

be more eclipsed with the π orbitals (\angle O-C-C-H, 115°) than the C-C bond is (\angle O-C-C-C, 127°), resulting in orbital distortion in the axial direction.^[1, 17] On the other hand, ring distortions in dithianone and in benzocycloheptenone are opposite to that in cyclohexanone.^[18] This geometrical distortion causes equatorial orbital extension,^[19] and equatorial addition of hydride ion is favored.^[18]



Scheme 1. The antibonding interaction indicated (left) leads to the extension of the LUMO in the direction *trans* to the allylic bond (right).

What role, if any, do orbital interactions involving the antiperiplanar C-O, C-S, C-C, and C-H bonds have?^[20] The β C-O or β C-S bonds in the axial transition structures are about 0.02 Å shorter than the corresponding bonds in the equatorial transition structures. However, the C-C bonds in the axial transition structure of the cyclohexanone-LiH reaction are also shorter by about 0.02 Å. These bond length variations reflect the geometrical differences in the axial and equatorial transition structures, and do not support the argument of significant differences in hyperconjugative interactions by antiperiplanar C-O, C-S, C-C, and C-H bonds.

In summary, we demonstrate that torsional strains, and electrostatic effects in the presence of polar substituents, are most responsible for the stereoselectivity of nucleophilic additions to cyclohexanone and related systems. Orbital interactions due to the inherent difference in C-C, C-H, C-O, and C-S bonds are less important. We also point out that LUMO extension and small pyramidalizations of sp^2 centers^[4a] are a direct consequence of geometrical distortions.

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 [14] The energy difference between the cyclohexanone moiety in the two cyclohexanone-LiH transition structures is basis set dependent. It is 0.0, 0.8, -0.3, and 0.2 kcal mol⁻¹ with the 3-21G, 6-31G**/3-21G, MP2/6-31G**/3-21G, and MP3/6-31G**/3-21G calculations. Similar basis set dependence is also found for dioxanone and dithianone systems and for relative energies of transition structures.
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The Reaction of [Cp⁺Nb₂(B₂H₆)₂] (Cp⁺ = η -EtMe₄C₅) with Sulfur: Stabilization of the Tetrathioborato Ligand in Novel Sulfido Niobium Clusters

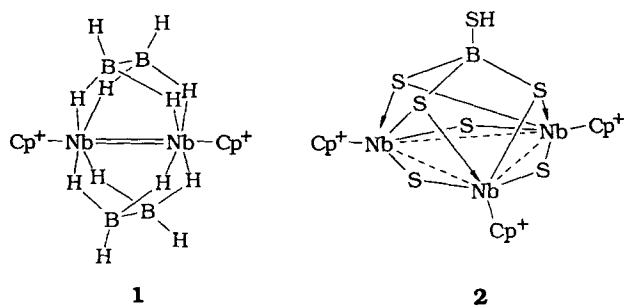
By Henri Brunner, Günther Gehart, Bernd Nuber, Joachim Wachter,* and Manfred L. Ziegler

The structural chemistry of binary boron-sulfur compounds is characterized by the formation of rings either in isolation or linked to chains, in which boron usually has the coordination number three.^[1] In contrast the coordination number four is not often found. Tetrathioborates with corner-linked BS₄ tetrahedra occur in the layer structures of heavy metal thioborates.^[1] However, monomeric M[H_nB(SH)_{4-n}] ($n = 0-3$) compounds could only be proven by spectroscopy in solution in the form of their alkali metal salts because they are easily polymerized.^[2] Hitherto tetrathioborates have not been observed as ligands in organometallic chemistry. Herein we report the first tridentate, triply bridging tetrathioborato ligand.

The surprisingly stable diboranato complex **1** was chosen as the starting material. The synthesis of **1** had been mentioned previously ten years ago, however, without specific details being given.^[3] We have recently studied **1** systematically with regard to its method of formation, structure, and spectroscopic properties.^[4] The two (unstable in the free state) B₂H₆ dianions, which are arranged as bridges perpendicular to the (formal) Nb-Nb double bond are characteristic of **1**. The reaction of **1** with sulfur in decane at 170 °C affords the neutral, diamagnetic complex **2** in yields of up to 26%. The boiling temperature of *o*-xylene (144 °C)

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is the lowest temperature at which **2** is still formed. However, under these conditions the preparation of complex **3** (20–45% yield) predominates, which differs from **2** in that it contains an additional S atom. Elemental analyses and FD mass spectra strongly indicate the stoichiometry $[\text{Cp}_3^+\text{Nb}_3\text{S}_n\text{BH}]$ ($n = 7$ and 8, respectively) of **2** and **3**. The IR spectra show weak absorptions at 2560 (**2**) and 2550 cm^{-1} (**3**); ν_{SH} bands of diorganoborosulfanes occur in a similar region of the spectrum.^[5] The ^1H NMR spectra provide interesting information about the different symmetry characteristics of **2** and **3**: whereas all Cp^+ ligands are equivalent in **2**, they are split in a ratio of 2:1 in **3**. The ^{11}B NMR spectrum of **2** shows a sharp signal at $\delta = 1.9$ ($h_{1/2} = 20 \text{ Hz}$)^[6] and thus lies in a similar region ($\delta = -0.6$) as that observed for $[\text{B}(\text{SH})_4]^-$.^[2]



A crystal structure analysis has so far only been carried out for **2**^[7] (Fig. 1), and this shows that the molecule consists of an equilateral Nb_3 triangle whose edges are spanned by the corners of a BS_4 tetrahedron. The sulfido ligands bridge

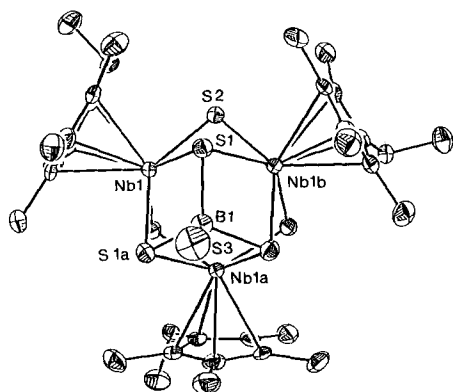


Fig. 1. Structure of **2** (ORTEP). Selected distances [\AA] and angles [$^\circ$]: Nb1-S1 2.554(4), Nb1-S2 2.396(4), Nb1-Nb1a 3.157(3), S1-B1 1.929(10), S3-B1 1.884(22); S1-Nb1-S1a 72.5(1), S1-Nb1-S2 80.7(1), Nb1-S1-Nb1-b 76.5(1), Nb1-S2-Nb1b 82.7(1), Nb1-S1-B1 90.8(5), S1-B1-S1a 102.8(7), S1-B1-S3 115.5(6).

the Nb–Nb edges on the “underside” of the molecule. The threefold metal-substituted ligand which is derived from $\text{B}(\text{SH})_4^-$ is bound to the Nb_3 unit with normal Nb–S distances (average 2.554(4) \AA). In contrast the Nb–S distances to the S^{2-} bridges are approximately 0.16 \AA shorter. They are also shorter than the values found so far in cyclopentadienylsulfidoniobium complexes.^[8] Whereas the average B–S distances are similar to those found in BS_4 tetrahedra, the angles at B1 differ from ideal tetrahedral angles by $\pm 6^\circ$. The localization of the proton on S3 is not possible because of a disorder about the threefold axis through B1–S3. The orga-

nization of the molecules in the columnlike unit cell (c is almost 100 \AA !) to give layers is peculiar. These layers are built up from BS_4 tetrahedra which lie opposite one another in such a way that the B1–S3 vectors are arranged parallel to the threefold axis and all the S3 atoms are in the same plane. Disordered solvent molecules (Et_2O) are situated approximately in this same layer (Fig. 2). The shortest intermolecular contacts between non-hydrogen atoms of the single molecules are not less than 4.0 \AA .

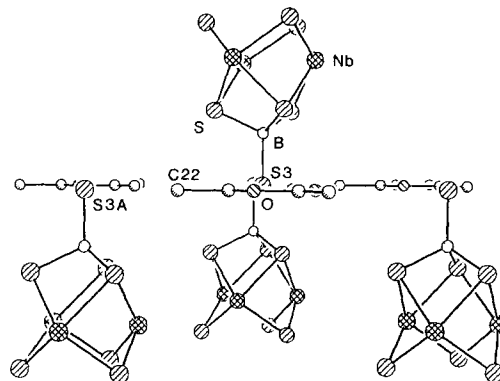


Fig. 2. Section of the unit cell of **2** with the view perpendicular to the trigonal axis. Symmetry related molecules lying opposite each other are shown without the Cp^+ ligands; the distorted ether molecules are shown in the side view. Selected distances: S3...S3A 6.98, S...C22 4.02, S3...C22 4.67 \AA .

The tridentate tetrathioborato ligand of **2** acts as a 12e donor, and when the 30e of the cyclopentadienyl and sulfido ligands as well as the 2e of the Nb_3^{3+} core are added, a total of 44 valence electrons is obtained for **2**. Thus, **2** is isoelectronic with $[\text{Cp}_3^+\text{Nb}_3(\mu\text{-Cl})_3(\mu\text{-O})_3]^+$ ($\text{Cp}^* = \text{C}_5\text{Me}_5$),^[9] which above all has an effect on the Nb–Nb bonds: from the MO calculations carried out for $[\text{Cp}_3^+\text{Re}_3(\mu\text{-O})_6]^{2+}$ ^[10] it was deduced that the cluster orbital with the lowest energy ($1a_1$ symmetry) is of a strongly bonding character and should be delocalized over the Nb three-membered ring. Its occupation with the two electrons of the Nb_3^{3+} core leads to the formation of equal M–M bonds of the formal bond order 2/3. This is indicated by the Nb–Nb distances of 3.157(3) \AA which are between bonding and nonbonding interactions.^[9, 12]

The structure of **3** remains unclear. If the framework of **2** is considered as a basis for that of **3**, the eighth S atom must be arranged in such a way that only two Cp^+ ligands are equivalent. $\mu_3\text{-S}$ or S_2 ligands in all their varieties of coordination could then be conceivable, such as in multinuclear cyclopentadienylsulfidoniobium complexes.^[8] Attempts to interconvert **2** and **3** by the directed removal and addition of sulfur, respectively, have so far been unsuccessful.

Experimental Procedure

The violet solution obtained from **1** (391 mg, 0.72 mmol) and S_8 (372 mg, 1.45 mmol) in decane (50 mL) was refluxed for 15h, whereby the color of the solution had already changed to red-brown after 1h. The decane was then distilled off and the residue was taken up in toluene and the suspension was filtered over SiO_2 . The red filtrate was subsequently chromatographed on SiO_2 (column 30 \times 3 cm). A series of small quantities of firstly an unknown compound, then **3** (15%), and **2** (18–26%) were eluted with a toluene/pentane mixture (3:1). Recrystallization was achieved from Et_2O (**2**) or Et_2O /pentane 10:1 (**3**) and this afforded analytically pure substances (correct C, H, S analyses). **2**: ^1H NMR (250 MHz, CDCl_3): $\delta = 1.13$ (t, $^3J(\text{H,H}) = 7.6 \text{ Hz}$, 9H; CH_3), 2.11 (s, 36H; CH_3), 2.48 (q, $^3J(\text{H,H}) = 7.6 \text{ Hz}$, 6H; CH_2); FD-MS (toluene) m/z 962.6 (M^+); **3**: ^1H NMR (250 MHz, CDCl_3): $\delta = 1.13$ (t, $^3J(\text{H,H}) = 7.6 \text{ Hz}$, 3H; CH_3), 1.14 (t, $^3J(\text{H,H}) = 7.6 \text{ Hz}$, 6H; CH_3), 2.09 (s, 12H; CH_3), 2.10 (s, 12H; CH_3), 2.20 (s, 6H; CH_3), 2.18 (s, 6H; CH_3), 2.44 (q,

CAS Registry numbers:

1, 141903-35-7; 2, 141928-15-6; 2 · Et₂O, 141928-16-7; 3, 141928-17-8.

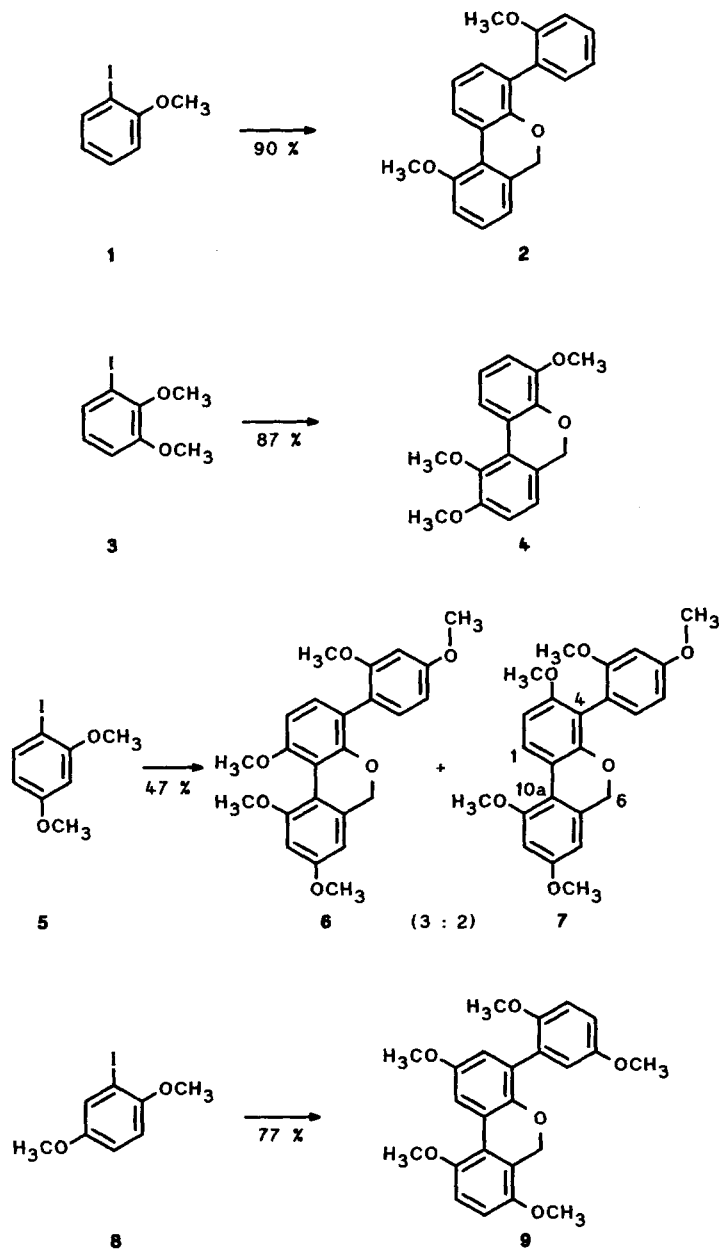
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 [7] **2** crystallized in the form of dark red, very small octahedral crystals which contained half a molecule of ether per formula unit. The systematic absences $-h+k+l = 3n$ for (h,k,l) and $l = 6n$ for (001) and the number of the formula units to be expected led to the rhombohedral space group $R\bar{3}c(D3d/6)$. The lattice constants were refined on the basis of 18 reflections ($4.0 < 2\theta < 23^\circ$) $a = 12.08(1)$, $c = 99.77(6)$ Å, $\gamma = 120^\circ$, $V = 12608.5$ Å³; $Z = 12$. Syntex-R3 diffractometer MoK α , $3.0 < 2\theta < 46.0^\circ$; 4223 measured reflections of which 1359 with $I < 2.5\sigma(I)$ were used for the refinement. Patterson and Fourier methods, anisotropic refinement up to $R = 0.062$, $R_w = 0.047$. Further details of the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-W-7514 Eggenstein-Leopoldshafen 2 (FRG) on quoting the depository number CSD-56281, the names of the authors, and the journal citation.
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Palladium-Catalyzed C-H Activation of Methoxy Groups: A Facile Synthesis of Substituted 6*H*-Dibenzo[*b,d*]pyrans**

By Gerald Dyker*

Transition metal catalyzed reactions have proved themselves particularly efficient in the synthesis of annelated ring systems.^[1] Palladium-catalyzed coupling reactions of aryl halides with alkenes,^[2] alkynes,^[3] and, intramolecularly, with arenes,^[4] have been well characterized and have found numerous applications in organic synthesis. In several cases, domino processes have been observed, in which polycyclic products are formed from several molecules of simple synthetic building blocks.^[5] We now report a new domino coupling reaction, where for the first time a palladium-catalyzed CH-activation at a methoxy group occurs.

ortho-Iodoanisole **1** is condensed with palladium catalysis to give a 90% yield of the substituted 6*H*-dibenzo[*b,d*]pyran **2**, a colorless, crystalline solid (m.p. 135°C).^[6] In order to investigate the generality of this annelation, and to clarify the regiochemical course of the reaction, a series of readily available 1-iodo-2,*n*-dimethoxybenzenes ($n = 3-6$)^[7] were transformed under the reaction conditions described above (Scheme 1). In the case of 1-iodo-2,3-dimethoxybenzene (**3**),



Scheme 1. Synthesis of dibenzopyrans **2**, **4**, **6**, **7**, and **9**. Reaction conditions: 4 mol% Pd(OAc)₂, K₂CO₃, *n*Bu₄NBr, dimethylformamide, N₂, 3 d, 100°C.

the condensation product **4** was obtained (87% yield, m.p. 119°C), which originates from only two molecules of the starting compound. Clearly, a crucial position for the third condensation step is blocked.

1-Iodo-2,4-dimethoxybenzene (**5**), on the other hand, affords a 47% yield of the regioisomeric annelation products **6** and **7** in a 3:2 ratio (71% yield with respect to unrecovered

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