be more eclipsed with the π orbitals (π O-C-C-H, 115°) than the C–C bond is (π O-C-C-C, 127°), resulting in orbital distortion in the axial direction. On the other hand, ring distortions in dicholane and in benzylocyclohexanone are opposite to that in cyclohexane. This geometrical distortion causes equatorial orbital extension, and equatorial addition of hydride ion is favored.

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? 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 cyclohexane–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 σ2p centers are direct consequences of geometrical distortions.

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[9] The calculations were performed with the GAUSSIAN 90 program; M. J. Frisch, M. Head-Gordon, G. W. Trucks, J. B. Foresman, H. B. Schlegel, K. Raghavachari, M. A. Robb, J. S. Binkley, C. Gonzalez, D. J. Defrees, D. J. Fox, R. A. Whiteside, R. Seeger, C. F. Melius, J. Baker, R. L. Martin, L. R. Kahn, J. J. P. Stewart, S. Topiol, J. A. Pople, Gaussian Inc., Pittsburgh, PA, USA, 1990.

[10] A set of diffuse s and p orbitals was added to the hydride ion.


[13] A thorough discussion can be found in [4a]. Frenking et al. [1] suggested a change in the C–O* orbital by a 3-F substituent at C3 to be responsible for the increased axial addition, although the change is very small.

[14] The energy difference between the cyclohexane moiety in the two cyclohexane–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 calculations. Similar basis set dependencies are also found for dioxane and dithiane systems and for relative energies of transition structures.

[15] This strain can be roughly estimated by the calculations on the transition structure of acetone–LiH reaction. A 15° rotation of the two methyl groups away from the transition structure position in either direction causes about 1 kcal mol⁻¹ increase in energy.


The Reaction of [Cp*²Nb[B₂H₆]₃] (Cp* = n-EtMe₂C₅) 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. 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. However, monomeric [M(H₂B(SH)₄)₆]⁻ (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. 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. We have recently studied 1 systematically with regard to its method of formation, structure, and spectroscopic properties. The two (unstable in the free state) B₂H₄ 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)
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 [Cp₂ Nb₂ S₈ BH] (n = 7 and 8, respectively) of 2 and 3. The IR spectra show weak absorptions at 2560 (2) and 2550 cm⁻¹ (3); ν₉ bands of dizorganoborosulfanes occur in a similar region of the spectrum. 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 ¹¹B NMR spectrum of 2 shows a sharp signal at δ = 1.9 (h, J₂ = 20 Hz) and thus lies in a similar region (δ = −0.6) as that observed for [B(SH)₆]⁻.[2]

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 Nb₁³⁺ core are added, a total of 44 valence electrons is obtained for 2. Thus, 2 is isostructural with [Cp₂ Nb₂ (μ-Cl)_₄ (μ-OH)]⁺ (C₉ = C₆ Me₄) which above all has an effect on the Nb-Nb bonds: from the MO calculations carried out for [Cp₂ Re₂ (μ-OH)]²⁺.[10] It was deduced that the cluster orbital with the lowest energy (1α, symmetry) is of a strongly bonding character and energy could be delocalized over the Nb three-membered ring. Its occupation with the two electrons of the Nb₁³⁺ 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) Å 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. μ₁-S or μ₂-S 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 S₈ (372 mg, 1.45 mmol) in decane (50 mL) was refluxed for 15 h, whereby the color of the solution had already changed to red-brown after 1 h. The decane was then distilled off and the residue was taken up in toluene and the suspension was filtered over SO₃. The red filtrate remained 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. μ₁-S or μ₂-S 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.
Transition metal catalyzed annelation reactions, Part 2. This work was
with arene,
pling reaction, where for the first time a palladium-catalyzed
products are formed from several molecules of simple syn-
numerous applications in organic synthesis. In several cases,
alkeynes,
alkeynes,
halides with alkenes,
alkeynes,
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by the Fonds der Chemischen Industrie with a Liebig Scholarship,
(4.0 ); CH,); 2.58
3J(H,H) = 7.6 Hz, 2H; CH,); FD-MS (toluene): m/z 994.1 (M+).

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[6] We thank Prof. Dr. B. Wrackmeyer, Universitäüt Bayreuth, for carrying out the 11B NMR measurement.
[7] 2 crystallized in the form of dark red, very small octahedral crystals which
systematic abscis
h+k+l = 3n for (h,k,l) and l = 6n for (001) and the number of the
rhombohedral space group R3(03d6). The lattice constants were refined on the basis of 18 reflections (4.0 < 2θ < 23°) a = 12.08(1), c = 99.77(6) Å, γ = 120°. V = 12508.5 Å3, Z = 12. Syntax-R3 diffractometer MoKα, λ = 0.4606; 4223 measured reflections of which 1359 with R = 0.062, R = 0.047. Further details of the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, Ge-
sellschaft für wissenschaftlich-technische Information mbH, D-W-75434 Eggenstein-Leopoldshafen (FRG) on quoting the depository number CSD-56281, the names of the authors, and the journal citation.

** Palladium-Catalyzed C-H Activation of Methoxy Groups: A Facile Synthesis of Substituted 6H-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 C-H-activation at a methoxy group occurs.

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ortho-Iodoanisole 1 is condensed with palladium catalysis to give a 90% yield of the substituted 6H-dibenzo[b,d]pyran 2, a colorless, crystalline solid (m.p. 119°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-2,4-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 dibenzo[pyrans 2, 4, 6, 7, and 9. Reaction conditions: 4 mol % Pd(OAc)2, K2CO3, nBu4NBr, dimethylformamide, N2, 3d, 100°C.](image)