Organometallics **1998,** *17,* 519−523

Borole Derivatives. 24.[1] Synthesis of Cationic (Arene)(phenylborole)rhodium Complexes. Structures of the Trinuclear Complex (η^5-C_4H_4BPh)Rh(μ_3-I)$_3$-Rh(μ,η^5:η^6-C_4H_4BPh)Rh(η^5-C_4H_4BMe)·CH_2Cl_2 and of the Polymeric *catena*-(μ,η^5:η^6-1-Phenylborole)rhodium Tetrafluoroborate

Gerhard E. Herberich,* Hartmut J. Eckenrath,[3] and Ulli Englert

Institut für Anorganische Chemie, Technische Hochschule Aachen, D-52056 Aachen, Germany

Received August 19, 1997

The heterocubane [Rh(μ_3-I)(C_4H_4BPh)]$_4$ (**1**) reacts with Ag^+ salts in acetonitrile to give the labile salt [Rh$(NCMe)_3$(C_4H_4BPh)]BF_4 (**2**). This salt **2** reacts with hexamethylbenzene (hmb) to give the arene complex [Rh(C_4H_4BPh)(hmb)]BF_4 (**3**), and with mesitylene [Rh(1,3,5-$C_6H_3Me_3$)(C_4H_4BPh)]BF_4 (**4**) is obtained. Complex **2** loses acetonitrile under vacuum to produce the polymeric salt *catena*-[{Rh(μ,η^5:η^6-C_4H_4BPh)}BF_4]$_x$ (**5**). Insight into the essential structural features of this polymer provided its radial distribution function obtained from a wide-angle X-ray scattering experiment. When treated with acetonitrile, complex **5** regenerates **2** and with pyridine affords [Rh$(py)_3$((C_4H_4BPh)]BF_4 (**6**). Crystallization from a solution of [Rh(μ_3-I)(C_4H_4BPh)]$_4$ (**1**) and the corresponding methylborole complex [Rh(μ_3-I)-(C_4H_4BMe)]$_4$ (1/1) in CH_2Cl_2 produces the trinuclear complex (η^5-C_4H_4BPh)Rh(μ_3-I)$_3$Rh(μ,η^5:η^6-C_4H_4BPh)Rh(η^5-C_4H_4BMe)·CH_2Cl_2 (**7**) with a bridging μ,η^5:η^6-C_4H_4BPh ligand; complex **7** was characterized by an X-ray structure determination. The resulting molecular structure was used to create a structure model for the monomeric building block of polymer **5**.

Introduction

The heterocubanes [Rh(μ_3-I)(C_4H_4BR)]$_4$ (R = Ph, Me)[4] are versatile sources of (borole)rhodium fragments RhI(C_4H_4BR). These fragments may add strong σ-donor ligands such as pyridine, triphenylphosphine, and CO very readily but have little propensity to bind unsaturated hydrocarbon systems: we have been able to show that with the moderate donor norbornadiene the complex iodo(phenylborole)(norbornadiene)rhodium can be isolated, whereas no reaction occurs with 1,5-cyclooctadiene and similar ligands.[2] In the well-documented chemistry of (diene)rhodium complexes halide abstraction with silver salts has been used to activate the (diene)rhodium moiety with respect to arene complexation.[5] In analogy to these results we now extend our investigation on the reactivity of (borole)rhodium fragments. In the present contribution we show that dehalogenation of the heterocubane [Rh(μ_3-I)(C_4H_4BPh)]$_4$ (**1**) with silver salts yields the cationic fragment [Rh(C_4H_4BPh)]$^+$. The more pronounced electrophilic character of this fragment opens a route to the corresponding (arene)(phenylborole)rhodium cations and, in the absence of stabilizing ligands, to a surprising polycation.

Results and Discussion

Synthesis of (Arene)(phenylborole)rhodium Cations. Acetonitrile solutions of the heterocubane **1** contain the mononuclear bis(ligand) complex RhI$(NCMe)_2$((C_4H_4BPh) as the predominant solution species; removal of the solvent under vacuum regenerates **1**.[2,4] Halide abstraction with $AgBF_4$ in acetonitrile produces a solution of the salt [Rh$(NCMe)_3$(C_4H_4BPh)]BF_4 (**2**) with presumably three acetonitrile ligands. The acetonitrile ligands in **2** are labile and undergo exchange with uncoordinated acetonitrile at a high rate since ^1H and $^{13}C\{^1H\}$ NMR spectra (500 MHz for ^1H and 126 MHz for ^{13}C, CD_3CN, −35 °C) show only one signal for both the coordinated and the uncoordinated MeCN. When hexamethylbenzene (hmb) is added to the solution, a slow (20 °C, 3 days) displacement reaction takes place to produce the robust sandwich salt **3** in quantitative yield. With mesitylene as the arene, an equilibrium is established; while the solution is concentrated under vacuum part of the acetonitrile is removed and the equilibrium is shifted to the product side to give the salt **4**.

Obviously, a more pronounced donor character of the arene is favorable to complex formation. In line with this notion, complex **4** reacts with hmb in CH_2Cl_2 to form the hmb complex **3** in a very slow displacement

---

[1] Part 23: see ref 2.

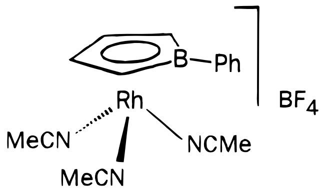
[2] Herberich, G. E.; Eckenrath, H. J.; Englert, U. *Organometallics* **1997**, *16*, 4800.

[3] Eckenrath, H. J. Doctoral Dissertation, Technische Hochschule Aachen, Aachen, Germany, 1997.

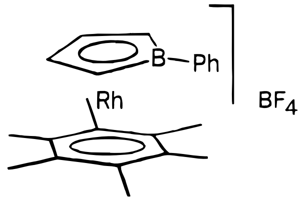
[4] Herberich, G. E.; Eckenrath, H. J.; Englert, U. *Organometallics* **1997**, *16*, 4292.

[5] (a) Huges, R. P. In *Compehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, U.K., 1982; Vol. 5, p 277. (b) Sharp, P. R. In *Compehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, U.K., 1995; Vol. 8, p 115.

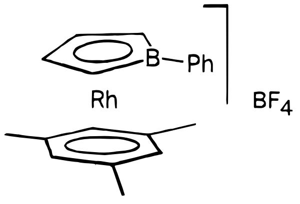
S0276-7333(97)00742-5 CCC: \$15.00
Publication on Web 02/16/1998



2



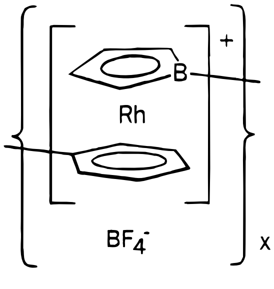
3



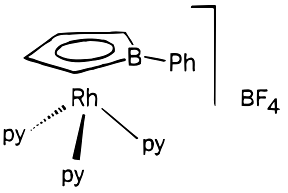
4

reaction (20 °C, 20 days) which is markedly accelerated in the presence of acetonitrile.

The fragment $[Rh(C_4H_4BPh)]^+$ may be considered as a bifunctional building block in that the *B*-phenyl group may act as an arene and ligate to the Rh center of another fragment. In this way we may conceive a polymeric cation, the *catena*-($\mu,\eta^5{:}\eta^6$-1-phenylborole)rhodium polycation. This type of bridging has been observed previously in the dinuclear complex $Cr(CO)_4(\mu,\eta^5{:}\eta^6\text{-}C_4H_4BPh)\ Cr(CO)_3$.[6]



5



6

When we attempted to isolate the salt **2** by evaporating the solvent under vacuum we obtained the polymeric tetrafluoroborate **5**. In most common organic solvents polymer **5** is extremely insoluble. It can be dissolved in acetonitrile to regenerate a solution of **2** and in acetone with an admixture of pyridine to produce the solvate $[Rh(py)_3(C_4H_4BPh)]BF_4$ (**6**), which can be isolated as yellow crystals. The composition of this compound justifies our assumption that the solution species **2** does indeed contain three acetonitrile ligands.

Polymer **5** was also encountered when we tried to synthesize the toluene complex $[Rh(PhMe)(C_4H_4BPh)]BF_4$. Halide abstraction from **1** in a mixture of CH_2Cl_2 and toluene gave the toluene complex as the kinetic product, according to the ^1H NMR spectrum of the solution; however, the primary product could not be isolated and decomposed to give again polymer **5**.

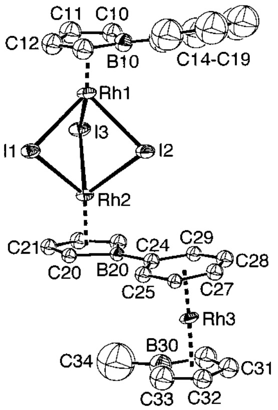


Figure 1. Displacement ellipsoid plot (PLATON)[8] of the molecule **7**. Ellipsoids are scaled to 30% probability.

A Trinuclear Complex. In our earlier study of the heterocubanes we measured NMR spectra of mixtures of $[Rh(\mu_3\text{-}I)(C_4H_4BPh)]_4$ and the corresponding methylborole complex $[Rh(\mu_3\text{-}I)(C_4H_4BMe)]_4$.[4] These measurements revealed a fast exchange of (borole)rhodium fragments at ambient temperature and the presence of all five conceivable heterocubanes $Rh_4(\mu_3\text{-}I)_4(C_4H_4BMe)_{4-x}(C_4H_4BPh)_x$ (with $x = 0, 1, ..., 4$) at low temperature. The outcome of crystallizations from these mixed solutions is unpredictable and may be quite surprising. When a 1/1 solution of the two heterocubanes in CH_2Cl_2 was kept at −30 °C, the trinuclear, zwitterionic crystalline complex **7** was obtained. This complex was characterized by elemental analysis and later by X-ray structure analysis to establish its constitution: $(\eta^5\text{-}C_4H_4BPh)Rh(\mu_3\text{-}I)_3Rh(\mu,\eta^5{:}\eta^6\text{-}C_4H_4BPh)Rh(\eta^5\text{-}C_4H_4BMe)\cdot CH_2Cl_2$.

It should be noted that **7** only exists in the crystalline state. Solutions of **7** show the same ^1H NMR spectra as a 2/1 mixture of the original two heterocubanes; the signals of the phenyl substituent show the chemical shifts expected for the uncoordinated phenyl group.[7] At low temperature the five heterocubanes $Rh_4(\mu_3\text{-}I)_4(C_4H_4BMe)_{4-x}(C_4H_4BPh)_x$ are observed with intensities corresponding approximately to statistical weights.

Structure of 7. Complex **7** crystallizes in the triclinic space group $P\bar{1}$. Crystals of the compound clathrate an equimolar amount of CH_2Cl_2, which does not efficiently fill the space between the large trinuclear complexes. A systematic grid search in the unit cell revealed a relatively large void of ca. 100 Å^3 when the solvent molecules were not taken into account. As a result both the atoms of the CH_2Cl_2 molecules and the adjacent peripheral groups of the larger constituents, namely the methyl group C34 and the phenyl ring C14−C19, show large displacement parameters. In view of these drawbacks only the heavy atoms I, Rh, and Cl were refined anisotropically, and the results of this structure determination are not very precise. They are sufficient, however, to unravel the unexpected constitution of the compound (Figure 1, Table 1).

The molecule consists of a cationic (arene)(borole)rhodium fragment and a triply bridged bis(borole)tris(μ-iodo)dirhodate unit which are linked through a $\mu,\eta^5{:}\eta^6\text{-}C_4H_4BPh$ bridge. The dihedral angle subtended by

---

[6] Herberich, G. E.; Hessner, B.; Negele, M.; Howard, J. A. K. *J. Organomet. Chem.* **1987**, *336*, 29.

[7] In the region of coordinated arenes there are small unassigned signals of species that are static on the NMR time scale; they would account for less than 5% of **1** in case they belong to a $Rh(\eta^6\text{-}PhB)$ fragment.

[8] Spek, A. L. *Acta Crystallogr.* **1990**, *A46*, C34.

Table 1. Selected Interatomic Distances and Bond Angles for 7

(a) Bond Distances (pm)			
I1−Rh1	272.8(2)	I1−Rh2	273.4(2)
I2−Rh1	274.9(2)	I2−Rh2	273.0(2)
I3−Rh1	274.8(2)	I3−Rh2	276.6(2)
(b) Bond Angles (deg)			
I1−Rh1−I2	86.04(6)	I1−Rh2−I2	86.29(6)
I1−Rh1−I3	84.13(7)	I1−Rh2−I3	83.68(5)
I2−Rh1−I3	85.76(6)	I2−Rh2−I3	85.76(6)
Rh1−I1−Rh2	77.46(6)	Rh1−I2−Rh2	77.17(6)
Rh1−I3−Rh2	76.58(6)		

the best planes through the phenyl and the borole ring amounts to 8(2)°. The central Rh_2I_3 core is an oblate trigonal bipyramid and is very similar to the same structural element in the compound Cp*Rh(μ-I)$_3$Rh-(C_4H_4BPh).[2] The Rh−I bond lengths average 274.3 pm (range 272.8(2)−276.6(2) pm); this conforms to expectation.[9] The rhodium-centered angles I−Rh−I amount to 85.28° (av), while the angles Rh−I−Rh centered at iodine are rather small and amount to 77.02° (av).

Structure of *catena*-[{Rh(μ,η^5:η^6-C_4H_4BPh)}BF_4]$_x$ (5). The compound has shown no tendency to form single crystals suitable for X-ray diffraction, and a powder sample proved to be amorphous. In order to obtain insight into the construction principle of polymer **5**, we decided to perform a wide-angle X-ray scattering (WAXS) experiment. This technique is known to provide information about short- and medium-range order in noncrystalline samples[10] for many different classes of compounds: it has been successfully applied to the study of inorganic glasses,[11] nanocrystalline particles,[12] and amorphous molecular solids.[13,14]

The radial distribution function (RDF) of **5** exhibits a pronounced local maximum at 560 pm. At least two conceivable structural models for the polymer are not compatible with this feature: triple-decker type geometries with two metal atoms on either side of a bridging ring as well as a phenylborole with both metals coordinated to the same side of the rings exhibit maxima in the RDF at clearly shorter distances and thus can be excluded. The peak in the RDF at 560 pm is in good agreement with the distance between the metal centers Rh2−Rh3 in compound **7** (563 pm), and we concluded that the basic structural feature of the polymer consists of a transoid bridging phenylborole with essentially coplanar rings, similar to the Rh2/C20−C29/Rh3 moiety in the trinuclear complex. Therefore, this fragment of the molecular structure of crystalline **7** was used to derive a model for the amorphous compound **5**: the bridging phenylborole with two metal atoms on opposite sides of the borole and arene rings served as a backbone for the polymeric chain. A sandwich type coordination for both Rh atoms is required for the building block of a polymer (Figure 2), and hence a phenyl fragment and a borole ring were positioned above and below the Rh/phenylborole/Rh moiety.

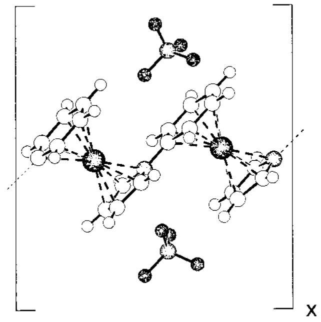


Figure 2. Model for the dinuclear building block of polymer **5** (SCHAKAL).[15]

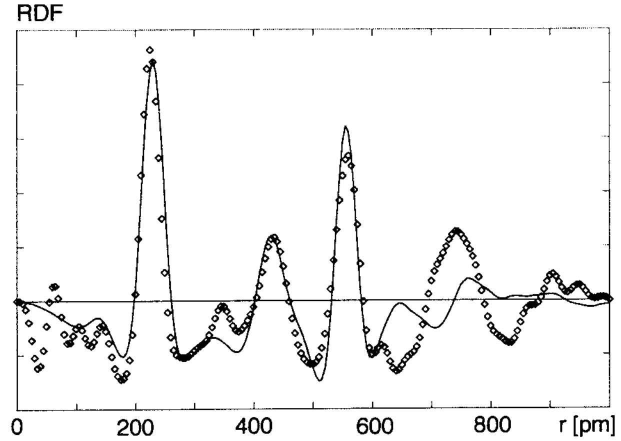


Figure 3. Experimental (dotted line) and calculated (solid line) radial distribution functions for polymer **5**. The calculated RDF refers to the structure model based on a dinuclear building block and two anions, as illustrated in Figure 2.

A graphical representation of the building block of polymer **5** showing the polycationic chain and two tetrafluoroborate anions is given in Figure 2. We note that any extension of the cationic substructure comprising independent molecular species such as the corresponding anions necessarily involves extra degrees of freedom. Even in the case of relatively strong interactions information concerning the intermolecular arrangement is less reliable than intramolecular features of the model. Following the idea of efficient space-filling and electrostatic arguments, we placed the BF_4^- anions on either side of the chain at van der Waals distances with shortest H−F contacts of ca. 230 pm. A comparison between the RDF calculated for this final model including two anions per dinuclear subunit and the experimental data is given in Figure 3. It shows satisfactory agreement for distances up to ca. 600 pm; relative heights for the maxima in the calculated RDF show inferior agreement with the experimental results when the BF_4^- anions are omitted from the structure model. However, in view of the fact that details of the calculated distribution function are already sensitive to variations in the positional and orientational parameters of the tetrafluoroborate groups, no further attempts were made to adjust the model for ordering phenomena in the range of longer distances, e.g. due to interchain ordering or more complicated ionic patterns. In sum-

---

(9) Orpen, A. G.; Brammer, L.; Allen, F. H.; Kennard, O.; Watson, D. G.; Taylor, R. *J. Chem. Soc., Dalton Trans.* **1989**, S1.

(10) Warren, B. E. *X-Ray Diffraction*; Dover Publications: New York, 1990.

(11) Burian, A.; Lecante, P.; Mosset, A.; Galy, J. *Z. Kristallogr.* **1990**, *193*, 199.

(12) Rodriguez, A.; Amiens, C.; Chaudret, B.; Casanove, M. J.; Lecante, P.; Bradley, J. S. *Chem. Mater.* **1996**, *8*, 1978.

(13) Galy, J.; Vogt, T.; Lecante, P.; Mosset, A.; Strähle, J. *J. Phys.* **1986**, *47*, C8−627.

(14) Vogt, T.; Faulmann, C.; Soules, R.; Lecante, P.; Mosset, A.; Castan, P.; Cassoux, P.; Galy, J. *J. Am. Chem. Soc.* **1988**, *110*, 1833.

(15) Keller, E. SCHAKAL; University of Freiburg: Freiburg, Germany, 1986.

mary, a reliable model for the polycation could be derived from an experimentally observed structure with a minimum of manipulations.

Concluding Remarks. Our results show that (arene)(borole)rhodium complexes may be obtained by dehalogenation of the (phenylborole)rhodium iodide heterocubane. The donor character of the arene limits the stability of the resulting arene complexes toward nucleophilic degradation by σ-donor ligands. The hmb and mesitylene complexes have been isolated, whereas with toluene as a less stabilizing ligand the corresponding arene complex is only seen as an intermediate kinetic product. The coordinated toluene is slowly displaced by the *B*-phenyl substituent of the borole ligand, and this autocomplexation results in formation of a polymeric salt. With σ donors such as acetonitrile or pyridine, this polymer regenerates monomeric (phenylborole)rhodium cations stabilized by solvent molecules.

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 from CaH_2, toluene from sodium, and Et_2O from sodium benzophenone ketyl. 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.

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) and a Bruker WP-80 PFT (^{1}H, 80 MHz) spectrometer. If not stated otherwise, chemical shifts (ppm) were measured at ambient temperature and are relative to internal TMS for ^{1}H and ^{13}C and relative to $BF_3 \cdot Et_2O$ as external reference for ^{11}B. C-unsubstituted borole ligands display AA′BB′-type ^{1}H NMR spectra in the form of two not fully resolved multiplets, one for the AA′ part and one for the BB′ part. The frequency difference of the two most prominent lines of the multiplets amounts to $N = {}^3J_{23} + {}^4J_{24}$. Because of the coupling with Rh the apparent values taken from the spectra contain a contribution from ^2J(Rh−H) and may be different for 2-/5-H and 3-/4-H.

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.

Synthesis of [Rh(NCMe)$_3$(C$_4$H$_4$BPh)]BF$_4$ (2) in Solution and of *catena*-[{Rh(μ,η^5:η^6-C$_4$H$_4$BPh)}BF$_4$]$_x$ (5). A solution of $AgBF_4$ (790 mg, 4.058 mmol) in acetonitrile (20 mL) was added to a suspension of **1** (1.50 g, 1.014 mmol) in acetonitrile (20 mL). The mixture was stirred for 30 min. The AgI formed was filtered off (with the help of a G4 frit, covered with Kieselgur) and washed with acetonitrile (3 × 10 mL). The solvent was then removed under vacuum to give a foamy residue, which was triturated with acetone (10 mL) for 1 h. The solid material was collected on a frit, washed with acetone (3 × 5 mL), and dried under vacuum to give **5** (1.22 g, 91%) as a light yellow powder: no mp <250 °C; soluble in acetonitrile, insoluble in common organic solvents.

2: ^{1}H NMR (500 MHz, CD_3CN) δ 7.72 (m, 2 H$_o$), 7.34−7.43 (m, 2 H$_m$ + H$_p$), borole 5.74 (m, N = 6.0 Hz, 3-/4-H) and 3.99 (m, N = 5.5 Hz, 2-/5-H); ^{13}C{^{1}H} NMR (126 MHz, CD_3CN) δ 136.55 (C$_o$), 130.42 (C$_p$), 128.81 (C$_m$), borole 94.27 [d, ^1J(Rh-C) = 9.3 Hz, C-3,4], 64.1 (br, C-2,5); ^{11}B{^{1}H} NMR (CD_3CN) δ 24, −1.

5: Anal. Calcd for $C_{10}H_9B_2F_4Rh$: C, 36.43; H, 2.75. Found: C, 36.44; H, 2.61.

Synthesis of [Rh(C$_4$H$_4$BPh)(hmb)]BF$_4$ (3). A solution of **5** (140 mg, 0.425 mmol as monomer) and hexamethylbenzene (200 mg, 1.232 mmol) in acetonitrile (10 mL) was stirred for 3 days. The resulting solution was filtered and evaporated to dryness. The solid residue was washed with hexane (5 × 5 mL) and recrystallized from acetone/hexane to give **3** (175 mg, 84%) as a light yellow powder; no mp <250 °C; soluble in acetonitrile, moderately soluble in acetone. Anal. Calcd for $C_{22}H_{27}B_2F_4Rh$: C, 53.71; H, 5.53. Found: C, 53.75; H, 5.41. SIMS (DTE/DTT): positive ions, m/z (I_{rel}) 405 (100, [Rh(C$_6$Me$_6$)(C$_4$H$_4$BPh)]$^+$); negative ions, m/z (I_{rel}) 87 (100, BF_4^-).

3: ^{1}H NMR (500 MHz, CD_3CN) δ 7.65 (m, 2 H$_o$), 7.42−7.46 (m, 2 H$_m$ + H$_p$), borole 5.77 (m, N = 6.7 Hz, 3-/4-H) and 4.70 (m, N = 5.2 Hz, 2-/5-H), 2.17 (s, 6 Me); ^{13}C{^{1}H} NMR (126 MHz, CD_3CN) δ 136.53 (C$_o$), 131.12 (C$_p$), 129.17 (C$_m$), 114.96 [d, ^1J(Rh−C) = 4.4 Hz, C_6Me$_6$], borole 98.72 [d, ^1J(Rh−C) = 8.7 Hz, C-3,4], 87.5 (br, C-2,5), 17.18 (C$_6$$Me_6$); ^{11}B{^{1}H} NMR ($CD_3CN$) δ 20, −1.

Synthesis of [Rh(1,3,5-C$_6$H$_3$Me$_3$)(C$_4$H$_4$BPh)]BF$_4$ (4). A solution of $AgBF_4$ (58 mg, 0.297 mmol) in acetone (5 mL) was added to a suspension of **1** (110 mg, 0.074 mmol) in CH_2Cl_2 (15 mL) and mesitylene (1 mL, 7.2 mmol). The mixture was stirred for 60 min. The AgI formed was then filtered off (with the help of a G4 frit, covered with Kieselgur) and washed with acetone (2 × 5 mL). The filtrate was concentrated to a small volume (5 mL), and the product was precipitated by addition of hexane (15 mL). The raw product was isolated and dissolved in CH_2Cl_2. The concentrated solution (1 mL) was then kept at −30 °C for 20 days to give **4** (115 mg, 86%) as lemon yellow crystals: mp 188 °C; soluble in CH_2Cl_2 and acetone, insoluble in ether. Anal. Calcd for $C_{19}H_{21}B_2F_4Rh$: C, 50.73; H, 4.71. Found: C, 50.95; H, 4.81. SIMS (DTE/DTT): positive ions, m/z (I_{rel}) 363 (100, [Rh(C$_6$H$_3$Me$_3$)(C$_4$H$_4$BPh)]$^+$); negative ions, m/z (I_{rel}) 88 (100, [HBF$_4$]$^-$).

4: ^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.69 (m, 2 H$_o$), 7.40−7.44 (m, 2 H$_m$ + H$_p$), 6.53 (s, C$_6$$H_3Me_3$), borole 6.07 (m, N = 6.5 Hz, 3-/4-H) and 5.06 (m, N = 5.5 Hz, 2-/5-H), 2.23 (s, 3 Me); ^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2) δ 135.67 (C$_o$), 130.82 (C$_p$), 128.66 (C$_m$), 118.38 [d, ^1J(Rh−C) = 3.8 Hz, C-1,3,5], 102.32 [d, ^1J(Rh−C) = 4.4 Hz, C-2,4,6], borole 98.61 [d, ^1J(Rh−C) = 8.8 Hz, C-3,4], 86.5 (br, C-2,5), 19.82 (3 Me); ^{11}B{^{1}H} NMR (CD_3CN) δ 22, −1.

Synthesis of [Rh(py)$_3$(C$_4$H$_4$BPh)]BF$_4$ (6). A mixture of pyridine (159 mg, 2.01 mmol), acetone (30 mL), and solid **6** (220 mg, 0.667 mmol as monomer) was stirred for 1 h. The resulting solution was filtered and evaporated to dryness. The solid residue was washed with ether (5 × 5 mL) and recrystallized from acetone (50 to −30 °C) to give **6** (285 mg, 76%) as yellow crystals: mp 183 °C; in solution somewhat air-sensitive, soluble in acetonitrile, CH_2Cl_2, and acetone, insoluble in ether. Anal. Calcd for $C_{25}H_{24}B_2F_4N_3Rh$: C, 52.96; H, 4.27; N, 7.41. Found: C, 52.93; H, 4.22; N, 7.30. SIMS (NBA): positive ions, m/z (I_{rel}) 486 (31, [Rh$_2$(C$_4$H$_4$BPh)$_2$]$^+$), 401 (3, [Rh(py)$_2$(C$_4$H$_4$BPh)]$^+$), 322 (10, [Rh(py)(C$_4$H$_4$BPh)]$^+$), 243 (17, [Rh(C$_4$H$_4$BPh)]$^+$), 80 (100, pyH$^+$); negative ions, m/z (I_{rel}) 87 (100, BF_4^-).

6: ^{1}H NMR (500 MHz, d_6-acetone) δ 8.57 (m, 6 2-/6-H), 7.94 (m, 3 4-H), 7.43 (m, 6 3-/5-H), Ph 7.48 (m, 2 H$_o$), 7.15 (m, H$_p$), 7.02 (m, 2 H$_m$), borole 5.85 (m, N = 6.1 Hz, 3-/4-H) and 4.02 (m, N = 5.5 Hz, 2-/5-H); ^{13}C{^{1}H} NMR (126 MHz, d_6-acetone) δ 154.46 (C-2,6), 139.39 (C-4), 127.03 (C-3,5), Ph 136.17 (C$_o$), 129.45 (C$_p$), 128.05 (C$_m$), borole 96.43 [d, ^1J(Rh-C) = 9.4 Hz, C-3,4], 61.9 (br, C-2,5); ^{11}B{^{1}H} NMR (d_6-acetone) δ 25, −1.

Preparation of 7. A solution of [Rh(μ_3-I)(C$_4$H$_4$BPh)]$_4$ (**1**; 168 mg, 0.114 mmol) and [Rh(μ_3-I)(C$_4$H$_4$BMe)]$_4$ (140 mg, 0.114 mmol) in acetonitrile (20 mL) was stirred at 20 °C for 1 h. After removal of the solvent the brown residue was suspended in ether (10 mL) with stirring for 1 h, then collected on a frit, washed with ether (2 × 2 mL), and dried under vacuum. A solution of the solid in CH_2Cl_2 (2 mL) was stored 15 days at

Table 2. Crystal Data, Data Collection Parameters and Convergence Results for 7

formula	$C_{26}H_{27}Cl_2B_3I_3Rh_3$
system	triclinic
space group (No.)	$P\bar{1}$ (2)
a, pm	1072.6(6)
b, pm	1126.1(2)
c, pm	1363.4(6)
α, deg	87.51(2)
β, deg	71.62(5)
γ, deg	82.56(3)
U, nm^3	1.550(1)
Z	2
d_{calc}, g cm^{-3}	2.426
T, K	213
μ, cm^{-1}	47.06
λ, pm (radiation)	71.073 (Mo Kα)
θ_{max}, deg	28
cryst dimens, mm^3	$0.15 \times 0.1 \times 0.1$
abs cor	empirical ψ-scans
min transmission	0.858
max transmission	0.999
no. of rflns	5832
no. of indep obs rflns $I > 1.0\ \sigma(I)$	2955
no. of vars	189
R^a	0.081
$R_w{}^b$	0.065
res el dens, e nm^{-3}	1.85×10^{-3} (close to I3)

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

−30 °C to give **7** (95 mg, 37%) as dark red crystals: mp 97 °C. Anal. Calcd for $C_{26}H_{27}B_3Cl_2I_3Rh_3$: C, 27.58; H, 2.40. Found: C, 27.76; H, 2.40.

7: ^{1}H NMR (500 MHz, CD_2Cl_2, 20 °C) δ 7.69 (m, 4 H_o), 7.41−7.34 (m, 2 H_p + 4 H_m), 0.40 (s, Me), borole ligand **a** (C_4H_4BPh) 5.18 (br, 4H, 3-/4-H), 4.22 (br, 4H, 2-/5-H), borole ligand **b** (C_4H_4BMe) 4.96 (br, 2H, 3-/4-H), 3.61 (br, 2H, 2-/5-H); ^{1}H NMR (500 MHz, CD_2Cl_2, −80 °C), five species, signals in aromatic region not resolved, δ 7.65−7.57 (H_o), 7.38−7.32 (H_m, H_p), $Rh_4(\mu_3\text{-}I)_4(C_4H_4BPh)_4$ (16%) δ 5.09 (m, 3-/4-H), 3.97 (m, 2-/5-H), $Rh_4(\mu_3\text{-}I)_4(C_4H_4BMe)(C_4H_4BPh)_3$ (36%) δ for **a** 5.16 (m, 3-/4-H), 4.01 (m, 2-/5-H), for **b** 4.90 (m, 3-/4-H), 3.42 (m, 2−5-H), 0.28 (s, Me), $Rh_4(\mu_3\text{-}I)_4(C_4H_4BMe)_2(C_4H_4BPh)_2$ (33%) δ for **a** 5.23 (m, 3-/4-H), 4.06 (m, 2-/5-H), for **b** 4.96 (m, 3-/4-H), 3.46 (m, 2-/5-H) 0.32 (s, Me), $Rh_4(\mu_3\text{-}I)_4(C_4H_4BMe)_3(C_4H_4BPh)$ (13%) δ for **a** 5.32 (m, 3-/4-H), 4.12 (m, 2-/5-H), for **b** 5.03 (m, 3-/4-H), 3.51 (m, 2-/5-H), 0.37 (s, Me), $Rh_4(\mu_3\text{-}I)_4(C_4H_4BMe)_4$ (2%) δ 5.11 (m, 3-/4-H), 3.56 (m, 2-/5-H), 0.42 (s, Me); $^{13}C\{^1H\}$ NMR (126 MHz, CD_2Cl_2, 20 °C) δ 136.31 (C_o), 129.41 (C_p), 127.99 (C_m), 89.66 (br, C-3/4, **a**), 88.96 (br, C-3/4, **b**), 74.03 (br, C-2/5, **a** and **b**); $^{13}C\{^1H\}$ NMR (126 MHz, CD_2Cl_2, −80 °C) δ 135.26, 135.28, 135.31, 135.35 (C_o), 128.56, 128.58, 128.61 (C_p), 127.16 (C_m), −2.20 (br, Me), for **a** 88.57 (br, C-3/4), 71.21 (br, C-2/5), for **b** 88.17 (br, C-3/4), 71.74 (br, C-2/5); $^{11}B\{^1H\}$ NMR (CD_2Cl_2, 20 °C) δ 24 (ligand **a**), 20 (ligand **b**).

Crystal Structure Determination of 7. A solution of $[Rh(\mu_3\text{-}I)(C_4H_4BPh)]_4$ **(1)** and $[Rh(\mu_3\text{-}I)(C_4H_4BMe)]_4$ (1/1) in CH_2Cl_2 was stored at −30 °C for 15 days to give crystals suitable for the structure determination. 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. Three regularly measured check reflections indicated a loss of intensity of ca. 8%, presumably due to partial loss of clathrated dichloromethane even at low temperature; the intensity data were corrected by scaling them to the closest standard. Before averaging over symmetry-equivalent reflections an empirical absorption correction based on azimuthal scans[16] (transmission maximum 0.999, minimum 0.858) was applied. The structure was solved by direct methods[17] and refined on F with the local version of the SDP program suite.[18] The final structure model included metal and halogen atoms with anisotropic and the remaining nonhydrogen atoms with isotropic displacement parameters and H atoms as riding in calculated positions (C−H = 98 pm, $U_{iso}(H) = 1.3U_{iso}(C)$).

WAXS Experiment. WAXS measurements were performed in transmission mode on an ENRAF-Nonius CAD4 instrument using graphite-monochromatized Mo Kα radiation ($\lambda = 71.073$ pm). The sample was prepared by pelleting 171 mg of the pure compound **5**. The data set included 459 points equally spaced in s ($s = 4\pi(\sin\theta)/\lambda$) on a θ range extending from 1.5 to 70°. Data were corrected for air scattering, absorption, and polarization using procedures previously described.[19] After normalization using the Norman[20] and Krogh-Moe[21] methods, the so-called reduced intensity $i(s)$ was extracted. A Fourier transform of $i(s)$ provided a reduced radial distribution function (RDF), whose maxima can be related to interatomic distances inside the sample. The Debye formula[10,22] was used to calculate scattering intensities for a number of different models for the cation (see Results and Discussion). The RDF shown in Figure 3 is based on the structural model graphically represented in Figure 2 without further curve-fitting procedures.

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

Supporting Information Available:[23] Tables of bond distances and angles, anisotropic displacement parameters, and hydrogen atom coordinates for **7** and Cartesian coordinates for the dinuclear building block for **5** (7 pages). Ordering information is given on any masthead page.

OM970742+

---

(16) North, A. C. T.; Phillips, D. C.; Mathews, F. S. *Acta Crystallogr.* **1968**, *A24*, 351.

(17) Sheldrick, G. M. SHELXS-86, Program for Crystal Structure Solution; University of Göttingen: Göttingen, Germany, 1986.

(18) Frenz, B. A. ENRAF-Nonius SDP Version 5.0; ENRAF-Nonius: Delft, The Netherlands, 1989, and local programs.

(19) Lecante, P.; Mosset, A., Galy, J. *J. Mater. Sci.* **1992**, *27*, 3286.

(20) Norman, N. *Acta Crystallogr.* **1957**, *10*, 370.

(21) Krogh-Moe, J. *Acta Crystallogr.* **1956**, *9*, 951.

(22) Debye, P. *Ann. Phys. (Leipzig)* **1915**, *46*, 809.

(23) Further details of the crystal structure analysis 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-408057 for **7**, the names of the authors, and this journal citation.