Communications

A Novel Bridged Donor–Acceptor Complex: Synthesis and Structure of 1,1′-(2,2′-$C_8H_6N_4$)-[*closo*-1-Sn-2,3-$(Me_3Si)_2$-2,3-$C_2B_4H_4$]$_2$

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Summary: The reaction of *closo*-1-Sn-2,3-$(Me_3Si)_2$-2,3-$C_2B_4H_4$ (I) with 2,2′-bipyrimidine, $C_8H_6N_4$, in a molar ratio of 2:1 in benzene produced a novel bridged donor–acceptor complex, 1,1′-(2,2′-$C_8H_6N_4$)-[*closo*-1-Sn-2,3-$(Me_3Si)_2$-2,3-$C_2B_4H_4$]$_2$ (II) as a moderately air-stable, red, crystalline, and sublimable solid, in 70% yield. The X-ray crystal structure of II unambiguously shows that the stannacarboranes occupy trans positions with respect to the 2,2′-bipyrimidine and have elongated tin-carbon(cage) bonds.

There has recently been an increased interest in group 14 carborane chemistry. Impetus for this has been the increased availability of structural data on these compounds and the increased yields in their syntheses.[1-9] Our recent synthetic and structural studies of the donor–acceptor complexes of the *closo*-stannacarboranes[2-4] and *closo*-germacarboranes[7] have raised some fundamental questions regarding the bonding of group 14 atoms to the carboranes. To date, it is not known how the steric, orbital, "lone-pair", or combination of these effects influence the orientation of the Lewis base bound to the apical heteroatom and direct the increased slip distortion of this atom on complexation with the base.

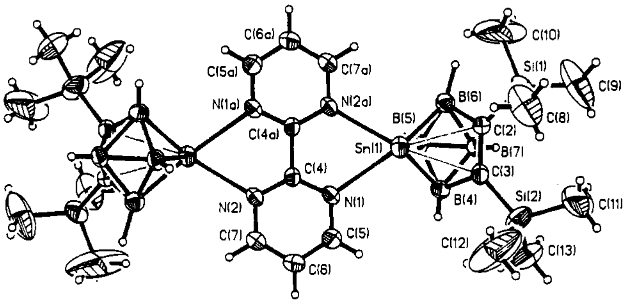

Figure 1. ORTEP view of II showing the atom numbering scheme and thermal ellipsoids at the 40% probability level. The midway between C(4)–C(4a) bond lies at a center of symmetry. Pertinent parameters include Sn–N(1,2) = 2.639 (5), Sn–C(2) = 2.640 (6), Sn–C(3) = 2.653 (7), Sn–B(4) = 2.437 (8), Sn–B (5) = 2.379 (9), and Sn–B (6) = 2.468 (8) Å, and the torsion angle for N(1)–C(4)–C(4a)–N(2a) is 1.2 (9)°.

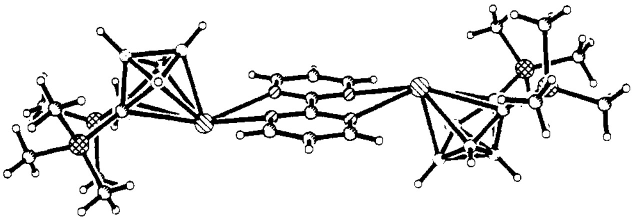

Figure 2. Perspective view showing the trans configuration of the stannacarboranes in II.

During the course of our investigation in this area, we have carried out a reaction between *closo*-Sn-[$(Me_3Si)_2C_2B_4H_4$] (I)[1] and 2,2′-bipyrimidine. A red, crystalline, moderately air-stable, sublimable solid product was isolated in 70% yield.[10] Since the structure of the new bis(stannacarborane)–2,2′-bipyrimidine complex, II, could not be determined from its IR, NMR, and mass spectral data,[11] we have conducted an X-ray analysis of this solid which unambiguously showed the solid to be the novel bridged donor-acceptor complex 1,1′-(2,2′-$C_8H_6N_4$)-[*closo*-1-Sn-2,3-$(Me_3Si)_2$-2,3-$C_2B_4H_4$]$_2$ (II) as shown in its ORTEP drawing in Figure 1.[12]

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(1) Hosmane, N. S.; Sirmokadam, N. N.; Herber, R. H. *Organometallics* **1984**, *3*, 1665.

(2) Hosmane, N. S.; de Meester, P.; Maldar, N. N.; Potts, S. B.; Chu, S. S. C.; Herber, R. H. *Organometallics* **1986**, *5*, 772.

(3) Hosmane, N. S.; Maguire, J. A. In *Molecular Structure and Energetics*; Liebman, J. F., Greenberg, A., Williams, R. E., Eds.; VCH Publishers: New York, 1987, Vol. 5, Chapter 14 and references therein.

(4) Siriwardane, U.; Hosmane, N. S.; Chu, S. S. C. *Acta Crystallogr. Sect. C: Cryst Struct. Commun.* **1987**, *C43*, 1067.

(5) Siriwardane, U.; Islam, M. S.; West, T. A.; Hosmane, N. S.; Maguire, J. A.; Cowley, A. H. *J. Am. Chem. Soc.* **1987**, *109*, 4600.

(6) Islam, M. S.; Siriwardane, U.; Hosmane, N. S.; Maguire, J. A.; de Meester, P.; Chu, S. S. C. *Organometallics* **1987**, *6*, 1936.

(7) Hosmane, N. S.; Siriwardane, U.; Islam, M. S.; Maguire, J. A.; Chu, S. S. C. *Inorg. Chem.* **1987**, *26*, 0000.

(8) Jutzi, P; Galow, P.; Abu-Orabi, S.; Arif, A. M.; Cowley, A. H.; Norman, N. C. *Organometallics* **1987**, *6*, 1024.

(9) Rees, W. S., Jr.; Schubert, D. M.; Knobler, C. B.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1986**, *108*, 5369.

(10) In a procedure identical with that employed in the synthesis of III and IV,[2] 2.50 mmol (0.84 g) of I was reacted with 1.26 mmol (0.20 g) of anhydrous 2,2′-bipyrmidine in benzene to isolate pure red crystalline solid II in 70% yield (0.72 g, 0.87 mmol). This solid (mp 70 °C) is sparingly soluble in nonpolar organic solvents but slightly soluble in polar solvents.

(11) FT NMR data: ^1H NMR ($CDCl_3$, relative to external Me_4Si) δ 8.36 [d, 2 H, bpmd ring, $^3J(^1H-^1H) = 4.6$ Hz], 6.19 [t, 1 H, bpmd ring, $^3J(^1H-^1H) = 4.6$ Hz], 3.93 (q(br), 3 H, basal H_t, $^1J(^1H-^{11}B) = 142$ Hz], 2.88 [q(br), 1 H, apical H_t, $^1J(^1H-^{11}B) = 143$ Hz], 0.42 [s, 18 H, $(CH_3)_3Si$]; ^{11}B NMR ($CDCl_3$, relative to external $BF_3{\cdot}OEt_2$) δ 20.68 [d, 1 B, basal BH, $^1J(^{11}B-^1H) = 145$ Hz], −0.30 [d, 2 B, basal BH, $^1J(^{11}B-^1H) = 142$ Hz], −17.99 [d, 1 B, apical BH, $^1J(^{11}B-^1H) = 143$ Hz]; ^{13}C NMR ($CDCl_3$, relative to external Me_4Si) δ 157.10 [d, bpmd ring, $^1J(^{13}C-^1H) = 186$ Hz], 132.17 [s, bpmd ring, NCN], 121.91 [d, bpmd ring, $^1J(^{13}C-^1H) = 172$ Hz], 127.14 [s (br), cage carbons], 2.42 [q, $(CH_3)_3Si$, $^1J(^{13}C-^1H) = 119$ Hz]; ^{29}Si NMR ($CDCl_3$, relative to external Me_4Si) δ −11.98 [m, $Si(CH_3)_3$, $^2J(^{29}Si-^1H) = 6.1$ Hz]; ^{119}Sn NMR ($CDCl_3$, relative to external TMT) δ −141.99 [s, (br), cage–Sn–bpmd]; mass spectrum; the electron-impact (EI) mass spectrum of II do not exhibit the parent ion; however, both the bipyrimidine ion fragment with 100% relative intensity and the stannacarborane precursor ion were present in the EI mass spectrum; IR ($CDCl_3$ vs $CDCl_3$) 2940 (m, s), 2880 (w, s), 2520 (m, br), 1550 (s, br), 1405 (s, s), 1397 (s, s), 1240 (s, s), 1200 (w, br), 1140 (m, s), 990 (w, br), 885 (m, sh), 875 (m, sh), 840 (vs, br), 800 (m, sh), 775 (w, br), 754 (m, s), 678 (m, s), 645 (w, s), 620 (w, br), 593 (w, s), 412 (m, s), 390 (m, br) cm^{-1}.

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The X-ray crystal structure of II shows displacements of the tin atoms from the centroidal positions above the C_2B_3 faces, and the Lewis base is directly opposite the C–C(cage) bonds making rather severe bond angles (85–92°) with cage ligands. The average tin–carbon(cage) distance [2.646 (6) Å] is 0.267 Å longer than the tin–unique boron distance [2.379 (9) Å]. However, somewhat different bond distances were found in the structures of 1-Sn-$(C_{10}H_8N_2)$-2-(Me_3Si)-3-(R)-2,3-$C_2B_4H_4$ donor-acceptor complexes.[2,4] For example when R = Me (III),[4] the average Sn–C distance [2.818 (6) Å] is 0.459 Å longer than the Sn–B(unique) distance [2.359 (7) Å], whereas the difference between Sn–C [2.73 (1) Å] and Sn–B(unique) [2.37 (2) Å] distances is 0.36 Å when R = $SiMe_3$ (IV).[2] Surprisingly, the Sn–N distances of 2.639 (5) Å in the title compound II are significantly longer than those found in III [2.475 (4) Å][4] and IV [2.51 (1) Å].[2] Furthermore, the dihedral angles between the bipyrimidine rings and the carborane C_2B_3 faces [44.21 (3)°] in the bridged compound II are significantly higher than those between the bipyridine rings and C_2B_3 faces of the stannacarboranes in the nonbridged donor–acceptor complexes III [18.4 (2)°] and IV [26.8 (5)°]. Thus, the interaction between the orbitals of tin and aromatic ring nitrogens in II is weaker than those of III and IV. Consequently, the bridged donor–acceptor complex II in the present study is significantly less slip distorted than the nonbridged 2,2′-bipyridine complexes of the stannacarborane. The important features of the structure of II are the trans position of the two stannacarborane molecules with respect to the central 2,2′-bipyrimidine base (Figure 2) and their closo-geometries

The recent molecular orbital (MO) calculations of the Fenske–Hall type on the "experimental" geometries of the (2,2′-bipyridine)$SnB_4H_4(CER_3)_2$ (E = C, Si; R = H, Me) showed that the "slip distortion" is caused by an antibonding interaction in the HOMO between the tin's "lone pair" and the cage carbons of the carboranes.[13] From the tilt of the bipyrimidine rings in II with respect to the carborane ligands, that is, opposite the cage carbons, it is apparent that the bipyrimidine nitrogens are bonding with tin orbitals originally involved in π bonding with the carborane. As the tin–carborane π interactions become weaker, the main bonding interaction is with the tin σ orbital, and the complex is stabilized by an increased slippage of the tin away from the cage carbons. In this way, a change from η^5 to η^3 bonding is expected in the stannacarborane on complexing with bipyrimidine. This is further evidence of the predominance of σ interactions in the tin–carborane bonding in II. The geometry at tin in II suggests a localized "lone pair" exo to the cage and hence, according to Wades rules,[14] the apical tin is still a two-electron atom and the closo structure is maintained. The trans configuration of the stannacarboranes about the bipyrimidine molecule is not the one that would be favored on steric grounds; orbital effects contribute significantly. It is anticipated that going down from silicon to lead will increase not only the "slip distortion" but also the tilting as the "lone pair" orbital becomes more important.

Among group 14 heterocarboranes, the donor–acceptor complexes of the sila- and plumbacarboranes are not yet known. However, such an endeavor is currently underway in this laboratory.

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Registry No. I, 90388-43-5; II, 110374-95-3; 2,2′-$C_8H_6N_4$, 34671-83-5.

Supplementary Material Available: Tables of positional parameters for non-H atoms (Table 1), bond distances (Table 2), bond angles (Table 3), torsion angles (Table 4), thermal parameters (Table 5), positional parameters for H atoms (Table 6), and molecular planes (Table 7) (8 pages); a listing of observed and calculated structure factors (Table 8) (13 pages). Ordering information is given on any current masthead page.

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[12] Crystallographic data: suitable crystals of II ($C_{24}H_{50}B_8Si_4Sn_2$) were grown by sublimation onto a glass surface. Crystals were sealed in 0.7-mm capillary tubes under dry argon. Data collection was carried out at −110 °C, using an upgraded Nicolet $P\bar{1}$ to P3F diffractometer, Mo Kα radiation. The space group is $P2_1/c$ with $a = 15.884$ (4) Å, $b = 9.841$ (3) Å, $c = 13.550$ (4) Å, $\beta = 104.71$ (2)°, $U = 2048.4$ (9) Å^3, $Z = 2$, and $d_{calcd} = 1.26$ g cm^{-3}. A total of 3481 reflections which measured $I > 3\sigma(I)$ were used for structure solution using direct methods (SHELXTL-Plus) and subsequent difference Fourier methods. The data were not corrected for absorption. Final full-matrix least-squares refinement (SHELXTL-Plus-Structure Determination Software Program; Nicolet Instrument Corp., 1986) converged to $R = 0.059$ and $R_w = 0.076$. All methyl H atoms were placed in calculated positions and not refined, the function minimized being $\sum w(|F_o| - |F_c|)^2$, the weight used being $w^{-1} = \sigma(F^2) + 0.013754F^2$, $(\Delta/\sigma)_{max} = 0.30$, and $\Delta\rho_{max} = 0.81$ e/Å^3. Scattering factors for C, H, B, N, Si, and Sn used were those stored in SHELXTL-Plus.

[13] Barreto, R. D.; Fehlner, T. P.; Hosmane, N. S., submitted for publication.

[14] Wade, K. *Adv. Inorg. Chem. Radiochem.* **1976**, *18*, 1. Wade, K. *Electron Deficient Compounds*; Nelson: London, 1971.

The First Example of Photochemically Activated Carbon Dioxide Insertion into Transition-Metal–Carbon Bonds

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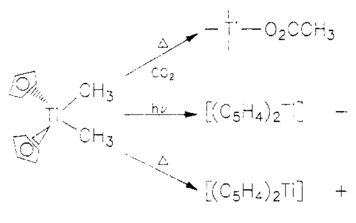
Summary: The photolysis of $Cp_2Ti(CH_3)_2$ (Cp = η^5-C_5H_5) (**1**) in the presence of CO_2 results in the insertion of CO_2 into one metal–carbon bond to form $Cp_2Ti(O_2CCH_3)CH_3$ (**2**).

$Cp_2Ti(CH_3)_2$ (**1**)[1] undergoes well-defined photolytic and thermal reactions:[2–6]



[†] NRC-NRL Research Associate.

[1] $Cp_2Ti(CH_3)_2$ was prepared by using a modification of Bestian's procedure: Clauss, K.; Bestian, H. *Justus Liebigs Ann. Chem.* **1962**, *654*, 8. Dry ethanol was used instead of using water to decompose the excess $LiCH_3$.

[2] (a) Rausch, M. D.; Boon, W. H.; Alt, H. G. *J. Organomet. Chem.* **1977**, *141*, 299. (b) Samuel, E.; Maillard, P.; Giannotti, C. *Ibid.* **1977**, *142*, 289. (c) Bamford, C. H.; Puddephatt, R. J.; Slater, D. M. *Ibid.* **1978**, *159*, C31.

[3] (a) Erskine, G. J.; Hartgerink, J.; Weinberg, E. L.; McCowan, J. D. *J. Organomet. Chem.* **1979**, *170*, 51. (b) Erskine, G. J.; Wilson, D. A.; McCowan, J. D. *Ibid.* **1976**, *114*, 119.

[4] Kolomnikov, I. S.; Lobeeva, T. S.; Vol'pin, M. E. *Zh. Obshchh. Khim.* **1972**, *42*, 2232.