Complexes with Interactions between Metals and Aliphatic Groups of Boron Compounds. 1. Synthesis and Reactivity of ($\eta^5$-Cyclopentadienyl)cobalt $\eta^5$-1,3-Diborolene Complexes, a Novel Type of Sandwich Compounds with a Pentacoordinated Carbon Atom. Molecular Structure of ($\eta^5$-Cyclopentadienyl)cobalt 1,3,4,5-Tetraethyl-2-methyl-1,3-diborolene. Extended Hückel and INDO MO Studies‡

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Reaction of (C$_5$H$_5$)Co(C$_2$H$_4$)$_2$ with alkyl derivatives of the 1,3-diborolene (H$_2$B(1H)C$_2$H$_4$), yields the red-orange sandwich complexes 4a and 4b in 45% and 80% yield, respectively. The metal center attains the 18-electron configuration via a three-center, two-electron Co-C--H or a B--H--C interaction, wherehy the "axial" hydrogen of the endo cyclic methylene group is rendered acidic. Deprotonation by potassium in THF results in the formation of the yellow-brown anions 4*, which react with lithium alkyls to give the violet methyl derivatives 4c and 4e. The sandwich anions and metal halides yield the tetradecker sandwich complexes 8 and 9. An isolobal relationship between cyclopentadiene and diborolene is seen in the reactions with metal carbonyls, leading with M$_2$(CO)$_{12}$ to the unsymmetrical triple-decker complex 9b and with Ni(CO)$_4$ to the CO-bridged tetradecker complex 10a. 4 is stacked by (C$_5$H$_5$)Co(C$_2$H$_4$) and (C$_2$H$_5$)Fe(C$_2$H$_4$) to yield the triple-decker sandwich complexes 5 and 7, respectively. Reactivity pattern and $^1$H NMR data indicate an unusual bonding situation for the "axial" hydrogen in 4a and 4b (H $\delta$ -8.37 and -8.62, respectively). Evidence of a three-center, two-electron bonding arrangement in 4 stems from the small $^1$H-C--H coupling constant ($\sim$1 Hz) for 4a, which either is caused by a Co-C--H bond or a B--H--C bridge. On account of the room-temperature X-ray diffraction study of 4a (space group Pnma, $a = 9.257 (3)$ Å, $b = 15.264 (4)$ Å, $c = 12.478 (3)$ Å, $Z = 4, R_p = 0.040$) it is not possible to decide whether the "axial" hydrogen is bonded to carbon (C(4)--H(4) = 0.83 (4) Å) and comes in contact to both boron atoms (B--H = 1.70 (5) Å), or whether it is in a C--H--B bridge (disordered hydrogen, C--H = 0.93 (4), B--H = 1.36 (5) Å). The diborolyl ring in 4a differs from the diborolynyl ring in other sandwich or oligodecker compounds in the geometry around C(4), which is pentacoordinated. The C(4)--B(5) bond is elongated. MO calculations show that the EH and the INDO method predict at the equilibrium geometry a front orbital with pronounced localization at Co--C--H (three-center bond).

Introduction

The interaction of aliphatic C--H bonds with transition-metal atoms is an important step in catalytic processes, which involve the activation of saturated hydrocarbons toward rearrangement or further reaction.† Recent studies have demonstrated that in metal complexes M--H--C three-center interactions occur in the solid as well as in solution. The nature of this bonding in the complex [Et$_2$B(pz)$_2$]Co(cycl) (cycl = pyrazolyl) has been established by $^1$H NMR studies and an X-ray structural determination. In the carbene complex [Ta(CHCMe$_2$)(PM$_3$)$_2$Cl]$_2$ structurally determined by neutron diffraction, a remarkably small C--H--Ta angle of 84.8° and a considerably lengthened C--H bond of 1.131 (8) Å are found. These deformations are regarded as strong evidence for M--H--C interaction in a series of electron-deficient tantalum--alkylidene complexes,‡ which have been studied by a molecular orbital analysis.§ Further examples of such interactions have been found in iron complexes of the type [(MeO)$_3$P]$_2$Fe(η$_5$-C$_5$H$_5$)$_2$ from spectroscopic characterization as well as from single-crystal neutron and X-ray diffraction studies, which reveal a long C--H bond distance of 1.164 (3) Å. The metal atom is in the center

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of a distorted octahedron; one of the coordination sites is occupied by the hydrogen atom of a CH₃ group, thus relieving the coordinative and electronic unsaturation of the metal center. A related case with a very long C-H bond of 1.19 (1), established by neutron diffraction, is that of (η⁵-endo-methyl-cyclohexenyl)manganese tricarbonyl. Distorted ethyl and methyl complexes of R-TiCl₃-((CH₃)₂PCH₂CH₂P(CH₃)₂) also show strong M-H-C interaction, as do several polynuclear cases.¹¹

This work describes the preparation, spectroscopic characterization, and reactions of (η⁵-cyclopentadienyl)-cobalt-η₂,1,3-diborolene sandwich complexes, in which a pentacoordinated carbon is present. The compounds formally contain 16 valence electrons, if no additional interaction between cobalt and the methylene group CHR occurs. An 18-electron configuration may be achieved by the formation of a three-center, two-electron Co--C--H bond, or alternatively by a bonding arrangement in a diborane fashion, C=Co-B. This was discovered in an attempt to prepare the 16-valence-electron sandwich bis(1,3-diborolene)nickel, which may also function as a four-electron donor with retention of the analogue the neutral 1,3-diborolene ring serves as a three-electron donor. However, the ligand 1a may also function as a four-electron donor with retention of the R'C-H bond. This was discovered in an attempt to prepare the 16-valence-electron sandwich bis(1,3-diborolene)nickel, 3a, from the reaction of Na[(CH₂)₂BH], NiBr₂, and 1a, yielding bis(1,3-diborolene)nickel, (1a)₂Ni, an 18-electron complex.¹⁵

Results and Discussion

Synthesis Aspects. Preparation of (C₅H₅)Co-[((EtC)₃(CR)(CHR')₂] Complexes. Recently we have shown that the ring of the hydrogen atom from 1,3,4,5-tetraethyl-2-methyl-1,3-diborolene¹³ (1a) occurs in the reaction with [(η⁵-C₅H₅)Ni(CO)]₂ to give the nickel sandwich complex¹⁴ 2a. In this diamagnetic nickelocene

First evidence of the unusual ligand properties of 1a was obtained from the photolytic reaction of 1a and (C₅H₅)Co(CO)₅. Instead of the expected paramagnetic triple-decker sandwich complex¹⁶,¹⁷ 5a small amounts of a red product could be isolated by chromatography on silica gel. Its mass spectrum indicated that compound 4a was present. However, we were unable to characterize the product because of byproducts formed by insertion¹⁸,¹⁹ of CO into the ligand 1a. A general approach to 4 is provided by treating 1 with the Jonas reagent²⁰ (η⁵-cyclopentadienyl)cobalt bis(ethylene) in petroleum ether. The ethylene ligands are easily replaced by the heterocycle 1 resulting 4a in 45% and 4b in 80% yield. 4a is isolated from the reaction mixture through distillation at 80 °C (0.01 torr) as a red liquid which crystallizes on cooling; 4b sublimes as red crystals at 60 °C (0.01 torr). Both complexes are stable under a dried and purified atmosphere of nitrogen or argon. Small amounts of the triple-decker complex 5b and the tetraether complex 6b (M = Co) are obtained as side products.

Deprotonation of the Sandwich 4. The spectroscopic and structural data (see below) prove that in 4a,b the ring hydrogen of 1a,b is still attached to the C* atom, which implies pentacoordination for C*. However, the precise location of the "axial" hydrogen (terminal C-H or semi-bridging C--H-B) is uncertain. It is tempting to relate this hitherto unknown arrangement of a methylene group in bridging two boron atoms and coordinating to a transition metal to the arachno-carboraben-Co₅H₃ having two methylene groups each bound to three boron atoms.²¹ The carbaborene structure has been determined by an X-ray diffraction study.²² MO calculations²³ suggest that the axial methylene hydrogen atoms are more positive than the equatorial methylene hydrogen atoms, in agreement with the observed high acidity for the axial protons.²¹

In polyhedral boranes HB groups may be substituted for the isolanvalence electronic (C₅H₅)Co moiety.²⁴-²⁵ We will

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(23) Binger, P. Angew. Chem. 1985, 80, 288.


apply the isolobal analogy to the carborane molecule \( \text{C}_2\text{B}_7\text{H}_1\), and for clarity let us only compare the fragment 6 of the carborane with 4. Because of the interaction of the methylene group with related triangular "faces", \( \text{B}_3 \) in 6 and \( \text{B}_3 \) in 4, we may expect the bonding and reactivity of the methylene moiety in both compounds to be similar.

The deprotonation of 4 is achieved with potassium in THF. Under \( \text{H}_2 \) evolution the red-orange color of 4 changes to yellow-brown of the anion 4-. Addition of petroleum ether precipitates \( 4-\text{K}^+ \) as light yellow powder, which is extremely air sensitive. Its reaction with main-group halides \( \text{R}^+\text{X}^- \) such as \( \text{Me}_3\text{SiCl} \), \( \text{Et}_2\text{BCl} \), and alkyl halides depends on the steric requirements of the \( \text{R}^+ \) group. Obviously, the \( \text{Me}_3\text{Si} \) and \( \text{Et}_2\text{B} \) moieties are too bulky to enter the axial position on \( \text{C}^* \), since the only product obtained from 4a and \( \text{R}^+\text{X}^- \) is the neutral sandwich 4a compound (85 and 50% yield, respectively). Most likely its formation occurs via the sandwich radical 4a- which picks up a hydrogen from the solvent THF. Iodomethane and 4- lead to the violet complexes 4e and 4d in 80 and 22% yield, respectively. The compounds are thermally sensitive and decompose above 80 °C. From the brown oily decomposition products of 4e, the red sandwich complex 4a was isolated through chromatography on silica gel. This result indicates that the dimethyl derivative 4e loses a methylene group to yield 4a with methyl in the equatorial position.

With the assumption of an exo rather than an endo approach of iodomethane at the sandwich anion 4b-, we expect the formation of 4f in the first step, having methyl in axial and hydrogen in equatorial positions. However, this should be an unfavorable situation, and indeed we have never observed a compound analogous to 4f from 1a and \( \text{C}_2\text{H}_5\text{Co}(\text{C}_2\text{H}_5)\). In the methylation reaction of 4b-, we obtained in addition to 4e (22%) the monomethyl complex 4d in 45% yield. It may be formed from the initial product 4f via deprotonation by the starting compound 4b- and protonation of 4d- by either 4f or 4b. Reaction of the deprotonated complex 4a- with deuterium chloride results in the formation of the deuterated sandwich complex 4a, having deuterium in the "axial" position.

**Reaction of the Sandwich Anions 4-.** The "axial" substituent \( \text{H} \) supplies one electron and one orbital for bonding, its replacement by the one-electron, three-orbital donor moiety \( \text{C}_2\text{H}_5\text{Fe} \) leads to the diamagnetic triple-decker sandwich complex \( \text{C}_2\text{H}_5\text{Fe}(\text{C}_2\text{B}_3\text{Co}(\text{C}_2\text{H}_5) \) (7).

However, the reaction of 4b- with \( \text{C}_2\text{H}_5\text{Fe}(\text{CO})_2\) only yields minor amounts of the triple-decker complex 7: the main products are the neutral sandwich complex 4b and \( \text{[(C}_2\text{H}_5\text{Fe}(\text{CO})_2]} \), indicating the transient formation of the corresponding radicals. Two sandwich anions 4- and transition-metal halides \( \text{MX}_2 \) form the tetra-decker sandwich complexes 8 with \( \text{M} = \text{Cr} \) to \( \text{Zn} \) in the central position (30-50% yield). Their structure has been confirmed by X-ray diffraction studies. Magnetic data reveal that the central metal M in 8 adopts a high-spin electronic configuration \( \text{M} = \text{Cr} \) to \( \text{Co} \). An example given in this paper is the blue manganese complex 8b (M = Mn, 65% yield).

**Reaction of 4 with Metal Complexes.** The tetra-decker sandwich complexes are analogues of the metalloenes, since the building unit 4- and \( \text{C}_2\text{H}_5\) are isolobal species. When this consideration is applied to the neutral sandwich complex 4, we recognize the isolobal relationship with cyclopentadiene. Indeed 4a reacts with \( \text{M}_2\text{(CO)}_{10} \) to give the diamagnetic triple-decker complex 9b (65% yield) through replacement of \( \text{H} \) in 4a by the \( \text{Mn(CO)}_5 \) moiety. Similarly 4a and \( \text{Ni(CO)}_4 \) form the CO-bridged dimer 10a which is the electronic analogue of \( \text{[(C}_2\text{H}_5\text{Ni(CO)}_5]} \). Both complexes are formal insertion products of the 12-electron 1,3-diborolenylcobalt stack into the metal-cyclopentadienyl bonds of \( \text{C}_2\text{H}_5\text{Mn(CO)}_5 \) and \( \text{[(C}_2\text{H}_5\text{Ni(CO)}_5]} \), respectively. Reaction of the sandwich complex 4b with \( \text{C}_2\text{H}_5\text{Co}(\text{C}_2\text{H}_5)\) in petroleum ether at 40-50 °C leads to the "CoCo" triple-decker sandwich complex 5b in 54% yield. This proves the hypothesis that the formation of 5 from 1 and \( \text{C}_2\text{H}_5\text{Co(CO)}_2 \) occurs

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through stacking of the sandwich complex 4. In an analogous reaction the "FeCo" triple-decker sandwich complex 7a was obtained by heating a solution of (C₅H₅)Co(CO)₂[C(CO)₂(C₅H₅)Fe(CO)₂] and 1a in mesitylene at 180 °C. Besides other products the sandwich complex 4a is formed as an intermediate, which is stacked by the (C₅H₅)Fe fragment. This was proven by reacting 4b with [(C₅H₅)Fe(CO)₂]₂ or (C₅H₅)Fe(cod) (cod = 1,5-cyclooctadiene) to give 7b in 28 and 24% yield, respectively.17,30 Alternatively, one might expect the formation of 7a from 1a, (C₅H₅)Co(CO)₂, and [(C₅H₅)Fe(CO)₂]₂ via stacking of the iron sandwich complex 11a. This 16-electron complex is obtained from 1a and (C₅H₅)Fe(cod) in low yield.30 As the main product (36%) the blue, paramagnetic triple-decker sandwich complex (C₅H₅)Fe(la)Fe(C₅H₅) is formed through stacking of 11a by (C₅H₅)Fe. Although the "FeFe" triple-decker complex was never observed in the reaction mixture of (C₅H₅)Co(CO)₂, [(C₅H₅)Fe(CO)₂]₂, and 1a, we cannot rule out that under the reaction conditions 11a is an intermediate, which reacts with (C₅H₅)Co to give the "FeCo" triple-decker complex. Heating 4b and (C₅H₅)Co(CO)₂ or Co(CO)₅ in mesitylene at 170 °C results in the formation of the tetradecker sandwich complex 8b (M = Co) in 74 and 48% yield, respectively.27,30 With Fe(CO)₅ the corresponding iron tetradecker complex 8b is obtained.30

H, ¹¹B, and ¹³C NMR Studies of the 4. The ¹H and ¹¹B NMR chemical shifts of 4a–e are given in Table I. The most pronounced features in the ¹H NMR spectra are the chemical shifts of the axial C*-H bonds at -8.37 ppm for 4a and -8.62 ppm for 4b demonstrate the shielded character of these protons on one side and the multiplicity of these signals emphasize on the other side the aliphatic nature of the C*-H bonds. Thus, as expected the C* proton resonance of 4a appears as a quartet, as a result of its coupling with the C* methyl group which itself appears as a doublet at 0.94 ppm. The resonance of the C* proton in 4b shows up as a doublet at -8.62 ppm as a result of its coupling with the other C* proton which in turn appears as a doublet at 0.11 ppm. Irradiation at -8.37 ppm in the case of 4a and at -8.62 ppm in the case of 4b causes the collapse of the doublet of the C* methyl group and C*-H, respectively, of 4a and 4b into singlets, which also appears, when the "axial" hydrogen in 4a is replaced by deuterium. The assignment of the remaining peaks in the spectrum of 4b is straightforward. The singlets at 4.11 and 1.09 ppm are due to the C₂H₅ and boron methyl protons, respectively, and the triplet at 1.17 ppm is assigned to the methyl protons of the C ethyl group. The C ethyl group constitutes an ABX₃ spin system having two non equivalent methylene protons. Accordingly, for these protons two multiplets are found at 2.3 and 1.77 ppm. Similarly the proton spectrum of 4a shows two multiplets at 2.3 and 1.7 ppm as well as two triplets at 1.35 and 1.17 ppm. Through double-resonance experiments it has been possible to correlate the multiplets and triplets belonging to the two ABX₃ spin systems of 4a. The assignment of the multiplet at 2.3 ppm and the triplet at 1.17 ppm, respectively, to one of the methylene protons and the methyl protons of the C ethyl groups is based on a comparison of the chemical shifts of isoavulene electronic and isostructural (C₅H₅)Co sandwich complexes of 1,2,5-thiadiborolone,32 of 1,2,5-azadiborolene,50 and of 4b. The multiplet for the other methylene proton of the C ethyl group is coincident with the two multiplets expected for the methylene protons of B-C₂H₅; the remaining triplet at 1.35 ppm is due to the methyl protons of the B ethyl groups.

The assignments of the signals for 4c, 4d, and 4e follows that of 4a and 4b. The two methyl groups on C* are separated by about 0.5 ppm in 4c and 4e, and the high-field signal is tentatively assigned to the methyl group in "axial" position. The ¹¹B NMR data (Table I) for the complexes show different shifts, depending on the substitution on C*. For 4a, 4b with H in "axial" position, we observe values of δ 27, whereas for 4c and 4e the signals appear near 42 ppm. This is certainly an indication that in 4c and 4e the electronic situation at the boron atoms differs considerably from that in 4a and 4b. The observed downfield shift of 15 ppm caused by the substitution of H for CH₃ at C* may be explained as follows: Due to steric interactions of the "axial" methyl the Me₂C* group will pivot so that the other methyl comes in contact with the Co(C₅H₅) group. As a result the binding interaction between Co and C* is reduced and the sandwich complex will

| Table I. ¹H and ¹¹B NMR Chemical Shifts of 4a,b,c,e |
|---|---|---|---|---|---|
| complex | C₅H₅ | C*-R” | C*-R’ | B-R | C-Et | δ(¹¹B) |
| 4a | 4.09 | -8.37 | 0.94 | 1.7 (m, 4) | 2.5 (m, 2) | 27.5 |
| (s, 5) | (q, 1) | (d, 3) | (s, 6) | (t, 6) | |
| 4b | 4.11 | -8.62 | 0.11 | 1.09 (s, 6) | 2.3 (m, 2) | 27.3 |
| (s, 3) | (d, 1) | |
| 4c | 4.09 | -0.09 | 0.43 | 1.8 (m, 4) | 2.5 (m, 2) | 42.0 |
| (s, 5) | (s, 3) | |
| 4d | 4.02 | -8.65 | 0.10 | 1.10 | 1.7 (m, 2) | |
| (s, 5) | (q, 1) | (s, 3) | (d, 6) | |
| 4e | 4.02 | -0.14 | 0.35 | 1.25 (s, 6) | 2.3 (m, 2) | 41.6 |
| (s, 5) | (s, 3) | |
| 4aD | 4.09 | 0.94 | 1.7 (m, 4) | 2.3 (m, 2) | 1.7 (m, 2) | 1.17 (t, 3) |
| (s, 5) | (s, 3) | (t, 6) | |

1 In C₅D₅ (δ, Me₂Si). 2 Low-temperature ¹H NMR experiments show no significant changes in the spectroscopic properties for 4a. 3 (¹H) for R" = H: -8.41 (293 K), -8.25 (175 K) (in C₅D₅). In the ¹¹B NMR spectrum an extreme broadening of the signal at 225 K is observed. 4 Deuterated 4a (R" = ²H).

open up, which may cause a decreased shielding of the boron atoms. If we assume that the high $^{11}$B values of 4a and 4b in comparison to $\delta$ $^{11}$B for the isoelectronic sandwich complex 2a are a result of some additional interaction of the “axial” hydrogen with the boron atoms (a 3-c, 2-e C--H--B bond as shown in Figure 1D), the decrease of the shielding is expected, when H is replaced by CH.

$^{13}$C chemical shifts of 4a and 4b are given in Table II. The $^{13}$C resonances of carbon atoms bound to boron appear broadened as expected. The spectra were obtained by using the gated decoupling NMR spectroscopic technique. The $^{13}$C resonance of C* in the case of 4a appears as a doublet with an unusually low value of $J(^{13}$C--'H) = 81 Hz as it is observed (75-100 Hz) in metal complexes with the M--H--C interaction.$^{56,9}$ It was not possible to determine the $J(^{13}$C--$^{13}$C) value for C* in 4b, because the expected triplet signals of this carbon atom were obscured by the C ethyl triplet and quartet. The very low $J(^{13}$C--'H) value for C* in comparison to those for the free ligands 1a (115 Hz) and 1b (120 Hz) clearly indicate a decrease in the C--H bond order, which may be explained by a 3-c, 2-e Co--C--H bond with a high percent $p$ character on C* or by a 3-c, 2-e C--H--B bridge.

In Figure 1 four structural possibilities are shown for 4b. The NMR results rule out structure A with a Co--H bond but seem to be in agreement with B (3-c, 2-e Co--H--C), with C (3-c, 2-e Co--C--H) and with D, having a 3-c, 2-e C--H--B bridge. The high-field $^1$H NMR signal for 4b could indicate an arrangement B, since similar shieldings have been found for protons in complexes with M--H--C bonds. To relate structure C with the C$_2$B$_3$H$_7$ carbaborane, we shall compare the chemical shifts for the CH$_2$ bonding problem, an X-ray structure analysis was carried out of complex 4a. The result of this study is shown in Figure 2, which reveals that the basis on the location of the methyl group on C(4) both structures C and D are possible. Since, however, the location of the “axial” hydrogen is not very reliable, it is not possible to distinguish between C and D. The compound crystallizes isomorphous to cyclopentadienyl(1,3-diborolenyl)nickel$^{14}$ (2a), and the general features of both compounds are very similar.

The mean planes through the cyclopentadienyl and the 1,3-diborolenyl rings are almost coplanar with an angle of 0.6° between the planes. The distances from the central cobalt atom to the mean planes (Co--(C,H)$_3$) = 1.665 Å and Co--(C$_2$B$_3$) = 1.560 Å lie in the range found for cobalt triple-decker complexes.$^{17}$ The cyclopentadienyl ring shows severe rotational motion or disorder which shortens the C--C and C--H distances. The diborolenyl ring in this compound differs from the diborolenyl ring in other sandwich or oligodecker compounds in the geometry around C(4). The C(4)--B(5) distance (1.632 (2) Å) is significantly elongated in comparison to that in 2a (1.549 (2) Å). The carbon C(7) of the methyl group does not lie in the ring plane but is shifted by 0.15 Å out of the plane toward the cobalt atom. The angle between the ring plane and the line through C(4) and C(7) is 61.9°. The hydrogen atom H(4) attached to the ring carbon lies above the plane. It is shifted toward the center of the ring and comes in contact with the boron atoms (B--H = 1.70 (6) Å). The short distance of 0.83 (4) Å found for C(4)--H(4) is not very reliable. A related structural problem was found in the compound (C$_3$H$_5$C$_5$H$_3$)Co(C$_3$H$_5$C$_5$H$_3$)$_2$B$_2$H$_2$), in which a hydrogen atom attempts to bridge all five atoms of the open pentagonal C$_3$B$_3$ face.$^{34}$ An alternative which has to be considered is that the axial hydrogen H(4) is not simply bonded to C(4) but is engaged in three-center bonding or bridging with neighboring borons, as shown in D. With the assumption of a disordered hydrogen atom a C--H--B

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**Table II. $^{13}$C NMR Chemical Shifts ($\delta$) of 4a and 4b**

<table>
<thead>
<tr>
<th>complex</th>
<th>$^{13}$C</th>
<th>C=C</th>
<th>CH$_2$C</th>
<th>CH$_3$C</th>
<th>B-R</th>
<th>C-H</th>
<th>C*-C</th>
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<td>4a</td>
<td>81.8 (s)</td>
<td>100</td>
<td>313 (t)</td>
<td>132 (q)</td>
<td>7.3</td>
<td>43.6 (d)</td>
<td>13.3 (q)</td>
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<tr>
<td>1a</td>
<td>178</td>
<td>22.4 (tq)</td>
<td>14.6 (qt)</td>
<td>13 (t)</td>
<td>8.1 (qt)</td>
<td>10.3</td>
<td></td>
</tr>
<tr>
<td>4b</td>
<td>81.4 (s)</td>
<td>104</td>
<td>23.4 (t)</td>
<td>16.8 (q)</td>
<td>0</td>
<td>43 (d)</td>
<td>12.3</td>
</tr>
<tr>
<td>1b</td>
<td>179</td>
<td>22.3 (tq)</td>
<td>14.3 (qt)</td>
<td>7.0 (q)</td>
<td>34.9 (t)</td>
<td>12.0</td>
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</table>

$a$ $J($C--H$)$ in hertz. $b$ For the compound cyclopentadienylcobalt,1,3,4,5-tetramethyl-1,3-diborolene $J($C*-H$_a$) $\approx$ 90 Hz and $J($C*-H$_e$) $\approx$ 150 (15) Hz were found. $c$ $J($C*-H$)$ could not be observed due to overlapping signals.

![Figure 1. Structural possibilities for 4b.](image)

**Figure 1.** Structural possibilities for 4b.

![Figure 2. Molecular structure of $(\eta^5$-C$_5$H$_5$)Co(En)$_2$](image)

**Figure 2.** Molecular structure of $(\eta^5$-C$_5$H$_5$)Co(En)$_2$. Non-hydrogen atoms are represented by their 30% probability ellipsoids for thermal motion and the hydrogen atoms by spheres of arbitrary radius.

bond is formed (C-H = 0.93 (4) Å, B-H = 1.36(5) Å). On account of the present structure determination it is not possible to decide whether the hydrogen is in a C-H-B bridge or whether it is bonded to the carbon and weakly to both boron atoms. Preliminary results\(^{36}\) of an X-ray structure analysis of an analogous complex, where (C5-CH3C6H5)Fe, show that the geometry is similar to that of 4a. For the hydrogen bound to the ring carbon two disordered positions in the Co sandwich complex are different (C-B = 0.83, B-H = 1.35 Å and C-B = 1.61, C-H = 0.91, B-H = 1.61 Å). The observed C(4)-H bonds (0.83 and 0.93 Å for a disordered hydrogen) are short, due to the systematic underestimation of C-H bond distances by X-ray diffraction. Therefore, these values cannot be used for accurate comparison, which must await a neutron diffraction study.

**Molecular Orbital Studies.** In order to understand the electronic origin for the deformation of 1 in 4, we have studied the sandwich compound by means of theoretical molecular orbital calculations. We have used an one-electron method based on an extended Hückel (EH) Hamiltonian\(^{36}\) as well as a recently developed improved INDO variant for transition-metal compounds of the 3d

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Table V. Mean Planes through the Rings

<table>
<thead>
<tr>
<th>Plane 1: C(1), C(2), C(3), C(3'), C(2')</th>
</tr>
</thead>
<tbody>
<tr>
<td>Distances from the Plane</td>
</tr>
<tr>
<td>C(1) 0.009 H(1) 0.089</td>
</tr>
<tr>
<td>C(2) 0.007 H(2) 0.030</td>
</tr>
<tr>
<td>C(3) 0.003 H(3) 0.054</td>
</tr>
<tr>
<td>Co 1.665</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Plane 2: C(4), B(5), C(6), C(6'), B(5')</th>
</tr>
</thead>
<tbody>
<tr>
<td>Distances from the Plane</td>
</tr>
<tr>
<td>C(4) 0.013 C(7) -0.148 H(4) 0.80</td>
</tr>
<tr>
<td>B(5) -0.011 C(8) 0.012</td>
</tr>
<tr>
<td>C(6) 0.004 C(10) -0.123</td>
</tr>
<tr>
<td>Co 1.560</td>
</tr>
</tbody>
</table>

The Angle between the Planes: 0.57°

Figure 3. Schematic representation at the EH profiles of 4a, 4b, 4c, and 4f, respectively, as a function of α which is the angle between the mean molecular plane of the 1,3-diborolene ring and the syn C-R' (R' = CH₃ in 4a, H in 4b, H in 4f, and CH₃ in 4c) bond. ΔE is given in electronvolts. We have always used the energy minimum at 4a-d as the internal standard in the ΔE(α) curves: □ 4a; ● 4b; ▲ 4f; • 4c.

series. In the calculations we have employed the geometrical X-ray parameters of 4a. The diagonal elements for the EH approach have been adopted from ref 38.

We have displayed the EH energy profiles of 4a-e,f in Figure 3; α is the angle between the 1,3-diborolene ligand plane and the C-R' bond (R' = CH₃ in 4a, CH₃ in 4c, H in 4b, H in 4f). It is seen that the potential curves for 4a and 4c are characterized by only one minimum which is close to the experimentally derived deformation in 4a. 4b shows a second shallow minimum which is separated by the first one by ca. 0.5 eV. This conformation with a close Co-H contact is lowest in energy in the molecule 4f. It can be seen that the ΔE(α) curve of 4f corresponds to the superposition of the energy profiles predicted for 4b on one side and 4a/4c on the other side. The two isomeric CH₃ derivatives 4a/4f show pronounced differences with respect to their energy curves. The sharp minimum predicted in 4a already has been mentioned while a shallow ΔE(α) potential between 70° and 140° is encountered in 4f.

A detailed investigation of the computational results shows that this bending deformation must be traced back to an increasing bonding interaction between the transition-metal center and the carbon atom in the BCB moiety with increasing values of α. This is explicitly seen in the overlap populations (CoC*, CoC₅) that have been calculated for 4a in the EH approximation. Δα is the displacement from the equilibrium geometry which is char-

It is clear that the coupling between Co and the carbon atom in the diborolene ligand leads to a weakening of the CH bond. Small antibonding contributions to this interaction are predicted due to the CH$_2$ group. The AO phases allow a straightforward rationalization of the double minimum in 4b, but the single-valleyed E($\alpha$) shape in 4a. A further increase of $\Delta$ in 4a is additionally prevented due to antibonding four-electron interactions between the 3$d_\alpha$ orbital of the central atom and a $\sigma$ linear combination of the CH$_2$ group.

The nature of the metal--ligand--H three-center interaction is slightly changed in the case of the bridged structure (Figure 1D). The LCAO amplitude at C* is reduced while the coefficient at the boron atom is enlarged. The frontier orbital is thus formed by a proper 3$d_\alpha$/3$d_\beta$,$\gamma$ reduced while the coefficient at the boron atom is enlarged.

Due to topologically closely related due to the fact that Co and carbon is present. This results in a weakening of the "axial" C-H bond of the endo cyclic methylene group H$_2$ (0.01 torr)) and the olive-green triple-decker complex 5a (30 mg). Mass spectrum: $m/z$ (relative intensity) 328 (M$^+$, 91%). Anal. Calcd for C$_{17}$H$_{25}$B$_2$Co (313.8): C, 65.03; H, 9.12. Found: C, 65.32; H, 9.31. 328 (M$^+$, 91%). Anal. Calcd for C$_{18}$H$_{30}$B$_2$Co (327.98): C, 65.91; H, 9.53. Found: C, 65.32; H, 9.31.

The preparation of 4e was carried out as for 4c except that an excess of CH$_3$I was used. To the sandwich anion obtained from 4b (272 mg, 1 mmol) and potassium (39 mg, 1 mmol) was added. Evolution of ethene occurred. The reaction mixture was treated with an excess of dry DCI gas to yield 0.50 g of deuterated 4a, which contained 90% of nondeuterated 4a. In the IR spectra of 4a and deuterated 4a (R = D) v(C-D) for the axial hydrogen and deuterium, respectively, could be identified. 4b shows a broad band (weak) near 2600 cm$^{-1}$, which is tentatively assigned to v(C-H).

Preparation of the "CoMn" Triple-Decker Complex 9b. A solution of 4b (210 mg, 0.77 mmol) and Mn$_2$(CO)$_{10}$ (250 mg, 0.64 mmol) in 5 mL of mesitylene was heated for 0.5 h at 170 °C. The solvent was removed in vacuo and the residue chromatographed on silica gel with petroleum ether. The first violet fraction contained 260 mg (80%) of 9b: mp 260 °C; $\nu$(C-H) 3,78 (s, 3), 2,33 (s, 1), 1,46 (s, 1). 9b was reacted with 20 mg (0.22 mmol) of (CH$_3$)$_3$SiCl. To a solution of 9b (270 mg, 0.18 mmol) and (C$_2$H$_4$)$_2$O were synthesized via published procedures.

**Experimental Section**

**Methods.** All reactions and manipulations were carried out under an atmosphere of purified and dried nitrogen by using Schlenk type glassware. The solvents were dried by standard methods, distilled from sodium/benzophenon ketyl, and kept under nitrogen. Column chromatography was carried out under nitrogen atmosphere on silica gel Woelm 100-200, which was determined by using a Reichert melting point apparatus (capillary film (Cu K$_\alpha$ radiation, 0.7107 Å, graphite monochromator). Reflections were measured by an omega scan with a scan rate of 1.2° min$^{-1}$, with background measurements for 10° on both sides of the scan, and with varying scan range, which were calculated by the formula $\Delta\omega = A + B \sin \mu/\tan \theta'$ (where $\theta'$ is half the angle between the
counter and the horizontal plane, \( \alpha \) is the equinclination angle, and \( A \) and \( B \) are constants with values around 1.6–2.0\(^\circ \), respectively, 0.5–0.6\(^\circ \) in this case). The crystal had the dimensions 0.78 \( \times \) 0.16 \( \times \) 0.36 mm, and the rotation axis coincided with the \( z \) axis. A total of 2698 unique reflections of the layers 0\( h \)-1–12\( h \) up to \( \theta_{\text{max}} = 30^\circ \) were measured. For 508 reflections \( \sigma_f \) was greater than the intensity \( I \) (\( \sigma_f \) was estimated from counting statistics and a relative term, 0.02). These reflections were given the weight \( w = 0 \) and were not included in the refinement. The intensities were corrected for absorption (\( T_{\text{min}} = 0.71; T_{\text{max}} = 0.85 \)).

**Crystal Data:** \((\text{C}_6\text{H}_5)\text{Co}[(\text{C}_5\text{H}_5)\text{C}_2(\text{C}_5\text{H}_5\text{B})_2\text{CHCH}_3]; M_\text{r} = 313.97; \text{orthorhombic, space group Pnma; } a = 9.257 (3) \AA, b = 15.254 (4) \AA, c = 12.478 (3) \AA, V = 1762.0 \AA^3; \rho_{\text{calc}} = 1.183 \text{ g cm}^{-3}; \mu(\text{Mo }K\alpha) = 0.59 \text{ cm}^{-1}.

The Patterson synthesis gave the parameters of the cobalt atom. The carbon and boron atoms were found by a Fourier map. After least-squares refinement with anisotropic temperature factors all hydrogen atoms could be found.

Locating the hydrogen directly bound to the diborolene ring caused some difficulties. In analogy to other complexes with M–H–C interaction the hydrogen was expected between cobalt and C(4) forming a Co–H–C bond. Although all other hydrogen atoms were easily found, there was no peak in that area. The highest remaining peak lay near C(4) but on the other side of the ring. Assigning this peak to H(4) is supported by two other structural features. First the methyl group is shifted out of the ring plane toward \( \text{CC} \). If H(4) lies between Co and C(4), a shift away from Co is to be expected. Second the two rings are almost coplanar. In other sandwich structures with metal-hydrogen bonding the two rings are tilted.41

Refinement with all atoms (hydrogen isotropic) gave \( R = 0.044 \) and \( R_w = 0.040 \) (\( w \) was set equal \( \sigma^2 \)) for the observed reflections. A difference Fourier synthesis showed no significant peaks. In space group \( \text{Pnma} \) the hydrogen H(4) lies on the mirror plane. Otherwise disorder has to be assumed. An anisotropic—though probably not justified—refinement of this hydrogen showed the ellipsoid strongly elongated in the direction perpendicular to the mirror plane. Assuming disorder of H(4) the refinement of the y coordinate converged at \( \gamma = 0.230 \) (2) (instead of \( \gamma = 0.25 \) for H(4) on the mirror plane). All other parameters did not change significantly. These results make disorder very likely.

In the noncentrosymmetric space group \( \text{Pn2}_1a \) the molecule does not lie on a mirror plane. But refinement in this space group converged slowly, and the \( \text{C}_2\text{H}_5 \) ring had to be refined as a rigid group (\( \text{C}–\text{C} = 1.385 \AA \)). Otherwise, the ring became very distorted. The hydrogen atom H(4) came to lie near \( \gamma = 0.25 \). In spite of the greater number of parameters in \( \text{Pn2}_1a \) the \( R \) value did not improve.

For the present structure determination the space group \( \text{Pnma} \) with a disordered hydrogen atom H(4) seems most likely, but a position on the mirror plane cannot be excluded. Scattering factors for B, C, and Co (neutral) by Cromer and Mann42 and for H by Cromer43 were used. The programs of the SHELX 76 system44 were used.

Table III contains the final positional and thermal parameters for the refinement in \( \text{Pnma} \). Interatomic distances and angles are listed in Table IV and the mean planes in Table V. Figure 2 is a general view of the molecule.

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**Registry No.** 1a, 18067-54-4; 1b, 81620-71-5; 4a, 87261-48-1; 4a, 82090-74-2; 4aD, 87261-54-9; 4b, 87261-49-2; 4b, 81780-50-9; 4c, 87261-50-5; 4d, 87261-51-6; 4d', 87261-53-8; 4e, 87261-52-7; 5b, 82196-39-2; 8b, 87261-29-6; 9b, 87261-55-0; 10a, 81987-35-1; (\text{C}_6\text{H}_5)\text{Co}(\text{C}_5\text{H}_5)_2, 69393-67-5; \text{CH}_3\text{I}, 74-88-4; \text{(CH}_3)_2\text{SiCl}, 75-77-4; (\text{C}_6\text{H}_5)_2\text{BCL}, 5514-83-0; \text{DCI}, 7698-05-7; \text{Mn}_2(\text{CO})_{10}, 10170-69-1; \text{MnBr}_2(\text{DME}), 57839-30-7.

**Supplementary Material Available:** A listing of structure factors for 4a (9 pages). Ordering information is given on any current masthead page.

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(43) Cromer, D. T., private communication, cited in ref 44.