	B7	106.7 (3)	B4	B9	B5	59.9 (2)
B1	C2	B4	77.4 (2)	B3	B2	B6	106.7 (3)	B4	B9	B6	108.3 (3)
B1	C2	B8	95.9 (2)	B3	B2	B7	60.3 (2)	B4	B9	B7	107.8 (3)
B3	C2	B4	114.8 (3)	B6	B2	B7	61.3 (2)	B4	B9	B8	58.8 (2)
B3	C2	B8	63.9 (2)	Sn	B3	C1	61.8 (1)	B5	B9	B6	60.1 (2)
B4	C2	B8	61.1 (2)	Sn	B3	C2	78.7 (2)	B5	B9	B7	107.9 (3)
Sn	C2	C1	71.3 (2)	Sn	B3	B2	65.3 (2)	B5	B9	B8	106.5 (3)
Sn	C2	C3	78.3 (1)	Sn	B3	B7	122.1 (2)	B6	B9	B7	60.3 (2)
Sn	C2	C4	105.1 (3)	Sn	B3	B8	133.4 (2)	B6	B9	B8	107.9 (3)
Sn	C2	B1	53.5 (1)	C1	B3	C2	33.1 (2)	B7	B9	B8	60.2 (2)

^a Numbers in parentheses are estimated standard deviations in the least significant digits.

(5 mL) yielded 0.61 g (65%) of 7.

Preparation of 1-(Triphenylphosphine)-2,3-dimethyl-1-stanna-2,3-dicarbododecaborane (8). Solid triphenylphosphine (0.92 g, 3.50 mmol) was added to a solution of 1 (0.68 g, 2.44 mmol) in *n*-hexane. A colorless precipitate formed within 30 min. The

reaction mixture was stirred for 24 h, after which time the precipitate was filtered, washed twice with *n*-hexane, and dried in vacuo, yielding 0.87 g (66%) of 8.

X-ray Analysis of 1-(2,2'-Bipyridine)-2,3-dimethyl-1-stanna-2,3-dicarbododecaborane (2). A suitable single crystal

Table XI. Positional Parameters and Their Estimated Standard Deviations for Compound 2

atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> , Å ²
Sn	0.04774 (6)	0.12731 (7)	0.64597 (4)	3.05 (1)
O1	-0.1371 (6)	0.2415 (7)	0.5752 (5)	4.4 (2)
C1	0.2923 (7)	0.2039 (9)	0.6728 (5)	2.5 (2)
C2	0.2645 (7)	0.1139 (9)	0.7567 (6)	2.7 (2)
C3	0.3632 (8)	0.150 (1)	0.5935 (6)	3.6 (2)
C4	0.305 (1)	-0.0281 (9)	0.7555 (7)	4.0 (2)
C5	-0.120 (1)	0.344 (1)	0.5102 (8)	5.5 (3)
C6	-0.232 (1)	0.324 (1)	0.4398 (9)	8.7 (3)
C7	-0.330 (1)	0.254 (1)	0.4870 (9)	6.8 (3)
C8	-0.261 (1)	0.177 (1)	0.5611 (8)	6.4 (3)
B1	0.1798 (9)	0.321 (1)	0.6603 (7)	2.8 (2)
B2	0.0689 (9)	0.301 (1)	0.7519 (7)	2.7 (2)
B3	0.130 (1)	0.1573 (9)	0.8069 (6)	2.8 (2)
B4	0.3914 (9)	0.220 (1)	0.7716 (7)	2.9 (2)
B5	0.3359 (9)	0.357 (1)	0.7086 (7)	3.1 (2)
B6	0.195 (1)	0.417 (1)	0.7605 (7)	3.6 (2)
B7	0.162 (1)	0.313 (1)	0.8543 (7)	3.4 (2)
B8	0.286 (1)	0.192 (1)	0.8582 (6)	2.9 (2)
B9	0.325 (1)	0.353 (1)	0.8298 (7)	3.5 (2)
H1	0.174 (7)	0.360 (8)	0.592 (5)	2 (2)*
H2	-0.035 (7)	0.345 (8)	0.751 (5)	3 (2)*
H3	0.086 (6)	0.092 (7)	0.846 (4)	2 (1)*
H4	0.495 (8)	0.182 (9)	0.763 (6)	
H5	0.406 (8)	0.417 (8)	0.665 (5)	3 (2)*
H6	0.174 (7)	0.530 (8)	0.762 (5)	3 (2)*
H7	0.114 (7)	0.332 (8)	0.920 (5)	3 (2)*
H8	0.320 (7)	0.143 (7)	0.920 (5)	2 (2)*
H9	0.384 (9)	0.412 (9)	0.879 (6)	5 (2)*
H10	0.460 (7)	0.119 (8)	0.610 (5)	3 (2)*
H11	0.392 (8)	0.295 (8)	1.052 (5)	3 (2)*
H12	0.32 (1)	0.10 (1)	0.559 (8)	8 (3)*
H13	0.62 (1)	0.45 (1)	0.745 (8)	8 (3)*
H14	0.719 (9)	0.434 (9)	0.779 (6)	4 (2)*

* Atoms with an asterisk were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $(1/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos \gamma)B(1,2) + ac(\cos \beta)B(1,3) + bc(\cos \alpha)B(2,3)]$.

was sealed in a Lindemann capillary and mounted on an Enraf-Nonius CAD 4-F diffractometer. Initial lattice parameters were determined from a least-squares fit to 25 accurately centered reflections ($15 \leq 2\theta \leq 20^\circ$) and subsequently refined using higher angle data. These indicated a monoclinic lattice. Data were collected for one independent quadrant, $+h, +k, \pm l$, using the $\theta/2\theta$ scan mode. The final scan speed for each reflection was determined from the intensity gathered during an initial prescan and ranged from 2 to 7° min^{-1} . The ω -scan was determined for each reflection according to the equation $A + B \tan \theta$ for which A and

B were set at values 0.8 and 0.35, respectively. Aperture settings were derived in a like manner with $A = 4.0 \text{ mm}$ and $B = 1.0 \text{ mm}$. Crystal stability was monitored every 1 h throughout the data collection by means of two independent check reflections. Systematic absences observed were $h0l$ absent for $l = 2n + 1$ and $0k0$ absent for $k = 2n + 1$, thus uniquely determining the space group as $P2_1/c$.

Data were corrected for the effects of Lorentz, polarization, and decay but not for absorption. A 40% decay correction was necessary on account of facile loss of THF of crystallization (see text). Merging of equivalent reflections gave a total of 2286 unique measured data of which 1438 were considered observed, $I > 2.0\sigma(I)$. The position of the Sn atom was revealed from a Patterson map and all other non-hydrogen atoms from a subsequent difference Fourier map. Only those atoms in the carbaborane cage and N(1) and N(2) were refined by using anisotropic thermal parameters. All others, including the THF of crystallization, were refined anisotropically.

X-ray Analysis of 1-(Tetrahydrofuran)-2,3-dimethyl-1-stanna-2,3-dicarbadodecaborane (7). The details of the data collection for 7 were very similar to those described for 2. However, in the case of 7, the decay was negligible (<1%). The data were corrected for Lorentz and polarization effects. An empirical absorption correction was applied. Merging of equivalent reflections gave a total of 2430 unique measured data of which 1859 were considered observed. The structure of 7 was solved in the same manner as 2. All non-hydrogen atoms were refined with the use of anisotropic thermal parameters. The hydrogen atoms were placed in calculated positions 0.95 Å from their respective carbon atoms and included in the structure factor calculation.

All calculations were performed by using the SDP-plus program package.²¹

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Supplementary Material Available: Tables of thermal parameters (2 pages); listings of observed and calculated structure factors (18 pages). Ordering information is given on any current masthead page.

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