Synthesis and Properties of 1,4-Diboracyclohexene-2 Derivatives


Anorganisch-Chemisches Institut der Universität Im Neuenheimer Feld 270, D-6900 Heidelberg, FRG

Department of Chemistry, Keimyung University, Daegu 704-701, Korea

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Abstract. Two synthetic routes for the 1,4-diboracyclohexene-2 ring 8 have been developed. Method i) starts with 1,2-bis(dichloroaluminy)ethane, in which the AlCl₂ group is replaced by BCl₂. Exchange of the chlorine with B₂Cl₂ in 1,2-bis-(dichloroboryl)ethane yields the corresponding iodo compound, which reacts with the alkynes to heterocycles 8a, b in good yield. In method ii) B₂Cl₂ is added to alkynes, replacement of chlorine with B₂Cl₂ yields the bis(diiiodoboryl)ethane derivatives which undergo redox reactions with alkynes to give 8c, d. The diiodo derivative 8a forms the pyridine adduct 9a, and reacts with ether to give the ethoxy derivative 8f. 8a-d react with AlMe₃ to yield the corresponding dimethyl derivatives 8g-j, which give unstable radical anions when treated with potassium in THF. The ESR parameters are reported.

In electrochemical experiments irreversible reductions of 8g-j are observed. 8g-j react with (C₅H₅)Co(C₂H₄) to give the intermediate 16 VE complexes (C₅H₅)Co(8), in which C-H activation occurs with formation of the corresponding red 1,4-diboracyclohexadiene complexes 10. The X-ray structure analyses of 10h and 10j are reported.
INTRODUCTION

Heterocycles with the diboraethene group play an important role in organoborin chemistry. The compounds 1', 2', 3', 4', 5 and 6 are derived formally from cyclobutadiene, cyclopentadiene, thiophene, pyrrole, phosphole and benzene by replacing two carbon for boron atoms. The 1,4-diboracyclohexadiene 6a was first synthetized by Timms1; Herberich et al.2 isolated the compounds 6b, c with electron-donating groups at the boron atoms. However, alkyl compounds (R3 = CH3) and hydrogen derivatives (6d) are unstable because of the electron-deficiency at the boron atoms; they rearrange to give nido-tetracarbaboranes (7). Recently we synthesized the 1,2,3,4-tetramethyl-1,4-diboracyclohexene (8g)3 which is stable up to 150 °C. Here we report the preparation and properties of other derivatives, of which some are used as precursors for 6.

![Chemical structures](image)

RESULTS AND DISCUSSION

Syntheses and Properties. We have developed two syntheses for 1,4-dibora-2-cyclohexene derivatives4, 5. In the method i) the 1,2-bis (dichloraluminylo) ethane is reacted with liquid BCl3 to give 1,2-bis (dichloroboryl) ethane, in which the chlorine is exchanged for iodine by means of Bi3. Reactions of 1,2-bis (diiodoboryl) ethane with alkynes C2(R)2 in n-hexane lead via iodoboration of the alkynes to unstable addition products; at −30 °C elimination of iodine occurs with formation of the heterocycle (8a, b) in 60–80% yield. In method ii) addition of BiCl4 to alkenes leads to 1,2-bis (dichloroboryl) ethane derivatives(5), which are then transformed into the heterocycles 8c, d in the same manner as in the case of method i).

![Scheme 1](image)

The iodoboryl groups in 8a act as an acceptor for Lewis bases such as pyridine. Addition of two moles of pyridine yields compound 9a, in which both boron atoms are sp3 hybridized, as documented by 11B-NMR (δ = 19.6). From the spectroscopic data one cannot decide whether the pyridine donors occupy the same or opposite side of the ring. Despite the fact that in 9a both boron atom are four-coordinated, 9a is quite sensitive to air. It is hardly soluble in benzene, chloroform, and carbon disulfide. In methylenechloride decomposition occurs.

![Chemical structures](image)

The iodine atoms of 8a–d are easily substituted by other groups. Thus the addition product of 8a...
and Et₂O is unstable and cleavage of the O–C bond occurs with the formation of the alkoxy derivative 8a and EtII. Analogous to the ethoxylation the amination of 8a is carried out via nucleophilic substitution of iodine by amino groups. Reaction of 8a with trimethylsilyldimethylamine results in the formation of 8f in good yield. The complete methylation of 8a–d with trimethylaluminium occurs at -50 °C to give 8g–j and AlH₃.

<table>
<thead>
<tr>
<th></th>
<th>R¹</th>
<th>R²</th>
<th>R³</th>
</tr>
</thead>
<tbody>
<tr>
<td>8</td>
<td>Me</td>
<td>Me</td>
<td>H</td>
</tr>
<tr>
<td>h</td>
<td>Et</td>
<td>Me</td>
<td>H</td>
</tr>
<tr>
<td>i</td>
<td>Me</td>
<td>Me</td>
<td>Me</td>
</tr>
<tr>
<td>j</td>
<td>Et</td>
<td>Me</td>
<td>Me</td>
</tr>
<tr>
<td>u</td>
<td>Me</td>
<td>NMe₂</td>
<td>H</td>
</tr>
</tbody>
</table>

Rearrangement of 8g. The boron alkyl derivatives of 6 easily rearrange to give carborane of the type 7. If 8g–j would loose hydrogen on heating, we expect the formation of carboranes, too. However, 1,2,3,4-tetramethyl-1,4-dibora-2-cy-dohexene 8g rearranges to 1,2,3,4,5-pentamethyl-2-hydro-1,3-diborole 2a on heating to 160 °C in toluene. This ring contraction has been monitored by ¹H-NMR technique. The rate constant, and activation energy, ΔG* have been reported to be (1.2±0.2) 10⁻⁴ s⁻¹, 139.7±0.5 kJ/mol respectively.¹⁰ The rearrangement may be explained by a dehydroboration/ring opening and a hydroboration/ring closure, mechanism.

ESR and Electrochemistry of Alkyl Derivatives of 8. Compound 8h reacts with an excess of potassium mirror in THF at -60 °C and a red solution is formed.¹¹ Addition of CH₃I in THF to reduce 8h at 20 °C results in colorless solutions from which presumably a mixture of stereoisomers of 8j is obtained. Reductions of 8g–j with potassium yield orange to brown solutions of radicals, which are very unstable at 20 °C. ESR spectra are acquired at -60 °C. The ESR spectra of 8g (Fig. 1) and 8h, i, j gave ESR parameters shown in Table 1. From the data we conclude that the rings are not destroyed upon reduction. The instability of the radical anion is the reason for the irreversible reduction of 8g–i in the electrochemical experiments. The compounds exhibit a large range of existence (Table 2). The irreversible reductions show a more consistent picture than the also irreversible oxidations. Methyl groups at the ring positions 2 and 3 facilitate reduction (by 0.7 and 0.8 V), methyl at the position 5 and 6 increases the reduction potential (by -0.55 and 0.45 V) when one compares the pairs 8g/h, 8i/j, 8g/i, and 8h/j.

Fig. 1. X-Bond ESR-spectrum of the radical anion of 8g in THF at -60°C. The anion is formed by contact with a potassium mirror A: Experimental spectrum.

Fig. 1. B: Simulated spectrum, data see Table 1.
Formation of Complex\textsuperscript{11}. The compounds 8g-j react as ligands with organometal complex fragments to give sandwich (10) and triple-decker complexes (11, 12). Most probably the LnM moiety complexes the heterocycle \textsuperscript{8} first in \sigma\textsuperscript{2}-fashion via the C=C double bond and the two B-R\textsuperscript{2} groups, which function as good acceptors. In this intermediate the C-H bonds of the sp\textsuperscript{3} ring carbon atoms are activated and two hydrogens are eliminated with formation of \sigma\textsuperscript{4}-complexed 1,4-diboracycloc hexadienes, which act as 4e ligands. Scheme 2.

Typical examples are the reactions of 8g-j with the Jonas reagent\textsuperscript{12} (C\textsubscript{3}H\textsubscript{3})\textsubscript{2}Co (C\textsubscript{6}H\textsubscript{6}). Via the unstable 16 valence electron (VE) complex (C\textsubscript{6}H\textsubscript{6})\textsubscript{2}Co (8) the formation of the red sandwich 10 occurs.

In addition the unusual dinuclear complex 11 is formed, in which two C\textsubscript{6}H\textsubscript{6} groups have been hydrogenated to give the C\textsubscript{6}H\textsubscript{4} ligand. The cyclopentenyl ring functions as a 3e donor to cobalt. Therefore 11 is a 28 VE complex, whereas the green triple-decker 12—obtained via stacking of the sandwich 10 with the (C\textsubscript{6}H\textsubscript{6})\textsubscript{2}Co moiety—has 32 VE.

**Spectroscopic Studies.** The chemical shifts of the \textsuperscript{1}H- and \textsuperscript{11}B-NMR spectra are shown in Table 3. The alkyl derivatives 8g-j exhibit the expected \textsuperscript{1}H- and \textsuperscript{11}B-NMR signals, the \textit{\delta}—values differ hardly. However replacing R\textsuperscript{3}=alkyl with OEt or

![Scheme 2](image)

### Table 1. ESR-Data of radical anions of 8g, h, i, j.

<table>
<thead>
<tr>
<th>11B</th>
<th>1H</th>
<th>1H</th>
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<tbody>
<tr>
<td>8</td>
<td>N&lt;sup&gt;0&lt;/sup&gt;</td>
<td>(a(1B)&lt;sup&gt;b&lt;/sup&gt; )</td>
</tr>
<tr>
<td>g</td>
<td>2</td>
<td>0.28</td>
</tr>
<tr>
<td>h</td>
<td>2</td>
<td>0.37</td>
</tr>
<tr>
<td>i</td>
<td>2</td>
<td>0.4&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
<tr>
<td>j</td>
<td>2</td>
<td>0.4&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
<tr>
<td>g = 2.0226 for all radicals</td>
<td></td>
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</tr>
</tbody>
</table>

<sup>a</sup>Number of nuclei  
<sup>b</sup>Coupling constants in mT.  
<sup>c</sup>Estimated values of the ESR simulation. The simulated spectrum is very similar to the experimental spectra. Strong superpositions prevent a complete analysis. The other parameters were precisely obtained.  
<sup>d</sup>The nuclei H<sup>1</sup> are assigned to the \(a\) positions of sp\textsuperscript{3}-carbons. H<sup>2</sup> is assigned to the \(b\) position. Proton coupling of the boron substituents is not observed.

### Table 2. Electrochemical data of 8f-i<sup>9</sup>

<table>
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<th>Solvent</th>
<th>Cond. salt</th>
<th>Reduction</th>
<th>Oxidation</th>
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<tbody>
<tr>
<td>PN</td>
<td>TBAPF\textsubscript{6}</td>
<td>-3.10</td>
<td>+1.80</td>
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<tr>
<td>PN</td>
<td>TBAPF\textsubscript{6}</td>
<td>-2.80</td>
<td>+1.22</td>
</tr>
<tr>
<td>DME</td>
<td>TBAPF\textsubscript{6}</td>
<td>-2.35</td>
<td>+1.20</td>
</tr>
<tr>
<td>PN</td>
<td>TBAPF\textsubscript{6}</td>
<td>-2.10</td>
<td>—</td>
</tr>
<tr>
<td>DME</td>
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<tr>
<td>PN</td>
<td>TBAPF\textsubscript{6}</td>
<td>-2.55</td>
<td>—</td>
</tr>
</tbody>
</table>

<sup>9</sup>All redox reactions are irreversible; PN: propionitrile, DME: dimethoxy ethane. TBA PF<sub>6</sub>: (n-Bu<sub>4</sub>)NPF<sub>6</sub>.

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Table 3. $^1$H- and $^{11}$B-NMR data$^a$ of 8

<table>
<thead>
<tr>
<th>R1</th>
<th>CH₃</th>
<th>CH₂</th>
<th>CH₂</th>
<th>CH₃</th>
<th>R²</th>
<th>H</th>
<th>CH₃</th>
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<tr>
<td>a</td>
<td>1.96(s, 6)</td>
<td>-</td>
<td>-</td>
<td>1.35(s, 4)</td>
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<td>72.5</td>
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<tr>
<td>b</td>
<td>0.86(t, 6)</td>
<td>2.41(q, 4)</td>
<td>-</td>
<td>1.41(s, 4)</td>
<td>-</td>
<td>72.7</td>
<td></td>
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<tr>
<td>c</td>
<td>1.97(t, 6)</td>
<td>-</td>
<td>1.50(q, 2)</td>
<td>1.08(d, 6)</td>
<td>74.5</td>
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<tr>
<td>d</td>
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<td>2.49(q, 4)</td>
<td>-</td>
<td>1.46(q, 2)</td>
<td>0.95(d, 6)</td>
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<td>e</td>
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<td>1.07(t, 6)</td>
<td>0.96(s, 4)</td>
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<tr>
<td>f</td>
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<td></td>
<td>2.63(s, 6)</td>
<td>1.06(s, 4)</td>
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<tr>
<td>g</td>
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<td></td>
<td>0.83(s, 6)</td>
<td>1.42(s, 4)</td>
<td>73.5</td>
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<tr>
<td>h</td>
<td>0.97(t, 6)</td>
<td>2.47(q, 4)</td>
<td>0.85(s, 6)</td>
<td>1.42(s, 4)</td>
<td>77.5</td>
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<td></td>
<td></td>
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<tr>
<td>i</td>
<td>1.87(t, 6)</td>
<td></td>
<td>0.85(s, 6)</td>
<td>1.57(q, 2)</td>
<td>0.97(d, 6)</td>
<td>76.5</td>
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<tr>
<td>j</td>
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<td>2.38(q, 4)</td>
<td>0.78(s, 6)</td>
<td>1.53(q, 2)</td>
<td>0.99(d, 6)</td>
<td>78.3</td>
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</tr>
</tbody>
</table>

$^a$in ppm C₆D₆, 25°C *R² = OEt, NMe₂, CH₃

Fig. 2. Molecular structure of 10h.

NMe₂ causes a considerable upfield shift in the $^{11}$B-NMR spectra because of the donor qualities of OEt and NMe₂, the latter forming a strong (B=N) σ bond. This effect has been studied in several ring compounds. The $^{13}$C-NMR signals of the carbon atoms bonded to boron are broad as usual due to rapid relaxation; upon cooling these $^{13}$C lines sharpen and can be observed easily. 8h exhibits three broad signals ([165 (C, sp²), 25.7 (t, CH₂), 11.3 (q, CH₃)]. A triplet (24.35) and a quartet (15.30) are observed for R¹ = Et.

X-ray Structure Analyses. Two modifications were found for the sandwich 10h: modification 1: P2₁/c with a = 10.499 (7), b = 9.580 (14), c = 15.350 (14) Å, $\beta = 102.66$ (6)°, $V = 1506$Å³ and Z = 4. Modification 2: P1, a = 8.902 (5), b = 12.239 (6), c = 15.067 (9) Å, $\alpha = 90.73$ (4), $\beta = 80.59$ (5), $\gamma = 72.54$ (4)°, $V = 1542$Å³, Z = 4. (Two independent molecules in the cell). (Fig. 2, 3).

Mod. 1 was refined with 1858 unique reflection $R = 0.055$, $R_w = 0.045$ (179 parameters). Mod. 2: 3805 reflections, $R = 0.36$, $R_w = 0.029$ (496 parameters). In modification 1 the C₆H₅ ring is disordered and was refined by two rigid C₆H₅ rings. The geometry of the three independent sandwich molecules is identical and agrees well with the structure of (C₆H₅)Co[C₆H₄(B-CH₂)₂]₁. The C₂B₂ ring is non-planar, the two boron atoms are

Fig. 3. Molecular structure of 10j.
shifted 0.1 Å out of the C₄ plane away from the Co atom. The distances Co/ring plane are 1.50–1.51 Å (C₄ plane) and 1.63–1.67 Å (Cp-plane). The sandwich 10j crystallizes in the space group Pbnm with the cell parameters a = 9.328 (6), b = 11.924 (4), c = 15.318 (7) Å, V = 1704 Å³, Z = 4. The structure was refined with 874 unique reflections R = 0.080, R_w = 0.078 (109 parameters). The molecule has a crystallographic mirror plane perpendicular to the ring through the midpoint of the C–C bonds and the cobalt atom. The geometry of the sandwich 10j is in agreement with those of 10h, but the accuracy of the structure determination is worse than for the two modifications of 10h due to the crystal quality.

**EXPERIMENTAL SECTION**

All reactions and manipulations were carried out under an atmosphere of purified and dried nitrogen or argon by using Schlenk-type glassware. The solvents for preparative use were dried by standard methods, distilled from potassium/benzenephone ketyl, and kept under nitrogen. Microanalyses were performed by the microanalysis laboratory of the Chemische Institute der Universität Heidelberg. Spectral measurements: ¹H-NMR (δ, Me₂Si), Bruker AC 200, Bruker WH 200, and Bruker WX 360; ¹¹B-NMR (δ, BF₃·OEt₃), Jeol FX–90Q, Bruker AC 200; X-band ESR, Varian E3, standard LiTCNQ; MS MAT CH7 (EI). Electrochemical equipment: Princeton Applied Research (PAR) Model 173 potentiostat, Model 179 digital coulometer, Model 175 function generator; Methrom electrochemical cell; Methrom rotating disk electrode (RDE) for cyclic voltammetry (without rotating). Electrochemical procedures were carried out as described. Starting materials: (Cl₂Al)₂C₂H₆, (Cl₂)₈C₂H₄, (I₂B)₂C₂H₄, (I₂B)₂C₂H₆, B₂Cl₄.

2,3-Bis (dichloroboryl) butane. To B₂Cl₄ (13.0g, 79.3 mmol) at 0–5 °C 2-butene (5.0g, 89.3 mmol) was slowly condensed (2h). An exothermic addition of B₂Cl₄ onto the 2-butene occurred. The product was distilled at 20 °C/0.1 torr; yield 16.0g (73 mmoles, 91.7%). ¹H-NMR (CDCl₃): δ = 1.51 (d, 6), 5.43 (q, 2); ¹¹B-NMR (CDCl₃): δ = 64.

2,3-Bis (diododoboryl) butane. B₄ (38.0g, 97 mmol) was added to 2,3-bis (dichloroboryl) butane (16.0g, 73 mmol) and the reaction mixture was stirred for 3 h, whereby BCl₃ was formed. The volatile products were removed at 50 °C/100 torr and the residue was distilled at 70 °C/0.05 torr; yield: 27g (46 mmoles, 63.4%). ¹H-NMR (CDCl₃): δ = 0.89 (d, 6), 2.48 (q, 2); ¹¹B-NMR (CDCl₃): δ = 57.4.

1,4-Diiodo-1,4-diborocyclohexene. 8a-d. 8a: 2-Butyne (3.74g, 69.3 mmol) in 30 ml of n-pentane was slowly added to (I₂B)₂C₂H₄ (38.7g, 69.3 mmol) in 50 ml of n-pentane and heated for 1 h at reflux. Elimination of iodine occurred. The solvent was removed in vacuo and iodine sublimed off the reaction product at 80 °C/1 torr. 8a was distilled at 125 °C/1 torr, treated with mercury to remove iodine, and redistilled; yield 18g (50.3 mmoles, 72.6%) b.p. 55 °C/0.01 torr.

8b: (procedure analogues to 8a: The reaction of (I₂B)₂C₂H₄ (15.8g, 28.3 mmol) and 3-hexyne (2.32 g, 25.8 mmol) gave 8b (8.87g, 23 mmol, 81.2%, b.p. 123 °C/0.1 torr) 8c: The reaction of 2,3-bis (diododoboryl) butane (10.0g, 17 mmol) and 2-butyne (0.92g, 17 mmol) yielded 8e (6g, 15.5 mmol, 91.0%, bp 65 °C/0.03 torr). 8d: The reaction of 2,3-bis (diododoboryl) butane and 3-hexyne (4.0g, 49 mmol) gave 8d (15.6g, 37.7 mmol, 87.6%, bp 70 °C/0.05 torr).

Pyridine Adduct 9a. Pyridine (0.9g, 11.4 mmol) in 30 ml of n-pentane was very slowly added to 8a (2.1g, 5.8 mmol). In a vigorous reaction a yellow solid was formed, which was separated and dried in vacuo. Yield: 2.48g (4.8 mmol, 86%) of
9a, m.p. 162 °C (dec). \( ^{1}B\)-NMR: \( \delta = 19.6 \) (CDCl\(_3\)).

\[ C_{15}H_{20}B_3I_3N_2 \] (515.8)

caled. C 37.26, H 3.91 I 49.21 N 5.43

found. C 38.06 H 3.99 I 49.09 N 5.41

1,4-Bis (diethoxy)-2,3-dimethyl-1,4-diboracyclohexene-2 \( (8e) \). Et\(_2\)O (0.83g, 11.2 mmol) was added to 8e (2g, 5.6 mmol) in 15 ml of \( n \)-pentane. The reaction mixture was stirred for 1 h, then solvent removed and 8e was isolated by distillation at 55°C/5 torr. Yield: 0.8g (4.1 mmol, 74%), m.p. 14°C. MS (EI): m/e (%) = 194 (\( M^+ \), 4.2), 138 (\( M^+ \)-BOEt, 0.5), 56 (BOEt\(^+\), 43), 45 (EtO\(^+\), 17.3)

1,4-Bis (dimethylamino)-2,3-dimethyl-1,4-
diboracyclohexene-2 \( (8f) \). Me\(_2\)SiNMe\(_2\) (2.58g, 22.0 mmol) in 20 ml of petroleum ether (40/60) was added to 8a (3.88g, 11.0 mmol) in 20 ml of petroleum ether at 0 °C. After 1 h at 25 °C, the volatile components were removed in vacuo and 8f distilled at 29°C/0.1 torr. Yield: 1.66g (8.6 mol%, 78.3%), m.p. 15°C. MS (EI): m/e (%) = 192 (\( M^+ \), 3.3), 137 (\( M^+ \)-B\(_2\)CMe\(_3\), 4.5), 70 (C\(_5\)H\(_9\)CMe\(_2\)z\(^+\), 10.8), 44 (NMMe\(_2^+\), 100).

1,4-Dimethyl-1,4-
diboracyclohexene \( 8g-j \).

1,2,3,4-Tetramethyl-1,4-diboracyclohexene-2 \( 8g \): AlMe\(_3\) (2.4g, 33.3 mmol) in 30 ml of \( n \)-pentane was slowly added to 8a (18g, 50.3 mmol) in 30 ml of \( n \)-pentane at -40 °C and stirred for 2 h, then 1 h at 25 °C. The solvent was removed in vacuo (50 torr) and the residue distilled at 22 °C/0.1 torr. Yield: 5g (37.3 mol%, 74.2%) of 8g: colorless liquid, flammable in air. MS (EI): m/e (%) = 134 (\( M^+ \), 17.9), 119 (\( M^+ \)-Me, 20.9), 82 (\( M^+ \)-B\(_2\)Me\(_2\), 12.8), 54 (C\(_5\)H\(_9\)BMe\(_2^+\), 45.9), 51 (MeBC\(_5\)H\(_4\)z\(^+\), 13.6), 41 (Me\(_2\)B\(_2^+\), 38.1), 27 (HBMe\(_3^+\), 41.8). 8h (analogous to 8g): The reaction of AlMe\(_3\) (1.1g, 15.3 mmol) and 8h (8.87g, 23 mmol) yielded 2.7g (16.7 mol%, 77%) of 8h, bp 35°C/0.3 torr. MS (EI): m/z (%) = 162 (\( M^+ \), 1.5), 110 (\( M^-\)-B\(_2\)Me\(_2\), 77.9), 81 (M\(^2^+\), 7.1), 69 (C\(_5\)H\(_4\)CH\(_2\)BMe\(_2^+\), 50.7), 54 (C\(_7\)H\(_5\)BMe\(_3^+\), 44.4), 41 (BMe\(_2^+\), 83.7).

8i: The reaction of AlMe\(_3\) (0.75g, 10.4 mmol) and 8e (6.0g, 18.5 mmol) yielded 1.46g (5.6 mol%, 57.9%) of 8i, bp 40°C/0.5 torr. MS (EI): m/e (%) = 162 (\( M^+ \), 0.8), 110 (\( M^-\)-B\(_2\)Me\(_2\), 56.3), 99 (\( M^-\)-BMe\(_2\), 8.1), 56 (Me\(_2\)C\(_2\)H\(_3^+\), 58.3), 54 (Me\(_2\)C\(_2^+\), 15.4), 43 (Me\(_2\)CH\(^+\), 100). 8j: The reaction of AlMe\(_3\) (1.8g, 25 mmol) and 8d (15.6g, 37.7 mmol) gave 3.6g (18.9 mmol, 50.8%) of 8j, bp 50°C/0.7 torr. MS (EI): m/e (%) = 190 (\( M^+ \), 50.9), 175 (\( M^-\)-Me, 14.7), 161 (\( M^-\)-C\(_2\)H\(_5\), 69.8), 132 (\( M^-\)-C\(_2\)H\(_5\), 7.5), 95 (Me\(_2\), 10), 80 (C\(_5\)B\(_2\)H\(_4^+\), 15.3), 67 (C\(_5\)H\(_9\)B\(_2^+\), 43), 53 (C\(_5\)H\(_9\)B\(_2^+\), 27.3), 41 (Me\(_2\)B\(_2^+\), 100).

Reduction of 8h and Formation of 8j. 0.1g of 8i in 10 ml of THF was added to 75 mg of potassium mirror at -60 °C. The solution turned yellow-brown. Excess of potassium was filtered off, and 0.275 g of CH\(_3\)I was added to the solution at -30 °C. The reaction mixture was stirred 1 h, then the solvent removed, and the residue distilled at 23°C/0.1 torr. Yield: 45 mg (35.4%) of 8j identified by NMR and MS spectra.

Electrochemical studies. The ESR spectra obtained from solutions of 8g–j/potassium at -40 °C. The reduced solutions were yellow–orange to red-brown (Exp. data in Table 2).

Rearrangement of 8g-j. 1,2,3,4-Tetramethyl-1,4-diboracyclohexene-2 \( (8g) \) on heating to 160°C in toluene rearranged to give 1,2,3,4-pentamethyl-2-hydro-1,3-diborole 2a, bp 40°C/20 torr.

( \( \eta^5 \)-Cyclopentadienyl)cobalt- \( \eta^4 \)-(2,3-dimethyl-1,4-diboracyclohexadiene) 10h: 0.40g (2.47 mmol) of 8h was added to 0.482g (2.44 mmol) C\(_5\)H\(_4\)Co(C\(_2\)H\(_4\))\(_3\) in 25 ml petroleum ether (40/60) and stirred for 48 h at 25 °C. The dark green solution was concentrated and chromatographed (SiO\(_2\), petroleum ether) to give 3 fractions: 20 mg (0.07 mmol, 3%) of orange-red sandwich 10h (mp. 126°C), 0.20g (0.49 mmole, 20%) of dark-red triple-decker 11h (mp. 156°C), and 0.22g (0.54 mmole, 22%) of...
green triple-decker sandwich 12h (mp. 203 °C).

10h: 'H- NMR (CD₂Cl₂): δ = 4.91 (s, 2), 3.92 (s, 5), 2.0 (m, 4), 1.21 (t, 6), 1.05 (s, 6); ¹¹B-NMR (CD₂Cl₂): δ = 24.1. MS (EI): m/e (%) = 284 (M⁺-18.8), 246 (M⁺-CBMe, 94.7), 232 (M⁺-BC₂H₅Me, 19.2), 217 (M⁺-BC₂EtMe, 20.8), 124 (C₃H₅Co⁺, 5.9), 41 (Me₂B⁺, 10.4), 29 (Et⁺, 7.0).

(σ-2-CyclopentadienyI) cobalt-π(2,3-diethyl-1,4,5,6-tetramethyl-1,4-diboracyclohexadiene 10j: 8j (0.80g, 4.2 mmol) and (C₅H₅)Co(C₂H₅)₂ (0.76g, 4.16 mmol) were reacted for 20 h at 25 °C. Chromatographic work-up gave the orange-red sandwich 10j (155 mg, 11.9%, mp. 126.5 °C), a violet hydride complex (135 mg, 10.3%) and the green triple-decker sandwich 12j (70 mg, 3.9%, mp. 206 °C). 10j: 'H- NMR (CD₂Cl₂): δ = 3.75 (s, 5), 2.35 (m, 4), 1.68 (s, 6), 1.19 (t, 6), 1.09 (s, 6); ¹¹B-NMR (CD₂Cl₂): δ = 24.4 MS (EI): m/e (%) = 312 (M⁺, 100), 283 (M⁺-Et, 27.4), 156 (M⁺, 6.4), 124 (C₃H₅Co⁺, 54), 65 (C₂H₅⁺, 20.8), 59 (Co⁺, 27.7), 55 (EtMeB⁺, 10.1), 41 (Me₂B⁺, 47.4). C₁₅H₁₅B₂Co (311.9)

calcd. C 65.45 H 8.72
found. C 65.96 H 8.29

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