Contributions to the Chemistry of Boron, 230[◇]

Electrophilic Borylation of Metallocenes: Synthesis and Molecular Structures of 1,1′,3,3′-Tetrakis(dibromoboryl)metallocenes of the Iron Triad[☆]

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Reactions of metallocenes MCp_2 (M = Fe, Ru, Os) with an excess of BBr_3 at reflux temperature lead specifically to 1,1′,3,3′-tetrakis(dibromoboryl)metallocenes **3**, **7**, and **8** in high yield. $MeBBr_2$ and $PhBBr_2$ are less effective borylating agents. X-ray structural analyses of **3**, **7**, and **8** reveal an increasing tilt of the Br_2B groups towards the metal center while retaining the trigonal-planar environment at the boron atoms. This indicates a weak metal-boron interaction of the kind found for carbon-metal interactions in ferrocenyl carbocations.

Early interest in the chemistry of borylated ferrocenes resulted from the fact that (dihydroxyboryl)ferrocenes (ferrocenylboronic acids) allow an easy synthesis of mono- and 1,1′-dihalogenoferrocenes[2,3]. In addition, Siebert et al. demonstrated that boron halides, and boron tribromide in particular, allow an electrophilic borylation of ferrocene[4], and $CpFe(C_5H_4BBr_2)$ as well as $Fe(C_5H_4BBr_2)_2$ proved to be very stable organoboron dibromides. The ready formation of these compounds is quite remarkable because electrophilic substitutions on aromatic systems with boron trihalides require "drastic" conditions even in the presence of catalysts[5]. For instance, we have been unable to achieve borylation of benzene or toluene by means of BCl_3 or BBr_3 in the presence of a platinum catalyst as reported by Pace[6].

In the course of our studies of the synthesis of highly borylated aromatic systems we also studied the borylation of metallocenes[7], and we report in this paper on the synthesis and structures of tetrakis(dibromoboryl)ferrocene, -ruthenocene, and -osmocene.

Synthesis of (Dibromoboryl)metallocenes

Borylation of aromatic systems with BCl_3 is accelerated in the presence of $AlCl_3/Al$ as a catalyst[5]. For this reason we studied the influence of $AlCl_3$ and $ZnCl_2$ as catalysts on the reaction of ferrocene with BBr_3 in the hope to reduce the time required for a quantitative reaction, and CS_2 was used as a solvent as suggested by Siebert et al.[4]. The course of the borylation was followed by ^{11}B-NMR spectroscopy. Results are presented in Figure 1.

As Figure 1 demonstrates, all BBr_3 ($\delta^{11}B$ = 38.9) is consumed within 9.5 h, and 1,1′-bis(dibromoboryl)ferrocene ($\delta^{11}B$ = 50.3) is the main reaction product in all cases. However, and not unexpectedly, (dibromoboryl)ferrocene (**1**) ($\delta^{11}B$ = 46.8) is the first product which is formed rapidly, and its spectroscopic yield determined after 1 h exceeds that of $Fe(C_5H_4BBr_2)_2$ (**2**), which increases as the reaction proceeds. A comparison of the results demonstrates that no "catalyst" is required to achieve diborylation of ferrocene with BBr_3. On the contrary, both $ZnCl_2$ and $AlCl_3$ reduce the availability of BBr_3 due to the formation of $ClBBr_2$ ($\delta^{11}B$ = 42.3) and Cl_2BBr ($\delta^{11}B$ = 44.8), an effect that is much more pronounced in the case of $AlCl_3$ where a substantial amount of $ClBBr_2$ is generated, and this boron halide is obviously not as effective in borylating ferrocene as is BBr_3. Halogen exchange of the catalyst with the (dibromoboryl)ferrocenes may lead to ferrocenes carrying a ClBBr group. However, the ^{11}B-NMR spectra did not give any evidence for the presence of these species in the resulting solutions. But this does not exclude their formation because there is practically no difference in chemical shifts between (dichloroboryl)- and 1,1′-bis(dibromoboryl)ferrocene[4] and, consequently, also for bromo-chloro-borylated ferrocenes.

Replacement of CS_2 by dichloromethane as a solvent did not improve the yield of mono- and bis(dibromoboryl)ferrocenes. Actually, the yield of $Fe(C_5H_4BBr_2)_2$ was only 25% after 36 h in refluxing CH_2Cl_2. The best result was obtained by using boiling hexane as solvent. The higher temperature achieved (in comparison with CS_2) allowed a reduction of the reaction time to 5 h, and a yield of 60% was readily achieved for $Fe(C_5H_4BBr_2)_2$.

That hexane is a better solvent for the bromoborylation of metallocenes MCp_2 (M = Fe, Ru, Os) than CS_2 was also observed by Wrackmeyer and Herberhold[7]. For this reason we expected that more than two Br_2B groups might be

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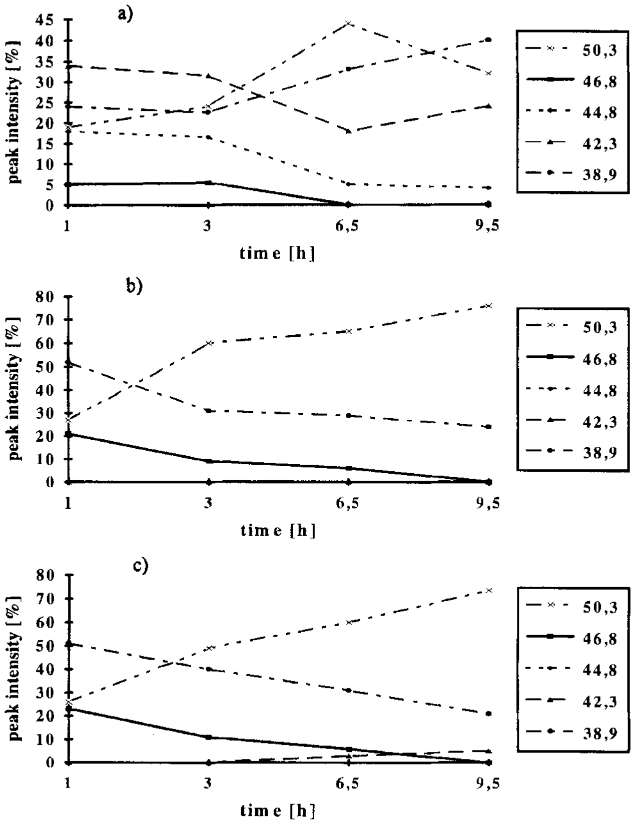
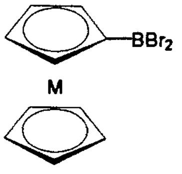
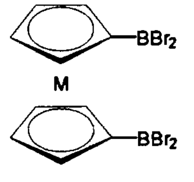
Figure 1. Borylation of ferrocene with BBr_3 (1:2 molar ratio) in boiling CS_2. a) $AlCl_3$ as catalyst (ferrocene/$AlCl_3$ = 1:1); b) $ZnCl_2$ as catalyst (ferrocene/$ZnCl_2$ 1:1); c) without catalyst). Development of the relative intensities of the ^{11}B-NMR signals. δ = 38.9 (BBr_3); 42.3 ($ClBBr_2$); 44.8 (Cl_2BBr); 46.8 (**1**); 50.3 (**2**)



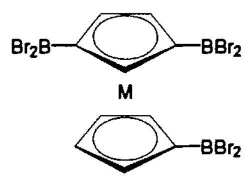
introduced into ferrocene. Indeed, if 4 mol of BBr_3 were used and the hexane solution kept at reflux for 98 h a ratio of 19:74:7 for the dibromoboryl compounds **2**, **3**, and **4** was present in solution.



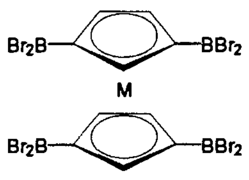
1 M = Fe



2 M = Fe
5 M = Ru



3 M = Fe
6 M = Ru



4 M = Fe
7 M = Ru
8 M = Os

This ratio was determined by ^{1}H-NMR spectroscopy because the ^{11}B-NMR spectra show only a broad signal at $\delta^{11}B = 52$ ($h_{1/2}$ = 425 Hz). The ^{1}H-NMR data also prove the 1,3-substitution pattern. The isomer **B** was not detected under these conditions.

A rapid and almost quantitative tetraborylation of ferrocene to **4** was finally achieved by using boron tribromide as solvent. 37 h under reflux conditions allowed the isolation of **4** in yields exceeding 80%.

Ruthenocene can also be borylated with BBr_3. The use of a 1:2.5 molar ratio of ruthenocene and BBr_3 in boiling hexane gave a mixture of bis- and tris(dibromoboryl)ruthenocene **5** and **6** in a 20:3 ratio within 1 h. Five hours later some tetrakis(dibromoboryl)ruthenocene **7** was also present, and the molar ratio of **5**:**6**:**7** was then 6.5:4:1. Heating of the mixture for additional 21 h changed this ratio into a final 4:6:1. If a ruthenocene-to-BBr_3 ratio of 1:4 was employed, the final molar ratio changed to 1:2:1, and in no case was it possible to detect $CpRu(C_5H_4BBr_2)$ as an intermediate even in the early stages of the reactions. Therefore, $CpRu(C_5H_4BBr_2)$ is obviously more prone to electrophilic attack than the ferrocene analogue.

Since a separation of the mixtures into its components by fractional crystallization failed we tried to arrive specifically at the stage of tetraborylation. Using BBr_3 as solvent as described for **4**, we obtained **7** in yields exceeding 80% in a period of 20 h. The same holds for the synthesis of the tetraborylated osmocene **8**. Attempts to introduce more than four boryl groups by electrophilic substitution of the metallocenes with pure BBr_3 led to undefined green to black-green products as precipitates which have so far not yet been characterized.

$MeBBr_2$ and $PhBBr_2$ are less effective borylating reagents. Thus, only (bromomethylboryl)ferrocene (**9**) and 1,1′-bis(bromomethylboryl)ferrocene (**10**) were obtained in boiling hexane, depending on the reaction time. In the absence of a solvent a tenfold excess of $MeBBr_2$ produced a mixture of borylated ferrocenes amongst which also 1,1′,3,3′-tetrakis(bromomethylboryl)ferrocene could be detected by NMR methods. Phenylboron dibromide, on the other hand, gave access only to the monoborylated **11**.

$MeBrBC_5H_4FeCp$	$(MeBrBC_5H_4)_2Fe$	$PhBrBC_5H_4FeCp$
9	**10**	**11**

NMR Data

Wrackmeyer and Herberhold[4c] have already presented ^{1}H-, ^{11}B- and ^{13}C-NMR data for the compounds described here with the exception of **8**, and additional data as well as a detailed analysis of the spectra are reported in ref.[7]. The NMR data of **8** are found in the experimental section, and no additional conclusions other than those already made[7] can be drawn.

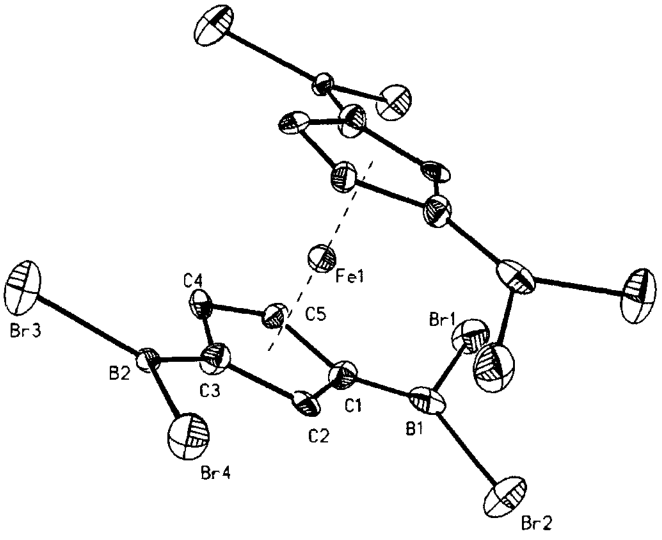
Molecular Structures

Although the substitution pattern of the dibromoborylated metallocenes of iron, ruthenium, and osmium can be unambiguously derived from NMR data, structural parameters are of prime interest for the discussion of possible metal boron bonding in these compounds. Therefore, the molecular structures of **4**, **7**, and **8** were determined by X-

Table 1. Selected bonds lengths [Å] and bond angles [°] for the tetrakis(dibromoboryl)metallocenes. Estimated standard deviations in parentheses

	4	**7**	**8**
M - C1	2.06(2)	2.17(1)	2.19(2)
M - C2	2.03(2)	2.16(1)	2.18(2)
M - C3	2.05(2)	2.19(1)	2.20(2)
M - C4	2.06(2)	2.17(1)	2.22(2)
M - C5	2.05(1)	2.17(1)	2.19(2)
C1 - B1	1.48(3)	1.49(2)	1.52(3)
C3 - B2	1.56(2)	1.51(2)	1.53(3)
B1 - Br1	1.93(2)	1.94(2)	1.87(3)
B1 - Br2	1.92(2)	1.90(2)	1.93(2)
B2 - Br3	1.89(2)	1.90(2)	1.91(2)
B2 - Br4	1.90(2)	1.91(2)	1.88)2)
C5-C1-B1	127(1)	129(2)	126(2)
C2-C1-B1	128(2)	124(2)	125(2)
C2-C3-B2	126(1)	126(1)	125(2)
C4-C3-B2	127(1)	129(1)	127(1)
C1-B1-Br1	123(2)	120(1)	123(2)
C1-B1-Br2	121(1)	123(1)	119(2)
Br1-B1-Br2	116(1)	117(1)	118(1)
C3-B2-Br3	120(1)	120(1)	119(1)
C3-B2-Br4	121(1)	121(1)	122(2)
Br3-B2-Br4	119.0(9)	118(1)	119(1)

Figure 2. ORTEP representation of tetrakis(dibromoboryl)ferrocene **4**. Thermal ellipsoids are shown on a 25% probability scale



ray methods. Relevant data are summarized in Table 1, and the molecular structures are shown in Figures 2 to 4.

Compounds **4**, **7**, and **8** crystallize in the orthorhombic system, **4** in the space group $P2_12_12$, and **7** and **8** in the space group *Pbcn*. Each of these molecules displays C_2 point group symmetry due to a special position of the central metal atom in the unit cell.

Although the refinement converged for all structures close to 5% the esd values are fairly large for bonds to the carbon and boron atoms, and most of the M−C, C−C, B−C, and B−Br bonds can be considered to be of equal lengths. The M−C bonds to the boron bearing carbon atoms seem to be longer (except the Os−C1,3 bonds), and it appears that these carbon atoms are moved away from the metal center while the M−C2 distances are shortest.

Figure 3. Molecular structure of tetrakis(dibromoboryl)ruthenocene **7**. View almost perpendicular to one Cp ring to show the orientation of the boryl groups and their deviation from the ring planes. Thermal ellipsoids represent a 25% probability

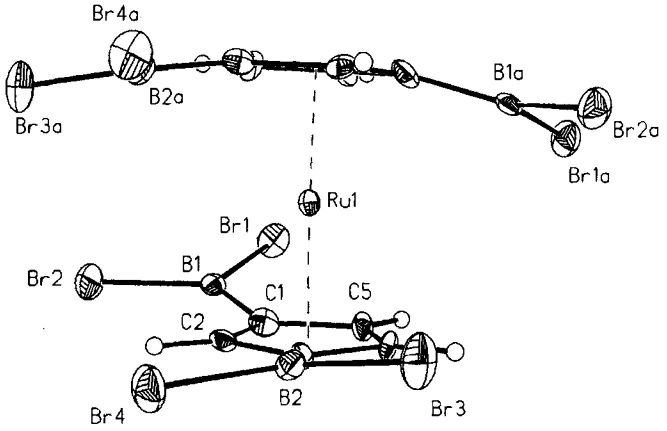
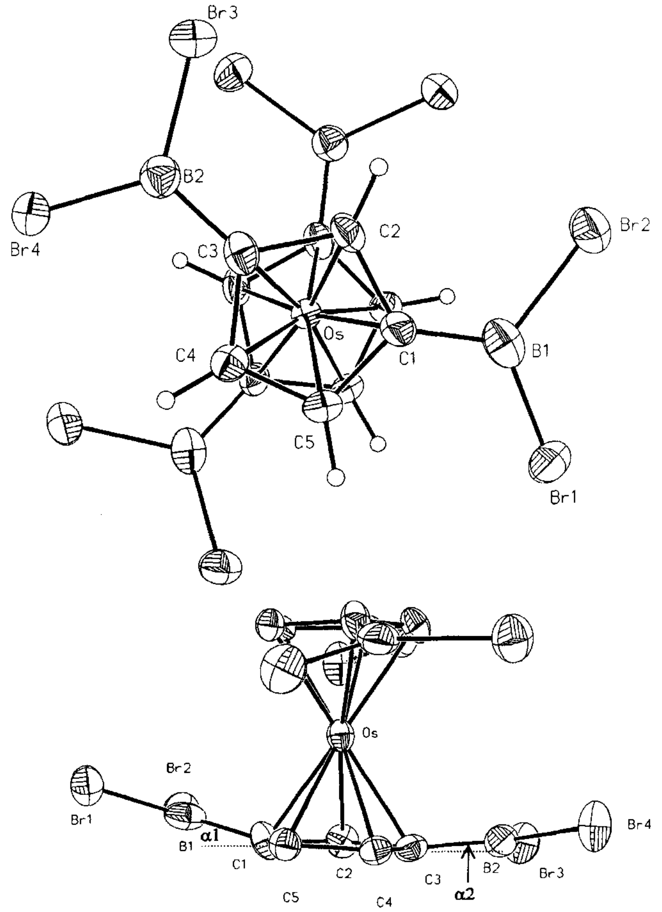


Figure 4. ORTEP-type description of the molecular structure of tetrakis(dibromoboryl)osmocene **8** to show the pseudo-staggered conformation of the Cp rings

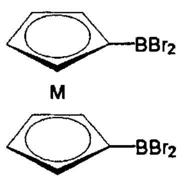


The main difference in the structure is the tilting of the Cp planes against one another with tilt angles of 1.4° for **4**, 5.1° for **7**, and 4.3° for **8**. A more noticeable feature of the structures is that the BBr_2 groups are bent towards the metal atoms. There are two tilt angles, α_1 and α_2. The former increases considerably as we move from the ferrocene **4** to the osmocene **8** (1.5° in **4**, 12.2° in **7**, and 12.6° in **8**) while the latter remains almost constant (6.9° in **4**, 7.4° in **7**, and 6.7° in **8**). This corresponds with distances between the metal and the boron atom of 3.13/3.15 Å in **4**, 3.06/3.19 Å, and 3.08/3.21 Å in **8**.

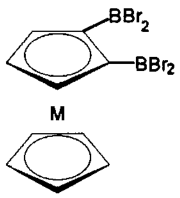
The B−C bonds lengths seem also to be correlated with the tilt angle α: an increase of the tilt angles causes a decrease of the B−C bond lengths, a correlation that becomes less pronounced as we move from the ferrocene to the osmocene derivative. In contrast, the B−Br bond lengths are equal within the limits of standard deviations in all compounds, and the sum of bond angles for each boron atom is 360°. Finally, the Cp rings in the compounds under consideration adopt a conformation that is between a staggered and eclipsed situation.

Discussion

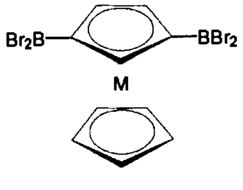
Electrophilic substitution of BBr_2 groups for the hydrogen atoms in iron-group metallocenes by treatment with BBr_3 is readily achieved, and up to four BBr_2 units can be introduced with formation of the 1,1′,3,3′ isomer. Qualitatively, the rate of the reaction is highest for ruthenocene.



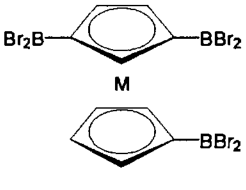
A



B



C



D

Diborylation can lead to three isomers, **A** to **C**. In our studies only the isomer **A** was detected, but Wrackmeyer and Herberhold[7] also detected the isomer **C** in the reaction mixtures. Similarly, triborylation leads exclusively to the 1,3,1′ isomer **D** (only one conformation shown). 1,2,3- and 1,2,4-tris(boryl)metallocene isomers are not formed, and in the case of tetraborylation the 1,3,1′,3′ isomer is generated specifically. Thus, the substitution pattern is 1-monoboryl < 1,1′-diboryl < 1,3,1′-triboryl < 1,3,1′,3′-tetraboryl with dominating 1,3-substitution. The main reason for the regiospecificity is obviously of steric nature but also of electronic origin. In 1,2-diborylmetallocenes one must expect that the X_2B groups must be arranged almost perpendicularly to the Cp ring plane to relief severe steric interaction of these groups that would result if these groups were arranged in a coplanar manner with the Cp ring allowing maximum B−C π overlap. The 1,3-isomer takes care of the latter effect and prevents a strong twisting of the boryl group out of the Cp ring plane. This is best demonstrated by the C−C−B−Br dihedral angles for compounds **4** (14.9, 7.4°), **7** (14.1, 9.1°), and **8** (16.6, 11.4°).

In contrast to the C_2-symmetric molecules **4**, **7**, and **8**, 1,1′-bis(dibromoboryl)ferrocene is a centrosymmetric molecule, and this results in a perfect staggered orientation of the Cp ring planes, which are arranged in a parallel fashion, while there is a small but noticeable tilt between the Cp planes in the tetraborylated species. Moreover, the orientation of the two Cp rings is between eclipsed and staggered. This may be due to the fact that the packing of the molecules in the crystal is determined by Br-Br contacts.

Borylated metallocenes are isoelectronic and isolobal with metallocenyl carbocations. The latter have been extensively studied[8], and the increase of stability along the series with M = Fe, Ru, and Os was attributed to an increasing metal-carbon interaction[9] as suggested by theoretical studies[10]. The interaction between the iron atom and the α-carbon atom has been verified by an X-ray structural analysis of a ferrocenyldiphenyl carbocation[11] and a ferrocenylcyclopropenium cation[12]. However the coupling constant $^1J(^{37}Fe^{13}C)$ determined for $FcCH_2^+BF_4^-$ (Fc = ferrocenyl) as well as the negligible heights of rotational barriers vote against a direct $Fe{-}C_{(exo)}$ bond[13].

It is evident from the present study that there is no coordinative metal-to-boron bond in tetraborylated metallocenes as well as in $Fe(C_5H_4BBr_2)_2$[7] because the boron atoms retain their planar environment. If the metal atom would coordinate to the boron atom, then one should observe at least some deviation of the boron atoms from planarity. Apart from this argument one has to consider also the fairly large metal-boron distances which exceed by far those found for σ-bonded boryl groups (2.2−2.5 Å)[14]. Thus, the interaction cannot be very pronounced even if there is a shielding effect for the boron nuclei if we move from the ferrocene to the osmocene derivative. It appears that this may be primarily a paramagnetically induced effect on the boron nuclei. On the other hand, the tilt angle found in $Fe[C_5H_3(BMe_2)_2]_2$[15] is considerably larger than in **4** but is less in $Fe[C_5H_4B(N\textit{i}Pr_2)]_2$ and $Fe[C_5H_4B(NMeCH_2)_2]_2$[15]. In these latter compounds the boron atoms are electronically "saturated", and the small tilt angles suggests the absence of a metal-boron interaction in contrast to the (dimethylboryl)ferrocene derivative.

We thank Dr. *Hovestreydt*, Siemens AG, Karlsruhe for the data collection of compound **8**, and Mrs. *D. Ewald* for recording the mass spectra.

Experimental

All manipulations were carried out under dry argon. The solvents used were dried according to standard procedures and stored under argon. − Melting points (not corrected): MEL-TEMP. − ^1H NMR: solvent C_6D_6; internal standard C_6HD_5 (δ = 7.15); Jeol EX-400 spectrometer. − ^{13}C NMR: solvent C_6D_6 (δ = 123.00); Jeol EX-400 spectrometer. − ^{11}B NMR: solvent C_6D_6 or hexane; external standard $BF_3 \cdot OEt_2$ ($\delta = 0.00$); Bruker ACP 200 spectrometer.

Ferrocene was obtained from Fluka, ruthenocene and osmocene were bought from Strem Chemicals and used without further purification.

1,1'-Bis(dibromoboryl)ferrocene (**2**)

a) Ferrocene (0.75 g, 4.03 mmol) was dissolved in 25 ml of CH_2Cl_2. Then BBr_3 (2.08 g, 0.78 ml, 8.05 mmol) was added and the red solution heated at reflux for 24 h. After addition of some more BBr_3 (0.29 g, 0.11 ml, 1.16 mmol) refluxing was continued since the ^{11}B-NMR peak ($\delta = 46$) for (dibromoboryl)ferrocene (**1**) had vanished in the reaction mixture (12 h). Solvent and excess of BBr_3 were removed in vacuo, and the residue was dissolved in 20 ml of CH_2Cl_2. Cooling of the solution to −30°C yielded 1.51 g of **2** (25%). Red crystals, m.p. 99−100°C. For spectroscopic data see ref.[4,7].

b) According to the above procedure ferrocene (6.00 g, 32.2 mmol) and BBr_3 (20.4 g, 7.69 ml, 83.0 mmol) were mixed together in 75 ml of hexane and heated at reflux for 5 h. Black, insoluble products were removed by filtration from the hot solution. Cooling to −30°C yielded 10.7 g of **2** (63%).

c) *Reactions in the Presence of Lewis Acids:* Ferrocene (0.30 g, 1.60 mmol) was dissolved in 20 ml of CS_2 and BBr_3 (0.83 g, 0.31 ml, 3.20 mmol) as well as the appropriate Lewis acid [Run 1: $AlCl_3$ (0.21, 1.56 mmol), run 2: $ZnCl_2$ (0.22 g, 1.60 mmol), run 3: no Lewis acid added for reference] were added to the solution. The mixture was heated at reflux for 9.5 h. ^{11}B-NMR spectra were recorded after 1, 3, 6.5, and 9.5 h (results see Figure 1).

(Bromomethylboryl)ferrocene (**9**): Dibromomethylborane (3.71 g, 20.0 mmol, containing about 5 mol-% of BBr_3) was added to ferrocene (1.86 g, 10.0 mmol) in 25 ml of hexane. The mixture was heated to reflux for 3.5 h, and insoluble black products were removed by filtration. Then the solvent was partially removed in vacuo and the remaining solution cooled to −30°C. After two recrystallizations 0.93 g of red-brown **9** (32%) (containing approximately 10% of **1**) was obtained. For spectroscopic data see ref.[4].

1,1'-Bis(bromomethylboryl)ferrocene (**10**): $MeBBr_2$ (2.20 g, 11.8 mmol) was added to a solution of ferrocene (1.00 g, 5.38 mmol) in 25 ml of hexane. The mixture was kept at reflux for 22 h. Then the solvent was removed and the residue dissolved in 10 ml of hexane. After cooling to −30°C 0.85 g of **10** (40%) was obtained as red-brown crystals. For spectroscopic data see ref.[4].

(Bromophenylboryl)ferrocene (**11**): To a solution of ferrocene (1.21 g, 6.50 mmol) in 25 ml of hexane was added $PhBBr_2$. A blue precipitate formed immediately. The suspension was heated at reflux for 23 h and the solution examined by $^{1}H/^{13}C/^{11}B$-NMR spectroscopy. It contained a 58:42 mixture of unreacted ferrocene and **11**. − ^{1}H NMR (hexane, C_6D_6): $\delta = 3.91$ (s, 5H, unsubstituted Cp), 4.55 (br., 4H, B-substituted Cp), 6.95 and 7.17 (m, 5H, Ph). − ^{13}C NMR (hexane, C_6D_6): $\delta = 70.8$ (unsubstituted Cp), 78.3 (substituted Cp), 77.0 (substituted Cp), 130.1, 131.4, 132.0 (Ph), C−B not found. − ^{11}B NMR (hexane, C_6D_6): $\delta = 58.4$ ($h_{1/2} =$ 223 Hz).

1,1',3,3'-Tetrakis(dibromoboryl)ferrocene (**4**): Ferrocene (1.00 g, 5.40 mmol) and boron tribromide (13.5 g, 53.8 mmol) were mixed in a Schlenk flask and kept at reflux for 37 h. When the formation of HBr had ceased, excess BBr_3 was evaporated in vacuo. The dark violet residue was dissolved in 250 ml of hot benzene, and insoluble black products were removed by filtration. Then the solvent was completely removed in vacuo from the filtrate and the residue recrystallized from hot 1,2-dichloroethane. Yield: 4.06 g of **4** (87%); m.p. 194°C (dec.). − $C_{10}H_6B_4Br_8Fe$ (864.5): calcd. C 13.9, H 0.70; found: C 13.99, H 1.11. − ^{1}H NMR (C_6D_6): $\delta = 4.70$ [d, $^{4}J(HH) =$ 1.46 Hz, 4H, 4,5-H], 4.94 (t, 2H, 2-H). − ^{13}C NMR (C_6D_6): $\delta =$ 83.4 (C−B), 85.9 (C-4,5), 87.7 (C-2). − ^{11}B NMR (C_6D_6): $\delta = 53.6$ (br). − IR (Nujol/Host., cm^{-1}): $\tilde{\nu} = 3096$ (w), 1449 (vs), 1302 (s), 1260 (s, sh), 1163 (vs), 810 (vs, br), 647 (m), 512 (s), 452 (m). − MS, *m/z* (%): 844 (6.4), 865 (51.1), 784 (11.3), 650 (76.3), 568 (9.3), 295 (100).

1,1',3,3'-Tetrakis(dibromoboryl)ruthenocene (**7**): According to the above procedure, ruthenocene (0.50 g, 2.16 mmol) and BBr_3 (5.41 g, 21.6 mmol) were heated together for 20 h. A yellow solution formed. Workup gave a yield of 1.61 g of **7** (82%), yellow crystals, m.p. 172°C (dec.). − $C_{10}H_6B_4Br_8Ru$ (912.8): calcd. C 13.6, H 0.66; found C 14.55, H 1.09. − ^{1}H NMR (C_6D_6): $\delta = 4.80$ [d, $^{4}J(HH) = 1.22$ Hz, 4H, 4,5-H], 5.03 [t, $^{4}J(HH) = 1.22$ Hz, 2H, 2-H]. − ^{13}C NMR (C_6D_6): $\delta = 87.9$ (C-4,5), 89.8 (C-2). − ^{11}B NMR (C_6D_6): $\delta = 51.7$ (br.). − IR (Nujol/Host., cm^{-1}): $\tilde{\nu} = 3092$ (w), 3085 (w), 1451 (vs), 1300 (s), 1164 (vs), 807 (vs), 649 (s), 501 (m), 462 (m), 422 (m), 373 (s).

1,1',3,3'-Tetrakis(dibromoboryl)osmocene (**8**): Prepared in analogy to **4**. Osmocene (0.31 g, 0.97 mmol) and BBr_3 (2.64 g, 10.5 mmol) were kept at reflux for 61.5 h. Recrystallization from hot 1,2-dichloroethane yielded 0.62 g of **8** (64%) as yellow crystals, m.p. 154−156°C. − $C_{10}H_6B_4Br_8Os$ (998.8): calcd. C 12.0, H 0.61; found C 13.2, H 0.98. − ^{1}H NMR (C_6D_6, BBr_3): $\delta = 4.94$ [d, $^{4}J(HH) =$ 0.98 Hz, 4H, 4,5-H], 5.14 [t, $^{4}J(HH) = 0.98$, $^{3}J(HH) = 1.46$ Hz, 2H, 2-H]. − ^{13}C NMR (C_6D_6, BBr_3): $\delta = 81.9$ (C-4,5), 82.4 (C-2), 83 (C-1, br.). − ^{11}B NMR ($CHBr_3$): $\delta = 50.3$. − IR (Nujol/Host., cm^{-1}): $\tilde{\nu} = 3099$ (w), 1447 (vs), 1259 (s, sh), 807 (vs, br), 645 (s), 370 (s).

X-Ray Structural Analyses: Siemens P4 diffractometer, graphite monochromator. Mo-K_α radiation, SHELXL-Plus and SHELXTL 93 programs for structure solution and refinement. All structures were solved by Patterson methods and Fourier synthesis. Nonhydrogen atoms were refined anisotropically, hydrogen atoms were placed in calculated positions by using fixed U_i values[16].

4: Dark red single crystals were obtained from 1,2-dichloroethane. $C_{10}H_6B_4Br_8Fe$, $M = 864.52$, orthorhombic, space group $P2_12_12$ (No. 18), $a = 15.405(3)$, $b = 7.031(2)$, $c = 9.526(2)$ Å, $V =$ 1031.8(4) Å^3, $Z = 2$, $D_{calc.} = 2.783$ Mg/m^3, $\mu = 16.21$ mm^{-1}. Single-crystal size: 0.2 × 0.18 × 0.16 mm, scan range: $4.28° < 2\Theta <$ 49.90° ($-17 \leqslant h \leqslant O$, $O \leqslant k \leqslant 8$, $-10 \leqslant l \leqslant 11$), 1924 reflections collected, 1612 symmetry-independent reflections; min/max transmission: 0.025/0.073. 105 parameters refined. Largest difference peak: 0.585 eÅ^{-3}, $w^{-1} = \sigma^2 F_o^2 + (0.0644P)^2$, $R = 0.0567$, $wR2 =$ 0.1143.

7: Single crystals were obtained from 1,2-dichloroethane. Yellow plates, $C_{10}H_6B_4Br_8Ru$, $M = 909.74$, orthorhombic, space group *Pbcn* (No. 60), $a = 7.724(4)$, $b = 19.099(11)$, $c = 13.919(9)$ Å, $V =$ 2053.3(21) Å^3, $Z = 4$, $D_{calc.} = 2.943$ Mg/m^3, $\mu = 16.32$ mm^{-1}. Crystal size: 0.1 × 0.9 × 0.85 mm; scan range: $4.26 < 2\Theta < 48.12°$ ($-1 \leqslant h \leqslant 8$, $-21 \leqslant k \leqslant 21$, $-15 \leqslant l \leqslant 1$), 3836 reflections collected, 1621 symmetry-independent reflections; max/min transmission: 0.974/0.447; 105 parameters refined; largest difference peak: 0.888 eÅ^{-3}, $w^{-1} = \sigma^2 F_o^2 + (0.0628P)^2$, $R = 0.0570$, $wR2 =$ 0.1154.

8: Single crystals were obtained from 1,2-dichloroethane, yellow plates, $C_{10}H_6B_4Br_8Os$, $M = 998.8$, orthorhombic, space group *Pbcn* (No. 60), $a = 7.728(3)$, $b = 19.043(7)$, $c = 13.978(5)$ Å, $V =$ 2057.1(12) Å^3, $Z = 4$, $D_{calc.} = 3.225$ Mg/m^3, $\mu = 21.728$ mm^{-1}. Crystal size: 0.2 × 0.2 × 0.18 mm, Siemens SMART-System (Mo-K_α radiation, graphite monochromator), 2568 reflections measured in the range $5.18° < 2\Theta < 46.48°$ ($-3 \leqslant h \leqslant 8$, $-20 \leqslant k \leqslant 12$,

$-6 \leq l \leq 15$), 1365 symmetry-independent reflections; min/max transmission: 0.0082/0.0343. Structure solution by direct methods; 109 parameters refined, largest difference peak: $1.690\ e\text{Å}^{-3}$, $w^{-1} = \sigma^2F_o^2 + (0.0660P)^2 + 17.7000P$, $R = 0.0525$, $wR2 = 0.1246$.

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[16] Details on the crystal structure determination are deposited at the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, and may be obtained by quoting the depository numbers CSD-401516 (**4**), -401517 (**7**), -401521 (**8**), the names of the authors, and the literature citation.

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