

1,4-Dibora-2-cyclohexene 유도체들의 합성과 그 성질

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Synthesis and Properties of 1,4-Diboracyclohexene-2 Derivatives¹

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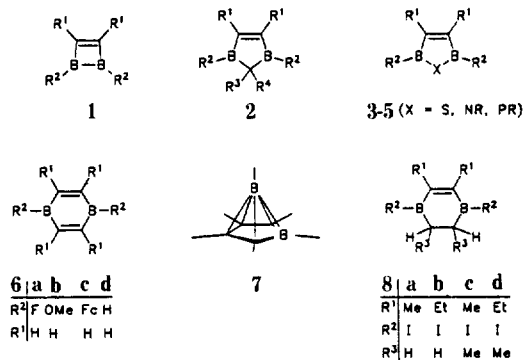
요 약. 1,4-dibora-2-cyclohexene 고리화합물 **8**을 합성하기 위한 두 가지 방법이 개발되었다. 방법 i)은 1,2-bis(dichloroaluminum)ethane을 출발물질로 하는데 이 물질은 AlCl_2 부분을 BCl_2 로 치환시켜준다. 1,2-bis(dichloroboryl)ethane에 결합된 염소를 BI_3 로 교환시켜 대응되는 요오드 화합물을 얻고 이 화합물을 alkynes와 반응시켜 헤테로고리화합물 **8a, b**를 많이 얻었다. 방법 ii)는 B_2Cl_4 를 alkynes에 부가시켜 얻어지는 염소화합물에 BI_3 를 치환시켜 bis(diiodoboryl)ethane 유도체를 얻고 이 화합물에 alkynes와 산화환원반응을 하여줌으로 **8c, d**를 얻는다. 요오드 유도체인 **8a**는 pyridine 부가물인 **9a**를 생성하고 또 ether와 반응하여 ethoxy 유도체인 **8e**를 생성시킨다. 요오드 유도체의 dimethyl amino 치환제가 **8f**이다. **8a-d**와 AlMe_3 를 반응시켜 대응되는 methyl 유도체인 **8g-j**를 얻고 이들 화합물은 THF속에서 칼륨과 반응시켜 불안정한 라디칼 음이온이 생성되고 여기서 ESR 결과가 측정된다. **8g-j**의 전기화학적 실험이 비가역적인 환원반응으로 나타났다. **8g-j** 화합물은 $(\text{C}_5\text{H}_5)\text{Co}(\text{C}_2\text{H}_4)_2$ 와 반응하여 중간체인 16개 VE(valence electron)를 갖는 착물 $(\text{C}_5\text{H}_5)\text{Co}(\mathbf{8})$ 이 얻어지는데 이 화합물은 다시 C-H 활성화에 의해 대응되는 붉은색의 1,4-diboracyclohexadiene 착물 **10**을 생성하게 된다. 착물 **10h**와 **10j**의 X-ray 구조가 결정되었다.

ABSTRACT. Two synthetic routes for the 1,4-diboracyclohexene-2 ring **8** have been developed. Method i) starts with 1,2-bis(dichloroaluminum)ethane, in which the AlCl_2 group is replaced by BCl_2 . Exchange of the chlorine with BI_3 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) B_2Cl_4 is added to alkenes, replacement of chlorine with BI_3 yields the bis(diiodoboryl)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 **8e**. **8a-d** react with AlMe_3 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 $(\text{C}_5\text{H}_5)\text{Co}(\text{C}_2\text{H}_4)_2$ to give the intermediate 16 VE complexes $(\text{C}_5\text{H}_5)\text{Co}(\mathbf{8})$, 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

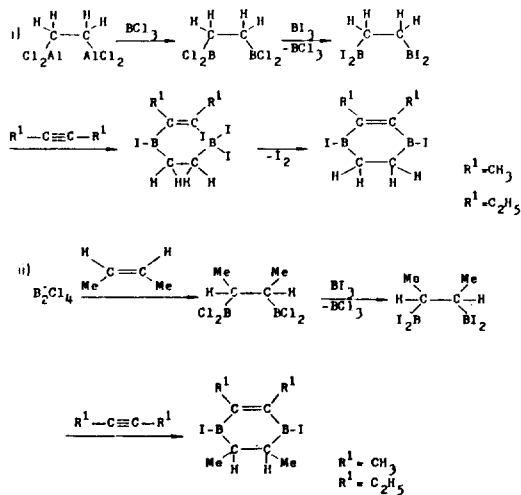
Heterocycles with the diboraethene group play an important role in organoboron chemistry. The compounds **1**², **2**³, **3**⁴, **4**⁵, **5** and **6** are derived formally from cyclobutadiene, cyclopentadiene, thiophene, pyrrole, phosphole and benzene by replacing two carbon for boron atoms. The 1,4-diboracyclohexadiene **6a** was first synthesized by Timms⁷; Herberich *et al.*⁸ isolated the compounds **6b**, **c** with electron-donating groups at the boron atoms. However, alkyl compounds ($R^2 = \text{CH}_3$) and hydrogen derivatives (**6d**) are unstable because of the electron-deficiency at the boron atoms; they rearrange to give nido-tetracarbahe-xaboranes (**7**)⁹. Recently we synthesized the 1,2,3,4-tetramethyl-1,4-diboracyclohexene (**8g**)¹⁰ 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**.



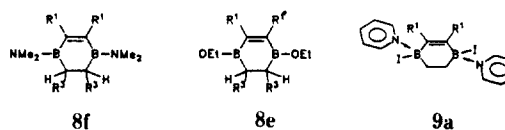
RESULTS AND DISCUSSION

Syntheses and Properties. We have developed two syntheses for 1,4-dibora-2-cyclohexene derivatives^{10, 11}. In the method i) the 1,2-bis (dichloroaluminum) ethane is reacted with liquid BCl_3 to give 1,2-bis (dichloroboryl) ethane, in which the chlorine is exchanged for iodine by means of BI_3 . Reactions of 1,2-bis (diiodoboryl) ethane with alkynes $\text{C}_2(\text{R}^1)_2$ in *n*-hexane lead via

iodoboration of the alkynes to unstable addition products; at -30°C elimination of iodine occurs with formation of the heterocycles (**8a**, **b**) in 60–80% yield. In method ii) addition of B_2Cl_4 to alkenes leads to 1,2-bis (dichloroboryl) ethane derivatives¹², which are then transformed into the heterocycles **8c**, **d** in the same manner as in the case of method i).

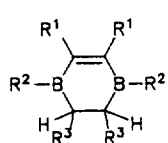


The iodoboryl groups in **8a** act as an acceptor for Lewis bases such as pyridine. Addition of two moles of pyridine yields compound **9a**, in which both boron atoms are sp^3 hybridized, as documented by ^{11}B -NMR ($\delta = 19.6$). From the spectroscopic data one cannot decide whether the pyridine 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.



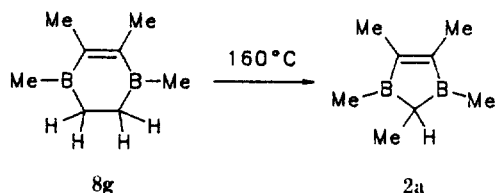
The iodine atoms of **8a–d** are easily substituted by other groups. Thus the addition product of **8a**

and Et_2O is unstable and cleavage of the O-C bond occurs with the formation of the alkoxy derivative **8e** and EtI . 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 trimethylaluminum occurs at -50°C to give **8g-j** and AlH_3 .



8	R ¹	R ²	R ³
g	Me	Me	H
h	Et	Me	H
i	Me	Me	Me
j	Et	Me	Me
f	Me	NMe ₂	H
e	Me	OEt	H

Rearrangement of 8g¹⁰. The boron alkyl derivatives of **6** easily rearrange to give carborane of the type **7**. If **8g-j** would lose hydrogen on heating, we expect the formation of carboranes, too. However, 1,2,3,4-tetramethyl-1,4-dibora-2-cyclohexene **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^\ddagger have been reported to be $(1.2 \pm 0.2) \cdot 10^{-4} \text{ s}^{-1}$ $139.7 \pm 0.5 \text{ kJ/mol}$ respectively¹⁰. The rearrangement may be explained by a dehydroboration/ring opening and a hydroboration/ring closure, mechanism¹⁰.



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 formed¹¹. Addition of CH_3I in THF to reduce **8h** at 20°C results in colorless solu-

tion 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**.

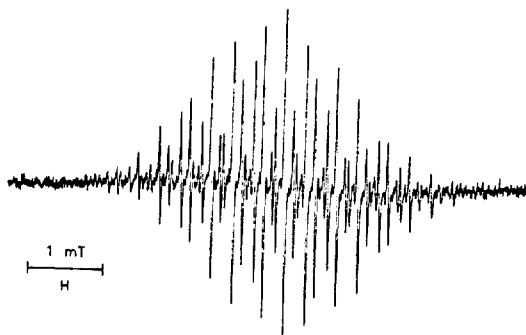


Fig. 1. X-Bond ESR-spectrum of the radical anion of **8g** in THF at -60°C . The anion is formed by contact with a potassium mirror A: Experimental spectrum.

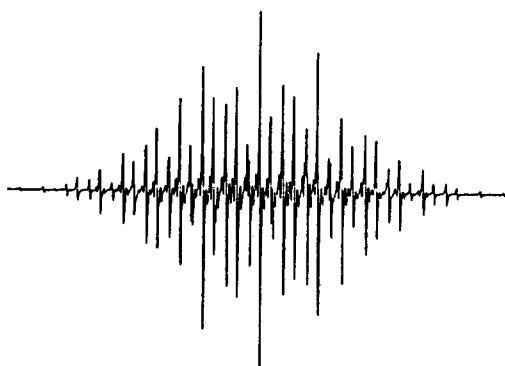


Fig. 1. B: Simulated spectrum, data see Table 1.

Formation of Complex¹¹. The compounds **8g-j** react as ligands with organometal complex fragments to give sandwich (**10**) and triple-decker complexes (**11**, **12**). Most probably the L_nM moiety complexes the heterocycle **8** first in η^4 -fashion via the C=C double bond and the two B-R² groups, which function as good acceptors. In this intermediate the C-H bonds of the sp³-ring carbon atoms are activated and two hydrogens are eliminated with formation of η^6 -complexed 1,4-diboracyclohexadienes, which act as 4e ligands. Scheme 2.

Typical examples are the reactions of **8g-j** with the Jonas reagent¹³ (C₅H₅) Co (C₂H₄). Via the unstable 16 valence electron (VE) complex (C₅H₅) Co (**8**) the formation of the red sandwich **10** occurs.

In addition the unusual dinuclear complex **11** is formed, in which two C₅H₅ groups have been hydrogenated to give the C₅H₇ 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 (C₅H₅) Co moiety—has 32 VE.

Spectroscopic Studies. The chemical shifts of the ¹H- and ¹¹B-NMR spectra are shown in Table 3. The alkyl derivatives **8g-j** exhibit the expected ¹H- and ¹¹B-NMR signals, the δ -values differ hardly. However replacing R²=alkyl with OEt or

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

	¹¹ B		¹ H		¹ H		
8	N ^{a)}	a(¹¹ B) ^{b)}	a(¹⁰ B)	N	a(H ¹)	N	a(H ²)
g	2	0.28	0.9	6	0.69	—	—
h	2	0.37	0.12	4	0.53 ^{d)}	6	0.029
i	2	0.4 ^{d)}	0.13 ^{d)}	6	0.5 ^{d)}	6	0.03 ^{d)}
j	2	0.4 ^{d)}	0.13 ^{d)}	4	0.5 ^{d)}	6	0.03 ^{d)}

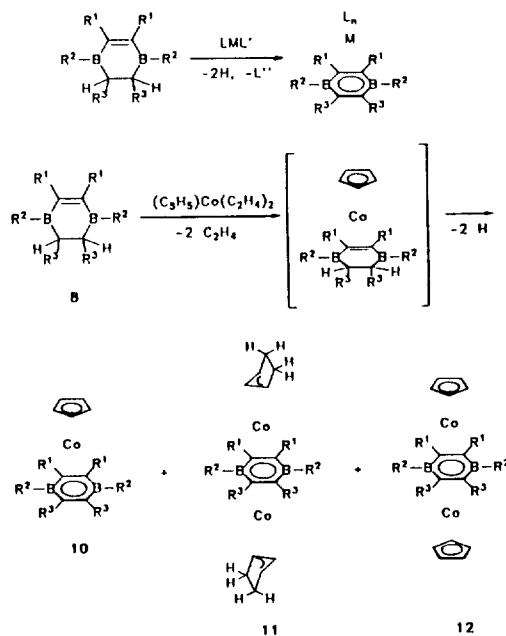
g = 2.0026 for all radicals

^{a)}Number of nuclei ^{b)}Coupling constants in mT.
^{c)}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.
^{d)}The nuclei H¹ are assigned to the α positions of sp²-carbons. H² is assigned to the β position. Proton coupling of the boron substituents is not observed.

Table 2. Electrochemical data of **8f-i**^{a)}

	c	g	h	h	i	j
Solvent	PN	PN	DME	PN	DME	PN
Cond. salt	TBAPF ₆	TBAPF ₆	TBAPF ₆	TBAPF ₆	TBAPF ₆	TBAPF ₆
Reduction	-3.10	-2.80	-2.35	-2.10	-3.35	-2.55
0/-1[V]						
Oxidation	+1.80	+1.22	+1.20	—	+1.10	—
0/+1[V]						

^{a)}All redox reactions are irreversible; PN: propionitrile, DME: dimethoxy ethane, TBA PF₆: (n-Bu)₄NPF₆.



Scheme 2.

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

8	R^1		$^*\text{R}^2$	R^3		^{11}B
	CH_3	CH_2		H	CH_3	
a	1.96(s, 6)	—	—	1.35(s, 4)	—	72.5
b	0.86(t, 6)	2.41(q, 4)	—	1.41(s, 4)	—	72.7
c	1.97(s, 6)	—	—	1.50(q, 2)	1.08(d, 6)	74.5
d	0.92(t, 6)	2.49(q, 4)	—	1.46(q, 2)	0.95(d, 6)	77.2
e	2.01(s, 6)	—	1.07(t, 6)	0.95(s, 4)	—	53.8
			3.76(8.4)			
f	1.92(s, 6)	—	2.63(s, 6)	1.06(s, 4)	—	43.0
			2.55(s, 6)			
g	1.91(s, 6)	—	0.83(s, 6)	1.42(s, 4)	—	73.5
h	0.97(t, 6)	2.47(q, 4)	0.86(s, 6)	1.42(s, 4)	—	77.5
i	1.87(s, 6)	—	0.85(s, 6)	1.57(q, 2)	0.97(d, 6)	76.5
j	0.85(t, 6)	2.38(q, 4)	0.76(s, 6)	1.53(q, 2)	0.96(d, 6)	78.3

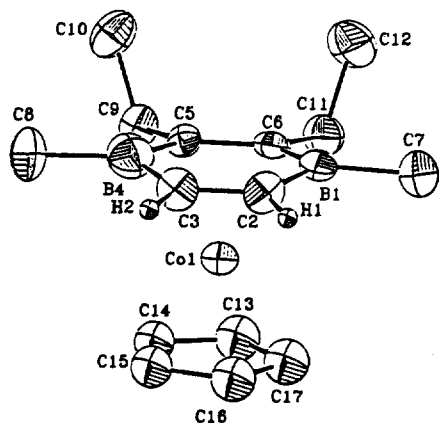
^{a)}in ppm C_6D_6 , 25°C * $\text{R}^2 = \text{OEt}$, NMe_2 , CH_3 

Fig. 2. Molecular structure of 10h.

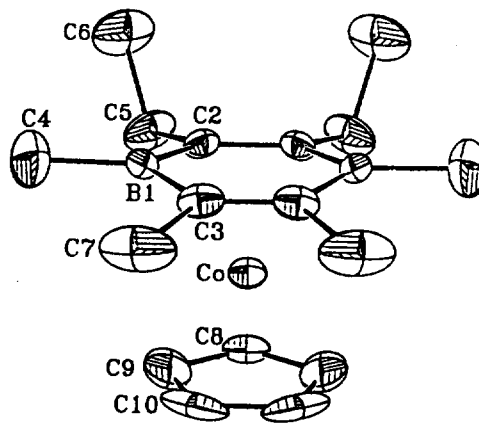


Fig. 3. Molecular structure of 10j.

NMe_2 causes a considerable upfield shift in the ^{11}B -NMR spectra because of the donor qualities of OEt and NMe_2 , the latter forming a strong ($\text{B}=\text{N}$) π 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, sp^2), 25.7 (t, CH_2), 11.3 (q, CH_3)]. A triplet (24.35) and a quartet (15.30) are observed for $\text{R}^1 = \text{Et}$.

X-ray Structure Analyses. Two modifications were found for the sandwich 10h: modification 1: $\text{P}2_1/\text{c}$ 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: $\text{P}1$, $a = 8.902$ (5), $b = 12.239$ (6), $c = 15.067$ (9) Å, $\alpha = 80.73$ (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 C_5H_5 ring is disordered and was refined by two rigid C_5H_5 rings. The geometry of the three independent sandwich molecules is identical and agrees well with the structure of $(\text{C}_5\text{H}_5)_2\text{Co}[\text{C}_4\text{H}_4(\text{B}-\text{CH}_3)_2]_2$. The C_4B_2 ring is non-planar, the two boron atoms are

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/benzophenone ketyl, and kept under nitrogen. Microanalyses were performed by the microanalysis laboratory of the *Chemische Institute der Universität Heidelberg*. Spectral measurements: ¹H-NMR (*δ*, Me₄Si), Bruker AC 200, Bruker WH 300, and Bruker WX 360; ¹¹B-NMR (*δ*, BF₃·OEt₂), 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 described¹⁴. Starting materials: (Cl₂Al)₂C₂H₄¹⁵, (Cl₂B)₂C₂H₄^{10, 11}, (I₂B)₂C₂H₄^{10, 11}, B₂Cl₄¹⁶.

2,3-Bis (dichloroboryl) butane¹⁷. To B₂Cl₄

(13.0g, 79.3 mmol) at 0–5 °C 2-butene (5.0g, 89.3 mmol) was slowly condensed (2h). An exothermal 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 (diiodoboryl) butane¹¹. BI₃ (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-diboracyclohexenes 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, 28.3 mmol) gave **8b** (8.87g, 23 mmol, 81.2%, b.p; 123 °C/0.1 torr) **8c**: The reaction of 2,3-bis (diiodoboryl) butane (10.0g, 17 mmol) and 2-butyne (0.92g, 17 mmol) yielded **8c** (6g, 15.5 mmol, 91.0%, bp 65 °C/0.03 torr). **8d**: The reaction of 2,3-bis (diiodoboryl) 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). ^{11}B -NMR: $\delta = 19.6$ ($\text{CD}_2\text{-Cl}_2$).

$\text{C}_{16}\text{H}_{20}\text{B}_2\text{I}_2\text{N}_2$ (515.8)

calcd. 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_2O (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 ($\text{M}^+ - \text{BOEt}$, 0.5), 56 (BOEt^+ , 43), 45 (EtO^+ , 17.3)

1,4-Bis (dimethylamino)-2,3-dimethyl-1,4-diboracyclohexene-2 (8f). $\text{Me}_3\text{SiNMe}_2$ (2.58g, 22.0 mmol) in 20 ml of petroleum ether (40/60) was added to **8a** (3.93 g, 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: 1.65g (8.6 mmoles, 78.3%), mp.: -15°C. MS (EI): m/e (%) = 192 (M^+ , 3.3), 137 ($\text{M}^+ - \text{B}_2\text{CNMe}_3$, 4.5), 70 ($\text{C}_2\text{H}_4\text{CMe}_2^+$, 10.8), 44 (NMe_2^+ , 100).

1,4-Dimethyl-1,4-diboracyclohexenes 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 mmol, 74.2%) of **8g**: colorless liquid, flammable in air. MS (EI): m/e (%) = 134 (M^+ , 17.9), 119 ($\text{M}^+ - \text{Me}$, 20.9), 82 ($\text{M}^+ - \text{B}_2\text{Me}_2$, 12.8), 54 ($\text{C}_4\text{H}_4\text{BMe}^+$, 45.9), 51 (MeBC_2H^+ , 13.6), 41 (Me_2B^+ , 93.1), 27 (HBMe^+ , 41.8). **8h** (analogous to **8g**): The reaction of AlMe_3 (1.1g, 15.3 mmol) and **8b** (8.87g, 23 mmol) yielded 2.7g (16.7 mmol, 77%) of **8h**, bp; 35°C/0.3 torr. MS (EI): m/z (%) = 162 (M^+ , 1.5), 110 ($\text{M}^+ - \text{B}_2\text{Me}_2$, 77.9), 81 (M^{2+} , 7.1), 69 ($\text{C}_2\text{H}_5\text{CH}_2\text{BMe}^+$, 50.7), 54

($\text{C}_2\text{H}_4\text{BMe}^+$, 44.4), 41 (BMe_2^+ , 83.7),

8i: The reaction of AlMe_3 (0.75g, 10.4 mmol) and **8c** (6.0g, 15.5 mmol) yielded 1.46g (8.6 mmol, 57.9%) of **8i**, bp; 40°C/0.5 torr. MS (EI): m/e (%) = 162 (M^+ , 0.8), 110 ($\text{M}^+ - \text{B}_2\text{Me}_2$, 56.3), 99 ($\text{M}^+ - \text{BMe}_2$, 8.1), 56 ($\text{Me}_2\text{C}_2\text{H}_2^+$, 58.3), 54 (Me_2C_2^+ , 13.4), 43 (Me_2CH^+ , 100). **8j**: The reaction of AlMe_3 (1.8g, 25 mmol) and **8d** (15.6g, 37.7 mmol) gave 3.6g (18.9 mmol, 50.3%) of **8j**, bp; 50°C/0.7 torr. MS (EI): m/e (%) = 190 (M^+ , 50.9), 175 ($\text{M}^+ - \text{Me}$, 14.7), 161 ($\text{M}^+ - \text{C}_2\text{H}_5$, 69.8), 132 ($\text{M}^+ - 2\text{C}_2\text{H}_5$, 7.5), 95 (M^{2+} , 10), 80 ($\text{C}_4\text{B}_2\text{H}_{10}^+$, 15.3), 67 ($\text{C}_4\text{H}_8\text{B}^+$, 41), 53 ($\text{C}_3\text{H}_6\text{B}^+$, 27.3), 41 (Me_2B^+ , 100).

Reduction of 8h and Formation of 8j. 0.1g of **8h** 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 0.275g of CH_3I were 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 8g¹⁰. 1,2,3,4-Tetramethyl-1,4-diboracyclohexene-2 (**8g**) on heating to 160°C in toluene rearranged to give 1,2,3,4,5-pentamethyl-2-hydro-1,3-diborole **2a**, bp.; 40°C/20 torr.

(η^5 -Cyclopentadienyl)cobalt- η^6 -(2,3-diethyl-1,4-dimethyl-1,4-diboracyclohexadiene **10h**: 0.40g (2.47 mmoles) of **8h** were added to 0.432g (2.4 mmoles) (C_5H_5)₂Co (C_2H_4)₂¹³ 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 mmoles, 3%) of orange-red sandwich **10h** (mp. 126 °C), 0.20g (0.49 mmoles, 20%) of dark-red triple-decker **11h** (mp. 156 °C), and 0.22g (0.54 mmoles, 22%) of

green triple-decker sandwich **12h** (mp. 203 °C). **10h**: ^1H -NMR (C_6D_6): δ = 4.91 (s, 2), 3.92 (s, 5), 2.0 (m, 4), 1.21 (t, 6), 1.05 (s, 6); ^{11}B -NMR (C_6D_6): δ = 24.1. MS (EI): m/e (%) = 284 (M^+ -18.8), 246 (M^+ -CBMe, 94.7), 232 (M^+ -BC₂H₂Me, 19.2), 217 (M^+ -BCEtMe, 20.8), 124 ($\text{C}_5\text{H}_5\text{Co}^+$, 5.9), 41 (Me_2B^+ , 10.4), 29 (Et^+ , 7.0).

(η^5 -Cyclopentadienyl) cobalt- η^6 -(2,3-diethyl-1,4,5,6-tetramethyl-1,4-diboracyclohexadiene **10j**: **8j** (0.80g, 4.2 mmol) and (C_5H_5) Co (C_2H_4)₂ (0.75g, 4.16 mmol) were reacted for 20 hs 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**: ^1H -NMR (C_6D_6): δ = 3.75 (s, 5), 2.35 (m, 4), 1.68 (s, 6), 1.19 (t, 6), 1.09 (s, 6); ^{11}B -NMR (C_6D_6): δ = 24.4 MS (EI): m/e (%) = 312 (M^+ , 100), 283 (M^+ -Et, 27.4), 156 (M^{2+} , 6.4), 124 ($\text{C}_5\text{H}_5\text{Co}^+$, 54), 65 (C_5H_5^+ , 20.8), 59 (Co^+ , 27.7), 55 (EtMeB^+ , 10.1), 41 (Me_2B^+ , 47.4). $\text{C}_{17}\text{H}_{27}\text{B}_2\text{Co}$ (311.9)

calcd. C 65.45 H 8.72

found. C 65.95 H 8.29

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REFERENCES

1. Redox-Reactions with Iodoboranes, XVIII, Part XVII: W. Siebert, U. Ender, and W. Herter, *Z. Naturforsch.* **40b**, 326 (1985).
2. (a) M. Hildenbrand, H. Pritzkow, and W. Siebert, *Angew. Chem.* **97**, 769 (1985); (b) *Angew. Chem. Int. Ed. Engl.* **24**, 759 (1985).
3. (a) P. Binger, *Tetrahedron Lett.* **24**, 2675 (1966); (b) *Angew. Chem.* **80**, 288 (1968); (c) *Angew. Chem. Int. Ed. Engl.* **7**, 286 (1968).
4. (a) W. Siebert, *Chemikerzeitung* **90**, 479 (1974); (b) W. Siebert, R. Full, J. Edwin, and K. Kinberger, *Chem. Ber.* **111**, 823 (1978).
5. W. Siebert, H. Schmidt, and R. Full, *Z. Naturforsch.* **35b**, 873 (1980).
6. (a) M. Driess, H. Pritzkow, and W. Siebert, *Angew. Chem.* **99**, 789 (1987); (b) *Angew. Chem. Int. Ed. Engl.* **26**, 781 (1987).
7. (a) P. L. Timms, *J. Am. Chem. Soc.* **90**, 4585 (1968); (b) P. S. Madren, A. Modinos, P. L. Timms, and P. Woodward, *J. Chem. Soc. Dalton*, 1272 (1975).
8. (a) G. E. Herberich, B. Heßner, S. Beswetherick, J. A. K. Howard and P. Woodward, *J. Organomet. Chem.* **192**, 421 (1980); (b) G. E. Herberich in G. Wilkinson, F. G. A. Stone, E. W. Abel (eds.): (c) *Comprehensive Organometallic Chemistry* vol.1, p.399, Pergamon Press, Oxford 1982.
9. R. N. Camp, D. S. Marynick, G. D. Graham, and W. N. Lipscomb, *J. Am. Chem. Soc.* **100**, 6781 (1988).
10. J. -K. Uhm, H. Remich, H. Wadepohl, and W. Siebert, *Z. Naturforsch.* **43b**, 306 (1988).
11. J. -K. Uhm, Ph. D. Dissertation, Universität Heidelberg (1987).
12. R. W. Rudolph, *J. Am. Chem. Soc.* **89**, 4216 (1967).
13. (a) K. Jonas and C. Krueger, *Angew. Chem.* **92**, 513 (1980); (b) *Angew. Chem. Int. Ed. Engl.* **19**, 520 (1980).
14. J. Zwecker, T. Kuhlmann, H. Pritzkow, W. Siebert, and U. Zenneck, *Organometallics* **7**, 2316 (1988).
15. H. Martin and H. Bretinger, *Z. Naturforsch.* **40b**, 182 (1985).
16. P. L. Timms, *J. Chem. Soc. Dalton* 1972, 830.
17. H. Haubold and A. Gemmler, *Chem. Ber.* **113**, 3352 (1980).