

Borole Derivatives. 22. Iodine Degradation of the Triple-Decker Complexes $(\mu\text{-C}_4\text{H}_4\text{BR})[\text{Rh}(\text{C}_4\text{H}_4\text{BR})]_2$ ($\text{R} = \text{Ph}, \text{Me}$): Synthesis and Structural Characterization of Heterocubanes $[\text{Rh}(\mu_3\text{-I})(\text{C}_4\text{H}_4\text{BR})]_4$ and of Bis(borole)rhodium Complexes $\text{RhI}(\text{C}_4\text{H}_4\text{BR})_2$ ¹

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Received May 21, 1997[®]

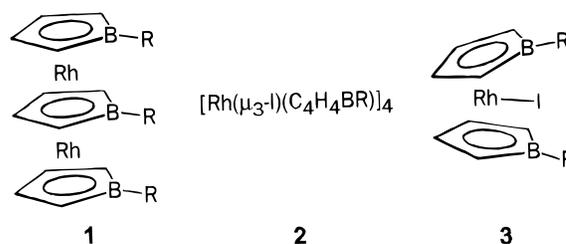
The triple-decker complexes $(\mu\text{-C}_4\text{H}_4\text{BR})[\text{Rh}(\text{C}_4\text{H}_4\text{BR})]_2$ ($\text{R} = \text{Ph}, \text{Me}$) (**1**) react with elemental iodine in toluene or dichloromethane to produce heterocubanes $[\text{Rh}(\mu_3\text{-I})(\text{C}_4\text{H}_4\text{BR})]_4$ (**2**) and bis(borole)iodorhodium complexes $\text{RhI}(\text{C}_4\text{H}_4\text{BR})_2$ (**3**). The heterocubanes **2** exchange fragments $\text{RhI}(\text{C}_4\text{H}_4\text{BR})$ at rates which are fast with respect to the NMR time scale. The bis(borole) compounds **3** exist in an equilibrium of rotational isomers $C_s\text{-3} = C_{2v}\text{-3}$ with $\Delta_R H = (-1.7 \pm 0.2) \text{ kJ mol}^{-1}$ and $\Delta_R S = (-16 \pm 1) \text{ J mol}^{-1} \text{ K}^{-1}$ for **3b**. Activation parameters for the forward and reverse isomerization reactions are reported. The isomerization takes place by the mechanism of ring–ring rotation; this is demonstrated for **3b** by TOCSY NMR spectra (¹H NMR, -80°C , mixing time 150 ms). Crystal structure determinations of **2a**, **2b**, and **3b** are reported. The higher-energy isomer $C_s\text{-3b}$ is found in the crystal of **3b**. One borole ligand of $C_s\text{-3b}$ is planar and η^5 -bonded with a normal Rh–B1 bond distance [236.7(6) pm]. The second ligand shows an unusual folding of 15.8(9)[°] along the line C2–C5, a very weak bonding interaction Rh–B2 [252.8(6) pm] approaching η^4 -coordination, and a close contact I–B2 [295.3(6) pm]. Both borole ligands show diene-like C–C bond length patterns with weak Rh-to-borole back-bonding.

Introduction

In 1983 we found that dehydrogenative complex formation of 2,5-dihydro-1*H*-boroles provides an efficient and versatile route to *C*-unsubstituted (borole)metal complexes. Among the very first examples was the triple-decker complex $(\mu\text{-C}_4\text{H}_4\text{BPh})[\text{Rh}(\text{C}_4\text{H}_4\text{BPh})]_2$ (**1a**),³ and later the methyl analog **1b** was also described.⁴ In this paper we report the oxidative degradation by iodine of the triple-decker complexes **1a,b**. This reaction will give us two new types of products, the dark red heterocubanes $[\text{Rh}(\mu_3\text{-I})(\text{C}_4\text{H}_4\text{BR})]_4$ (**2**) and the orange bis(borole)iodorhodium compounds $\text{RhI}(\text{C}_4\text{H}_4\text{BR})_2$ (**3**). Of these, the compounds **3** should attract particular attention because of a hitherto unknown bonding situation of a folded, approximately *tetrahapto*-coordinated borole ligand. In later papers we shall show that the complexes **2** are useful as versatile sources of the (borole)rhodium fragments $\text{Rh}(\text{C}_4\text{H}_4\text{BR})$.

Results and Discussion

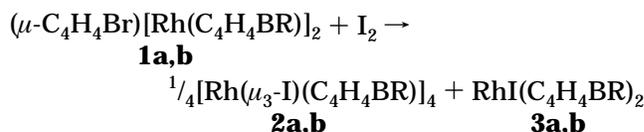
Syntheses. The triple-decker complexes **1a,b** readily react with elemental iodine. Two types of products **2** and **3** are obtained if toluene or CH_2Cl_2 is used as solvent at ambient temperature. The stoichiometry of



9, $\text{R} = \text{Ph}$; **b**, $\text{R} = \text{Me}$

this oxidation has been established in NMR tube experiments using *d*₈-toluene as solvent (Scheme 1).

Scheme 1



The two types of products **2** and **3** could not be separated by standard methods. When CO is bubbled through the reaction mixture, the heterocubanes **2** undergo a fast degradation (0.5 min, 20°C) to form labile and more soluble carbonyl derivatives, the dicarbonyl $\text{RhI}(\text{CO})_2(\text{C}_4\text{H}_4\text{BR})$ and dinuclear species $[\text{Rh}(\mu\text{-I})(\text{CO})(\text{C}_4\text{H}_4\text{BR})]_2$.⁵ The bis(ligand) complexes **3** react with CO at ambient temperature with noticeable rates. At elevated temperature they decompose quantitatively (80°C , 5–7 h); one of the two borole ligands is destroyed, and the formally remaining complex fragments are stabilized in the form of the same carbonyl species

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[®] Abstract published in *Advance ACS Abstracts*, September 1, 1997.

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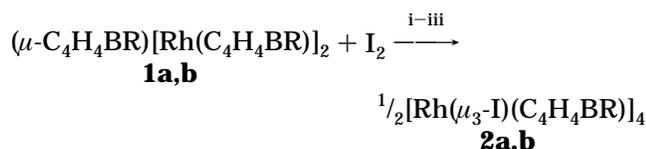
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mentioned above. In the absence of CO the bis(ligand) complexes **3** decompose less selectively; inter alia the triple-decker compounds are also formed. Finally, when solutions of the carbonyl species are heated in a stream of dinitrogen (110 °C, 4–8 h) a clean decomposition takes place to produce the heterocubanes **2**.

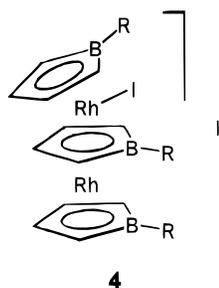
With these observations in mind we were able to develop two practical variants. Carbonylation of the reaction mixture at ambient temperature solubilizes the less soluble complexes **2**; the bis(ligand) complexes **3** can then be isolated by crystallization at lower temperature. On the other hand, carbonylation at elevated temperature and subsequent thermal decarbonylation cleanly gives the heterocubanes **2** as the sole complex products (Scheme 2).

Scheme 2



i, toluene 20 °C, 2 h; ii, CO (1 bar), 80 °C, 5–7 h;
iii, N₂ stream, 110 °C, 4–8 h

An exploratory investigation of **1a** by cyclic voltammetry revealed a reversible reduction at –1.44 V vs SCE in DME and a fully irreversible oxidation at 1.19 V in CH₂Cl₂. Considering the high anodic potential for the oxidation, the ready degradation by iodine may seem surprising. The same apparently paradoxical situation is found in the chemistry of Fe(CO)₅.⁶ On the basis of the redox potential of **1a** a one-electron oxidation by iodine is impossible. However, the basicity of the d⁸ metal center favors an electrophilic attack at one Rh center. Thus we may speculate that a charge transfer adduct **1a**·I₂ and an ionic species [(**1a**)I]I (**4**) are likely intermediates. From earlier work we know (i) that triple-decker complexes with central borole ligands are prone to nucleophilic degradation,^{4,7} and (ii) that cationic species are particularly reactive in this respect.⁸ Thus we expect that the cation of **4** should readily undergo nucleophilic degradation by iodide; this degradation would produce **3** and, formally, the monomer of **2**.



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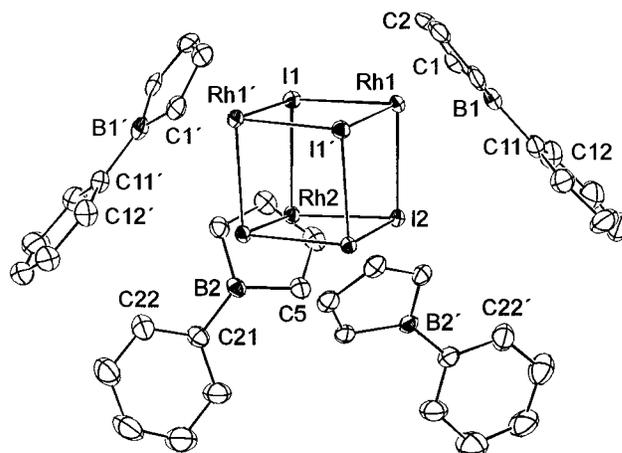


Figure 1. Thermal ellipsoid plot (ORTEP)⁹ of the molecule **2a**. Ellipsoids are scaled to 30% probability.

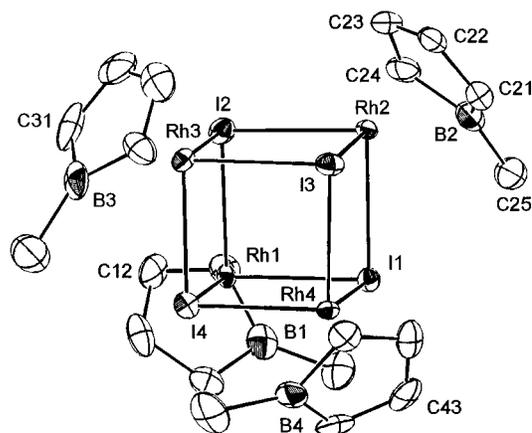


Figure 2. Thermal ellipsoid plot (ORTEP)⁹ of the molecule **2b**. Ellipsoids are scaled to 30% probability.

Table 1. Selected Interatomic Distances and Bond Angles for **2a**

(a) Bond Distances (pm)			
I1–Rh1	275.52(6)	I2–Rh1	276.07(5)
I1–Rh1'	273.56(6)	I2–Rh2	272.80(5)
I1–Rh2	277.41(5)	I2–Rh2'	276.20(5)
Rh1–C1	217.1(6)	Rh2–C5	214.2(6)
Rh1–C2	212.9(6)	Rh2–C6	211.4(6)
Rh1–C3	209.5(6)	Rh2–C7	212.3(6)
Rh1–C4	215.4(6)	Rh2–C8	216.5(5)
Rh1–B1	229.8(7)	Rh2–B2	233.3(6)
(b) Bond Angles (deg)			
Rh1–I1–Rh1'	92.47(2)	Rh1–I2–Rh2	94.52(2)
Rh1–I1–Rh2	93.61(2)	Rh1–I2–Rh2'	91.00(2)
Rh1'–I1–Rh2	91.27(2)	Rh2–I2–Rh2'	90.44(1)
I1–Rh1–I1'	87.43(2)	I1–Rh2–I2	86.05(2)
I1–Rh1–I2	85.79(2)	I1–Rh2–I2'	88.29(2)
I1'–Rh1–I2	89.10(2)	I2–Rh2–I2'	89.41(1)

Crystal Structures of the Heterocubanes **2a and **2b**.** Both complexes **2a,b** display a heterocubane structure with a Rh₄I₄ core (Figures 1 and 2, Tables 1 and 2). Complex **2a** crystallizes in space group *C2/c* and compound **2b** in *Pbca*. The molecules of **2a** possess crystallographic *C*₂ symmetry.

The Rh–I bond lengths average 275.8 pm [range: 270.49(9)–281.1(1) pm]. This is slightly longer than in the many known structures with μ_2 -iodo ligands;¹⁰ structures with μ_3 -iodo ligands are apparently unknown for rhodium. The angles centered at rhodium average 87.7° [range: 85.11(3)–91.70(3)°], and those centered

Table 2. Selected Interatomic Distances and Bond Angles for 2b

(a) Bond Distances (pm)			
I1–Rh1	276.5(1)	I2–Rh1	270.49(9)
I1–Rh2	276.2(1)	I2–Rh2	275.8(1)
I1–Rh4	274.8(1)	I2–Rh3	276.8(1)
I3–Rh2	277.7(1)	I4–Rh1	281.1(1)
I3–Rh3	273.8(1)	I4–Rh3	279.85(9)
I3–Rh4	276.29(9)	I4–Rh4	276.54(9)
(b) Bond Angles (deg)			
Rh1–I1–Rh2	87.74(3)	Rh1–I2–Rh2	89.03(3)
Rh1–I1–Rh4	94.57(3)	Rh1–I2–Rh3	95.93(3)
Rh2–I1–Rh4	93.60(3)	Rh2–I2–Rh3	91.47(3)
Rh2–I3–Rh3	91.71(3)	Rh1–I4–Rh3	92.88(3)
Rh2–I3–Rh4	92.93(3)	Rh1–I4–Rh4	93.15(3)
Rh3–I3–Rh4	92.26(3)	Rh3–I4–Rh4	90.91(3)
I1–Rh1–I2	91.70(3)	I1–Rh2–I2	90.63(3)
I1–Rh1–I4	85.53(3)	I1–Rh2–I3	86.45(3)
I2–Rh1–I4	86.05(3)	I2–Rh2–I3	88.06(3)
I2–Rh3–I3	88.67(3)	I1–Rh4–I3	87.01(3)
I2–Rh3–I4	85.11(3)	I1–Rh4–I4	86.75(3)
I3–Rh3–I4	88.06(3)	I3–Rh4–I4	88.23(3)

at iodine average 92.2° [range: 87.74(3)–95.93(3)°]. The cubane faces are almost perfectly planar (the angle sums deviating from 360° by at most 0.9°).

The structural pattern of the borole ligands is similar to that established in earlier structural work, as, e.g., in RhCl(C₄H₄BPh)(PPh₃)₂,¹¹ Fe(CO)₃(C₄H₄BPh),¹² and (μ-C₄H₄BMe)[Co(C₄H₄BMe)]₂,^{7b} and will not be discussed in detail. The distance of the Rh atoms to the best borole planes ranges from 177.4 to 178.3 pm while the Rh–B bond lengths average 232.5 pm, in agreement with η⁵-coordination of the borole ligand.

The observation of a heterocubane structure for **2a,b** may seem surprising at first glance. The related complexes of the types [RhX(alkene)₂]₂ and [RhX(diene)₂] (X = halogen) are *dinuclear square planar* complexes of a predominantly d⁸ metal center.¹³ The tetrafluoroethene complex [RhF(C₂H₄)(C₂F₄)_x] is an exception; it shows a “dimer-of-dimer” structure in the crystal but is a dimer in solution.¹⁴ As a consequence of the very strong back-bonding ability of the C₂F₄ ligand, the metal assumes more d⁶ character and the 18e configuration becomes more favorable. In the borole complexes **2a,b** the strong back-bonding ability of the borole ligand¹⁵ results in pronounced metal–ligand orbital mixing,¹⁶ and a description as d⁸ complexes is no longer appropriate. Thus, the compounds **2a,b** seem more akin to complexes such as [Cp^{*}RuCl]₄,¹⁷ to which they are isoelectronic in a broad sense.

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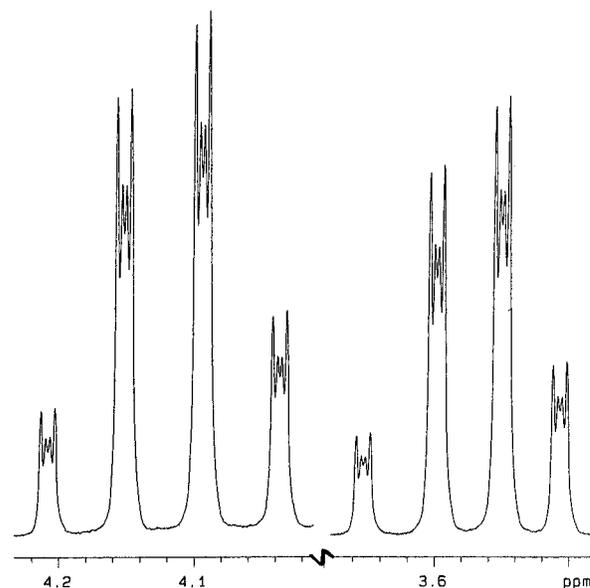


Figure 3. Low-temperature ¹H NMR signals (500 MHz, CD₂Cl₂, –80 °C) of a **2a/2b** mixture (1.20/1) in the borole region.

Constitution of 2a and 2b in Solution. The heterocubanes **2a,b** readily undergo degradation reactions with a wide variety of Lewis bases such as, e.g., CO, acetonitrile, pyridine, and phosphines.^{2,5} The carbonylation is reversible, and solutions of **2a,b** in acetonitrile regenerate the heterocubanes upon removal of the solvent in a vacuum.

Osmometric determinations of the molar mass of **2a** in CH₂Cl₂ give values somewhat below the value calculated for the heterocubane structure. These measurements confirm that **2a** essentially retains its tetranuclear nature in CH₂Cl₂ solution. On the other hand, they may be taken as a hint that **2a** does undergo a dissociation in solution, presumably into the dinuclear species. ¹H NMR spectra in CDCl₃ taken at ambient temperature on an 80 MHz spectrometer display one set of sharp signals consisting of the typical AA'BB' pattern of a coordinated borole ligand and the signals of the group R. The same spectra taken on a 500 MHz spectrometer show broad pseudosinglets in the region of the AA'BB' signals. The signals sharpen at higher temperature (*d*₈-toluene, 80 °C) and also upon cooling down to –80 °C.

To get more insight we looked at mixtures of **2a** and **2b** and measured their ¹H NMR spectra in CD₂Cl₂. Spectra taken at room temperature and at 80 MHz display only two ligand patterns corresponding to a 1-methyl- and a 1-phenylborole ligand; again, the spectra are blurred when measured at 500 MHz. At –80 °C, low-temperature limiting spectra with several different borole ligand patterns are seen, two of which are those of **2a** and **2b** (Figure 3). The spectra could be simulated with the assumption that five species Rh₄(μ₃-I)₄(C₄H₄BMe)_{4-x}(C₄H₄BPh)_x (with *x* = 0, 1, ..., 4) are present, with relative concentrations which correspond to statistical weights of the five species. The essential result is the proof that heterocubanes **2** exchange fragments RhI(C₄H₄BR) at rates which are fast with respect to the NMR time scale under the common experimental conditions.

Crystal Structure of the Bis(ligand) Complex 3b. Complex **3b** crystallizes in the monoclinic space group

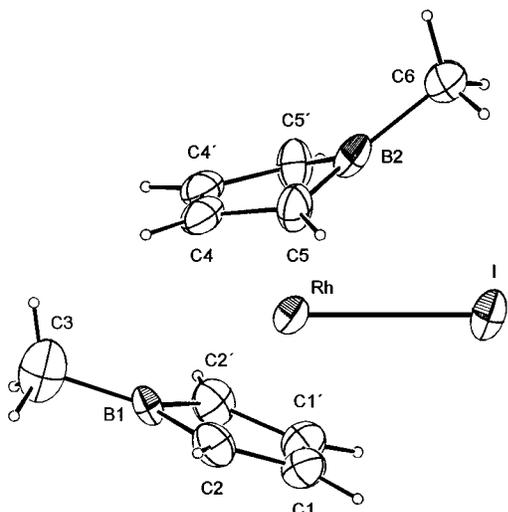


Figure 4. Thermal ellipsoid plot (PLATON)¹⁸ of the molecule *C_s-3b*. Ellipsoids are scaled to 30% probability.

Table 3. Selected Interatomic Distances and Bond Angles for 3b

(a) Bond Distances (pm)			
I–Rh	273.51(5)	I–B2	295.3(6)
Rh–C1	217.2(3)	Rh–C4	216.0(3)
Rh–C2	224.8(4)	Rh–C5	223.5(4)
Rh–B1	236.7(6)	Rh–B2	252.8(6)
C1–C1'	146.2(8)	C1–C2	138.7(5)
C2–B1	155.3(6)	C3–B1	155.8(9)
C4–C4'	143.4(8)	C4–C5	139.9(5)
C5–B2	156.3(6)	C6–B2	155.6(9)
(b) Bond Angles (deg)			
C1'–C1–C2	109.7(2)	C4'–C4–C5	110.2(2)
C1–C2–B1	109.7(4)	C4–C5–B2	108.3(4)
C2–B1–C2'	101.2(5)	C5–B2–C5'	100.3(5)
C2–B1–C3	129.4(2)	C5–B2–C6	129.1(2)

C₂/m. The molecule of **3b** possesses a bent sandwich structure with crystallographic *C_s* symmetry (Figure 4, Table 3). The tight packing of the ligands around the Rh center is illustrated by a space-filling representation (Figure 5). The Rh–I bond length amounts to 273.51(5) pm and lies in the expected range.¹⁰ One of the two borole ligands shows structural features similar to those found in RhCl(PPh₃)₂(C₄H₄BPh).¹¹ This ring is planar [plane C1,C1',C2,C2',B1; largest vertical displacement: 1.5(6) pm at B1]. The boron atom B1 is slightly bent away from the metal [vertical distance to plane C1,C1',C2,C2': 4.2(6) pm], yet B1 is a trigonal planar center [angle sum 360.0(5)°]. The metal-to-ring bonding shows a vertical distance of the Rh atom to the best borole plane of 185.8(1) pm, a rather large slip distortion of 13.7(3) pm,¹⁹ and a Rh–B1 distance of 236.7(6) pm [cf. Rh–B 232.5 pm (av) for **2a** and **2b**; cf. also RhCl(PPh₃)₂(C₄H₄BPh):¹¹ slip distortion 11.5 pm, Rh–B 240.0(5) pm]. The C–C bond lengths in the ring [C1–C1' 146.2(8), C1–C2 138.7(5) pm] show a diene-like pattern, indicating rather moderate back-bonding.

The second ring shows surprising structural features. The folding angle between the two planes C5,B2,C5' and C5,C4,C4',C5' of 15.8(9)° is exceptionally large, resulting in rather weakened bonding between the Rh atom and B2 [Rh–B2 252.8(6) pm]; the vertical distances to the

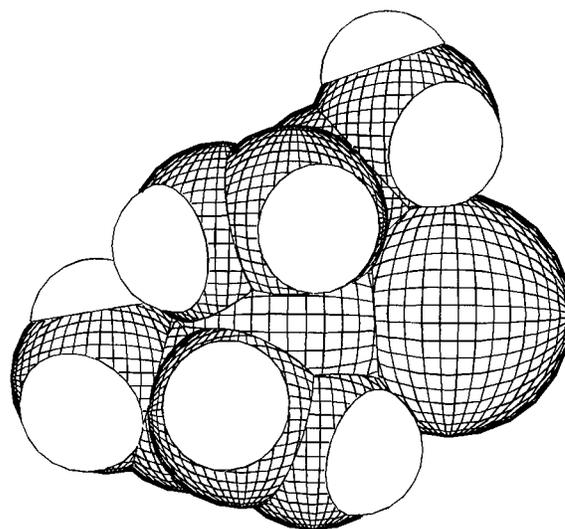


Figure 5. Space-filling representation (PLATON)¹⁸ of the molecule *C_s-3b*.¹⁸

diene plane C4,C4',C5,C5' amount to 27.2(7) pm for B2 and to 183.7(1) pm for the Rh atom. Thus the bonding situation is approaching a *tetrahapto*-coordination of the borole ligand. The orientation of this ring brings the boron atom B2 into contact with the iodine atom. The distance I···B2 [295.3(6) pm] is much larger than typical B–I bond lengths [BI₃·PMe₃: 223.7(9) and 227.2(16) pm²⁰] but also much shorter than a nonbonding distance [>360 pm].²¹ The boron center is no longer trigonal planar. The methyl group is bent away from the metal, and the angle between the plane C5,B2,C5' and the bond vector B2–C6 amounts to 10.5(2)°. The resulting distance I···C of the B–Me group [335.0(7) pm] corresponds to an at most very weak repulsion. Finally, the C–C distances in the ring [C4–C4' 143.4(8), C4–C5 139.9(5) pm] show again a diene-like pattern with moderate back-bonding.

Overall, two effects seem to be operating here, pronounced ligand–ligand repulsions and a weak bonding interaction between the boron center B2 and the iodo ligand. However, the origin of the slight pyramidalization at B2 remains unclear since both the I···B2 interaction and the distance I···C of the B2–Me group are in the borderline range.

Structures of 3a,b in Solution. The ¹H and ¹³C NMR spectra of **3a,b** at ambient temperature display only one borole pattern, and some atoms show signal broadening which cannot be caused by the quadrupole moment of a neighboring boron atom [**3a**, 3-/4-H, C-3,4; **3b**, C-3,4]. We therefore measured NMR spectra at temperatures down to –90 °C with the aim to unravel the dynamic behavior of the complexes **3**.

The low-temperature limiting ¹H NMR spectrum of **3b** shows six multiplets in the region of the borole rings, four of equal intensity and a pair of somewhat lower intensity (Figure 6). With the help of (¹H,¹H)-COSY spectra (taken at –90 °C) these multiplets can be grouped into three AA'BB' patterns; the presence of an ABCD spin system can be excluded unambiguously. The two AA'BB' systems of equal intensity are assigned to the isomer *C_s-3b* found in the crystal while the third one is assigned to an isomer *C_{2v}-3b*. Since the borole

(19) The slip distortion is the distance between the geometric center of the C₄B ring and the projection of the metal atom onto the C₄B best plane.

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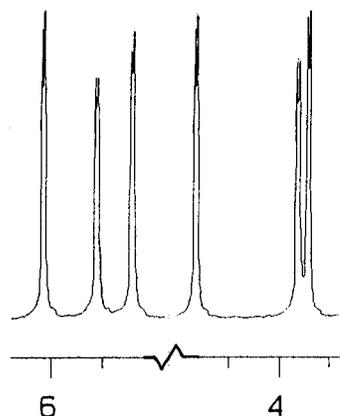
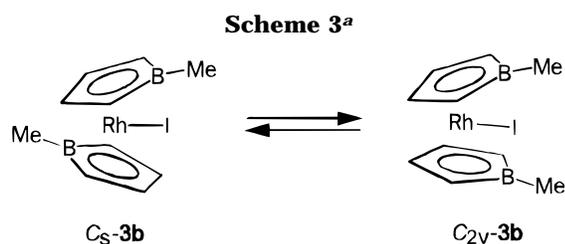


Figure 6. Low-temperature ^1H NMR signals (500 MHz, CD_2Cl_2 , -90°C) of **3b** in the borole region.



^a $C_5\text{-3b} \rightleftharpoons C_{2v}\text{-3b}$.

Table 4. Equilibrium Constants and Free Energies for the Equilibrium $C_5\text{-3b} \rightleftharpoons C_{2v}\text{-3b}$

$T(\text{K})$	$C_{2v}\text{-3b}/C_5\text{-3b}^a$	K	$\Delta_{\text{R}}G$ (kJ mol^{-1})
183	30/70	0.43	1.284
193	29/71	0.41	1.430
203	28/72	0.39	1.589
213	27/73	0.38	1.714
223	26/74	0.35	1.946

^a The concentration ratios rely on the assumption that the intensities of corresponding signals in the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum are comparable.

Table 5. Energetics of the Equilibrium $C_5\text{-3} \rightleftharpoons C_{2v}\text{-3}$

- (a) Thermodynamic Equilibrium Parameters for **3b**
 $\Delta_{\text{R}}H = (-1.7 \pm 0.2) \text{ kJ mol}^{-1}$
 $\Delta_{\text{R}}S = (-16 \pm 1) \text{ J mol}^{-1} \text{ K}^{-1}$
- (b) Activation Parameters for Isomerization of $C_5\text{-3b}$
 $\Delta H^\ddagger_1 = (34.0 \pm 1.9) \text{ kJ mol}^{-1}$
 $\Delta S^\ddagger_1 = (-47 \pm 9) \text{ J mol}^{-1} \text{ K}^{-1}$
- (c) Activation Parameters for Isomerization of $C_{2v}\text{-3b}$
 $\Delta H^\ddagger_{-1} = (35.6 \pm 2.0) \text{ kJ mol}^{-1}$
 $\Delta S^\ddagger_{-1} = (-32 \pm 9) \text{ J mol}^{-1} \text{ K}^{-1}$
- (d) Activation Parameters for Isomerization of $C_5\text{-3a}$
 $\Delta H^\ddagger = (33.5 \pm 1.5) \text{ kJ mol}^{-1}$
 $\Delta S^\ddagger = (-52 \pm 7) \text{ J mol}^{-1} \text{ K}^{-1}$

patterns coalesce at higher temperature and sharpen to the single pattern seen at ambient temperature, the two isomers are in a mobile equilibrium (Scheme 3). Note that isomer $C_{2v}\text{-3b}$ is shown as a syn-eclipsed conformer with both BMe groups close to the Rh–I bond; the alternative anti-eclipsed conformer would seem too congested sterically to be capable of existence.

Signal intensities of corresponding signals in the $^{13}\text{C}\{^1\text{H}\}$ NMR spectra were used to estimate equilibrium constants (Table 4) and to calculate thermodynamic parameters for the isomerization of Scheme 3 (Tables 4 and 5). Thus we obtained $\Delta_{\text{R}}H = (-1.7 \pm 0.2) \text{ kJ mol}^{-1}$ and $\Delta_{\text{R}}S = (-16 \pm 1) \text{ J mol}^{-1} \text{ K}^{-1}$. This result shows that the lower-energy isomer is $C_{2v}\text{-3b}$ while the

less symmetric $C_5\text{-3b}$ is entropically favored and predominates in the entire temperature range that is accessible experimentally.

When a 500 MHz ^1H NMR spectrum of the phenyl compound **3a** is measured at -90°C , the low-temperature limiting spectrum for $C_5\text{-3a}$ with resolved fine structure is observed while the borole signals for $C_{2v}\text{-3a}$ are seen as a pair of weak broad pseudosinglets. In the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (126 MHz, -90°C) only the signals of $C_5\text{-3a}$ could be observed. The equilibrium constant is about $K \approx 0.1$, corresponding to $\Delta_{\text{R}}G_{183} = 3.5 \text{ kJ mol}^{-1}$.

The room temperature $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum of **3b** displays a single resonance for the equilibrium mixture at δ 33 ppm while the low-temperature limiting spectrum (160 MHz, -80°C) shows a more intense signal at δ 37 and a weaker signal at δ 28 ppm. The chemical shift of the weaker signal corresponds to a normal 1-methylborole ligand in a situation with rather moderate back-bonding,²² and is therefore assigned to the planar borole ring of $C_5\text{-3b}$. The chemical shift of the stronger signal is very unusual and indicates considerable deshielding at the boron; it belongs to the folded borole ring of $C_5\text{-3b}$ and, because of its higher intensity, also to the borole rings of $C_{2v}\text{-3b}$. Thus, we have to conclude that both borole rings in $C_{2v}\text{-3b}$ are of the folded type with weakened Rh–B bonding. In the case of **3a** no splitting of the signal was seen at -80°C .

We next turn to the mechanism of the forward and reverse isomerization reactions. Since the coalescence temperatures observed are concentration-independent, the isomerization processes are first-order reactions. Line shape analysis with the help of the program DNMR²⁴ was used to estimate isomerization rates and to calculate activation parameters for both isomers of **3b** and for the predominant isomer $C_5\text{-3a}$ in the phenyl case (Table 5). The negative activation entropies obtained demonstrate the nondissociative and consequently intramolecular nature of the reactions observed. We conclude that the isomerization is brought about by ring–ring rotation.

This mechanism can be verified directly by means of the TOCSY NMR spectra²⁵ of **3b**. The spectra were recorded at -80°C with a mixing time of 150 ms. We describe selective excitations of borole protons in β -positions to the boron (i.e., 3-/4-H) and the transfer of magnetization to β -positions in the other borole rings; α -protons (i.e., 2-/5-H) and transfer of magnetization to these positions can remain out of consideration. Selective excitation of the β -protons of one borole in $C_5\text{-3b}$ produces a strong signal for these protons, a less intensive signal for the β -protons in $C_{2v}\text{-3b}$, and an even less intensive signal for the β -protons of the second borole in $C_5\text{-3b}$. Thus the interconversion of the two borole ligands of $C_5\text{-3b}$ takes place through the intermediacy of isomer $C_{2v}\text{-3b}$. On the other hand, if the β -protons of $C_{2v}\text{-3b}$ are excited selectively, then both β -proton signals of $C_5\text{-3b}$ appear with equal intensity.

(22) Cf., e.g., δ 28.5 ppm for $\text{Ni}(\text{C}_4\text{H}_4\text{BMe})_2$ ²³ and also δ 19.6 for $\text{CpRh}(\text{C}_4\text{H}_4\text{BMe})^4$ and 22.8 ppm for $\text{Ru}(\text{CO})_3(\text{C}_4\text{H}_4\text{BMe})$.¹¹

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Barriers to internal rotation of borole ligands have previously been observed.^{23,26} We note that the present case is the first nondegenerate example that could be analyzed.

Concluding Remarks. In this paper we have concentrated on the oxidative degradation reaction of the triple-decker complexes **1** and the identification and the structures of the products **2** and **3**. For the preparation of the heterocubanes **2** we have devised an optimized procedure which circumvents the separation of the products **2** and **3** and gives the heterocubanes **2** as the sole product in high yields (80–85%). In the next paper of this series we shall describe reactions of the heterocubanes **2** with a wide variety of Lewis bases. We shall then be able to comment in detail on the role of CO, acetonitrile, and pyridine in the oxidative degradation reaction.

Experimental Section

General Procedures. Reactions were carried out under an atmosphere of dinitrogen by means of conventional Schlenk techniques. Hexane was distilled from potassium, CH₂Cl₂ from CaH₂, and toluene from sodium. Acetone was heated under reflux with boric acid anhydride for 24 h and distilled under dinitrogen. Acetonitrile was filtered through a column with activated alumina and distilled under dinitrogen. Carbon monoxide was dried with concentrated sulfuric acid. NMR spectra were recorded on a Varian Unity 500 spectrometer (¹H, 500 MHz; ¹³C{¹H}, 125.7 MHz; ¹¹B{¹H}, 160.4 MHz) and a Bruker WP-80 PFT (¹H, 80 MHz) spectrometer. If not stated otherwise, chemical shifts were measured at ambient temperature and are relative to internal TMS for ¹H and ¹³C and relative to BF₃·Et₂O as external reference for ¹¹B. The *B*-phenyl compounds **2a** and **3a** are poorly soluble in noncoordinating solvents such as toluene or CH₂Cl₂; this was frequently a limiting factor in the recording of NMR spectra.

Secondary ion mass spectra (SIMS) were recorded on a Finnigan MAT-95 spectrometer. Elemental analyses and determinations of molecular mass were performed by Mikroanalytisches Labor Pascher, D-53424 Remagen-Bandorf, Germany. Melting points were determined in sealed capillaries on a Büchi 510 melting point apparatus and are uncorrected.

CV Data of 1a. Cyclic voltammetry was carried out using an EG & G 175 voltage scan generator and an EG & G 173 potentiostat. For the measurements a conventional three-electrode cell with a platinum-inlay working electrode, a platinum sheet counter electrode, and a saturated calomel (SCE) reference electrode was used. Solutions were ca. 10⁻³ M in electroactive species and 0.1 M in tetrabutylammonium hexafluorophosphate (TBAH) as supporting electrolyte. FeCp₂ served as internal standard. CV (CH₂Cl₂, 100 mV/s) *E*_p^a +1.19 V, irreversible oxidation; (DME, 100 mV/s) *E*_{1/2} -1.44 V, *i*_a/*i*_c 0.99, reversible reduction.

Synthesis of [Rh(μ₃-I)(C₄H₄BPh)]₄ (2a**).** Elemental iodine (2.19 g, 8.629 mmol) was added to a solution of **1a**^{3,4} (5.40 g, 8.63 mmol) in toluene (700 mL). The dark red reaction mixture was stirred at 20 °C for 2 h. Then a slow stream of dry CO was passed through the flask while the temperature was kept at 80 °C for 7 h. Then the orange solution was heated under gentle reflux while a slow stream of N₂ was passed through the flask until the CO band at 2055 cm⁻¹ had disappeared. After cooling to 20 °C the volatiles were removed under reduced pressure. The raw product was suspended in acetone (30 mL), transferred to a frit, and washed with acetone until the color of the filtrate was of a pale red. The solid was

then dissolved in hot acetonitrile (400 mL), the solution was filtered, and the solvent was removed in a vacuum. The microcrystals so obtained were collected on a frit, washed with acetone, and dried in a vacuum to give **2a** (5.31 g, 85%) as dark red microcrystals: mp 223 °C dec; in solution somewhat air-sensitive, soluble in acetonitrile, moderately soluble in CH₂Cl₂, CHCl₃, THF, and toluene, insoluble in acetone, ether, and hexane. Anal. Calcd for C₄₀H₃₆B₄I₄Rh₄: C, 32.48; H, 2.45. Found: C, 32.35; H, 2.50. Molar mass: *M*_{calc} 1479.21 g mol⁻¹; in acetonitrile *M*_{obs} [molarity (g/L)] 391 (5.548), 445 (11.77), 464 g/mol (13.05); in CH₂Cl₂ *M*_{obs} [molarity (g/L)] 1351 (3.475), 1430 g/mol (5.313). SIMS (DMBA): negative ions, *m/z* (*I*_{rel}) 1110 (1, [Rh₃I₃(C₄H₄BPh)₃]⁻), 740 (8, [Rh₂I₂(C₄H₄BPh)₂]⁻), 497 (70, [RhI₂(C₄H₄BPh)]⁻), 357 (26, [RhI₂]⁻), 127 (100, I⁻).

2a: ¹H NMR (500 MHz, CDCl₃) δ 7.63 (m, 2 H_o), 7.37 (m, H_p), 7.35 (m, 2 H_m), borole 5.03 (br, 3-/4-H), 4.18 (br, 2-/5-H), and borole signals at 80 MHz 5.03 (m, *N* = 5.9 Hz, 3-/4-H), 4.18 (m, *N* = 5.2 Hz, 2-/5-H). ¹³C{¹H} NMR (126 MHz, CDCl₃, 20 °C) δ 135.91 (C_o), 129.14 (C_p), 127.62 (C_m), borole 89.22 (C-3,4), 74 (br, C-2,5); ¹¹B{¹H} NMR (CDCl₃) δ 20.

Synthesis of [Rh(μ₃-I)(C₄H₄BMe)]₄ (2b**).** A solution of complex **1b**⁴ (310 mg, 0.705 mmol) and elemental iodine (179 mg, 0.705 mmol) in toluene (100 mL) was stirred at 20 °C for 2 h. Carbonylation (5 h) and decarbonylation (4 h) until the CO band at 2059 cm⁻¹ had disappeared, followed by removal of the volatiles, gave a raw product. This was dissolved in CH₂Cl₂ (80 mL), and the solution was filtered, concentrated to a small volume (3 mL), and stored at -30 °C for 16 h. The dark red microcrystals formed were collected, washed with acetone (2 × 2 mL), and dried in a vacuum to give **2b** (350 mg, 81%): mp 168 °C dec; in solution somewhat air-sensitive, soluble in acetonitrile, CH₂Cl₂, CHCl₃, THF, and toluene, insoluble in acetone, ether, and hexane. Anal. Calcd for C₂₀H₂₈B₄I₄Rh₄: C, 19.52; H, 2.23. Found: C, 19.52; H, 2.23. SIMS (K/T): negative ions, *m/z* (*I*_{rel}) 743 (13, [Rh₂I₃(C₄H₄BMe)₂]⁻), 616 (12, [RhI(C₄H₄BMe)]₂⁻), 435 (62, [RhI₂(C₄H₄BMe)]⁻), 127 (100, I⁻).

2b: ¹H NMR (500 MHz, CDCl₃) δ 5.09 (br, 3-/4-H), 3.66 (br, 2-/5-H), 0.50 (s, Me), and borole signals at 80 MHz 5.10 (m, *N* = 5.2 Hz, 3-/4-H), 3.67 (m, *N* = 5.2 Hz, 2-/5-H). ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 88.44 [d, *J*(Rh-C) = 8.8 Hz, C-3,4], 73.51 (br, C-2,5), -1.91 (br, Me). ¹¹B{¹H} NMR (CDCl₃) δ 24.

Synthesis of RhI(C₄H₄BPh)₂ (3a**).** Complex **1a**^{3,4} (520 mg, 0.831 mmol) was dissolved in CH₂Cl₂ (50 mL), and elemental iodine (211 mg, 0.831 mmol) was added. The reaction mixture was stirred for 2 h at ambient temperature. Dry CO was then passed through the flask for 15 min. The orange solution was concentrated to 5 mL under reduced pressure and then stored at -30 °C for 16 h to give orange crystals. After removal of the mother liquor, dissolution in CH₂Cl₂ (30 mL), and filtration, the solution was again concentrated to 3 mL under reduced pressure and stored at -30 °C for 16 h. The crystals were collected on a frit, washed with acetone (3 × 2 mL), and dried in a vacuum to give **3a** (270 mg, 64%) as orange needles: mp 168 °C dec; in solution somewhat sensitive, moderately soluble in CH₂Cl₂, CHCl₃, and toluene, insoluble in acetone, acetonitrile, ether, and hexane. Anal. Calcd for C₂₀H₁₈B₂IRh: C, 47.12; H, 3.56. Found: C, 47.08; H, 3.39. SIMS (NBA): positive ions, *m/z* (*I*_{rel}) 626 (<1, [Rh₂(C₄H₄BPh)₃]⁺), 383 (100, [Rh(C₄H₄BPh)₂]⁺).

3a: ¹H NMR (500 MHz, CD₂Cl₂) δ 7.70 (m, 2 H_o), 7.41 (m, 2 H_m), 7.33 (m, H_p), borole 5.88 (br, 3-/4-H), 4.70 (m, 2-/5-H), and borole signals at 80 MHz 5.88 (m, *N* = 7.3 Hz, 3-/4-H), 4.71 (m, *N* = 6.8 Hz, 2-/5-H); ¹³C{¹H} NMR (126 MHz, CD₂Cl₂) δ 136.36 (C_o), 130.54 (C_p), 128.28 (C_m), borole 103.74 (br, C-3,4), 81.47 (br, C-2,5). ¹¹B{¹H} NMR (CD₂Cl₂) δ 28.

VT-NMR spectra of 3a: ¹H NMR (500 MHz, CD₂Cl₂, -90 °C) *C*_s isomer (90%) δ 7.84 (m, 2 H_o), 7.53 (m, 2 H_o), 7.43–7.49 (m, 2 H_m + H_p), 7.33 (m, 2 H_m), 7.20 (m, H_p), 6.29 (m, 3-/4-H) and 4.93 (m, 2-/5-H) for first borole, 5.33 (m, 3-/4-H) and 4.45 (m, 2-/5-H) for second borole; *C*_{2v} isomer (10%) δ 6.02 (s br, 3-/4-H), 4.52 (s br, 2-/5-H), Ph protons hidden. ¹³C{¹H} NMR

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Table 6. Crystal Data, Data Collection Parameters, and Convergence Results

	2a	2b	3b
formula	C ₄₀ H ₃₆ B ₄ I ₄ Rh ₄	C ₂₀ H ₂₈ B ₄ I ₄ Rh ₄	C ₁₀ H ₁₄ B ₂ IRh
system	monoclinic	orthorhombic	monoclinic
space group (no.)	<i>C2/c</i> (15)	<i>Pbca</i> (61)	<i>C2/m</i> (12)
<i>a</i> , pm	1572.6(9)	1692.8(5)	993.6(4)
<i>b</i> , pm	1387.4(5)	1706.2(2)	891.4(3)
<i>c</i> , pm	1956.1(5)	2015.6(3)	1414.0(3)
β , deg	105.56(4)	2015.6(3)	104.55(3)
<i>V</i> , nm ³	4.112(3)	5.822(2)	1.2123(7)
<i>Z</i>	4	8	4
<i>d</i> _{calc} , g cm ⁻³	2.371	2.809	2.112
<i>T</i> , K	203	293	203
μ , cm ⁻¹	4521	33.65	38.65
λ , pm (radiation)	71.073 (Mo K α)	56.087 (Ag K α)	71.073 (Mo K α)
θ _{max} , deg	28	24	28
cryst dimens, mm ³	0.19 × 0.14 × 0.12	0.25 × 0.20 × 0.08	0.35 × 0.26 × 0.05
abs cor	numerical	empirical	numerical
min trans	0.442	rel 0.606	0.395
max trans	0.622	rel 0.999	0.899
no. of rflns	6143	10 799	5820
no. of indep obs rflns <i>I</i> > 1.0 σ (<i>I</i>)	3712	5555	1311
no. of vars	236	290	104
<i>R</i> ^a	0.035	0.070	0.028
<i>R</i> _w ^b	0.036	0.055	0.032
resd el dens, 10 ⁻⁶ e pm ⁻³	0.8	1.8 (close to Rh)	1.1 (close to I)

$$^a R = \sum ||F_o| - |F_c|| / \sum |F_o|. \quad ^b R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}.$$

(126 MHz, CDCl₃, -90 °C) *C_s* isomer δ 135.30 and 135.80 (C_o), 127.14 and 127.94 (C_m), 129.86 and 130.02 (C_p), borole 100.88 and 106.99 (C-3,4), 75.35 and 85.55 (C-2,5); *C_{2v}* isomer not observed. Simulation of line shapes: temperature range 193–303 K; signals of borole carbons C-3,4 and of phenyl carbons C_o, C_m, and C_p used.

Synthesis of RhI(C₄H₄BMe)₂ (3b). A solution of complex **1b**⁴ (840 mg, 1.911 mmol) and elemental iodine (485 mg, 1.911 mmol) in CH₂Cl₂ (50 mL) was stirred at ambient temperature for 2 h. The volatiles were then removed in a vacuum. The brown residue was extracted with hexane (5 × 20 mL). The combined solutions were filtered, concentrated to 50 mL, and then carbonylated (20 °C, 15 min). The resulting orange solution was concentrated to 10 mL and stored at -30 °C for 16 h to complete the crystallization. The crystals were collected, washed with hexane (2 × 1 mL), and dried in a vacuum to give **3b** (510 mg, 69%) as orange needles: mp 93 °C dec; in solution somewhat sensitive, very soluble in CH₂-Cl₂ and toluene, moderately soluble in ether and hexane. Anal. Calcd for C₁₀H₁₄B₂IRh: C, 31.14; H, 3.66. Found: C, 30.84; H, 3.69. SIMS (NBA): positive ions, *m/z* (*I*_{rel}) 440 (28, [Rh₂(C₄H₄BMe)₃]⁺), 386 (100, [RhI(C₄H₄BMe)₂]⁺), 259 (100, [Rh(C₄H₄BMe)₂]⁺).

3b: ¹H NMR (500 MHz, CD₂Cl₂) δ 5.87 (br, 3-/4-H), 4.13 (m, 2-/5-H), 1.05 (s, Me), and borole signals at 80 MHz 5.86 (m, *N* = 7.3 Hz, 3-/4-H), 4.14 (m, *N* = 6.7 Hz, 2-/5-H); ¹³C{¹H} NMR (126 MHz, CD₂Cl₂) δ 101.17 (C-3,4), 83.04 (br, C-2,5), 2.74 (br, Me); ¹¹B{¹H} NMR (CD₂Cl₂) δ 33.

VT-NMR Spectra of 3b: ¹H NMR (500 MHz, CD₂Cl₂, -90 °C) *C_s* isomer (70%) δ 6.03 (m, 3-/4-H) and 4.34 (m, 2-/5-H) for first borole, 5.69 (m, 3-/4-H) and 3.89 (m, 2-/5-H) for second borole, 1.17 (s, Me), 0.61 (s, Me); *C_{2v}* isomer (30%) δ 5.83 (m, 3-/4-H), 3.93 (m, 2-/5-H), 1.17 (s, 2 Me); ¹³C{¹H} NMR (126 MHz, CDCl₃, -90 °C) *C_s* isomer (70%) δ 106.43 [d, ¹J(Rh-C) = 6.0 Hz, C-3,4] and 88.06 (C-2,5) for first borole, 99.25 [d, ¹J(Rh-C) = 6.0 Hz, C-3,4] and 77.17 (C-2,5) for second borole, 4.40 and -1.38 (2 Me); *C_s* isomer (10%) δ 94.81 [d, ¹J(Rh-C) = 6.1 Hz, C-3,4], 79.53 (C-2,5), 4.67 (Me). Simulation of line shapes: temperature range 193–223 K; signals of all carbons used, ¹J(Rh-C) couplings taken into account, quadrupole broadening of C-2,5 and B-Me neglected. ¹¹B{¹H} NMR (CD₂-Cl₂, -90 °C): δ 37 (higher intensity) and 28.

Crystal Structure Determination of 2a, 2b, and 3b. Crystals of **2a** can be obtained from hot toluene solutions. Crystals of better quality were obtained incidentally when a

solution of **2a** and **2b** (1/1) in (*E*)-1,2-dichloroethene was cooled to -30 °C. Crystals of **2b** were obtained when a saturated solution in CH₂Cl₂ was cooled from 20 °C to -30 °C. In the case of **3b** the compound was dissolved in the minimum amount of hexane at 20 °C; the solution was kept at -30 °C to give crystals suitable for the structure determination.

The data collection was performed on ENRAF-Nonius CAD4 diffractometers equipped with a graphite monochromator. Crystal data, data collection parameters, and convergence results are given in Table 6.

The major source of systematic error in all three structure determinations stems from absorption: The numerical method by Gaussian integration²⁷ was used for the crystals of **2a** and **3b** which could readily be face-indexed whereas an empirical absorption correction²⁸ was applied in the case of **2b**. The structures were solved by direct methods²⁹ and refined on *F* with the local version of the SDP system.³⁰ In the final least squares refinements non-hydrogen atoms were assigned anisotropic displacement parameters; in the case of **3b** hydrogen atoms were refined isotropically, whereas the hydrogen atoms were included in riding geometry with fixed displacement parameters (C-H = 98 pm, *U*_{iso}(H) = 1.3*U*_{iso}(C)) in the refinement of the structural model for the other compounds.

Acknowledgment. This work was generously supported by Fonds der Chemischen Industrie.

Supporting Information Available: Tables of fractional coordinates of all atoms, anisotropic displacement parameters, and bond distances and angles for **2a**, **2b**, and **3b** (14 pages). Ordering information is given on any current masthead page.³¹

OM970422Q

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