

**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<sup>†</sup>**

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Reaction of  $(C_5H_5)Co(C_2H_4)_2$  with alkyl derivatives of the 1,3-diborolene  $(HC)_2(HB)_2CH_2$ , **1**, 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  $Co\cdots C\cdots H$  or a  $B\cdots H\cdots C$  interaction, whereby 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<sup>-</sup>**, which react with iodomethane to give the violet methyl derivatives **4c** and **4e**. The sandwich anions and metal halides yield the tetradecker sandwich complexes **8**. An isolobal relationship between cyclopentadiene and **4** is seen in reactions with metal carbonyls, leading with  $Mn_2(CO)_{10}$  to the unsymmetrical triple-decker complex **9b** and with  $Ni(CO)_4$  to the CO-bridged tetranuclear complex **10a**. **4** is stacked by  $(C_5H_5)Co(C_2H_4)_2$  and  $(C_5H_5)Fe(C_8H_{12})$  to yield the triple-decker sandwich complexes **5** and **7**, respectively. Reactivity pattern and <sup>1</sup>H NMR data indicate an unusual bonding situation for the "axial" hydrogen in **4a** and **4b** (<sup>1</sup>H  $\delta$  -8.37 and -8.62, respectively). Evidence of a three-center, two-electron bonding arrangement in **4** stems from the small <sup>13</sup>C-<sup>1</sup>H coupling constant (~81 Hz) for **4a**, which either is caused by a  $Co\cdots C\cdots H$  bond or by a  $C\cdots H\cdots B$  bridge. On account of the room-temperature X-ray diffraction study of **4a** (space group *Pnma*, *a* = 9.257 (3) Å, *b* = 15.254 (4) Å, *c* = 12.478 (3) Å, *Z* = 4, *R<sub>w</sub>* = 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  $C\cdots H\cdots B$  bridge (disordered hydrogen, C-H = 0.93 (4), B-H = 1.36 (5) Å). The diborolene ring in **4a** differs from the diborolenyl 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 energy profiles of **4a** and **4c** are characterized by only one minimum, whereas **4b** and **4f** possess a second shallow minimum. EH calculations on a  $C\cdots H\cdots B$ -bridged structure for **4b** predict an energy difference of an upper limit of 0.39 eV with respect to the absolute minimum. Wiberg bond indices of **4a** show remarkable bonding interaction between Co and C(4); the C(4)-H(4) bond is rather weak (0.647) in comparison to C-H bonds of  $C_5H_5$  (0.957). Both the INDO and the EH method predict at the equilibrium geometry a frontier orbital with pronounced localization at  $Co\cdots C\cdots H$  (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.<sup>2</sup> Recent studies have demonstrated that in metal complexes  $M\cdots H\cdots C$  three-center interactions occur in the solid as well as in solution. The nature of this bonding in the complex  $[Et_2B(pz)_2]Mo(CO)_2(\eta^3\text{-allyl})$  (*pz* = pyrazolyl)<sup>3</sup> has been established by <sup>1</sup>H NMR studies and an X-ray structural determination.<sup>4</sup> In the carbene complex  $[Ta(CHCMe_3)(PMe_3)Cl_3]_2$ ,<sup>5</sup> structurally determined by neutron diffraction, a remarkably small C-H<sub>α</sub>-Ta angle of 84.8° and a considerably lengthened C-H<sub>α</sub> bond of 1.131 (8) Å are found. These deformations are regarded as strong evidence for  $M\cdots H\cdots C$  interaction in a series of electron-deficient tantalum-alkylidene complexes,<sup>6</sup> which have been

studied by a molecular orbital analysis.<sup>7</sup> Further examples of such interactions have been found in iron complexes of the type  $[(MeO)_3P]_3Fe(\eta^3-C_8H_{13})^+$  from spectroscopic characterization as well as from single-crystal neutron and X-ray diffraction studies,<sup>8</sup> which reveal a long C-H bond distance of 1.164 (3) Å. The metal atom is in the center

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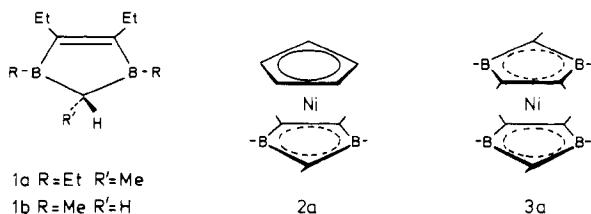
<sup>†</sup>Dedicated to Professor Ernst Otto Fischer on the occasion of his 65th birthday.

of a distorted octahedron; one of the coordination sites is occupied by the hydrogen atom of a CH<sub>3</sub> 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) Å, established by neutron diffraction, is that of ( $\eta^3$ -6-endo-methyl-cyclohexenyl)manganese tricarbonyl.<sup>9</sup> Distorted ethyl and methyl complexes of R-TiCl<sub>3</sub>-(CH<sub>3</sub>)<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>P(CH<sub>3</sub>)<sub>2</sub> also show strong M...H...C interaction,<sup>10</sup> as do several polynuclear cases.<sup>11</sup>

This work describes the preparation, spectroscopic characterization, and reactions of ( $\eta^5$ -cyclopentadienyl)-cobalt- $\eta^5$ -1,3-diborolene sandwich complexes, in which a pentacoordinated carbon is present. The compounds **4** 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, C...H...B. The unusual feature of a Co...C...H 3-c, 2-e interaction is that the carbon atom is "in the middle", unlike all the cases known previously and cited above. The proposed bonding model is discussed on the basis of the results of a single-crystal X-ray diffraction study and on molecular orbital calculations of extended Hückel and INDO type. A preliminary report on the synthesis of **4a,b** and structure of **4a** has been published.<sup>12</sup>

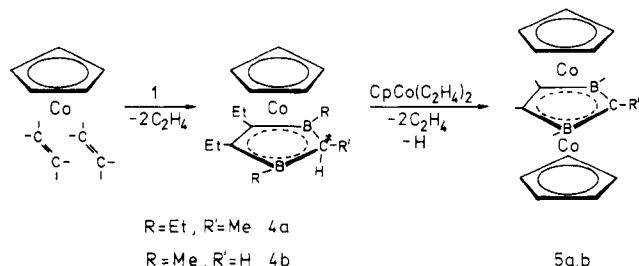
## Results and Discussion

**Synthesis Aspects. Preparation of (C<sub>5</sub>H<sub>5</sub>)Co-[(EtC)<sub>2</sub>(RB)<sub>2</sub>(CHR')] Complexes.** Recently we have shown that the abstraction of the ring hydrogen atom from 1,3,4,5-tetraethyl-2-methyl-1,3-diborolene<sup>13</sup> (**1a**) occurs in the reaction with [ $\eta^5$ -C<sub>5</sub>H<sub>5</sub>]Ni(CO)]<sub>2</sub> to give the nickel sandwich complex<sup>14</sup> **2a**. In this diamagnetic nickelocene



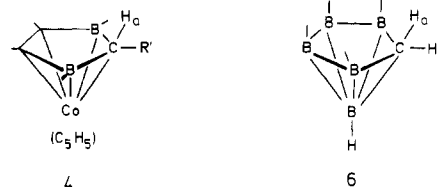
analogue the neutral 1,3-diborolenyl ring serves as a three-electron donor. However, the ligand **1a** may also function as a four-electron donor with retention of the R'C-H bond. This was discovered in an attempt to prepare the 16-valence-electron sandwich bis(1,3-diborolenyl) nickel, **3a**, from the reaction of Na(Et<sub>2</sub>BH), NiBr<sub>2</sub>, and **1a**, yielding bis(1,3-diborolene)nickel, (**1a**)<sub>2</sub>Ni, an 18-electron complex.<sup>15</sup>

First evidence of the unusual ligand properties of **1a** was obtained from the photolytic reaction of **1a** and (C<sub>5</sub>H<sub>5</sub>)Co(CO)<sub>2</sub>. Instead of the expected paramagnetic triple-decker sandwich complex<sup>16,17</sup> **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 insertion<sup>18,19</sup> of CO into the ligand **1a**. A general approach to **4** is provided



by treating **1** with the Jonas reagent<sup>20</sup> ( $\eta^5$ -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 tetradecker complex **8b** (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*-carbaborane C<sub>2</sub>B<sub>7</sub>H<sub>13</sub> having two methylene groups each bound to three boron atoms.<sup>21</sup> The carbaborane structure has been determined by an X-ray diffraction study.<sup>22</sup> MO calculations<sup>23</sup> 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.<sup>21</sup>



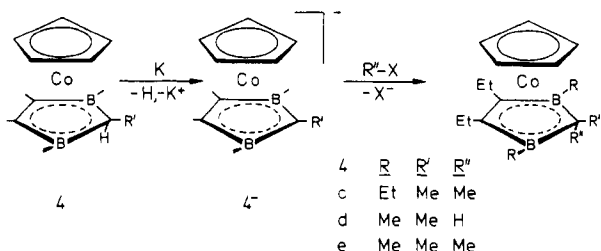
In polyhedral boranes HB groups may be substituted for the isovalence electronic (C<sub>5</sub>H<sub>5</sub>)Co moiety.<sup>24-26</sup> We will

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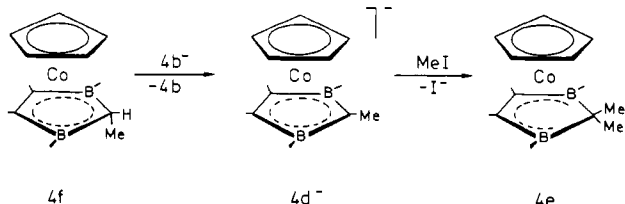
apply the isolobal analogy<sup>27</sup>  $\text{HB} \leftrightarrow \text{CpCo}$  to the carborane molecule  $\text{C}_2\text{B}_7\text{H}_{13}$ , and for clarity let us only compare the fragment 6 of the carborane with 4. Because of the interaction of the methylene group with related triangular "faces", ( $\text{B}_3$ ) in 6 and ( $\text{B}_2\text{Co}$ ) 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.<sup>28</sup> Under  $\text{H}_2$  evolution the red-orange color of 4 changes to yellow-brown of the anion 4<sup>-</sup>. 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  $4\text{a}^-$  and  $\text{R}''\text{-X}$  is the neutral sandwich  $4\text{a}$  compound (85 and 50% yield, respectively). Most likely its formation occurs via the sandwich radical  $4\text{a}^\cdot$  which picks up a hydrogen from the solvent THF. Iodomethane and  $4^-$  lead to the violet complexes  $4\text{c}$  and  $4\text{e}$  in 80 and 22% yield, respectively. The compounds are thermally sensitive and decompose above 80 °C. From the brown oily decomposition products of  $4\text{c}$ , the red sandwich complex  $4\text{a}$  was isolated through chromatography on silica gel. This result indicates that the dimethyl derivative  $4\text{c}$  loses a methylene group to yield  $4\text{a}$  with methyl in the equatorial position.

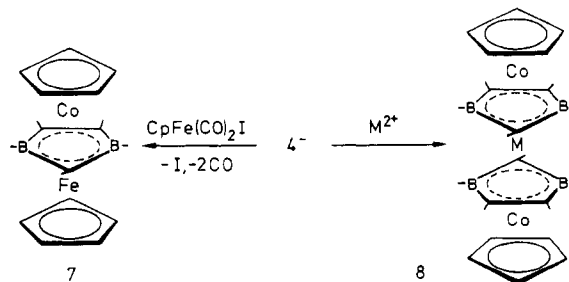
With the assumption of an exo rather than an endo approach of iodomethane at the sandwich anion  $4\text{b}^-$ , we expect the formation of  $4\text{f}$  in the first step, having methyl in axial and hydrogen in equatorial positions. However, this should be an unfavorable situation, and indeed we never have observed a compound analogous to  $4\text{f}$  from  $1\text{a}$  and  $(\text{C}_5\text{H}_5)\text{Co}(\text{C}_2\text{H}_4)_2$ . In the methylation reaction of  $4\text{b}^-$  we obtained in addition to  $4\text{e}$  (22%) the monomethyl complex  $4\text{d}$  (protonated  $4\text{d}^-$ , 45% yield). It may be



formed from the initial product  $4\text{f}$  via deprotonation by the starting compound  $4\text{b}^-$  and protonation of  $4\text{d}^-$  by either  $4\text{f}$  or  $4\text{b}$ . Reaction of the deprotonated complex  $4\text{a}^-$  with deuterium chloride results in the formation of the deu-

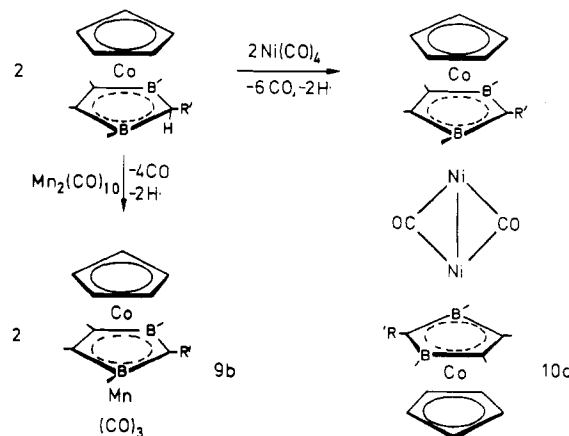
terated sandwich complex  $4\text{a}$ , having deuterium in the "axial" position.

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



However, the reaction of  $4\text{b}^-$  with  $(\text{C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{I}$  only yields minor amounts of the triple-decker complex 7: the main products are the neutral sandwich complex  $4\text{b}$  and  $[(\text{C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2$ , indicating the transient formation of the corresponding radicals.<sup>17</sup> Two sandwich anions  $4^-$  and transition-metal halides  $\text{MX}_2$  form the tetradecar sandwich complexes 8 with  $\text{M} = \text{Cr}$  to  $\text{Zn}$  in the central position (30–80% yield). Their structure has been confirmed by X-ray diffraction studies.<sup>30</sup> Magnetic data reveal that the central metal  $\text{M}$  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  $8\text{b}$  ( $\text{M} = \text{Mn}$ , 65% yield).

**Reaction of 4 with Metal Complexes.** The tetradecar sandwich complexes are analogues of the metallocenes, since the building unit  $4^-$  and  $\text{C}_5\text{H}_5^-$  are isolobal species. When this consideration is applied to the neutral sandwich complex 4, we recognize the isolobal relationship with cyclopentadiene. Indeed  $4\text{a}$  reacts with  $\text{Mn}_2(\text{CO})_{10}$  to give the diamagnetic triple-decker complex  $9\text{b}$  (65% yield) through replacement of H in  $4\text{a}$  by the  $\text{Mn}(\text{CO})_3$  moiety. Similarly  $4\text{a}$  and  $\text{Ni}(\text{CO})_4$  form the CO-bridged



dimer<sup>31</sup>  $10\text{a}$  which is the electronic analogue of  $[(\text{C}_5\text{H}_5)\text{-Ni}(\text{CO})_2]_2$ . Both complexes are formal insertion products of the 12-electron 1,3-diborolenylcobalt stack into the metal-cyclopentadienyl bonds of  $(\text{C}_5\text{H}_5)\text{Mn}(\text{CO})_3$  and  $[(\text{C}_5\text{H}_5)\text{Ni}(\text{CO})_2]_2$ , respectively. Reaction of the sandwich complex  $4\text{b}$  with  $(\text{C}_5\text{H}_5)\text{Co}(\text{C}_2\text{H}_4)_2$  in petroleum ether at 40–50 °C leads to the "CoCo" triple-decker sandwich complex  $5\text{b}$  in 54% yield.<sup>17</sup> This proves the hypothesis that the formation of 5 from 1 and  $(\text{C}_5\text{H}_5)\text{Co}(\text{CO})_2$  occurs

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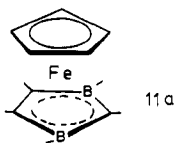
Table I.  $^1\text{H}$  and  $^{11}\text{B}$  NMR Chemical Shifts<sup>a</sup> of 4a,b,c,e

complex	$\text{C}_5\text{H}_5$	$\text{C}^*\text{-R}''$	$\text{C}^*\text{-R}'$	B-R	C-Et	$\delta(^{11}\text{B})$
4a <sup>b</sup>	4.09 (s, 5)	-8.37 (q, 1)	0.94 (d, 3)	1.7 (m, 4) 1.35 (t, 6)	2.3 (m, 2) 1.7 (m, 2) 1.17 (t, 6)	27.5
4b	4.11 (s, 5)	-8.62 (d, 1)	0.11 (d, 1)	1.09 (s, 6)	2.3 (m, 2) 1.7 (m, 2) 1.17 (t, 6)	27.3
4c	4.09 (s, 5)	-0.09 (s, 3)	0.43 (s, 3)	1.8 (m, 4) 1.58 (t, 6)	2.3 (m, 2) 1.7 (m, 2) 1.15 (t, 6)	42.0
4d	4.02 (s, 5)	-8.65 (q, 1)	0.10 (d, 3)	1.10 (s, 6)	2.3 (m, 2) 1.7 (m, 2) 1.16 (t, 6)	
4e	4.02 (s, 5)	-0.14 (s, 3)	0.35 (s, 3)	1.25 (s, 6)	2.3 (m, 2) 1.7 (m, 2) 1.16 (t, 6)	41.6
4aD <sup>c</sup>	4.09 (s, 5)		0.94 (s, 3)	1.7 (m, 4) 1.35 (t, 6)	2.3 (m, 2) 1.7 (m, 2) 1.17 (t, 3)	

<sup>a</sup> In  $\text{C}_6\text{D}_6$  ( $\delta$ ,  $\text{Me}_4\text{Si}$ ). <sup>b</sup> Low-temperature  $^1\text{H}$  NMR experiments show no significant changes in the spectroscopic properties for 4a.  $\delta(^1\text{H})$  for  $\text{R}'' = \text{H}$ : -8.41 (293 K), -8.25 (176 K) (in  $\text{C}_7\text{D}_8$ ). In the  $^{11}\text{B}$  NMR spectrum an extreme broadening of the signal at 225 K is observed. <sup>c</sup> Deuterated 4a ( $\text{R}'' = ^2\text{H}$ ).

through stacking of the sandwich complex 4.

In an analogous reaction the "FeCo" triple-decker sandwich complex 7a<sup>17</sup> was obtained by heating a solution of  $(\text{C}_5\text{H}_5)_2\text{Co}(\text{CO})_2$ ,  $[(\text{C}_5\text{H}_5)_2\text{Fe}(\text{CO})_2]_2$ , and 1a in mesitylene at 160 °C. Besides other products the sandwich complex 4a is formed as an intermediate, which is stacked by the  $(\text{C}_5\text{H}_5)_2\text{Fe}$  fragment. This was proven by reacting 4b with  $[(\text{C}_5\text{H}_5)_2\text{Fe}(\text{CO})_2]_2$  or  $(\text{C}_5\text{H}_5)_2\text{Fe}(\text{cod})$  (cod = 1,5-cyclooctadiene) to give 7b in 28 and 24% yield, respectively.<sup>17,30</sup> Alternatively, one might expect the formation of 7a from 1a,  $(\text{C}_5\text{H}_5)_2\text{Co}(\text{CO})_2$ , and  $[(\text{C}_5\text{H}_5)_2\text{Fe}(\text{CO})_2]_2$  via stacking of the iron sandwich complex 11a. This 16-electron complex



is obtained from 1a and  $(\text{C}_5\text{H}_5)_2\text{Fe}(\text{cod})$  in low yield.<sup>30</sup> As the main product (36%) the blue, paramagnetic triple-decker sandwich complex  $(\text{C}_5\text{H}_5)_2\text{Fe}(\text{1a})\text{Fe}(\text{C}_5\text{H}_5)$  is formed through stacking of 11a by  $(\text{C}_5\text{H}_5)_2\text{Fe}$ . Although the "FeFe" triple-decker complex was never observed in the reaction mixture of  $(\text{C}_5\text{H}_5)_2\text{Co}(\text{CO})_2$ ,  $[(\text{C}_5\text{H}_5)_2\text{Fe}(\text{CO})_2]_2$ , and 1a, we cannot rule out that under the reaction conditions 11a is an intermediate, which reacts with  $(\text{C}_5\text{H}_5)_2\text{Co}$  to give the "FeCo" triple-decker complex. Heating 4b and  $(\text{C}_5\text{H}_5)_2\text{Co}(\text{CO})_2$  or  $\text{Co}_2(\text{CO})_8$  in mesitylene at 170 °C results in the formation of the tetradecker sandwich complex 8b ( $\text{M} = \text{Co}$ ) in 74 and 48% yield, respectively.<sup>29,30</sup> With  $\text{Fe}(\text{CO})_5$  the corresponding iron tetradecker complex 8b is obtained.<sup>30</sup>

**$^1\text{H}$ ,  $^{11}\text{B}$ , and  $^{13}\text{C}$  NMR Studies of 4.** The  $^1\text{H}$  and  $^{11}\text{B}$  NMR chemical shifts of 4a-e are given in Table I. The most pronounced features in the  $^1\text{H}$  NMR spectra are the chemical shifts of the axial  $\text{C}^*\text{-H}$  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  $\text{C}^*\text{-H}$  bonds. Thus, as expected the  $\text{C}^*$  proton resonance of 4a appears as a quartet, as a result of its coupling with the  $\text{C}^*$  methyl group which itself appears as a doublet at 0.94 ppm. The resonance of the  $\text{C}^*$  proton in 4b shows up as a doublet at -8.62 ppm as a result of its coupling with the other  $\text{C}^*$  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  $\text{C}^*$  methyl group and  $\text{C}^*\text{-H}$ , 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  $\text{C}_5\text{H}_5$  and boron methyl protons, respectively, and the triplet at 1.17 ppm is assigned to the methyl protons of the C ethyl groups. The C ethyl group constitutes an  $\text{ABX}_3$  spin system having two non equivalent methylene protons. Accordingly, for these protons two multiplets are found at 2.3 and 1.7 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  $\text{ABX}_3$  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 isovalence electronic and isostructural  $(\text{C}_5\text{H}_5)_2\text{Co}$  sandwich complexes of 1,2,5-thiadiborolene,<sup>32</sup> of 1,2,5-azadiborolene,<sup>33</sup> 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  $\text{B-C}_2\text{H}_5$ ; 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  $\text{C}^*$  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  $^{11}\text{B}$  NMR data (Table I) for the complexes show different shifts, depending on the substitution on  $\text{C}^*$ . For 4a,b with H in "axial" position, we observe values of  $\delta$  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  $\text{CH}_3$  at  $\text{C}^*$  may be explained as follows: Due to steric interactions of the "axial" methyl the  $\text{Me}_2\text{C}^*$  group will pivot so that the other methyl comes in contact with the  $\text{Co}(\text{C}_5\text{H}_5)$  group. As a result the bonding interaction between Co and  $\text{C}^*$  is reduced and the sandwich complex will

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(33) Siebert, W.; Schmidt, H.; Full, R. *Z. Naturforsch. B: Anorg. Chem., Org. Chem.* 1980, 35B, 873.

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

complex	$\text{C}_5\text{H}_5$	C=C	$\text{CCH}_2\text{C}$	$\text{CCCH}_3$	B-R	C-H	C*-C
4a	81.8 (s) (177) <sup>a</sup>	100	23.1 (t) (128)	17.2 (q) (128)	7.5  13.7 (q) (128)	40.9 (d) (~81) <sup>b</sup>	13.3 (q) (128)
1a		178	22.4 (tq)	14.6 (qt)	8.1 (qt) 13 (t)	43 (d) (115)	
4b	81.4 (s) (177)	104	23.4 (t) (125)	16.8 (q) (125)	0	20.3 <sup>c</sup>	
1b		179	22.3 (tq) (130)	14.3 (qt) (130)	7.0 (q) (~120)	34.9 (t) (120)	

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

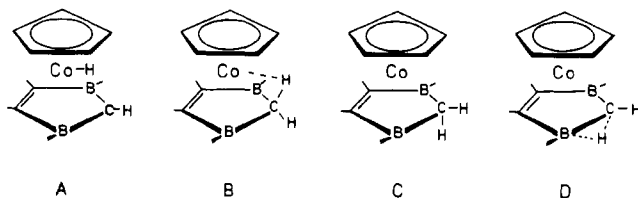


Figure 1. Structural possibilities for 4b.

open up, which may cause a decreased shielding of the boron atoms. If we assume that the high  $^{11}\text{B}$  values of 4a and 4b in comparison to  $\delta$  36 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  $\text{CH}_3$ .

$^{13}\text{C}$  chemical shifts of 4a and 4b are given in Table II. The  $^{13}\text{C}$  resonances of carbon atoms bound to boron appear broadened as expected. The spectra were obtained by using the gated decoupling NMR spectroscopic technique. The  $^{13}\text{C}$  resonance of  $\text{C}^*$  in the case of 4a appears as a doublet with an unusually low value of  $J(^{13}\text{C}-^1\text{H}) \approx 81$  Hz as it is observed (75–100 Hz) in metal complexes with the  $\text{M}\cdots\text{H}\cdots\text{C}$  interaction.<sup>5,6,9</sup> It was not possible to determine the  $J(^{13}\text{C}-^1\text{H})$  value for  $\text{C}^*$  in 4b, because the expected triplet signals of this carbon atom were obscured by the C ethyl triplet and quartet. The very low  $J(^{13}\text{C}-^1\text{H})$  value for  $\text{C}^*$  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  $\text{Co}\cdots\text{C}\cdots\text{H}$  bond with a high percent p character on  $\text{C}^*$  or by a 3-c, 2-e  $\text{C}\cdots\text{H}\cdots\text{B}$  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  $\text{Co}\cdots\text{H}\cdots\text{C}$ ), with C (3-c, 2-e  $\text{Co}\cdots\text{C}\cdots\text{H}$ ) and with D, having a 3-c, 2-e  $\text{C}\cdots\text{H}\cdots\text{B}$  bridge. The high-field  $^1\text{H}$  NMR signal for 4b could indicate an arrangement B, since similar shieldings have been found for protons in complexes with  $\text{M}\cdots\text{H}\cdots\text{C}$  bonds. To relate structure C with the  $\text{C}_2\text{B}_7\text{H}_{13}$  carborane,<sup>21</sup> we shall compare the chemical shifts for the  $\text{CH}_2$  groups. In 4b the signals for the two protons at  $\text{C}^*$  are separated by 8.73 ppm, whereas in the carborane the axial (–0.77 ppm) and equatorial protons (0.10 ppm) do not differ much. This small  $\delta$  value does not favor structure C; however, the influence of the cobalt atom on the shielding of C-H<sub>a</sub> cannot be neglected.

**X-ray Crystal Structure of ( $\eta^5$ -Cyclopentadienyl)cobalt 1,3,4,5-Tetraethyl-2-methyl-1,3-diborolene (4a).** For clarification of this interesting stereochemical and 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 on the basis of the location of the methyl group on C(4) both structures C and D are

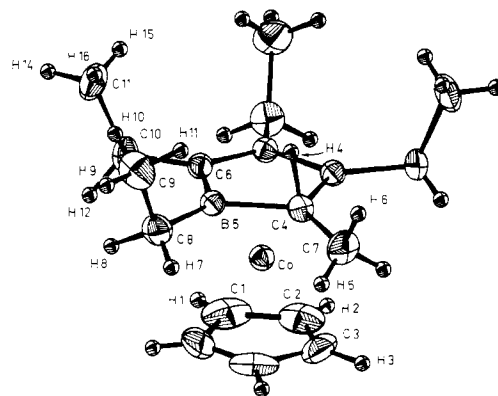


Figure 2. Molecular structure of ( $\eta^5$ - $\text{C}_5\text{H}_5$ )Co[(EtC)<sub>2</sub>-(EtB)<sub>2</sub>CHCH<sub>3</sub>], 4a. Non-hydrogen atoms are represented by their 30% probability ellipsoids for thermal motion and the hydrogen atoms by spheres of arbitrary radius.

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<sup>14</sup> (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 ( $\text{Co}-(\text{C}_5\text{H}_5) = 1.665$  Å and  $\text{Co}-(\text{C}_2\text{B}_2) = 1.560$  Å) lie in the range found for cobalt triple-decker complexes.<sup>17</sup> The cyclopentadienyl ring shows severe rotational motion or disorder which shortens the C-C and C-H distances. The diborolene 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 6.1°. 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 ( $\text{B}\cdots\text{H} = 1.70$  (5) 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 ( $\eta^5$ - $\text{C}_5\text{H}_5$ )Co( $\eta^5$ - $\text{C}_5\text{H}_4\text{C}_2\text{B}_9\text{H}_{11}$ ), in which a hydrogen atom attempts to bridge all five atoms of the open pentagonal  $\text{C}_2\text{B}_3$  face.<sup>34</sup> 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  $\text{C}\cdots\text{H}\cdots\text{B}$

Table III. Positional and Thermal Parameters with Their Estimated Standard Deviations<sup>a</sup>

	x	y	z	U <sub>11</sub>	U <sub>22</sub>	U <sub>33</sub>	U <sub>12</sub>	U <sub>13</sub>	U <sub>23</sub>
Co	0.62215 (3)	0.25	0.46580 (2)	0.0357 (2)	0.0375 (2)	0.0305 (2)	0	-0.0035 (2)	0
C(1)	0.6214 (6)	0.25	0.3039 (3)	0.068 (2)	0.199 (7)	0.031 (2)	0	-0.012 (2)	0
C(2)	0.5480 (4)	0.1767 (3)	0.3407 (3)	0.109 (3)	0.081 (2)	0.070 (2)	0.015 (2)	-0.047 (2)	-0.028 (2)
C(3)	0.4349 (3)	0.2045 (2)	0.4008 (2)	0.063 (1)	0.119 (3)	0.069 (2)	-0.038 (2)	-0.029 (2)	0.016 (2)
C(4)	0.6042 (3)	0.25	0.6281 (2)	0.037 (1)	0.046 (1)	0.032 (1)	0	0.006 (1)	0
B(5)	0.6887 (2)	0.3362 (1)	0.5825 (2)	0.041 (1)	0.033 (1)	0.035 (1)	0.000 (1)	-0.001 (1)	0.000 (1)
C(6)	0.8156 (2)	0.2972 (1)	0.5190 (1)	0.036 (1)	0.038 (1)	0.032 (1)	-0.005 (1)	-0.001 (1)	0.003 (1)
C(7)	0.4605 (4)	0.25	0.6859 (3)	0.051 (2)	0.078 (3)	0.057 (2)	0	0.021 (2)	0
C(8)	0.6472 (3)	0.4349 (1)	0.6060 (2)	0.062 (1)	0.037 (1)	0.060 (1)	0.008 (1)	-0.004 (1)	-0.005 (1)
C(9)	0.7209 (4)	0.4720 (2)	0.7043 (2)	0.105 (2)	0.048 (1)	0.067 (2)	0.011 (2)	-0.008 (2)	-0.019 (1)
C(10)	0.9199 (3)	0.3516 (2)	0.4533 (2)	0.058 (1)	0.056 (1)	0.055 (1)	-0.014 (1)	0.014 (1)	0.009 (1)
C(11)	1.0513 (3)	0.3780 (2)	0.5179 (3)	0.049 (1)	0.068 (2)	0.123 (3)	-0.021 (1)	0.007 (2)	0.014 (2)

	x	y	z	U, Å <sup>2</sup>	x	y	z	U, Å <sup>2</sup>	
H(1)	0.687 (7)	0.25	0.277 (5)	0.15 (3)	H(9)	0.692 (4)	0.531 (2)	0.723 (3)	0.13 (1)
H(2)	0.566 (3)	0.120 (2)	0.335 (3)	0.10 (1)	H(10)	0.828 (4)	0.470 (2)	0.698 (3)	0.12 (1)
H(3)	0.375 (3)	0.172 (2)	0.437 (3)	0.10 (1)	H(11)	0.700 (4)	0.435 (2)	0.763 (3)	0.11 (1)
H(4) <sup>b</sup>	0.676 (5)	0.25	0.668 (4)	0.11 (2)	H(12)	0.875 (3)	0.408 (2)	0.430 (2)	0.09 (1)
H(5)	0.402 (2)	0.299 (2)	0.668 (2)	0.08 (9)	H(13)	0.944 (3)	0.320 (2)	0.387 (2)	0.08 (1)
H(6)	0.464 (4)	0.25	0.758 (3)	0.07 (1)	H(14)	1.120 (3)	0.412 (2)	0.475 (2)	0.09 (1)
H(7)	0.551 (3)	0.441 (2)	0.611 (2)	0.07 (1)	H(15)	1.097 (3)	0.328 (3)	0.541 (3)	0.11 (1)
H(8)	0.674 (3)	0.470 (2)	0.547 (2)	0.07 (1)	H(16)	1.010 (4)	0.409 (3)	0.583 (3)	0.14 (2)

<sup>a</sup> The form of the anisotropic thermal parameter is  $\exp[-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2hka^*b^*U_{12} + 2hla^*c^*U_{13} + 2klb^*c^*U_{23})]$ . <sup>b</sup> Refinement of a disordered H(4):  $x = 0.675 (3)$ ,  $y = 0.220 (2)$ ,  $z = 0.666 (3)$ , and  $B = 0.04 (1) \text{ \AA}^2$ .

Table IV. Interatomic Distances (Å) and Angles (deg)

Distances around Cobalt					
Co-C(1)	2.020 (3)	Co-C(3)	2.036 (2)	Co-B(5)	2.057 (2)
Co-C(2)	2.040 (2)	Co-C(4)	2.031 (2)	Co-C(6)	2.042 (2)
Distances in the Cyclopentadienyl Ring					
C(1)-C(2)	1.387 (4)	C(3)-C'(3)	1.389 (7)	C(2)-H(2)	0.88 (3)
C(2)-C(3)	1.356 (5)	C(1)-H(1)	0.69 (7)	C(3)-H(3)	0.87 (3)
Distances in the Diborolenyl Ring					
C(4)-B(5)	1.632 (2)	C(4)-H(4)	0.83 (4)	C(9)-H(11)	0.95 (3)
C(4)-C(7)	1.514 (4)	C(7)-H(5)	0.95 (3)	C(10)-H(12)	1.00 (3)
B(5)-C(6)	1.537 (3)	C(7)-H(6)	0.91 (4)	C(10)-H(13)	0.99 (3)
B(5)-C(8)	1.582 (3)	C(8)-H(7)	0.90 (2)	C(11)-H(14)	0.98 (3)
C(6)-C(6')	1.441 (3)	C(8)-H(8)	0.95 (3)	C(11)-H(15)	0.91 (4)
C(6)-C(10)	1.541 (3)	C(9)-H(9)	0.97 (4)	C(11)-H(16)	1.01 (4)
C(8)-C(9)	1.513 (3)	C(9)-H(10)	1.00 (4)	B(5)-H(4)	1.70 (5)
C(10)-C(11)	1.515 (4)				
Angles around Cobalt					
C(1)-Co-C(4)	175.1 (2)	C(3)-Co-C(6)	175.5 (2)	C(2)-Co-B(5)	173.5 (2)
Angles in the Cyclopentadienyl Ring					
C(2)-C(1)-C(2)'	107.5 (6)	C(1)-C(2)-H(2)	132 (2)	C(2)-C(3)-H(3)	127 (2)
C(2)-C(1)-H(1)	126 (3)	C(3)-C(2)-H(2)	120 (2)	C(3)-C(3)-H(3)	125 (2)
C(1)-C(2)-C(3)	108.0 (4)	C(2)-C(3)-C(3)'	108.2 (6)		
Angles in the Diborolenyl Ring					
B(5)-C(4)-B(5)'	107.3 (3)	C(4)-B(5)-C(6)	103.6 (1)	B(5)-C(6)-C(10)	123.8 (2)
B(5)-C(4)-C(7)	126.0 (1)	C(4)-B(5)-C(8)	125.9 (2)	C(6)-C(6)-C(10)	123.2 (3)
B(5)-C(4)-H(4)	80 (2)	C(6)-B(5)-C(8)	130.5 (2)	B(5)-C(8)-C(9)	113.3 (2)
C(7)-C(4)-H(4)	115 (3)	B(5)-C(6)-C(6)'	112.7 (2)	C(6)-C(10)-C(11)	111.7 (2)

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<sup>35</sup> of an X-ray structure analysis of an analogous complex, where (C<sub>5</sub>H<sub>5</sub>)Co is substituted by the isolobal toluene-iron fragment, (CH<sub>3</sub>C<sub>6</sub>H<sub>5</sub>)Fe, show that the geometry is similar to that of **4a**. For the hydrogen bound to the ring carbon two positions are found, which are almost identical with the disordered positions in the Co sandwich complex **4a** but not related by a symmetry operation. However, the C-H-B bridges and the corresponding C-B bonds in this Fe sandwich complex are different (C-B = 1.64, C-H =

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<sup>36</sup> as well as a recently developed improved INDO variant for transition-metal compounds of the 3d

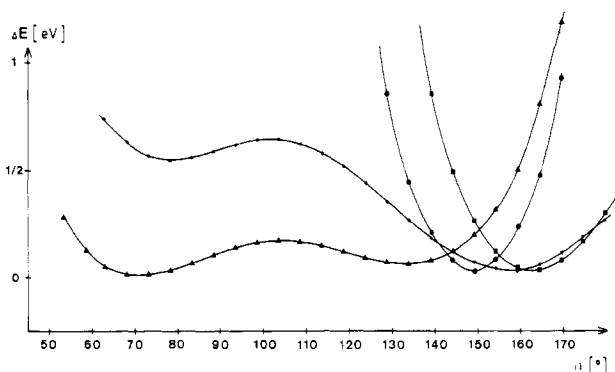
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Table V. Mean Planes through the Rings

Plane 1: C(1), C(2), C(3), C(3)', C(2)'					
5.3330x + 10.2026z = 6.4055					
Distances from the Plane					
C(1)	0.009	H(1)	0.089		
C(2)	-0.007	H(2)	0.030		
C(3)	0.003	H(3)	0.054		
Co	1.665				
Plane 2: C(4), B(5), C(6), C(6)', B(5)'					
5.2578x + 10.2731z = 9.6162					
Distances from the Plane					
C(4)	0.013	C(7)	-0.148	H(4)	0.80
B(5)	-0.011	C(8)	0.012		
C(6)	0.004	C(10)	-0.123		
Co	1.560				

The Angle between the Planes: 0.57°

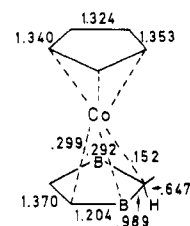


**Figure 3.** Schematic representation at the EH profiles of **4a**, **4b**, **4c**, and **4f**, respectively, as a function of  $\alpha$  which is the angle between the mean molecular plane of the 1,3-diborolene ring and the syn C-R' (R' = CH<sub>3</sub> in **4a**, H in **4b**, H in **4f**, and CH<sub>3</sub> in **4c**) bond.  $\Delta E$  is given in electronvolts. We have always used the energy minimum at **4a-d** as the internal standard in the  $\Delta E(\alpha)$  curves: ■, **4a**; △, **4b**; ▲, **4f**; ●, **4c**.

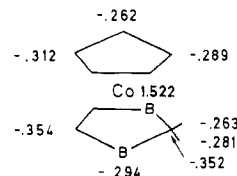
series.<sup>37</sup> In the calculations we have employed the geometrical X-ray parameters of **4a**. The diagonal elements for the EH approach have been adopted from ref 38.

We have displayed the EH energy profiles of **4a-c,f** in Figure 3;  $\alpha$  is the angle between the 1,3-diborolene ligand plane and the C-R' bond (R' = CH<sub>3</sub> in **4a**, CH<sub>3</sub> 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  $\Delta E(\alpha)$  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 CHCH<sub>3</sub> 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  $\Delta E(\alpha)$  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  $\alpha$ . This is explicitly seen in the overlap populations (CoC\*, CoC<sub>Me</sub>) that have been calculated for **4a** in the EH approximation.  $\Delta\alpha$  is the displacement from the equilibrium geometry which is char-



**Figure 4.** Wiberg bond indices in **1a** according to the semiempirical INDO method.



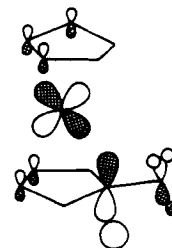
**Figure 5.** Net charges in **4a** according to the semiempirical INDO method.

acterized by an angle,  $\alpha$ , of 171.6° ( $\Delta\alpha$  (deg), overlap populations for CoC\* and CoC<sub>Me</sub>): 40, 0.036 and -0.078; 30, 0.084 and -0.055; 20, 0.119 and -0.039; 10, 0.144 and -0.029; 0, 0.162 and -0.021; -10, 0.173 and -0.015; -20, 0.177 and -0.011; ( $\Delta\alpha > 0 \rightarrow \alpha < \alpha_{\text{exptl}}$ ;  $\Delta\alpha < 0 \rightarrow \alpha > \alpha_{\text{exptl}}$ ).

EH calculations on a C...H...B-bridged structure (Figure 1D) for **4b** predict an energy difference of 0.39 eV with respect to the absolute minimum. In spite of the fact that these EH calculations were performed without any geometry optimization, the energy difference is not so large that the isomeric structure D should be discounted as a reasonable alternative.

The equilibrium geometry of **4a** has been studied by means of the INDO method. Wiberg bond indices<sup>39</sup> are displayed in Figure 4. It is immediately seen that there is a remarkable bonding interaction between the 3d center and the C\* atom in the heterocyclic ligand. The corresponding bond index is comparable with the Wiberg indices for the various Co-cyclopentadienyl bonds. The CH bond in the CH(CH<sub>3</sub>) moiety of **4a** is rather weak (0.647) and amounts only to two-thirds bonding parameters of the other CH bonds encountered in **4a** (averaged CH indices in the C<sub>5</sub>H<sub>5</sub> unit = 0.957; averaged CH indices in the CH<sub>3</sub> groups = 0.977). A simplified VB description of **4a** might be given by the two resonance structures: CpCo[(EtC)<sub>2</sub>(BET)<sub>2</sub>CHCH<sub>3</sub>] ↔ CpCo[(EtC)<sub>2</sub>(BET)<sub>2</sub>CCH<sub>3</sub>]-H<sup>+</sup>. The INDO net charges<sup>37</sup> (Figure 5) indicate a significant charge deficit at the H center in the CH(CH<sub>3</sub>) moiety ( $q = +0.281$ ). The transition-metal atom is made strongly positive, while a surplus of charge is found in the heterocycle ( $q_{\text{C}_2\text{B}_2\text{C}} = -1.02$ ) as well as in the C<sub>5</sub>H<sub>5</sub> ligand ( $q = -0.52$ ).

Both the INDO and the EH methods predict at the equilibrium geometry a frontier orbital with a pronounced localization at CoC\*H (three-center bond). A schematic display for this three-center combination is shown.

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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<sub>3</sub> 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  $\Delta\alpha$  in **4a** is additionally prevented due to antibonding four-electron interactions between the 3d<sub>z<sup>2</sup></sub> orbital of the central atom and a  $\sigma$  linear combination of the CH<sub>3</sub> 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 3d<sub>z<sup>2</sup></sub>/3d<sub>yz</sub> linear combination at the metal side and by C\*, B, and H contributions from the remaining atoms. It should be mentioned that both types of multicenter interactions are topologically closely related due to the fact that Co and H are coupled via fragment orbitals of the hetero ligand.

### Conclusion

From experimental and theoretical results we conclude that the 1,3-diborolene functions as a four-electron ligand in the sandwich complex **4**, in which a pentacoordinated carbon is present. This results in a weakening of the "axial" C-H bond of the endo cyclic methylene group HC\*R'. We anticipate that an enhancement of the reactivity of aliphatic C-H bonds in boron compounds will occur not only toward the d<sup>8</sup> fragments (C<sub>5</sub>H<sub>5</sub>)Co, (C<sub>6</sub>-H<sub>6</sub>)Fe, and (CO)<sub>3</sub>Fe but also toward other d<sup>n</sup> transition-metal species.

### 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/benzophenone ketyl, and kept under nitrogen. Column chromatography was carried out under nitrogen atmosphere on silica gel Woelm 100-200, which was heated 4-5 h at 150-160 °C in vacuo. Melting points were determined by using a Reichert melting point apparatus (capillary method) and are uncorrected. Microanalyses were performed by the microanalysis laboratories of the Fachbereich Chemie, Universität Marburg, and of the Organisch-Chemisches Institut, Universität Heidelberg.

**Spectroscopy.** The <sup>1</sup>H and <sup>11</sup>B NMR spectra ( $\delta$ , Me<sub>4</sub>Si) were recorded on a Varian XL-100 spectrometer and the <sup>13</sup>C NMR spectra on a Varian CFT-20. The mass spectra were obtained with a Varian MAT CH7, a MAT 711, or a VEGE 700 spectrometer.

**Synthesis.** The 1,3-diborolenes **1a**<sup>40</sup> and **1b**<sup>17</sup> and (C<sub>5</sub>H<sub>5</sub>)Co(C<sub>2</sub>H<sub>4</sub>)<sub>2</sub><sup>20</sup> were synthesized via published procedures.

( $\eta^5$ -Cyclopentadienyl)cobalt  $\eta^5$ -1,3,4,5-Tetraethyl-1-methyl-1,3-diborolene (**4a**). (C<sub>5</sub>H<sub>5</sub>)Co(C<sub>2</sub>H<sub>4</sub>)<sub>2</sub> (4.8 g, 26.5 mmol) was dissolved in petroleum ether (40 mL), and **1a** (3.9 g, 20.5 mmol) was added. Evolution of ethene occurred. The reaction mixture was heated for 3 h at 40-50 °C and stirred for 12 h at 20 °C. The reaction products were chromatographed on silica gel with petroleum ether yielding **4a** (2.8 g, 45%; mp 91 °C (from toluene); bp 80 °C (0.01 torr)) and the olive-green triple-decker complex **5a** (30 mg). Mass spectrum:  $m/z$  (relative intensity) 314 (M<sup>+</sup>, 46%). Anal. Calcd for C<sub>17</sub>H<sub>29</sub>B<sub>2</sub>Co (313.8): C, 65.03; H, 9.12. Found: C, 64.35; H, 9.12.

( $\eta^5$ -Cyclopentadienyl)cobalt  $\eta^5$ -4,5-Diethyl-1,3-dimethyl-1,3-diborolene **4b**. The reaction and workup procedure were carried out as for **4a**. **1b** (0.3 g, 20 mmol) and (C<sub>5</sub>H<sub>5</sub>)Co(C<sub>2</sub>H<sub>4</sub>)<sub>2</sub> (0.36 g, 2.0 mmol) in 20 mL of petroleum ether (40/60) yielded 0.44 g (80%) of **4b** (mp 88-90 °C) and small amounts (<5%) of **5b** and **8b** (M = Co).<sup>29</sup> Mass spectrum:  $m/z$  (relative intensity) 272 (M<sup>+</sup>, 100%). Anal. Calcd for C<sub>14</sub>H<sub>23</sub>B<sub>2</sub>Co (271.9): C, 61.84; H, 8.52. Found: C, 61.21, H, 8.07.

**Reaction of the Anion 4<sup>-</sup> with CH<sub>3</sub>I.** A potassium mirror (78 mg, 2.0 mmol) was generated, and **4a** (0.60 g, 1.91 mmol) in 20 mL of THF was added. Within 0.5 h the color of the solution changed from orange to yellow-brown. After the solution was stirred for 2 h at 20 °C, methyl iodide (284 mg, 2.0 mmol) in 5 mL of THF was added. Within 2 h the color changed to violet and a white solid (KI) precipitated. The solvent was evaporated in vacuo. The residue was dissolved in petroleum ether and the filtrate was chromatographed on silica gel. The first, violet fraction contained 520 mg (80%) of **4c**, a waxlike product which did not yield crystals. It decomposed slowly at 25 °C, rapidly at 80 °C to partially yield **4a**. Mass spectrum of **4c**:  $m/z$  (relative intensity) 328 (M<sup>+</sup>, 91%). Anal. Calcd for C<sub>18</sub>H<sub>31</sub>B<sub>2</sub>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<sub>3</sub>I was used. To the sandwich anion obtained from **4b** (272 mg, 1 mmol) and potassium (39 mg, 1 mmol) was added 1.4 g (10 mmol) of methyl iodide in 10 mL of THF. Chromatographic workup of the brown reaction mixture yielded violet **4e** (65 mg, 22%), red **4d** (130 mg, 45%), and a third, unidentified fraction (20 mg). **4e** was identified by its <sup>1</sup>H NMR and mass spectra ( $m/z$  300 (M<sup>+</sup>, 47%). **4d** was deprotonated with potassium. The resulting sandwich anion **4d<sup>-</sup>** was reacted with an excess of CH<sub>3</sub>I to give violet **4e** (~75% yield), a waxlike material. A satisfactory analysis of **4e** could not be obtained.

**Reaction of 4<sup>-</sup> with (CH<sub>3</sub>)<sub>3</sub>SiCl and (C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>BCl.** To a solution of **4a<sup>-</sup>**, obtained from 0.60 g of **4a** (1.91 mmol) and 78 mg of potassium (2.0 mmol) in 10 mL of THF, was added 208 mg (2.0 mmol) of (CH<sub>3</sub>)<sub>3</sub>SiCl. After the solution was stirred for 3 h, 130 mg of KCl (85%) and 0.50 g of **4a** (85%) were isolated. The anion **4a<sup>-</sup>**, obtained from **4a** (270 mg, 0.86 mmol) and potassium (39 mg, 1.0 mmol), was reacted with 94.5 mg (0.9 mmol) of (C<sub>2</sub>-H<sub>5</sub>)<sub>2</sub>BCl to give 60 mg of KCl (90%) and 130 mg of **4a** (50%).

**Deuteration of 4a.** A solution of **4a<sup>-</sup>** in THF, obtained from **4a** (560 mg, 1.78 mmol) and potassium (75 mg, 1.92 mmol), was treated with an excess of dry DCl gas to yield 0.50 g of deuterated **4a** (90%), which contained <5% of nondeuterated **4a**. In the IR spectra of **4a** and deuterated **4a** (R'' = <sup>2</sup>H)  $\nu$ (C-H) and  $\nu$ (C-D) for the axial hydrogen and deuterium, respectively, could not be identified. **4b** shows a broad band (weak) near 2600 cm<sup>-1</sup>, which is tentatively assigned to  $\nu$ (C-H).

**Preparation of the "CoMn" Triple-Decker Complex 9b.** A solution of **4b** (210 mg, 0.77 mmol) and Mn<sub>2</sub>(CO)<sub>10</sub> (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; <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, Me<sub>4</sub>Si)  $\delta$  3.78 (s, 5), 2.35 (m, 2), 2.23 (s, 1), 2.05 (m, 2), 1.32 (s, 3), 1.26 (t, 3); <sup>11</sup>B NMR (C<sub>6</sub>D<sub>6</sub>, (C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>O-BF<sub>3</sub>)  $\delta$  18.3. IR spectrum (C<sub>2</sub>Cl<sub>4</sub>)  $\nu$ (CO) 2028, 1936, 1925 cm<sup>-1</sup>; mass spectrum,  $m/z$  (relative intensity) 410 (M<sup>+</sup>, 6), 354 ([M - 2CO]<sup>+</sup>, 5), 326 ([M - 3CO]<sup>+</sup>, 100%). Anal. Calcd for C<sub>17</sub>H<sub>22</sub>B<sub>2</sub>CoMnO<sub>3</sub> (409.8): C, 49.82; H, 5.41. Found: C, 49.93; H, 5.41.

**Preparation of the "CoMnCo" Tetradecker Complex 10a.** A solution of **4a** (630 mg, 2.32 mmol) in 30 mL of THF was stirred for 5 h over a potassium mirror (120 mg, 3.07 mmol) at room temperature. To the filtered solution was added solid MnBr<sub>2</sub>·DME (380 mg, 1.25 mmol). The reaction mixture was stirred for 2 h. After removal of the solvent the residue was extracted several times with petroleum ether, from which at -30 °C blue, air-sensitive **10a** (450 mg, 65%) was obtained (mp 210 °C dec): <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, Me<sub>4</sub>Si)  $\delta$  50, 22, -6, -18, -25; mass spectrum,  $m/z$  (relative intensity) 597 (M<sup>+</sup>, 100%). Anal. Calcd for C<sub>28</sub>H<sub>44</sub>B<sub>4</sub>Co<sub>2</sub>Mn (596.7): C, 56.36; H, 7.43. Found: C, 56.18; H, 7.30.

**Collection of Diffraction Data and Solution of Structure.** The substance can be handled in the air, but after some time it is hydrolyzed. Therefore the crystals were sealed in capillaries. Lattice parameters were refined with 17 indexed lines of a Guinier film (Cu K $\alpha$  radiation, 1.54051 Å, quartz monochromator, calibration substance Pb(NO<sub>3</sub>)<sub>2</sub>,  $a = 7.856$  (1) Å). Intensity data were collected with a STOE Weissenberg diffractometer (Mo K $\alpha$  radiation, 0.7107 Å, graphite monochromator). Reflections were measured by an  $\omega$  scan with a scan rate of 1.2° min<sup>-1</sup>, with background measurements for 10 s on both sides of the scan, and with varying scan ranges, 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,  $\mu$  is the equiinclination angle, and  $A$  and  $B$  are constants with values around 1.6–2.0°, respectively, 0.5–0.6° in this case). The crystal had the dimensions 0.78 × 0.16 × 0.36 mm, and the rotation axis coincided with the  $a$  axis. A total of 2698 unique reflections of the layers  $0kl$ – $12kl$  up to  $\theta_{\max} = 30^\circ$  were measured. For 508 reflections  $\sigma_I$  was greater than the intensity  $I$  ( $\sigma_I$  was estimated from counting statistics and a relative term, 0.03 $I$ ). These reflections were given the weight  $w = 0$  and were not included in the refinement. The intensities were corrected for absorption ( $T_{\min} = 0.71$ ;  $T_{\max} = 0.85$ ).

**Crystal Data:**  $(C_5H_5)Co[(C_2H_5C)_2(C_2H_5B)_2CHCH_3]$ ;  $M_r = 313.97$ ; orthorhombic, space group  $Pnma$ ;  $a = 9.257$  (3) Å,  $b = 15.254$  (4) Å,  $c = 12.478$  (3) Å,  $V = 1762.0$  Å<sup>3</sup>;  $\rho_{\text{calcd}} = 1.183$  g cm<sup>-3</sup>;  $\mu(\text{Mo K}\alpha) = 9.59$  cm<sup>-1</sup>.

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  $M\cdots H-C$  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 Co. 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.<sup>41</sup>

Refinement with all atoms (hydrogen isotropic) gave  $R = 0.044$  and  $R_w = 0.040$  ( $w$  was set equal  $\sigma_I^{-2}$ ) for the observed reflections. A difference Fourier synthesis showed no significant peaks. In space group  $Pnma$  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  $y = 0.220$  (2) (instead of  $y = 0.25$  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  $Pn2_1a$  the molecule does not lie on a mirror plane. But refinement in this space group converged slowly, and the  $C_5H_5$  ring had to be refined as a rigid group ( $C-C = 1.385$  Å). Otherwise, the ring became very distorted. The hydrogen atom H(4) came to lie near  $y = 0.25$ . In spite of the greater number of parameters in  $Pn2_1a$  the  $R$  value did not improve.

For the present structure determination the space group  $Pnma$  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 Mann<sup>42</sup> and for H by Cromer<sup>43</sup> were used. The programs of the SHELX 76 system<sup>44</sup> were used.

Table III contains the final positional and thermal parameters for the refinement in  $Pnma$ . 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<sup>-</sup>, 82090-74-2; 4aD, 87261-54-9; 4b, 87261-49-2; 4b<sup>-</sup>, 81780-50-9; 4c, 87261-50-5; 4d, 87261-51-6; 4d<sup>-</sup>, 87261-53-8; 4e, 87261-52-7; 5b, 82196-39-2; 8b, 87281-29-6; 9b, 87261-55-0; 10a, 81987-35-1;  $(C_5H_5)Co(C_2H_4)_2$ , 69393-67-5;  $CH_3I$ , 74-88-4;  $(CH_3)_3SiCl$ , 75-77-4;  $(C_2H_5)_2BCl$ , 5314-83-0;  $DCl$ , 7698-05-7;  $Mn_2(CO)_{10}$ , 10170-69-1;  $MnBr_2 \cdot DME$ , 57539-30-7.

**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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