Tetranuclear (Borole)rhodium Clusters with Hydrido and Methylthiolato Ligands − Structures of $[\{Rh(C_4H_4BMe)\}_4(\mu_3\text{-}H)(\mu_3\text{-}I)_3]$ and of $[\{Rh(C_4H_4BPh)\}_2(\mu\text{-}SMe)(\mu_3\text{-}SMe)]_2$ (2 *Rh−Rh*)[‡]

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The heterocubanes $[Rh(C_4H_4BR)(\mu_3\text{-}I)]_4$ (**1a**: R = Ph; **1b**: R = Me) can be hydrogenated in THF (suspension, 1 bar H_2, 20 °C) to give the μ_3-hydrido clusters $[\{Rh(C_4H_4BR)\}_4(\mu_3\text{-}H)(\mu_3\text{-}I)_3]$ (**2a**,**b**). The structure of **2b** consists of a $Rh_4(\mu_3\text{-}H)(\mu_3\text{-}I)_3$ core with idealized C_{3v} symmetry and four capping η^5-borole ligands. The Rh–Rh distances within the $Rh_3(\mu_3\text{-}H)$ cluster unit amount to 2.9448(6), 2.9647(6), and 2.9724(6) Å; the μ_3-H ligand is 0.064(5) Å above the Rh_3 plane with a mean Rh–H bond length of 1.83(5) Å. The tris(acetonitrile) salts $[Rh(C_4H_4BR)(NCMe)_3]BF_4$ (**4a**,**b**) react with NaSMe to give the methylthiolato complexes $[Rh(C_4H_4BR)(SMe)]_x$ (**3a**,**b**). In the crystal **3a** possesses a centrosymmetric stepped-ladder structure $[\{Rh(C_4H_4BPh)\}_2(\mu\text{-}SMe)(\mu_3\text{-}SMe)]_2$ (2*Rh–Rh*) (**3a**-Rh_4), with a Rh–Rh bond length of 2.9233(11) Å. In solution a dissociation equilibrium is observed with a predominating dinuclear complex $[Rh(C_4H_4BPh)(\mu\text{-}SMe)]_2$ (**3a**-Rh_2); in pyridine a closely related solvate $[Rh(py)(C_4H_4BPh)(\mu\text{-}SMe)]_2$ (**5**) with a static $Rh_2(\mu\text{-}SMe)_2$ core is formed.

Introduction

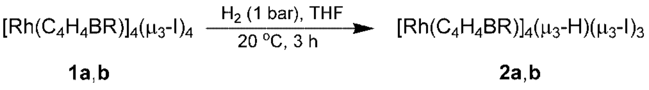
The recently described heterocubanes $[Rh(C_4H_4BR)(\mu_3\text{-}I)]_4$ (**1a**,**b**) are readily accessible[2a] and display a rich reaction chemistry.[2b] They possess a total of 72 valence electrons, with five electrons counted per μ_3-iodide ligand. Hence the Rh centers obey the 18-electron rule and therefore the complexes **1** are cage compounds. As they have no metal−metal bonds, they are not clusters in the sense of the widely accepted definition of a cluster given by Cotton.[3] The heterocubanes **1a** and **1b** undergo an exchange of (borole)rhodium vertices which is fast on the NMR timescale at ambient temperature,[2a] possibly via a dissociation−association equilibrium between tetra- and dinuclear species.

We have tried to vary the bridging ligand in these cage compounds in a number of ways,[4] and report here on two results. Homogeneous hydrogenation of the heterocubanes **1a**,**b** (R = Ph and Me, respectively) produces novel tetranuclear μ_3-hydrido clusters $[\{Rh(C_4H_4BR)\}_4(\mu_3\text{-}H)(\mu_3\text{-}I)_3]$ (**2a**,**b**), and treatment with NaSMe affords the methylthio complexes $[Rh(SMe)(C_4H_4BR)]_x$ (**3a**,**b**). In the case of **3b** a tetranuclear complex with a partially opened structure is found in the crystal and a dissociation−association equilibrium in solution.

Results and Discussion

Hydrogenation and Synthesis of Hydrido Clusters

The heterocubanes **1** readily react with dihydrogen in THF (1 bar, 20 °C, 3 h) to produce the μ_3-hydrido clusters **2** (Scheme 1) The basicity of the THF seems to be essential since no reaction is observed when dichloromethane is used as solvent. The products can be isolated as dark red crystals by cooling concentrated dichloromethane solutions. In solution they are slightly sensitive to air. They do not react with triethylamine or with iodomethane at ambient temperature and are decomposed by CF_3CO_2D in $CDCl_3$. We mention in passing that attempted hydrogenation of **1a**,**b** with $NaBHEt_3$ was unsuccessful and seemed to result in reductive decomposition.



$$\underset{\textbf{1a,b}}{[Rh(C_4H_4BR)]_4(\mu_3\text{-}I)_4} \xrightarrow[20\ ^\circ C,\ 3\ h]{H_2\ (1\ bar),\ THF} \underset{\textbf{2a,b}}{[Rh(C_4H_4BR)]_4(\mu_3\text{-}H)(\mu_3\text{-}I)_3}$$

Scheme 1. Hydrogenation of the heterocubanes $[Rh(C_4H_4BR)(\mu_3\text{-}I)]_4$ (**1a**,**b**)

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The ^{1}H NMR spectra of the product complexes **2a**,**b** display a quadruplet at high field [e.g. for **2a**: $\delta = -10.27$ ppm, $^1J_{\mathrm{Rh,H}} = 21.5$ Hz] indicating the presence of a triply bridging hydrido ligand in a $\mathrm{Rh_3(\mu_3\text{-}H)}$ arrangement. The $\mathrm{Rh_3(\mu_3\text{-}H)}$ structural element was first found in the Fischer/Wawersik complex $[\mathrm{(RhCp)_3(\mu_3\text{-}H)(\mu_3\text{-}Cp)}]$ [$\delta = -12.47$ ppm, $^1J_{\mathrm{Rh,H}} = 26.5$ Hz],[5] and is known from a few other structurally characterized complexes,[6,7] including, for instance, the tetranuclear complex $[\mathrm{(RhCp^*)_4(\mu_3\text{-}H)_4](BF_4)_2}$[7b,7c] and the trimethylenemethane complex $[\{\mathrm{Rh(COD)}\}_3(\mu_3\text{-}\mathrm{H})\{\mu_3\text{-}\mathrm{C(CH_2)_3}\}]$.[7a] We also see two types of borole ligands in a 3:1 ratio. In combination with the elemental analysis these observations define the formula and constitution of the clusters **2**.

Structure of the Hydrido Cluster 2b

Because of the novelty of these hydrido compounds we decided to characterize **2b** by an X-ray structure determination. Complex **2b** crystallizes in the monoclinic space group $P2_1/n$ with $Z = 4$ (Figure 1; produced with the Platon software package[8]). The central core of **2b** is a trigonal $\mathrm{Rh_4(\mu_3\text{-}H)(\mu_3\text{-}I)_3}$ unit with idealized C_{3v} symmetry, and each Rh vertex is capped by a borole ligand. Note that the apical vertex (with Rh1) is similar to the vertices of **1b**, while the basal vertices belong to a true cluster unit $(\mu_3\text{-}\mathrm{H})\mathrm{Rh_3}$.

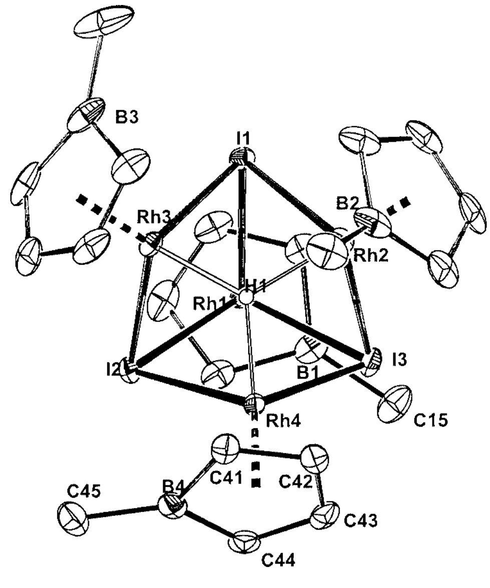


Figure 1. Molecular structure (PLATON plot,[8] at the 30% probability level) of **2b** in the crystal; see text for Rh−Rh interactions in the cluster; selected bond lengths (Å) and bond angles (°): I1−Rh1 2.7420(5), I1−Rh2 2.7181(6), I1−Rh3 2.7309(6), I2−Rh1 2.7272(6), I2−Rh3 2.7170(5), I2−Rh4 2.7285(6), I3−Rh1 2.7626(6), I3−Rh2 2.7398(6), I3−Rh4 2.7626(6), Rh1···Rh2 3.956(1), Rh1··Rh3 3.905(1), Rh1···Rh4 3.973(1), Rh2−Rh3 2.9647(6), Rh2−Rh4 2.9448(6), Rh3−Rh4 2.9724(6), Rh2−H1 1.82(5), Rh3−H1 1.82(5), Rh4−H1 1.83(5); I1−Rh1−I2 87.81(2), I1−Rh1−I3 85.87(2), I1−Rh2−I3 86.78(2), I1−Rh3−I2 88.24(2), I2−Rh1−I3 86.17(1), I2−Rh4−I3 86.14(1), Rh1−I1−Rh2 92.85(2), Rh1−I1−Rh3 91.06(2), Rh1−I2−Rh3 91.68(2), Rh1−I2−Rh4 93.47(2), Rh1−I3−Rh2 91.93(2), Rh1−I3−Rh4 91.95(1), Rh2−I1−Rh3 65.92(1), Rh2−I3−Rh4 64.71(2), Rh3−I2−Rh4 66.16(1)

The Rh−Rh distances between the apical Rh atom and the basal Rh centers amount to more than 3.90 Å and thus are nonbonding. The basal Rh atoms form a nearly regular triangle with Rh−Rh distances of 2.9448(6)−2.9724(6) Å. Known complexes with all-18e configurations and two center, two electron Rh−Rh bonds typically display Rh−Rh bond lengths of 2.72 Å,[5,6] while electron-deficient examples[7] tend to have longer bonds, with Rh−Rh distances up to about 3.0 Å.[9]

The Rh−I bond lengths average 2.737 Å [2.7170(5)−2.7626(6) Å] and are similar to those in **1a** and **1b** [2.7049(9)−2.777(1) Å],[3] while the Rh−(μ_2-I) distances [2.715−2.741 Å] seem to be marginally shorter.[10] The borole ligation to the metal is not detailed here. We only note that the Rh−B distances [2.307(6)−2.348(6) Å] are in the expected range (cf. the Rh−B bond lengths in the heterocubanes **1a**,**b**, which average to 2.325 Å[2a]).

The hydride ligand could be localized in the structure analysis and was refined isotropically. It lies 0.64(5) Å above the $\mathrm{Rh_3}$ plane, and the Rh−H bond lengths observed average to 1.83(5) Å. This result is in reasonable agreement with the data for the cluster $[\mathrm{(RhCp^*)_4(\mu_3\text{-}H)_4](BF_4)_2}$ (as determined by neutron diffraction).[7b]

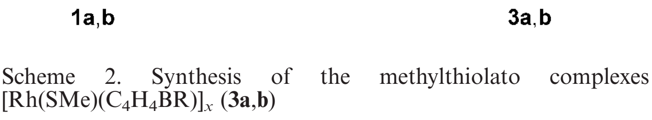
The hydrido clusters $[\{\mathrm{Rh(C_4H_4BR)}\}_4(\mu_3\text{-}\mathrm{H})(\mu_3\text{-}\mathrm{I})_3]$ (**2a,b**) possess a total of 68 valence electrons, four less than the cage complexes **1**. Formally removing one iodo ligand from the cages **1** generates a $[\{\mathrm{Rh(C_4H_4BR)}\}_4(\mu_3\text{-}\mathrm{I})_3]^+$ fragment with three empty, metal-centered orbitals ready for σ-bonding. In C_{3v} symmetry these σ-orbitals combine to an a_1 and an e set of orbitals. Interaction with the 1s orbital of the hydrido ligand results in bonding of the hydrido ligand and metal-metal bonding, in other words, in a four center, two electron bond within the $(\mu_3\text{-}\mathrm{H})\mathrm{Rh_3}$ tetrahedron. The e set of MOs remains empty and accounts for the reduced electron count of **2a**,**b**.

Synthesis of Methylthiolato Complexes

The anionic ligand of the cage complexes **1** may be substituted in a two-step procedure, first removing the halide ligand by dehalogenation with silver salts such as $\mathrm{AgBF_4}$ in acetonitrile, and then introducing a new ligand. Thus, the reaction of the tris(acetonitrile) salts **4a**,**b** with sodium methylthiolate in acetonitrile smoothly affords the robust, high-melting methylthiolato complexes **3a**,**b** (Scheme 2). The phenyl complex **3a** can be crystallized from hot toluene, while the methyl complex **3b** is scarcely soluble, even in toluene or $\mathrm{CH_2Cl_2}$.

Structure of the Methylthiolato Complex 3a in the Crystal

The low-temperature NMR spectra of complex **3a** indicate that this compound is not of the heterocubane type.



$$\underset{\textbf{1a,b}}{[\mathrm{Rh(C_4H_4BR)}]_4(\mu_3\text{-}\mathrm{I})_4} \xrightarrow[\text{2. NaSMe}]{\text{1. AgBF}_4\text{ in MeCN}} \underset{\textbf{3a,b}}{[\mathrm{Rh(SMe)(C_4H_4BR)}]_x}$$

Scheme 2. Synthesis of the methylthiolato complexes $[\mathrm{Rh(SMe)(C_4H_4BR)}]_x$ (**3a**,**b**)

The X-ray single-crystal structure determination revealed that complex **3a** consists of tetranuclear [{Rh-(C_4H_4BR)}$_2$(μ-SMe)($μ_3$-SMe)]$_2$ (2 *Rh−Rh*) (**3a**-Rh_4) molecules which display a crystallographic center of symmetry (Figure 2). The structure observed may formally be deduced from a cubanoid structure analogous to **1a**. Opening the heterocubane cage gives a stepped ladder, and coordinative unsaturation of the outer Rh centers is avoided by formation of dative Rh−Rh bonds [Rh1−Rh2 2.9233(11) Å]. Some additional stabilization by π-interactions with the sulfur lone-pairs may also be present. While the central rhombus is planar (as implied by the centrosymmetry of the molecule), the outer tetragons are folded along the line Rh1,Rh2 with a folding angle (between the plane Rh1,Rh2,S1 and Rh1,Rh2,S2) of 68.38(9)° in such a way that S2 is moved toward the central rhombus. Finally, we note that the molecule **3a**-Rh_4 may be viewed as a dimer of a dinuclear species **3a**-Rh_2. This view is supported by the fact that the connecting Rh2−S1′ and Rh2′−S1 bonds are markedly longer [2.461(2) Å] than the other Rh−S bonds in the same molecule [cf. Rh1−S1 2.326(2), Rh1−S2 2.303(3) Å and Rh2−S1 2.400(2), Rh2−S2 2.405(3) Å].

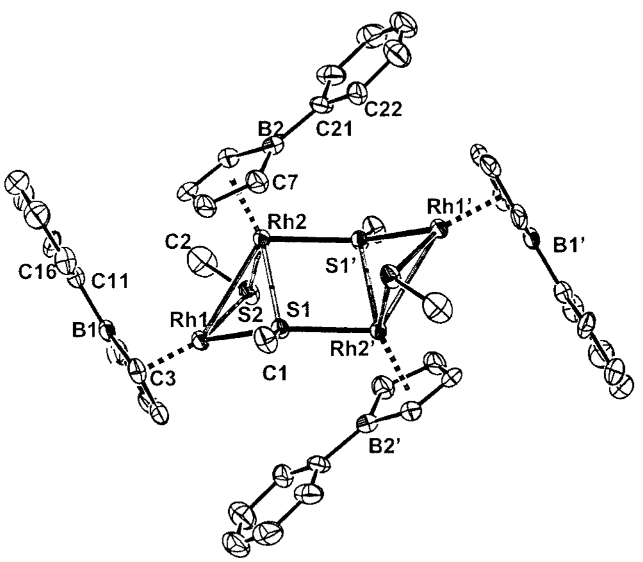
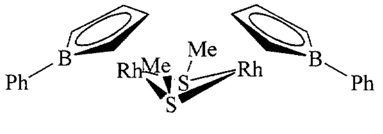


Figure 2. Molecular structure (PLATON plot,[8] at the 30% probability level) of **3a** in the crystal; selected bond lengths (Å) and bond angles (°):Rh1−Rh2 2.9233(11), Rh1−S1 2.326(2), Rh1−S2 2.303(2), Rh2−S1 2.400(2), Rh2−S2 2.405(3), Rh2−S1′ 2.461(2), S1−C1 1.818(8), S2−C2 1.826(10); Rh1−Rh2−S1 50.67(5), Rh1−Rh2−S2 50.06(6), Rh2−Rh1−S1 52.92(5), Rh2−Rh1−S2 53.21(7), S1−Rh1−S2 82.78(8), S1−Rh2−S2 79.14(8)



3a-Rh_2

Opening of heterocubane structures is also known from the family of complexes [MX(PR_3)]$_4$,[11] and small metal centers and bulky counter-ligands favor stepped-ladder structures. For instance, while the chloro complex [CuCl(PPh_3)]$_4$ is a heterocubane, the phenylthiolate adopts a [{Cu(PPh_3)}$_2$(μ-SPh)($μ_3$-SPh)]$_2$ structure closely akin to that of **3a**. This structural difference is probably related to the bulkiness of the phenylthiolato ligands.

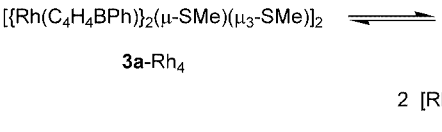
The Rh−S bond lengths in **3a** (2.32−2.46 Å) are shorter than the Rh−I bond lengths in **1a** (2.73−2.77 Å). The opening of the cubanoid structure to the stepped-ladder structure may again be caused by steric congestion. A detailed molecular modeling study would require a fully parametrized force-field to deal with the $η^5$-bonded phenylborole ligands. We therefore recurred to the following simplified approach for the generation of a hypothetical $μ_3$-SMe bridged heterocubane: Starting with the structure of **1a** the distances between the Rh centers and the heteroatoms were reduced to 2.35 Å (for pertinent reference data see ref.[10]), and the methyl groups were placed at an S−C distance of 1.8 Å in the radial direction. No conformational changes and no optimizations of the whole structure were performed. The resulting molecule exhibited prohibitively short C···H (1.9 Å), C···C (2.8 Å), and H···H (1.9 Å) interactions between the S−Me and B−Ph groups. On the basis of MM2 van der Waals parameters[12] an estimated destabilization of the cubanoid structure by approximately 100 kJ/mol was calculated.

Structure of the Methylthiolato Clusters 3a,b in Solution

The low-temperature ^1H NMR spectrum of **3a** (500 MHz, CD_2Cl_2, −80 °C) displays eight multiplets of equal intensity for the borole protons. This observation strongly suggests that the same structure that was found in the crystal is also present in the low-temperature solution. The stepped-ladder molecule **3a**-Rh_4 is a *meso* species with two chemically different borole ligands, both of which are in a chiral environment. Two sharp singlets are seen for the SMe groups, again in agreement with the assumption of a stepped-ladder structure in solution.

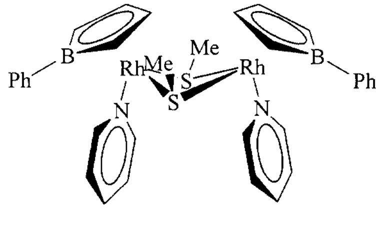
^1H NMR measurements at ambient temperature or above (in CD_2Cl_2, $CDCl_3$, or 1,1,2,2-$C_2D_2Cl_4$) produced spectra corresponding to effective C_{2v} symmetry. Using a 500 MHz spectrometer the signals were broad and blurred; on an 80 MHz machine the same solutions gave sharp, well-resolved signals with the characteristic hyperfine structure of the borole AA′BB′ four-spin system. Only one type of borole ligand and one type of SMe ligand were left. The chemical shifts are temperature dependent up to about 80 °C and then remain constant up to 120 °C (in 1,1,2,2-$C_2D_2Cl_4$), the highest temperature reached. These observations are readily explained by the assumption of a dissociation/association equilibrium between the tetranuclear species **3a**-Rh_4 and the dinuclear species **3a**-Rh_2, which was already mentioned above in the structural discussion (Scheme 3). We mention in passing that dinuclear species such as **3a**-Rh_2 could, in principle, form three stereoisomers, two *syn*-stereoisomers and one *anti*-stereoisomer, although only one species is seen in the NMR spectra. A comparison of the chemical shifts of the tetranuclear species from the spectrum measured at

−80 °C and of the dinuclear species **3a**-Rh$_2$ exclusively present above 80 °C shows that at ambient temperatures **3a**-Rh$_2$ is already the predominant species. It is interesting to note here that the electronically related ruthenium complexes [(RuCp*)$_2$(μ-SR)$_2$] are dinuclear, as confirmed by an X-ray structure determination of [{Ru(C$_5$Me$_4$Et)}$_2$(μ-SEt)$_2$].[13]



Sdheme 3. The dissociation equilibrium of the tetranuclear complex [{Rh(C$_4$H$_4$BR)}$_2$(μ-SMe)(μ$_3$-SMe)]$_2$ (2 *Rh−Rh*) (**3a**-Rh$_4$)

In the presence of pyridine complex **3a** shows a somewhat enhanced solubility, and in neat [D$_5$]pyridine it is moderately soluble. The ^{1}H NMR spectrum of this solution shows effective C_{2v} symmetry. The SMe groups appear as a sharp triplet not seen in the equilibrium mixture of Scheme 3. The triplet results from coupling with two Rh centers and indicates the formation of a new dinuclear species **5**, presumably of the formula [{Rh(py)(C$_4$H$_4$BPh)}$_2$(μ-SMe)$_2$]. On attempted isolation complex **5** lost the pyridine completely, re-forming the cluster **3a**. The observation of the sharp triplet demonstrates that **3a**-Rh$_2$ cannot dissociate into a mononuclear species, not even in the presence of a good donor ligand. On the other hand, it also suggests that the tetranuclear species **3a**-Rh$_4$ is no longer present as it would, very likely, cause blurring of the hyperfine structure of the signal.



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The analogous 1-methylborole complex **3b** poses the same structural problems. Because of the low solubility of this complex only ^{1}H NMR spectra could be measured and low-temperature measurements were not possible. Comparison of ^{1}H NMR measurements at 500 MHz and at 80 MHz revealed chemical-shift differences, suggesting that the methyl compound **3b** is also involved in a dissociation equilibrium in solution. An attempted X-ray structure determination showed the crystals to be polysynthetic twins, and no structure solution could be obtained. Thus the nuclearity of **3b** remains an open question.

Conclusion

The triple-decker complexes [{Rh(C$_4$H$_4$BR)}$_2$(μ-C$_4$H$_4$BR)] (R = Ph, Me) are among the most easily accessible borole complexes,[14] and therefore have been the starting point of a variety of studies.[1,2,15] In this paper we have described the first true cluster compounds with (borole)rhodium vertices. In preceding work we speculated that the fast exchange of (borole)rhodium vertices observed for the heterocubanes **1a**,**b** could occur via a dissociative formation of dinuclear intermediates.[2a] It was therefore particularly satisfying to find compelling evidence for the existence of the dinuclear species **3a**,**b**-Rh$_2$ in equilibrium with the tetranuclear clusters **3a**,**b**-Rh$_4$.

Experimental Section

General: Reactions were carried out under an atmosphere of dinitrogen by means of conventional Schlenk techniques. Hexane was distilled from potassium, CH$_2$Cl$_2$ from CaH$_2$, and THF and Et$_2$O from sodium benzophenone ketyl.

Secondary ion mass spectra (SIMS) were recorded on a Finnigan MAT-95 spectrometer. NMR spectra were recorded on a Varian Unity 500 spectrometer (^{1}H: 499.6 MHz; ^{13}C{^{1}H}: 125.6 MHz; ^{11}B{^{1}H}: 160.3 MHz). Chemical shifts are given in ppm; they were measured at ambient temperature and are relative to internal TMS for ^{1}H and ^{13}C and relative to BF$_3$·OEt$_2$ as external reference for ^{11}B.

[{Rh(C$_4$H$_4$BPh)}$_4$(μ$_3$-H)(μ$_3$-I)$_3$] (2a): The heterocubane [Rh(C$_4$H$_4$BPh)(μ$_3$-I)]$_4$ (**1a**; 830 mg, 0.561 mmol) was suspended in THF (60 mL). A slow stream of hydrogen was passed through the flask with stirring for 3 h. Complex **1b** slowly dissolved as the reaction proceeded. The volatiles were then removed under vacuum. The residue was dissolved in CH$_2$Cl$_2$ (50 mL); the solution was filtered through a frit covered with kieselguhr, concentrated to a small volume (5 mL), and kept at −30 °C for 24 h. After removal of the mother liquor the crystals were washed with diethyl ether (2 × 5 mL) and dried under vacuum to give **2a** (560 mg, 74%) as dark red crystals, m.p. 212 °C (dec.); in solution somewhat sensitive to air, soluble in CH$_2$Cl$_2$, slightly soluble in benzene, insoluble in hexane, Et$_2$O and acetonitrile. C$_{40}$H$_{37}$B$_4$I$_3$Rh$_4$ (1353.3): calcd. C 35.50, H 2.76; found C 35.18, H 2.71. SIMS (NBA; negative ions): *m*/*z* (%) = 1110 (14) [Rh$_3$I$_3$(C$_4$H$_4$BPh)$_3$]$^-$, 497 (24) [RhI$_2$(C$_4$H$_4$BPh)]$^-$, 357 (27) [RhI$_2$]$^-$, 127 (100) [I$^-$]. ^{1}H NMR (CDCl$_3$): δ = −10.27 (q, $^1J_{\mathrm{Rh,H}}$ = 21.5 Hz, μ$_3$-H), 3.84 (m, $N = {}^3J_{23} + {}^4J_{24}$ = 5.5 Hz, borole 2-/5-H), 4.49 (m, *N* = 5.5 Hz, 3 × borole 2′-/5′-H), 4.91 (m, *N* = 5.2 Hz, borole 3-/4-H), 5.11 (m, *N* = 5.2 Hz, 3 × borole 3′-/4′-H), 7.31−7.39 (m, H$_p$ + 3 H$_p$′ + 2 H$_m$ + 6 H$_m$′), 7.57 (m, 2 H$_o$), 7.62 (m, 6 H$_o$′) ppm. ^{13}C{^{1}H} NMR (CDCl$_3$): δ = 71.8 (br., borole C-2,5), 75.0 (br., borole C-2′,5′), 88.49 [d, $^1J_{\mathrm{Rh,C}}$ = 9.3 Hz, borole C-3,4], 90.19 (d, $^1J_{\mathrm{Rh,C}}$ = 8.3 Hz, borole C-3′,4′) 127.68 (C$_m$), 127.60 (C$_m$′), 129.09 (C$_p$′), 129.11 (C$_p$), 135.82 (C$_o$ + C$_o$′), 136.7 (C$_i$), 137.08 (C$_i$′) ppm. ^{11}B{^{1}H} NMR (CDCl$_3$): δ = 20 ppm.

[{Rh(C$_4$H$_4$BMe)}$_4$(μ$_3$-H)(μ$_3$-I)$_3$] (2b): The heterocubane [Rh(C$_4$H$_4$BMe)(μ$_3$-I)]$_4$ (**1b**, 200 mg, 0.162 mmol) was dissolved in THF (20 mL) and hydrogenated as described above for **1a**. The raw product was dissolved in CH$_2$Cl$_2$ (10 mL); the solution was filtered through a frit covered with kieselguhr, concentrated to a small volume (1 mL), and kept at −30 °C for 24 h. After removal of the mother liquor the crystals were washed with hexane (2 × 5 mL) and dried under vacuum to give **2b** (148 mg, 82%) as dark red crystals, m.p. 155 °C (dec.); in solution somewhat sensitive to air, soluble in CH$_2$Cl$_2$, tetrahydrofuran and toluene, moderately soluble in Et$_2$O, insoluble in hexane. Crystals suitable for a single-crystal

Table 1. Crystal data, data collection parameters, and convergence results for **2b** and **3a**

	2b	**3a**
Empirical formula	$C_{20}H_{29}B_4I_3Rh_4$	$C_{44}H_{48}B_4Rh_4S_4$
Molecular mass	1105.01	1159.94
Crystal system	monoclinic	orthorhombic
Space group	$P2_1/n$	*Pbca*
Radiation (λ[Å])	Mo-K_α (0.71073)	Cu-K_α (1.54184)
a (Å)	15.415(2)	8.408(4)
b (Å)	11.629(2)	22.058(7)
c (Å)	15.834(2)	23.915(7)
β (°)	104.769(10)	
V (Å^3)	2744.6(7)	4435(3)
Z	4	4
$d_{calcd.}$ [g/cm^3]	2.67	1.737
F(000)	2032	2304
μ [cm^{-1}]	5.746	13.819
Absorption correction	empirical	empirical
Max./min. transmission	0.9986/0.8981	0.9976/0.7565
Θ (°)	3−28	5−65
Temperature [K]	203	293
Scan mode	ω−2Θ	ω−Θ
Crystal size [mm]	0.36 × 0.28 × 0.20	0.35 × 0.15 × 0.06
Reflections collected	8687	3707
Reflections unique	6609[a]	3707
Reflections observed	5233	2460
Criterion for observation	$I > 2\sigma(I)$	$I > 2\sigma(I)$
Variables	288	255
R_1,[b] observed (all data)	0.0286 (0.0504)	0.0491 (0.0958)
wR_2,[c] observed (all data)	0.0567 (0.0598)	0.1228(0.1355)
GOF[d]	1.010	1.008
Max. residual density [e/Å^3]	0.89	1.495

[a] $R_{int} = 0.0236$. [b] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [c] $wR_2 = [\Sigma w(F_o^2 - F_c^2)2/\Sigma w(F_o^2)^2]^{1/2}$, where $w = 1/[\sigma^2(F_o^2) + (aP)^2]$ and $P = [\max(F_o^2,0) + 2F_c^2]/3$. [d] $GOF = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma[(n - p)]^{1/2}$.

structure determination were obtained by very slowly concentrating a saturated solution of **2b** in diethyl ether. $C_{20}H_{29}B_4I_3Rh_4$ (1105.5): calcd. C 21.74, H, 2.65; found C 21.69, H 2.67. SIMS (NBA; positive ions): *m*/*z* (%) = 1106 (62) [M$^+$], 979 (18) [M$^+$ − I], 798 (100) [M$^+$ − I − Rh − C_4H_4BMe]; negative ions: *m*/*z* (%) = 435 (26) [$RhI_2(C_4H_4BMe)$]$^-$, 127 (100) [I$^-$]. ^{1}H NMR ($CDCl_3$): δ = −9.78 [q, $^1J_{Rh,H}$ = 21.4 Hz, μ_3-H), 0.40 (s, Me), 0.50 (s, 3 × Me′), 3.41 (m, *N* = 5.2 Hz, borole 2-/5-H), 4.15 (m, *N* = 5.2 Hz, 3 × borole 2′-/5′-H), 4.89 (m, *N* = 5.5 Hz, borole 3-/4-H), 5.42 (m, *N* = 5.5 Hz, 3 × borole 3′-/4′-H) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = −2.31 (br., Me + Me′), 72.81 (br., borole C-2,5), 76.15 (br., borole C-2′,5′), 87.73 [d, $^1J_{Rh,C}$ = 9.3 Hz, borole C-3,4], 89.99 [d, $^1J_{Rh,C}$ = 8.7 Hz, borole C-3′,4′] ppm. $^{11}B\{^1H\}$ NMR ($CDCl_3$): δ = 25 ppm.

[{Rh(C_4H_4BPh)}$_2$(μ-SMe)(μ_3-SMe)]$_2$ (3a): Polymeric *catena*-[Rh(μ,η^5:η^6-C_4H_4BPh)BF_4][1] (650 mg, 1.971 mmol Rh) was dissolved in acetonitrile (10 mL) to give a solution of **4a**. This solution was added with stirring to a suspension of NaSMe (138 mg, 1.969 mmol) in acetonitrile (5 mL), and stirring was continued for 60 min. The solid raw product thus obtained was collected on a G4 frit covered with kieselguhr and washed with acetonitrile (5 × 10 mL). It was then eluted with CH_2Cl_2. The solvent was evaporated under vacuum, and the resulting solid was washed with acetone (2 × 5 mL) and dried under vacuum to afford **3a** (430 mg, 75%) as blackish red microcrystals, m.p. 238 °C, not air-sensitive, soluble in pyridine, slightly soluble in $CHCl_3$, CH_2Cl_2 and toluene, insoluble in diethyl ether, acetone, acetonitrile. Single crystals suitable for a single-crystal structure determination were obtained from a concentrated solution of **3a** in hot toluene by very slow cooling to ambient temperature. $C_{44}H_{48}B_4Rh_4S_4$ (1160.0) calcd. C 45.56, H 4.17; found C 45.93, H 4.16. ^{1}H NMR (80 MHz, $CDCl_3$, 25 °C): δ = 2.70 (s, Me), 3.96 (m, *N* = 5.8 Hz, borole 2-/5-H), 4.60 (m, *N* = 4.6 Hz, borole 3-/4-H), 7.24−7.43 (complex region, 2 H_p + 4 H_m), 7.73 (m, 4 H_o) ppm. $^{13}C\{^1H\}$ NMR (125.7 MHz, $CDCl_3$, 25 °C): δ = 23.84 (Me), 93.04 (br., borole C-3/4), 127.90 (C_m), 129.34 (C_p), 135.56 (C_o) ppm; signal for C-2/5 not observed. $^{11}B\{^1H\}$ NMR (160.4 MHz, $CDCl_3$, 25 °C): δ = 22 ppm.

Selected VT NMR Data for 3a: ^{1}H NMR (500 MHz, CD_2Cl_2, −80 °C): δ = 2.14 (s, μ_3-SMe), 2.47 (s, μ-SMe), 2.80 (m, 2 H, borole 2-H_2 or 5-H), 3.23 (m, 2 H, borole 2-H or 5-H), 3.53 (m, borole 2′-H or 5′-H), 3.75 (m, borole 2′-H or 5′-H), 3.92 (m, borole 3′-H or 4′-H), 4.35 (m, borole 3-H or 4-H), 4.52 (m, borole 3-H or 4-H), 5.46 (m, borole 3′-H or 4′-H), 7.36−7.40 (complex region, 2 H_p + 4 H_m), 7.47 (m, 4 $H_{m'}$), 7.53 (m, 2 $H_{p'}$), 7.65−7.70 (complex region, 4 H_o + 2 $H_{o'}$) ppm; assignments were made on the basis of (^{1}H,^{1}H)-COSY spectra. ^{1}H NMR (500 MHz, CD_2Cl_2, 25 °C): δ = 2.98 (br. s, 2 Me), 4.19 (br. s, 2 × borole 2-/5-H), 4.73 (br. s, 2 × borole 3-/4-H), 7.33 (m, 4 H_m), 7.42 (m, 2 H_p), 7.74 (m, 4 H_o) ppm. ^{1}H NMR (500 MHz, 1,1,2,2-$C_2D_2Cl_4$, 120 °C): δ = 3.13 (s, 2 Me), 4.28 (m, 2 × borole 2-/5-H), 4.82 (m, 2 × borole 3-/4-H), 7.28 (m, 4 H_m), 7.38 (m, 2 H_p), 7.71 (m, 4 H_o) ppm.

Data for 5: ^{1}H NMR (80 MHz, [D$_5$]pyridine, 25 °C): δ = 2.76 (t, $^3J_{Rh,H}$ = 1.4 Hz, 2 Me), borole 4.09 (m, *N* = 5.7 Hz, borole 2-/5-H), 5.26 (m, *N* = 5.0 Hz, borole 3-/4-H), 7.19−7.32 (complex region, 4 H_m + 2 H_p), 7.75 (m, 4 H_o) ppm.

[Rh(SMe)(C_4H_4BMe)]$_x$ (3b): A solution of $AgBF_4$ (221 mg, 1.135 mmol) in acetonitrile (10 mL) was added with stirring to a suspension of **1b** (350 mg, 0.284 mmol) in acetonitrile (10 mL), and stirring was continued for 30 min. The resulting reaction mixture was filtered through a frit covered with kieselguhr into a flask containing a stirred suspension of NaSMe (79.5 mg, 1.134 mmol) in acetonitrile (5 mL). After stirring the reaction mixture for 60 min, the microcrystalline product was collected on a frit covered with kieselguhr and washed with acetonitrile (5 × 10 mL). It was then eluted with CH_2Cl_2. The solvent was evaporated under vacuum, and the resulting solid was washed with acetone (2 × 5 mL) and dried under vacuum to afford **3b** (180 mg, 70%) as blackish red microcrystals, m.p. 227 °C; not air-sensitive, slightly soluble in $CHCl_3$, CH_2Cl_2 and toluene, insoluble in diethyl ether, acetone, acetonitrile. ^{1}H NMR (80 MHz, $CDCl_3$, 25 °C): $\delta = 0.31$ (s, B-Me), 2.83 (s, S-Me), 3.77 (m, $N = 5.7$ Hz, borole 2-/5-H), 5.24 (m, $N = 5.8$ Hz, borole 3-/4-H) ppm. ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): $\delta = 0.32$ (s, Me), 2.71 (s, SMe), 3.69 (m, borole 2-/5-H), 5.22 (m, borole 3-/4-H) ppm.

X-ray Crystal Structure Determinations: The data collection was performed on an ENRAF-Nonius CAD4 diffractometer with Mo-K_α radiation for **2b** and Cu-K_α radiation for **3a** (where the crystals were small and the unit cell comparatively large) using a graphite monochromator. Crystal data, data collection parameters, and convergence results are given in Table 1. In the case of **3a** all residual electron density greater than 0.55 e/Å^3 was close to the two Rh atoms.

CCDC-216303 (for **2b**) and -216302 (for **3a**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) + 44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk].

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[9] Cf. data for $[(RhCp^*)_4(\mu_3\text{-}H)_4](BF_4)_2$: two short bonds of 2.655(1) Å and four long bonds of 2.829(1) Å;[7b,7c] and for the 44e cluster $[\{Rh(COD)\}_3(\mu_3\text{-}H)\{\mu_3\text{-}C(CH_2)_3\}]$: 2.977(1)−2.981(1) Å].[7a]

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