Borole Derivatives. 23. Reversible Carbonylation and Lewis Base Degradation of the Heterocubane $[Rh(\mu_3\text{-}I)(C_4H_4BPh)]_4$ and of the Bis(borole) Complex $RhI(C_4H_4BPh)_2$ and Synthesis and Structure of the Dinuclear Complex $Cp^*Rh(\mu\text{-}I)_3Rh(C_4H_4BPh)$[1]

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The heterocubane $[Rh(\mu_3\text{-}I)(C_4H_4BPh)]_4$ (**2a**) readily adds Lewis bases to form the mononuclear products $RhI(py)_2(C_4H_4BPh)$ (**4**), and $RhI(bpy)(C_4H_4BPh)$ (**7**), the labile solution species $RhI(NCMe)_2(C_4H_4BPh)$ (**8**) and $RhI(CO)_2(C_4H_4BPh)$ (**9**), $RhI(PPh_3)_2(C_4H_4BPh)$ (**11**), the 1,1′-bis(diphenylphosphino)ferrocene complex RhI(dppf)(C_4H_4BPh) (**13**), and the norbornadiene complex RhI(nbd)(C_4H_4BPh) (**14**) as well as the dinuclear products $[Rh(\mu\text{-}I)(py)(C_4H_4BPh)]_2$ (**5**), $[Rh(\mu\text{-}I)(CO)(C_4H_4BPh)]_2$ (**10**), and the bis(diphenylphosphino)methane complex $[Rh_2(\mu\text{-}I)_2(\mu\text{-dppm})(C_4H_4BPh)_2]$ (**12**). The complexes **5** and **10** exist as mixtures of *cis* and *trans* isomers; the isomeric carbonyls **10** interconvert slowly at ambient temperature, while the isomeric pyridine complexes **5** show fast interchange on the NMR time scale at 20 °C and low-temperature limiting spectra at −80 °C. The heterocubane also adds $(RhI_2Cp^*)_2$ (which acts as a Lewis base *and* as a Lewis acid) to produce the novel unsymmetrical dinuclear complex $Cp^*Rh(\mu\text{-}I)_3Rh(C_4H_4BPh)$ (**15**). Complex **15** was shown by crystal structure analysis to possess a central trigonal-bipyramidal Rh_2I_3 core, capped with the Cp* and the borole ligands, respectively. The bis(ligand) complex $RhI(C_4H_4BPh)_2$ (**3a**) reacts with excess pyridine at 20 °C to give $RhI(py)_2(C_4H_4BPh)$ (**4**) and the borole-pyridine adduct $C_4H_4BPh\cdot py$ (**6**). With CO it reacts at elevated temperature (in toluene, 80 °C, 7 h) to give the dicarbonyl **9** with loss of one borole ligand.

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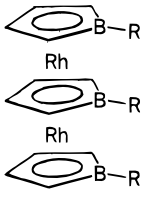
Introduction

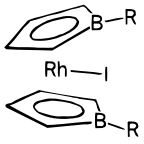
In the previous paper of this series we have shown that the triple-decker complexes **1a**,**b**[4] (**a**, R = Ph; **b**, R = Me) undergo an oxidative degradation when treated with elemental iodine in toluene or CH_2Cl_2.[2] The products are the heterocubanes $[Rh(\mu_3\text{-}I)(C_4H_4BR)]_4$ (**2**) and the bis(borole)iodorhodium compounds $RhI(C_4H_4BR)_2$ (**3**).[2,5]



1

$[Rh(\mu_3\text{-}I)(C_4H_4BR)]_4$

2



3

The outcome of the oxidative degradation of **1** is influenced by the presence of auxiliary ligands and can be steered to give the heterocubanes **2** as the sole products.[2] The complexes **2** in turn readily add ligands such as CO and PPh_3, and this addition may be reversible or irreversible, depending on the ligands involved. In this paper we wish to describe the role of auxiliary ligands in the synthesis of the heterocubanes **2** and the use of **2a** as the most versatile source of (borole)rhodium fragments $Rh(C_4H_4BPh)$.

Results and Discussion

Addition of Nitrogen Bases. The heterocubane **2a** adds nitrogen bases such as pyridine (py) at ambient temperature within seconds. With py/Rh ratios ≥2 the orange crystalline bis(pyridine) complex $RhI(py)_2(C_4H_4BPh)$ (**4**) can be isolated. When only 1 equivalent of pyridine per Rh is used, the dark orange material $[Rh(\mu\text{-}I)(py)(C_4H_4BPh)]_2$ (**5**) is obtained. Molecular weight measurements in CH_2Cl_2 show that **5** is dinuclear and also seem to indicate that **5** tends to dissociate at low concentrations. The dinuclearity of **5** implies the existence of configurational isomers *cis*-**5** and *trans*-**5**.

Crystals of complex **4** tend to lose pyridine under vacuum. The same tendency is observed in solution, where the chemical shifts are markedly different at −80 and 20 °C, respectively, indicating a reversible dissociation of pyridine. When pyridine is added to solutions of pure bis(pyridine) complex **4**, only one set of pyridine signals is seen at ambient temperature, while at low temperature (^1H NMR, 500 MHz, CD_2Cl_2, −80 °C) a slow-exchange regime with two sets of pyridine signals for **4** and free pyridine is observed. The low-tempera-

[⊗] Abstract published in *Advance ACS Abstracts,* September 15, 1997.

(1) Part 22: See ref 2.

(2) Herberich, G. E.; Eckenrath, H. J.; Englert, U. *Organometallics* **1997**, *16*, 4292.

(3) Eckenrath, H. J. Doctoral Dissertation, Technische Hochschule Aachen, Aachen, Germany, 1997.

(4) (a) Herberich, G. E.; Hessner, B.; Boveleth, W.; Lüthe, H.; Saive, R.; Zelenka, L. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 996; *Angew. Chem. Suppl.* **1983**, 1503. (b) Herberich, G. E.; Büschges, U.; Hessner, B.; Lüthe, H. *J. Organomet. Chem.* **1986**, *312*, 13.

(5) In solution the complexes **3** exhibit a dynamic equilibrium between two conformational isomers. Only the major isomer of C_s symmetry is shown.

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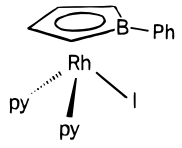

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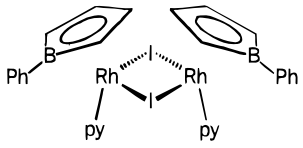
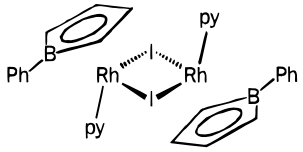


cis-**5**

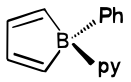


trans-**5**

ture NMR spectra of **4** show lateral symmetry. This would be consistent with effective lateral symmetry due to a low barrier to internal rotation and also with a symmetric preferential conformation such as that found previously in the complex $RhCl(PPh_3)_2(C_4H_4BPh)$,[6] where the Rh−Cl bond is in the pseudoaxial position of a distorted tetragonal pyramid with the boron eclipsed with this bond. Unfortunately, the spectral data obtained do not allow us to clarify this issue.

Low-temperature NMR spectra of **5** show the presence of two very similar isomers of almost identical energy, and both isomers show effective mirror symmetry for the (borole)rhodium fragments with two kinds of protons and two kinds of carbon nuclei. At 20 °C only averaged spectra are seen. We interpret these observations as due to the interconversion of *cis*-**5** and *trans*-**5**. As a consequence of the fast interconversion the two isomers can only be handled as an inseparable mixture.

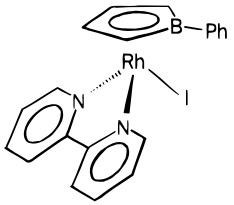
The bis(ligand) complex **3a** is readily attacked by excess pyridine at ambient temperature to give complex **4** and the labile borole−pyridine adduct **6** ($\delta(^{11}B)$ 2 ppm). Lewis base adducts of boroles have been described in several instances.[4b,7,8] When the solvent is removed under vacuum, the adduct **6** decomposes and, after addition of a small amount of pyridine, the oily residue can be crystallized from toluene to give **4**.



6

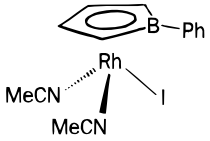
The substitution-labile bis(pyridine) complex **4** reacts with 2,2′-bipyridine (bpy) to form the robust yellow complex $RhI(bpy)(C_4H_4BPh)$ (**7**) within a few seconds. This compound can be made equally well from **2a** and 2,2′-bipyridine in CH_2Cl_2 or $CHCl_3$ solutions. No further compound appears when **2a** is treated with less than 1 equiv of 2,2′-bipyridine (Rh/bpy > 1); part of the heterocubane **2a** simply remains unreacted.

Acetonitrile adds to the heterocubane **2a** reversibly, and **2a** possesses an enhanced solubility in this solvent. Removal of the solvent regenerates **2a**. The solutions contain several species which are in a fast exchange



7

situation. Thus, the NMR spectra show chemical shifts that are somewhat concentration dependent, but individual species cannot be identified. Molecular weight measurements show that the predominant solution species is mononuclear, presumably the bis(acetonitrile) complex $RhI(NCMe)_2(C_4H_4BPh)$ (**8**).



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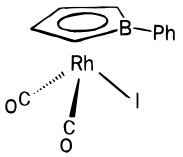
Carbonylation. When a solution of **2a** in CH_2Cl_2 is stirred under an atmosphere of carbon monoxide, the color changes from dark red to light orange within a few seconds. A $CDCl_3$ solution displays two ν(CO) bands of equal intensity at 2108 and 2080 cm^{-1}. These bands are assigned to the mononuclear dicarbonyl $RhI(CO)_2(C_4H_4BPh)$ (**9**). The homologous cobalt complex $CoI(CO)_2(C_4H_4BPh)$ shows CO bands at 2086 and 2058 cm^{-1} in CH_2Cl_2.[9]



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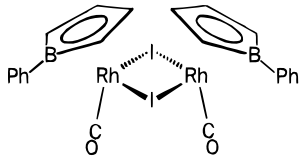
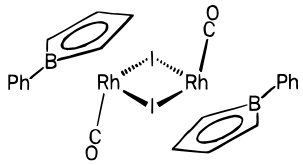


cis-**10**



trans-**10**

The dicarbonyl complex **9** only exists under an atmosphere of CO. When the solvent is removed under vacuum, an orange material is obtained as a residue. Solution NMR spectra of this residue at ambient temperature disclose the presence of two species with effective mirror symmetry and marginally different spectral data. We assign the observed spectra to *cis*/*trans* isomeric, dinuclear species $[Rh(\mu\text{-}I)(CO)(C_4H_4BPh)]_2$ (**10**). The isomers *cis*-**10** and *trans*-**10** are labile, but less so than the pyridine analogs **5** and, in contrast to *cis*-**5** and *trans*-**5**, interconvert slowly on the NMR time scale at ambient temperature.[10] This interpreta-

(6) Herberich, G. E.; Boveleth, W.; Hessner, B.; Hostalek, M.; Köffer, D. P. J.; Negele, M. *J. Organomet. Chem.* **1987**, *319*, 311.

(7) (a) Eisch, J. J.; Hota, N. K.; Kozima, S. *J. Am. Chem. Soc.* **1969**, *91*, 4575. (b) Grisdale, P. J.; Walters, J. L. R. *J. Organomet. Chem.* **1970**, *22*, C19.

(8) Herberich, G. E.; Negele, M. *J. Organomet. Chem.* **1988**, *350*, 81.

(9) Herberich, G. E.; Hessner, B.; Saive, R. *J. Organomet. Chem.* **1987**, *319*, 9.

(10) The barrier could not be determined, since decarbonylation takes place at elevated temperatures; $\Delta G^{\ddagger} > 65$ kJ/mol, estimated from $T_c > 20$ °C.

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tion is in accord with the IR spectrum in hexane, which shows three ν(CO) bands at 2068, 2060, and 2054 cm^{-1} with relative intensities of 9/10/9. The rather small separations between these bands can be understood as the consequence of rather weak coupling between the CO ligands across the two μ-I bridges.

Iodine Degradation of 1a Revisited. When the oxidative degradation of **1a**,**b** is effected by elemental iodine in toluene or CH_2Cl_2, the reaction cleanly follows Scheme 1.[2] If, however, coordinating solvents are present, the solvent may participate and react with any of the reactands. We discuss this aspect for the phenyl series only.

Scheme 1

$$(\mu\text{-}C_4H_4Br)[Rh(C_4H_4BR)_2]_2 + I_2 \rightarrow$$
1a,b

$$^1/_4[Rh(\mu_3\text{-}I)(C_4H_4Br)]_4 + RhI(C_4H_4BR)_2$$
2a,b **3a,b**

When acetonitrile is used as solvent, the heterocubane **2a** is solubilized as the solution species **8**, while **3a** is stable at ambient temperature in accord with the low nucleophilicity of acetonitrile. Similarly, when the oxidation is performed in toluene under an atmosphere of CO, the heterocubane is solubilized as the dicarbonyl **9**, while the less soluble bis(ligand) species **3a** is almost inert against CO at ambient temperature. At elevated temperature (in toluene, 80 °C, 7 h) **3a** reacts with CO to give more of the dicarbonyl **9**; one borole ligand is lost and destroyed. In a previous paper we have already described how this situation can be used to isolate either **3a** (by crystallization from the mixture at low temperature) or alternatively **2a** (by thermolysis of the solution of **9** under a stream of dinitrogen).[2]

A rather different situation ensues if pyridine or pyridine/THF mixtures are used as solvent. The fragment RhI(C_4H_4BPh), which in an inert solvent gives rise to the formation of **2a**, is stabilized as the bis(pyridine) adduct **4**. The second product **3a**, undergoes further degradation to give 1 equiv more of **4** and the borole−pyridine adduct **6** (Scheme 2).

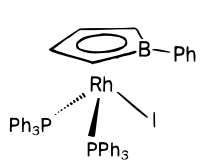
Scheme 2

$$(\mu\text{-}C_4H_4BPh)[Rh(C_4H_4BPh)_2]_2 + I_2 \rightarrow$$
1a

$$2RhI(py)_2(C_4H_4BPh) + C_4H_4BPh\cdot py$$
4 **6**

Addition of Phosphines. The heterocubane **2a** readily adds phosphines, and the products obtained are generally less labile then those formed with nitrogen bases. We give three examples which stand for three different structural types of products.

With 2 equiv of triphenylphosphine per rhodium, the mononuclear bis(phosphine) complex RhI(PPh_3)$_2$(C_4H_4BPh) (**11**) is formed. Complex **11** is a robust analog of **4** and **9**. The homologous chloride has been characterized structurally and possesses a roughly tetragonal-pyramidal structure, with the halogen in the axial position and the boron eclipsed with the Rh−Cl bond.[6] Reaction of **2a** with bis(diphenylphosphino)methane (dppm) affords the robust dinuclear compound [Rh$_2$(μ-I)$_2$(μ-dppm)(C_4H_4BPh)$_2$] (**12**). This complex is remarkably stable; even in the presence of a large excess of dppm it remains the major species in the solution. Structurally, complex **12** is related to the dinuclear species *cis*-**5** and *cis*-**10** and displays effective C_{2v} symmetry. The central Rh$_2$(μ-I)$_2$(μ-dppm) core is recognized in the ^{31}P NMR spectrum, which shows the AA′ part of an AA′XX′ type spectrum with six lines. The very flexible 1,1′-bis(diphenylphosphino)ferrocene[11] (dppf) adds to **2a** to produce the chelate complex RhI(dppf)-(C_4H_4BPh) (**13**). Note that this compound shows effective mirror symmetry in solution at ambient temperature, with two types of *P*-phenyl groups and four types of CH groups for the cyclopentadienyl rings. This implies high ligand flexibility but also inert Rh−P and Rh−I bonds.



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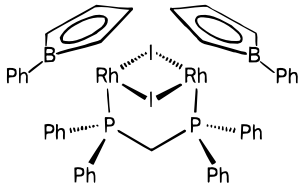

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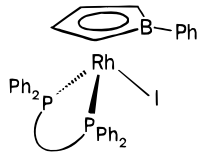

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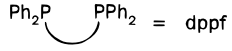
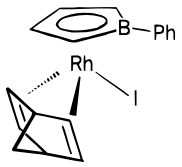


Reaction with Norbornadiene. The heterocubane **2a** shows very low affinity with unsaturated hydrocarbons. It reacts with norbornadiene (in CH_2Cl_2, 20 °C, 1 h) to produce the mononuclear complex RhI(nbd)(C_4H_4-BPh) (**14**), which can be isolated as orange crystals. This is the only positive result we can report in this context; e.g. neither 1,3-cyclohexadiene nor 1,5-cyclooctadiene reacts with **2a**. The ^{1}H and ^{13}C NMR spectra of **14** could be assigned completely with the help of (^{1}H,^{1}H)-COSY, (^{1}H,^{13}C)-HETCOR, and NOE difference spectra. The norbornadiene ligand displays two widely separated signals for the bridgehead CH groups and two equivalent protons in the CH_2 group. The olefinic *endo*-CH groups are close to the borole protons. Thus, the olefinic bonds of the norbornadiene are parallel to the Rh−I bond.



14

Solutions of analytically pure complex **14** in $CDCl_3$ show a reversible dissociation of the norbornadiene (e.g.

(11) Gan, K.-S.; Hor, T. S. A. 1,1′-Bis(diphenylphosphino)ferrocene-Coordination Chemistry, Organic Syntheses, and Catalysis; In *Ferrocenes*; Togni, A., Hayashi, T., Eds.; VCH: Weinheim, Germany, 1995.

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0.5% at −30 °C and 5% at 20 °C, NMR tube experiment). ^{1}H NMR spectra show the signals of nbd in addition to those of **14**; no further signals were observed which could tell the fate of the liberated fragment RhI(C_4H_4BPh). Complexes of the type [RhCl(diene)]$_2$ react with dienes at ambient temperature and exchange the diene.[12] Addition of a diene could be demonstrated in solution at low temperature, e.g. in the case of RhCl(nbd)$_2$.[12] We note that complex **14** is the missing link between the bis(norbornadiene) complex mentioned and the bis(borole) compound **3a**.

Addition of an Organometallic Halide and Synthesis of the Unsymmetrical Dinuclear Complex Cp*Rh(μ-I)$_3$Rh(C_4H_4BPh) (15). The heterocubanes **2** exchange fragments RhI(C_4H_4BR) at rates which are fast on the NMR time scale at ambient temperature.[2] This observation suggests that these fragments should also easily combine with other organometallic metal halides. As an example we chose the reaction of **2a** with (RhI$_2$Cp*)$_2$[13] (Scheme 3). Note that in the present context the fragment RhI$_2$Cp* can be considered as a bidentate Lewis base with an additional Lewis acid center.

Scheme 3

$$[Rh(\mu_3\text{-I})(C_4H_4BPh)]_4 + 2[RhI_2Cp^*]_2 \rightarrow$$
2a

$$4Cp^*Rh(\mu\text{-I})_3Rh(C_4H_4BPh)$$
15

Since the reactants are only slightly soluble, the two starting compounds were stirred as a suspension in CH_2Cl_2 to form (20 °C, 6 h) the mixed complex **15** as dark red microcrystals. The ^{1}H and ^{13}C NMR spectra show chemical shift values which are markedly different from those of the single components. There are no indications of dynamic processes, as the signals are sharp and remain unchanged when the sample is cooled to −80 °C. These observations indicate that **15** is a stable solution species which is formed through thermodynamic control in the reaction of Scheme 3. In contrast to the case of **2a**, the μ-I bridges in **15** are not cleaved when the complex is dissolved in acetonitrile. However, better ligands such as pyridine and CO (1 bar) readily react with **16** to form mononuclear degradation products.

Crystal Structure of 15. Complex **15** crystallizes in space group $P2_1/m$ (Figure 1, Table 1), and the molecule of **15** possesses crystallographic C_s symmetry. It consists of a central trigonal-bipyramidal Rh_2I_3 core which is capped with Cp* and the borole ligand. The three best planes C_5 of Cp*, (μ-I)$_3$, and C_4B are coplanar (only the interplanar angle of 4.1(2.9)° between the planes C_5 and C_4B differs from zero, though this is barely significant).

The Rh−I bond lengths (271.14(9)−275.48(6) pm) are in the expected range.[15] Note that the Rh−I bond lengths to the Rh(C_4H_4B) fragment are somewhat longer than those to the RhCp* fragment, reflecting the stronger metal−ligand interaction with the borole ring. The angles centered at Rh1 average 84.34° and those centered at Rh2 average 85.45°, while those centered at iodine average 77.60°.

The borole ring shows the usual characteristics. There is a slight folding along the line C2,C2′ which moves the B atom away from the metal; the vertical distance of the boron to the plane C_4 of the borole ring amounts to 12.3(9) pm, and the less well defined folding angle is 7.2(3.3)°. The Rh atom is shifted toward the C_4 part of the borole ring, and the resulting slip distortion[16] amounts to 9.7 pm. The C−C distances in the borole ring are not different. This observation indicates strong back-donation from the Rh atom into the π_3 orbital of the borole ring. Formally the three bridging iodo ligands place half a negative charge onto the (borole)rhodium fragment and half a positive charge onto the Cp*Rh fragment; this situation favors the back-bonding interaction just mentioned.

Concluding Remarks. It was the aim of this paper to show that the heterocubane [Rh(μ_3-I)(C_4H_4BPh)]$_4$ (**2a**)

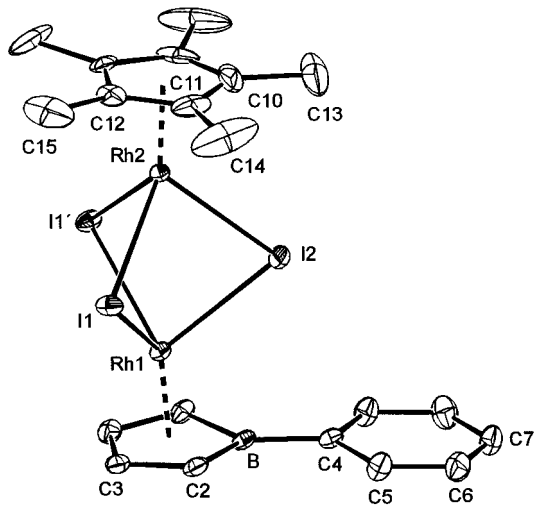

Figure 1. Thermal ellipsoid plot (PLATON)[14] of the molecule **15**. Ellipsoids are scaled to 30% probability.

Table 1. Selected Bond Distances and Angles for 15

(a) Bond Distances (pm)			
I1−Rh1	275.48(6)	I1−Rh2	272.30(6)
I2−Rh1	273.46(9)	I2−Rh2	271.14(9)
Rh1−C2	214.7(6)	Rh2−C10	217(1)
Rh1−C3	211.7(6)	Rh2−C11	213.4(7)
Rh1−B	229.6(9)	Rh2−C12	216.1(6)
C2−C3	142.1(9)	C3-C3′	141(1)
C2−B	154.4(9)	C4−B	154(1)
(b) Bond Angles (deg)			
Rh1−I1−Rh2	77.42(2)	Rh1−I2−Rh2	77.96(2)
I1−Rh1−I1′	84.19(2)	I1−Rh1−I2	84.42(2)
I1−Rh2−I1′	85.40(3)	I1−Rh2−I2	85.48(2)
C3−C2−B	108.7(6)	C2−C3−C3′	110.3(4)
C2−B−C2′	101.5(8)	C2−B−C4	129.2(4)
(c) Distances from Least-Squares Planes (pm)			
Rh1−(C_4B)	176.83(6)	Rh2−(C_5)	178.77(6)
Rh1−(I_3)	173.59(6)	Rh2−(I_3)	168.98(6)

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(16) The slip distortion is the distance between the geometric center of the C_4B ring and the projection of the metal atom onto the C_4B best plane.

displays a rich reaction chemistry. On the basis of the reactions described, we were able to explain the oxidative degradation of the triple-decker complexes (μ-C_4H_4-BR)[Rh(C_4H_4BR)]$_2$ (**1**) in more detail.[2]

All the new compounds described here show lateral symmetry. Internal rotation of the borole ring could create less symmetric rotamers. Barriers to internal rotation of borole rings have already been observed in a number of cases.[8,17] It may have been noted that it is not always clear whether the observed lateral symmetry reflects the preferential conformation of the complexes or is an effective symmetry due to a low barrier.

We have emphasized that the heterocubanes **2** have little tendency to react with unsaturated hydrocarbons. However, they can be activated by halide abstraction. This aspect will be presented in a later paper.[18]

Experimental Section

General Procedures. Reactions were carried out under an atmosphere of dinitrogen by means of conventional Schlenk techniques. Hexane was distilled from potassium, CH_2Cl_2, chlorobenzene, and pyridine were distilled from CaH_2, and Et_2O was distilled from sodium benzophenone ketyl. 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 (^{1}H, 500 MHz; ^{13}C{^{1}H}, 125.7 MHz; ^{11}B{^{1}H}, 160.4 MHz; ^{31}P{^{1}H}, 202.4 MHz) and a Bruker WP-80 PFT (^{1}H, 80 MHz) spectrometer. Chemical shifts are given in ppm; if not stated otherwise, they were measured at ambient temperature and are relative to internal TMS for ^{1}H and ^{13}C, relative to BF_3·Et_2O as an external reference for ^{11}B, and relative to 85% phosphoric acid as an external reference for ^{31}P.

Secondary ion mass spectra (SIMS) were recorded on a Finnigan MAT-95 spectrometer. Elemental analyses and determinations of molecular masses 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.

Addition of Pyridine to 2a in a 2/1 Ratio. Pyridine (65 mg, 0.82 mmol) was added to a solution of **2a** (150 mg, 0.101 mmol) in CH_2Cl_2 (5 mL). The color changed from dark red to orange within 30 s. After removal of the volatiles the oily residue was triturated with hexane (5 mL). The orange powder formed was collected, washed with hexane (2 × 2 mL), and shortly dried under vacuum to give **4** (210 mg, 98%): mp 138 °C; in solution somewhat air-sensitive; slowly gives off pyridine under vacuum; soluble in CH_2Cl_2, toluene, and ether; insoluble in hexane. Anal. Calcd for $C_{20}H_{19}BIN_2Rh$: C, 45.50; H, 3.63; N, 5.31. Found: C, 45.03; H, 3.61; N, 5.23.

Data for **4** are as follows. ^{1}H NMR (500 MHz, CD_2Cl_2, −80 °C): δ py 8.49 (m, 4 H_o), 7.53 (m, 2 H_p), 6.97−7.02 (m, 4 H_m + H_p of BPh), BPh 7.22 (m, 2 H_o), 6.88 (m, 2 H_m), borole 5.69 (m, 3-/4-H), 3.92 (m, 2-/5-H). ^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2): δ py 154.83 (br, C_o), 136.91 (C_p), 124.80 (br, C_m), BPh 135.25 (C_o), 128.12 (C_p), 127.37 (C_m), borole 90.60 (br, C-3,4), 67 (br, C-2,5). ^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2, −80 °C): δ py 154.53 (C_o), 136.57 (C_p), 124.41 (C_m), BPh 137.47 (C_i), 134.17 (C_o), 127.31 (C_p), 126.57 (C_m), borole 90.89 [d, ^1J(Rh−C) = 8.3 Hz, C-3,4], 65.65 (C-2,5). ^{11}B{^{1}H} NMR (CD_2Cl_2): δ 21. IR (KBr): ν(C═N) 1599 cm^{-1}.

Addition of Pyridine to 2a in a 1/1 Ratio. Complex **2a** (250 mg, 0.169 mmol) and pyridine (53.8 mg, 0.680 mmol) were combined in CH_2Cl_2 (5 mL). After removal of the volatiles the residue was washed with ether (1 mL) to give **5** (295 mg, 97%) as a dark orange powder: mp 158 °C; in solution somewhat air-sensitive; soluble in CH_2Cl_2 and toluene, moderately soluble in ether, insoluble in hexane. Anal. Calcd for $C_{30}H_{28}B_2I_2N_2Rh_2$: C, 40.13; H, 3.14; N, 3.12. Found: C, 40.45; H, 3.06; N, 3.06. Molar mass M_{calc} 897.81 g mol^{-1}; in CH_2Cl_2 M_{obs} (molarity (g/L)) 817 (39.64), 736 (20.70), 683 (9.98). SIMS (NBA): positive ions, m/z (I_{rel}) 983 (100, [$Rh_3I_2(C_4H_4BPh)_3$]$^+$).

Data for **5** are as follows. ^{1}H NMR (500 MHz, CD_2Cl_2): δ py 8.92 (br, 4 H_o), 7.44 (br, 2 H_p), 6.91 (br, 4 H_m), BPh 7.37 (m, 4 H_o), 7.16 (m, 2 H_p), 7.07 (m, 4 H_m), borole 5.22 (br, 3-/4-H), 3.84 (br, 2-/5-H); the broad borole signals appear as multiplets with N = 5.2 Hz at 80 MHz. ^{1}H NMR (500 MHz, CD_2Cl_2, −80 °C): isomer 1 (50%), δ py 9.04 (m, 4 H_o), 7.62 (m, 2 H_p), 7.14 (m, 4 H_m), Ph 7.33 (m, 4 H_o), 7.08 (m, 2 H_p), 7.02 (m, 4 H_m), borole 4.93 (m, N = 4.9 Hz, 3-/4-H), 3.55 (m, N = 4.9 Hz, 2-/5-H); isomer 2 (50%), δ py 8.53 (m, 4 H_o), 7.04 (m, 2 H_p), 6.48 (m, 4 H_m), BPh 7.28 (m, 4 H_o), 7.12 (m, 2 H_p), 7.02 (m, 4 H_m, as in isomer 1), borole 5.31 (m, 3-/4-H), 3.73 (m, N = 5.2 Hz, 2-/5-H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ py 156.15 (C_o), 136.04 (C_p), 123.97 (C_m), BPh 138.20 (br, C_i), 135.13 (C_o), 127.96 (C_p), 127.11 (C_m), borole 88.48 (br, C-3,4), 70.82 (br, C-2,5). ^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2, −80 °C), signals of Ph groups of isomers not resolved, δ BPh 137.74 (C_i), 134.65 (C_o), 127.48 and 127.41 (C_p), 126.58 (C_m); isomer 1 (50%), py 156.23 (C_o), 136.43 (C_p), 124.13 (C_m), borole 87.94 (C-3,4), 67.86 (C-2,5); isomer 2 (50%) py 155.25 (C_o), 135.48 (C_p), 123.40 (C_m), borole 87.94 (C-3,4), 68.22 (C-2,5). At −40 °C the isomer ratio is 45/55; this allows us to decompose the ^{1}H NMR spectrum into separate spectra of the isomers. Protons in the *ortho* positions of the BPh and pyridine groups are assigned by analogy; further assignments are based on (^{1}H,^{1}H)-COSY and (^{1}H,^{13}C)-HETCOR spectra. ^{11}B{^{1}H} NMR ($CDCl_3$): δ 20. IR (KBr): ν(C═N) 1599 cm^{-1}.

Synthesis of RhI(bpy)(C_4H_4BPh) (7). 2,2′-Bipyridine (68 mg, 0.436 mmol) was added to a solution of **4** (230 mg, 0.436 mmol) in THF (4 mL) to produce a yellow precipitate within seconds. After the mixture was stirred for 30 min, the volatiles were removed under vacuum. The residue was washed with hexane (2 × 1 mL) and dried under vacuum to give **7** (225 mg, 98%) as a light yellow powder: darkens above 190 °C, no mp < 250 °C; moderately soluble in CH_2Cl_2 and THF, insoluble in toluene and ether. Anal. Calcd for $C_{20}H_{17}BIN_2Rh$: C, 45.67; H, 3.26; N, 5.33; I, 24.13. Found: C, 45.55; H, 3.34; N, 5.23; I, 24.1.

Data for **7** are as follows. ^{1}H NMR (500 MHz, CD_2Cl_2): δ 9.01 (m, 2 6-/6′-H, bpy), 7.92 (m, 2 H), 7.74 (m, 2 H), 7.43 (m, 2 H), 7.21−7.09 (m, 2 H + 2 H_m + H_p), borole 5.68 (m, 3-/4-H), 4.00 (m, 2-/5-H). ^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2): δ bpy 155.50 (C-6,6′), 153.64 (C-2,2′), 137.01 (C-4,4′), 125.47 and 121.61 (C-3,3′ and C5,5′), BPh 135.04 (C_o), 128.06 (C_p), 127.40 (C_m), borole 91.81 [d, ^1J(Rh−C) = 8.6 Hz, C-3,4], 68.35 (br, C-2,5). ^{11}B-{^{1}H} NMR ($CDCl_3$): δ 21. IR (KBr): ν(C═N) 1599 cm^{-1}.

Acetonitrile Solutions of 2a: molar mass M_{calc} 369.80 g mol^{-1} for RhI(C_4H_4BPh); in acetonitrile M_{obs} (molarity (g/L)) 391 (5.548), 445 (11.77), 464 g/mol (13.05). ^{1}H NMR (500 MHz, CD_3CN): δ BPh 7.70 (m, 2 H_o), 7.34−7.30 (m, 2 H_m + H_p), borole 5.42 (br, 3-/4-H), 4.06 (m, N = 5.9 Hz, 2-/5-H). ^{1}H NMR (80 MHz) 5.43 (m, N = 5.8 Hz, 3-/4-H), 4.07 (m, N = 5.5 Hz, 2-/5-H). ^{13}C{^{1}H} NMR (126 MHz, CD_3CN): δ BPh 136.44 (C_o), 129.39 (C_p), 128.48 (C_m), borole 90.24 (br, C-3,4), 69.58 (br, C-2,5). ^{11}B{^{1}H} NMR (CD_3CN): δ 21.

Preparation of 9 in $CDCl_3$. A suspension of **2a** (30 mg) in CD_2Cl_2 or $CDCl_3$ (1 mL) was stirred under CO (1 bar) for 10 min while a slow stream of dry CO was passed through the flask. The yellow solution was then transferred into an NMR tube that had been purged with dry CO.

Data for **9** are as follows. ^{1}H NMR (500 MHz, CD_2Cl_2): δ BPh 7.76 (m, 2 H_o), 7.43−7.36 (m, 2 H_m + H_p), borole 6.32 (m,

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N = 5.5 Hz, 3-/4-H), 4.81 (m, N = 5.2 Hz, 2-/5-H). $^{13}C\{^1H\}$ NMR (126 MHz, CD_2Cl_2): δ 182.82 [d, ^1J(Rh−C) = 66.9 Hz, CO], BPh 135.85 (C_o), 130.75 (C_p), 128.40 (C_m), borole 104.34 [d, ^1J(Rh−C) = 5.5 Hz, C-3,4], 80.07 (br, C-2,5). $^{11}B\{^1H\}$ NMR ($CDCl_3$): δ 25. IR ($CDCl_3$): ν(CO)$_{as}$ = 2108, ν(CO)$_s$ = 2080 cm^{-1}.

Synthesis of [Rh(μ-I)(CO)(C_4H_4BPh)]$_2$ (10). A suspension of **2a** (280 mg, 0.189 mmol) in CH_2Cl_2 (10 mL) was stirred under CO (1 bar) for 10 min while a slow stream of dry CO was passed through the reaction vessel. The volatiles were then removed under vacuum. The foamy residue was triturated with hexane (5 mL) for 30 min, collected on a frit, washed with hexane (2 mL), and dried under vacuum to give **10** (230 mg, 76%) as an orange powder: retains traces of solvent and slowly decomposes under vacuum; mp 87 °C with partial decomposition; in solution somewhat air-sensitive; rather soluble in CH_2Cl_2, toluene, and acetone, moderately soluble in ether, slightly soluble in hexane.

Data for **10** are as follows. ^1H NMR (500 MHz, CD_2Cl_2): δ BPh, signals of isomers not resolved, 7.64 (m, 4 H_o), 7.35−7.29 (m, 4 H_m + 2 H_p); isomer 1 (55%), borole 5.86 (m, 3-/4-H), 4.56 (m, 2-/5-H); isomer 2 (45%), borole 5.82 (m, 3-/4-H), 4.56 (m, 2-/5-H). $^{13}C\{^1H\}$ NMR (126 MHz, CD_2Cl_2): δ BPh, signals of isomers not resolved, 136.36 (C_o), 135.3 (C_i), 130.02 (C_p), 127.89 (C_m); isomer 1 (55%), 187.30 [d, ^1J(Rh−C) = 71.3 Hz, CO], borole 100.13 [d, ^1J(Rh−C) = 6.6 Hz, C-3,4], 77.40 (br, C-2,5); isomer 2 (45%), 186.96 [d, ^1J(Rh−C) = 71.3 Hz, CO], borole 99.96 [d, ^1J(Rh−C) = 7.1 Hz, C-3,4], 77.80 (br, C-2,5). $^{11}B\{^1H\}$ NMR (CD_2Cl_2): δ 25. IR (hexane): ν(CO) 2054, 2060, 2068 cm^{-1}.

Addition of PPh_3 to 2a in a 2/1 Ratio. A solution of **2a** (260 mg, 0.176 mmol) and PPh_3 (369 mg, 1.406 mmol) in CH_2Cl_2 (10 mL) was stirred at ambient temperature for 30 min. The orange solution was then concentrated to 5 mL and layered with ether (20 mL). Orange needles formed slowly. After 3 days the mother liquor was removed; the crystals were washed with ether (2 × 5 mL) and dried under vacuum to give **11** (560 mg, 89%) as orange needles: mp 244 °C; in solution somewhat air-sensitive; soluble in CH_2Cl_2, slightly soluble in ether and acetone, insoluble in hexane. Anal. Calcd for $C_{46}H_{39}BIP_2Rh$: C, 61.77; H, 4.40. Found: C, 61.82; H, 4.38. SIMS (NBA): positive ions, m/z (I_{rel}) 768 (85, [RhH(PPh_3)$_2$(C_4H_4BPh)]$^+$), 505 (100, [Rh(PPh_3)(C_4H_4BPh)]$^+$).

Data for **11** are as follows. ^1H NMR (500 MHz, $CDCl_3$): δ BPh 7.75 (m, 2 H_o), 7.36−7.30 (m, 2 H_m + H_p + 12 H_o of PPh_3), PPh_3 7.28 (m, 6 H_p), 7.15 (m, 12 H_m), borole 4.61 (m, N = 5.8 Hz, 3-/4-H), 3.70 (m, 2-/5-H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ BPh 137.60 (C_i), 137.32 (C_o), 128.65 (C_p), 126.92 (C_m), PPh_3 135.51 ("t", N = 41.3 Hz, C_i), 134.40 ("t", N = 8.8 Hz, C_o), 129.46 (C_p), 127.65 ("t", N = 8.3 Hz, C_m), borole 97.01 [d, ^1J(Rh−C) = 7.1 Hz, C-3,4], 79.71 (br, C-2,5). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 20.29 [d, ^1J(Rh−P) = 142.6 Hz]. $^{11}B\{^1H\}$ NMR ($CDCl_3$) δ 27.

Synthesis of Rh$_2$(μ-I)$_2$(μ-dppm)(C_4H_4BPh)$_2$ (12). A solution of **2a** (240 mg, 0.162 mmol) and $CH_2(PPh_2)_2$ (dppm; 125 mg, 0.325 mmol) in CH_2Cl_2 (10 mL) was stirred for 1 h, then concentrated to 3 mL, and cooled to −30 °C for 16 h. The orange crystals that formed were collected, washed with hexane (2 × 5 mL), and dried under vacuum to give **12** (300 mg, 82%); no mp <250 °C; in solution somewhat air-sensitive; soluble in CH_2Cl_2, slightly soluble in ether and acetone, insoluble in hexane. Anal. Calcd for $C_{45}H_{40}B_2I_2P_2Rh_2$: C, 48.09; H, 3.59. Found: C, 48.12; H, 3.61. SIMS (NBA): positive ions, m/z (I_{rel}) 1124 (5, [Rh$_2$I$_2$(dppm)(C_4H_4BPh)$_2$]$^+$), 627 (53, [Rh(dppm)(C_4H_4BPh)]$^+$), 307 (100, $CH_2P_2Ph_3^+$).

Data for **12** are as follows. ^1H NMR (500 MHz, $CDCl_3$): δ BPh 7.62 (m, 4 H_o), 7.32−7.29 (m, 4 H_m + 2 H_p), PPh_2 7.41 (m, 8 H_o), 7.24 (m, 4 H_p), 7.14 (m, 8 H_m), 4.44 [t, ^2J(P−H) = 11.9 Hz, CH_2], borole 4.61 (m, N = 4.9 Hz, 3-/4-H), 3.94 (m, N = 5.2 Hz, 2-/5-H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ BPh 136.75 (C_o), 128.83 (C_p), 127.52 (C_m), PPh_2 134.68 (virtual d, N = 47.2 Hz, C_i), 133.64 (m, N = 11 Hz, C_o), 130.42 (C_p), 128.26 (m, N = 9.9 Hz, C_m), 35.16 [t, ^1J(P−C) = 12.6 Hz, CH_2], borole 96.14 [d, ^1J(Rh−C) = 6.6 Hz, C-3,4], 77.42 (br, C-2,5). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 16.76 (AA′XX′ system, "dt", ^1J(Rh−P) = 153.2, ^2J(P−P) = 15.9, ^3J(Rh−P) = 1.4, |^2J(Rh−Rh)| < 0.2 Hz). $^{11}B\{^1H\}$ NMR ($CDCl_3$): δ 21.

Synthesis of RhI(dppf)(C_4H_4BPh) (13). A solution of **2a** (230 mg, 0.155 mmol) and Fe($C_5H_4PPPh_2$)$_2$ (dppf; 345 mg, 0.622 mmol) in CH_2Cl_2 (10 mL) was stirred for 1 h. The solution was concentrated to 5 mL, and hexane (25 mL) was added to precipitate a light yellow powder, which was collected, washed with hexane (2 × 5 mL), and dried under vacuum at 60 °C to give **13** (545 mg, 95%): no mp <250 °C; in solution somewhat air-sensitive; soluble in CH_2Cl_2, slightly soluble in benzene and acetone, insoluble in ether and hexane. Recrystallization from CH_2Cl_2 after layering with hexane gave crystals with CH_2Cl_2. Anal. Calcd for $C_{44}H_{37}BFeIP_2Rh\cdot CH_2Cl_2$: C, 53.56; H, 3.90. Found: C, 53.50; H, 3.92. SIMS (NBA): positive ions, m/z (I_{rel}) 797 (100, [Rh(dppf)(C_4H_4BPh)]$^+$).

Data for **13** are as follows. ^1H NMR (500 MHz, $CDCl_3$): δ BPh 7.73 (m, 2 H_o), 7.34 (m, 2 H_m), 7.27 (m, H_p), PPh 7.58 (m, 4 H_o), 7.49 (m, 2 H_p), 7.23 (m, 4 H_m), PPh′ 7.47 (m, 4 $H_{o'}$), 7.39 (m, 4 $H_{m'}$), 7.28 (m, 2 $H_{p'}$), C_5H_4 5.65 (m, 2 5-H), 4.34 (m, 2 2-H), 4.31 (m, 2 4-H), 4.06 (m, 2 3-H), borole 4.71 (m, 3-/4-H), 3.59 (m, 2-/5-H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ BPh 136.95 (C_o), 128.48 (C_p), 126.88 (C_m), PPh 138.50 (m, N = 41.1 Hz, C_i or $C_{i'}$), 137.97 (m, N = 41.1 Hz, C_i or $C_{i'}$), 134.73 ("t", N = 10.4 Hz, C_o), 134.29 ("t", N = 11.5 Hz, $C_{o'}$), 130.08 (C_p), 129.38 ($C_{p'}$), 127.63 ("t", N = 9.3 Hz, $C_{m'}$), 127.24 ("t", N = 9.9 Hz, C_m), C_5H_4 87.88 (m, N = 48.8 Hz, C-1), 77.91 ("t", N = 10.4 Hz, C-5), 73.56 (C-2), 71.74 (C-4), 67.95 (C-3), borole 96.14 [d, ^1J(Rh−C) = 7.1 Hz, C-3,4], 78.20 (br, C-2,5). For ferrocenes ^3J(H−H) ≈ 2 × ^4J(H−H); the $^1H\{^{31}P\}$ NMR spectrum shows the protons 2-/5-H as a multiplet of five lines with intensities 1/2/2/2/1 and the protons 3-/4-H as a multiplet of six lines with intensities 1/1/2/2/1/1. Further assignments were made on the basis of (^1H,^1H)-COSY, (^1H,^{13}C)-HETCOR, and NOE difference spectra. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 33.06 [d, ^1J(Rh−P) = 148.3 Hz]. $^{11}B\{^1H\}$ NMR (CD_2Cl_2): δ 27.

Synthesis of RhI(nbd)(C_4H_4BPh) (14). A solution of **2a** (260 mg, 0.176 mmol) and nbd (65 mg, 0.71 mmol) in CH_2Cl_2 (20 mL) was stirred for 1 h, then concentrated to 3 mL, and cooled to −30 °C for 16 h. The orange-red crystals that formed were collected, washed with ether (2 × 2 mL), and dried under vacuum to give **14** (250 mg, 77%) as dark orange crystals: mp 167 °C dec; in solution somewhat air-sensitive; soluble in CH_2Cl_2 and acetone, moderately soluble in ether, slightly soluble in hexane. Anal. Calcd for $C_{17}H_{17}BIRh$: C, 44.20; H, 3.71. Found: C, 44.02; H, 3.73. SIMS (NBA): positive ions, m/z (I_{rel}) 335 (100, [Rh(nbd)(C_4H_4BPh)]$^+$).

Data for **14** are as follows. ^1H NMR (500 MHz, $CDCl_3$): δ BPh 7.88 (M, 2 H_o), 7.47−7.42 (m, H_p + 2 H_m), nbd 5.18 (m, 2 *exo*-CH=), 4.75 (m, 2 *endo*-CH=), 3.67 (m, *exo*-CH), 2.79 (m, *endo*-CH), 1.13 ("t", N = 1.5 Hz, CH_2), borole 5.73 (m, N = 6.4 Hz, 3-/4-H), 4.65 (m, N = 6.7 Hz, 2-/5-H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ BPh 135.19 (C_o), 129.43 (C_p), 128.28 (C_m), nbd 78.35 [d, ^1J(Rh−C) = 5.4 Hz, *exo*-CH=], 63.41 [d, ^3J(Rh−C) = 3.8 Hz, CH_2], 59.93 [d, ^1J(Rh−C) = 6.0 Hz, *endo*-CH=], 50.17 (*exo*-CH), 44.49 [d, ^2J(Rh−C) = 2.2 Hz, *endo*-CH], borole 100.53 [d, ^1J(Rh−C) = 6.1 Hz, C-3,4], 89.05 (br, C-2,5). Atoms that are closer to the borole ligand are designated as *endo*. $^{11}B\{^1H\}$ NMR ($CDCl_3$) δ 22.

Synthesis of Cp*Rh(μ-I)$_3$Rh(C_4H_4BPh) (15). A suspension of **2a** (730 mg, 0.494 mmol) and [RhI$_2$Cp*]$_2$[13] (972 mg, 0.988 mmol) in CH_2Cl_2 (60 mL) was stirred at 20 °C for 6 h. The volume was then reduced to 5 mL. The solid was collected on a frit, washed with ether (2 × 5 mL), and dried under vacuum to afford **15** (1.61 g, 95%) as blackish red crystals: no mp up to 250 °C; moderately soluble in CH_2Cl_2 and $CHCl_3$, slightly soluble in toluene, insoluble in acetonitrile and ether. Anal. Calcd for $C_{20}H_{24}BI_3Rh_2$: C, 27.88; H, 2.81. Found: C, 27.76; H. 2.73.

Table 2. Crystal Data, Data Collection Parameters, and Convergence Results for 15

formula	$C_{20}H_{24}BI_3Rh_2$
system	monoclinic
space group (No.)	$P2_1/m$ (11)
a, pm	887.8(3)
b, pm	1253.9(2)
c, pm	1124.7(5)
β, deg	110.61(3)
V, nm^3	1.1718(6)
Z	2
d_{calc}, g cm^{-3}	2.442
T, K	203
μ, cm^{-1}	53.03
λ, pm (radiation)	71.073 (Mo Kα)
θ_{max}, deg	26
cryst dimens, mm^3	0.24 × 0.24 × 0.10
abs cor	empirical
min transmissn	0.703
max transmissn	0.999
no. of reflns	2579
no. of indep obs rflns, $I > \sigma(I)$	2016
no. of vars	132
R^a	0.032
$R_w{}^b$	0.035
residual electron dens, e nm^{-6}	0.9

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

Data for **15** are as follows. ^{1}H NMR (500 MHz, $CDCl_3$): δ BPh 7.77 (m, 2 H_o), 7.31−7.28 (m, 2 H_m + H_p), borole 5.43 (m, 3-/4-H), 4.28 (m, 2-/5-H), 1.90 (s, Cp*). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ BPh 136.00 (C_o), 128.58 (C_p), 127.34 (C_m), Cp* 95.82 [d, ^1J(Rh−C) = 8.2 Hz, C_5Me_5] and 10.93 (C_5Me_5), borole 87.54 [d, ^1J(Rh−C) = 9.3 Hz, C-3,4], 71.44 (C-2,5). ^{11}B{^{1}H} NMR (CD_2Cl_2): δ 20.

Crystal Structure Determination of 15. A hot saturated solution of **15** in chlorobenzene was slowly cooled to ambient temperature to give suitable crystals. The data collection was performed on an ENRAF-Nonius CAD4 diffractometer with Mo Kα radiation (graphite monochromator). Crystal data, data collection parameters, and convergence results are given in Table 2. An empirical absorption correction[19] based on azimuthal scans was applied to the intensity data before averaging over symmetry-equivalent reflections. The structure was solved by direct methods;[20] refinement on structure factors with the help of the SDP program system[21] included all non-hydrogen atoms with anisotropic displacement parameters, while hydrogen atoms were treated as riding in idealized geometry (C−H = 98 pm, U_{iso}(H) = 1.3U_{iso}(C) for Cp*, one groupwise refined isotropic displacement parameter for the hydrogen atoms of the borole ring).[22]

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Supporting Information Available: Tables of fractional coordinates of all atoms, anisotropic displacement parameters, and bond distances and angles for **15** (5 pages). Ordering information is given on any current masthead page.

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(22) Further details of the crystal structure investigation are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, Germany, on quoting the depository number CSD-407353 for **15**, the names of the authors, and this journal citation.

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