Borabenzene Derivatives. 20.[1] (Boratabenzene)(hexamethylbenzene)iron Complexes: Synthesis, Structure, and Reactivity

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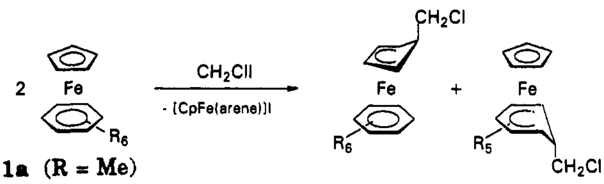
The 19e complex CpFe(HMB) (HMB = hexamethylbenzene) (**1a**) reacts with dihaloboranes RBX_2 (R = Me, Ph, NEt_2; X = Cl, Br) to give paramagnetic 19e (boratabenzene)(hexamethylbenzene) iron complexes $(C_5H_5BR)Fe(HMB)$ (R = Me, Ph, NEt_2) (**2a–c**). Oxidation with $[FeCp_2]PF_6$ affords the corresponding diamagnetic salts $[(C_5H_5BR)Fe(HMB)]PF_6$ (**2a–c·PF₆**), while oxidation of the diethylamino derivative **2c** with $FeCl_3$ in Et_2O/H_2O produces the hydroxo compound $[(C_5H_5BOH)Fe(HMB)]PF_6$ (**2d·PF₆**). The structures of both the neutral methyl compound **2a** and the corresponding salt **2a·PF₆** have been determined by X-ray crystallography. A comparison of the two structures demonstrates the labilizing effect of the excess electron. Both structures show distortions of the ring ligands which can be explained by qualitative MO considerations. The arene ligand possesses a boat conformation in **2a** and an inverted boat conformation in **2a⁺**. Cyclovoltammetric investigation of the cations $[(C_5H_5BR)Fe(HMB)]^+$ (**2a–c⁺**) shows a reversible (+/0) and a quasireversible (0/−) reduction wave; compared to CpFe(HMB) these waves are shifted anodically. The phenyl derivative **2b** reacts with MeI to form the iodide **2b·I** as well as diamagnetic methyl addition products $(C_5H_5BPh)Fe(C_6Me_7)$ (**6a**) and three isomers $(C_5H_5MeBPh)Fe(HMB)$ (**3a–5a**) with the methyl group added to the borabenzene ring. The cation **2b⁺** undergoes hydride addition with $NaBH_4$ to produce $(C_5H_5BPh)Fe(1,2,3,4,5,6\text{-}endo\text{-}C_6HMe_6)$ (**6b**) and two isomers $(C_5H_6BPh)Fe(HMB)$ (**3b**, **4b**) with bora-2,4- and bora-2,5-cyclohexadiene ligands.

Introduction

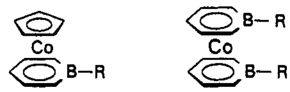
Sandwich complexes with 19 valence electrons have recently attracted renewed interest.[2,3] The longest known representative of this small family of complexes is cobaltocene $CoCp_2$,[4] and its remarkable reactivity has furnished the paradigm for the whole family. Thus, the 19e iron sandwich complexes of general type CpFe(arene)[2,5,6] are expected to show similar patterns of reactivity. Two reactions are particularly characteristic for these systems: oxidation of the 19e sandwich complex to give a stable cation with an 18e configuration[4] and oxidative addition of organic halides.[7,8] Thus, CpFe(HMB)[9] (**1a**) reacts with organic halides R'X to give salts **1a·X** and two regioisomeric complexes of type (HMB)Fe(5-*exo*-R'C_5H_5) and CpFe(6-*exo*-R'C_6R_6) (Scheme I).[8] The same reactivity has been observed for **1b**, however with different isomer distributions of the corresponding regioisomers.[7,8]

Scheme I



1a (R = Me)
1b (R = H)

Another characteristic reaction of cobaltocene is the formation of borabenzene complexes $CoCp(C_5H_5BR)$ and $Co(C_5H_5BR)_2$ when cobaltocene is treated with haloboranes RBX_2 (R = Me, Ph, Cl, Br; X = Cl, Br),[10] the first and most widely explored entry into the field of borabenzene chemistry.[11,12] In this paper we will show that CpFe(arene) complexes undergo the same boranediyl (RB) insertion reaction to afford (arene)(boratabenzene)iron compounds.



Experimental Section

General Procedures. Reactions were carried out under an atmosphere of dinitrogen by means of conventional Schlenk techniques. Pentane and hexane were distilled from Na/K alloy, ethereal solvents from sodium benzophenone ketyl, and acetonitrile and dichloromethane from CaH_2. Toluene was distilled

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from sodium and acetone from B_2O_3. Alumina for chromatography (Woelm) was heated in a high vacuum at 300 °C and deactivated (7% H_2O, deoxygenated) after cooling. Melting points were measured in sealed capillaries and are uncorrected. Elemental analyses were performed by Analytische Laboratorien, D-51647 Gummersbach, Germany.

NMR spectra were recorded on a Varian VXR 500 (^{1}H, 500 MHz), a Bruker WH 270 PFT (^{1}H, 270 MHz; ^{13}C, 67.88 MHz), a Bruker WP 80 PFT (^{1}H, 80 MHz), and a JEOL NM-PS-100 spectrometer (^{11}B, 32.08 MHz) with digital resolutions <0.5 Hz/point for ^{1}H and <1.0 Hz for ^{13}C spectra. Infrared spectra were recorded on a Perkin-Elmer 780 FTIR spectrometer.

Cyclic voltammetry was carried out using an EG & G 175 voltage scan generator and an EG & G 173 potentiostat. Solutions were ca. 10^{-3} M in electroactive species and 0.1 M in tetrabutylammonium hexafluorophosphate (TBAH) as supporting electrolyte. For the measurements a conventional three electrode cell with a platinum-inlay working electrode, a platinum sheet counter electrode, and a saturated calomel (SCE) or a Ag/AgCl reference electrode was used. All potentials were measured relative to the $FeCp_2^{+/0}$ couple, which was added after the measurement. DME, DMF, and CH_2Cl_2 (Merck, p.a.) were filtered through highly active alumina and distilled under argon. TBAH was recrystallized from ethanol and dried in vacuo at 80 °C. Abbreviations used in this text follow standard electrochemical conventions.[13] For example, E_p is the peak potential, v is the scan rate, and i_p is the peak current.

Materials. CpFe(HMB),[9] CpFe(C_6H_6),[9,14] [$FeCp_2$]PF_6,[15] $PhBCl_2$,[16] and $MeBBr_2$[17] were prepared by published procedures. Other chemicals were used as received. All 19e iron complexes prepared in this work are air-sensitive; crystals of the salts **2a–d**·PF_6 can be handled in air without noticeable deterioration.

Synthesis of (C_5H_5BMe)Fe(HMB) (2a). $MeBBr_2$ (0.82 g, 4.4 mmol) in toluene (80 mL) was added dropwise to **1a** (3.50 g, 12.3 mmol) in toluene (120 mL) at −78 °C. After stirring for 20 min at −78 °C, the mixture was warmed to room temperature. A precipitate of **1a**·Cl was removed by filtration. The volatiles were pumped off in vacuo. Extraction of the oily residue with hexane/toluene (10:1) and two crystallizations gave pure **2a** (0.32 g, 24%) as black crystals, mp 64 °C dec. Anal. Calcd for $C_{18}H_{26}BFe$: C, 69.95; H, 8.48. Found: C, 69.85; H, 8.34. MS (90 °C): m/z (I_{rel}) 309 (52, M$^+$), 283 (100, CpFe(C_6Me_6)$^+$). ^{1}H NMR (toluene-d_8, 32 °C): δ −2.9 ($w_{1/2}$ = 88 Hz, HMB), 11.4 ($w_{1/2}$ = 365 Hz, C_5H_5B), −18.1 ($w_{1/2}$ = 409 Hz, C_5H_5B), −26.7 ($w_{1/2}$ = 197 Hz, BMe).

Synthesis of (C_5H_5BPh)Fe(HMB) (2b). $PhBCl_2$ (0.53 g, 3.4 mmol) in toluene (5 mL) was added dropwise to **1a** (2.67 g, 9.4 mmol) in toluene (60 mL) at −78 °C. Workup as for **2a** yielded black, crystalline **2b** (0.61 g, 48%), mp 148 °C dec. Anal. Calcd for $C_{23}H_{28}BFe$: C, 74.44; H, 7.61. Found: C, 74.14; H, 7.49. MS (90 °C): m/z (I_{rel}) 371 (100, M$^+$), 209 (15, Fe(C_5H_5BPh)$^+$). ^{1}H NMR (toluene-d_8, 32 °C): δ −2.6 ($w_{1/2}$ = 92 Hz, HMB), 12.7 ($w_{1/2}$ = 72 Hz, 2H of C_5H_5B), −15.7 ($w_{1/2}$ = 426 Hz, 1H of C_5H_5B), C_5H_5B signals not observed at −30 °C, 12.5 ($w_{1/2}$ = 25 Hz, BPh), 6.0 ($w_{1/2}$ = 18 Hz, BPh).

Synthesis of ($C_5H_5BNEt_2$)Fe(HMB) (2c). Et_2NBCl_2 (0.21 g, 1.34 mmol) was added to **1a** (1.06 g, 3.8 mmol) in toluene (40 mL) at room temperature, and the reaction mixture was stirred for 4 days at room temperature. Workup as for **2a** afforded black, crystalline **2c** (0.16 g, 34%), mp 133 °C dec. Anal. Calcd for $C_{21}H_{33}BNFe$: C, 68.89; H, 9.09. Found: C, 68.68; H, 8.92. MS (90 °C): m/z (I_{rel}) 366 (39, M$^+$), 283 (100, CpFe(HMB)$^+$). ^{1}H NMR (toluene-d_8, 32 °C): δ −4.3 ($w_{1/2}$ = 142 Hz, HMB), C_5H_5B signals not observed, −3.8 ($w_{1/2}$ = 80 Hz, $BNCH_2$), −1.1 ($w_{1/2}$ = 50 Hz, $BNCH_2Me$).

Synthesis of (C_5H_5BOH)Fe(HMB) (2d). A suspension of **2d**·PF_6 (0.26 g, 0.57 mmol) in THF (10 mL) was stirred for 30 min with Na/Hg (1%, 4.1 g = 1.71 mmol of Na) at −30 °C. Removal of the solvent, extraction of the residue with hexane, and crystallization from hexane gave **2d** (0.07 g, 42%) as black crystals, mp 134 °C dec. Anal. Calcd for $C_{17}H_{24}BFe$: C, 65.65; H, 7.78. Found: C, 65.58; H, 7.75. MS (110 °C): m/z (I_{rel}) 162 (100, HMB$^+$). IR (CH_2Cl_2, cm^{-1}): ν(OH) = 3640. ^{1}H NMR (toluene-d_8, 32 °C): δ −3.6 ($w_{1/2}$ = 158 Hz, HMB), 8.8 ($w_{1/2}$ = 170 Hz).

Synthesis of [(C_5H_5BR)Fe(HMB)]PF_6 (R = Me, Ph, NEt_2). The neutral complexes **2** (2 mmol) in CH_2Cl_2 (70 mL) were stirred at 0 °C with [$FeCp_2$]PF_6 (0.63 g, 1.9 mmol) for 4 h. After removal of the solvent, ferrocene was extracted with hexane. The residue was dissolved in a small volume of CH_2Cl_2. Filtration and slow addition of ether precipitated the salts **2**·PF_6 as red solids.

2a·PF_6. Yield: 42%; mp 140 °C dec. Anal. Calcd for $C_{18}H_{26}BF_6PFe$: C, 47.62; H, 5.77. Found: C, 47.84; H, 5.76. ^{1}H NMR (acetone-d_6): δ 5.87 (m, 3-/5-H + 4-H), 4.49 (d, $^3J_{23}$ = 8.9 Hz, 2-/6-H), 2.54 (s, HMB), 0.70 (s, BMe). ^{13}C NMR (CD_2Cl_2/CH_2Cl_2): δ 89.0 (d br, J = 149 Hz, C2/6), 99.7 (d, ^1J = 170 Hz, C3/5), 83.4 (d, ^1J = 175 Hz, C4), 101.1 (s, C_6Me_6), 17.7 (q, ^1J = 132 Hz, C_6Me_6). ^{11}B NMR (CH_2Cl_2): δ 25.0.

2b·PF_6. Yield: 82%; mp 220 °C dec. Anal. Calcd for $C_{22}H_{28}BF_6PFe$: C, 53.53; H, 5.47. Found: C, 53.48; H, 5.37. ^{1}H NMR (acetone-d_6): δ 8.15 (m, 2 H_o), 7.52 (m, 2H_m + H_p), 6.12 (m, 3-/5-H + 4-H, 5.20 (d, $^3J_{23}$ = 9.3 Hz, 2-/6-H), 2.38 (s, HMB). ^{13}C NMR (acetone-d_6): δ 135.7 (dt, ^1J = 154, ^3J = 6 Hz, 2C_o), 132.0 (dt, ^1J = 151, ^3J = 6 Hz, C_p), 129.1 (dd, ^1J = 156, ^3J = 4 Hz, 2C_m), 85.0 (br, C2/6), 100.5 (dd, ^1J = 169, ^3J = 4 Hz, C3/5), 85.4 (d, ^1J = 173 Hz, C4), 102.1 (s, C_6Me_6), 17.1 (q, ^1J = 130 Hz, C_6Me_6). ^{11}B NMR (acetone): δ 21.0.

2c·PF_6. Yield: 38%; mp 158 °C dec. Anal. Calcd for $C_{21}H_{33}BNF_6PFe$: C, 49.35; H, 6.51. Found: C, 49.08; H, 6.51. ^{1}H NMR (acetone-d_6): δ 5.85 (m, 4-H), 5.25 (m, 3-/5-H), 3.74 (d, $^3J_{23}$ = 8.8 Hz, 2-/6-H), 2.47 (s, HMB); ABC_3 systems δ 3.46 (dq, 2H_A, NCH_2), 3.08 (dq, 2H_B, NCH_2), 1.09 (t, 2Me), $^2J_{AB}$ = 14.2, $^3J_{AC}$ = $^3J_{BC}$ = 7.2 Hz. ^{13}C NMR (acetone-d_6): δ 82.6 (br, C2/6), 99.7 (d, ^1J = 162 Hz, C3/5), 79.8 (d, ^1J = 179 Hz, C4), 101.0 (s, C_6Me_6), 17.6 (q, ^1J = 128 Hz, C_6Me_6), 43.4 (t, ^1J = 135 Hz, 2NCH_2), 16.2 (q, ^1J = 128 Hz, 2Me). ^{11}B NMR (acetone-d_6: δ 21.0.

Synthesis of [(C_5H_5BOH)Fe(HMB)]PF_6 (2d·PF_6). $FeCl_3·6H_2O$ (3.0 g, 11.1 mmol) in H_2O (50 mL) was added to **2c** (0.62 g, 1.58 mmol) in Et_2O (100 mL). After vigorously stirring for 20 min, the aqueous phase was separated and treated with NH_4PF_6(aq). Recrystallization of the precipitate formed from acetone/Et_2O gave **2d**·PF_6 (0.40 g, 56%), mp 175 °C dec. Anal. Calcd for $C_{17}H_{24}BOF_6PFe$: C, 44.78; H, 5.31. Found: C, 46.26; H, 5.77. ^{1}H NMR (acetone-d_6): δ 6.72 (s, OH), 5.96 (t, $^3J_{45}$ = 5.8 Hz, 4-H), 5.69 (dd, 3-/5-H), 3.96 (d, $^3J_{23}$ = 9.2 Hz, 2-/6-H), 2.53 (s, HMB). ^{13}C NMR (acetone-d_6): 79.4 (br, C2/6), 101.5 (d, ^1J = 169 Hz, C3/5), 81.5 (d, ^1J = 174 Hz, C4), 101.5 (s, C_6Me_6), 16.9 (q, ^1J = 128 Hz, C_6Me_6). ^{11}B NMR (acetone): δ 22.0. IR (MeCN, cm^{-1}): ν(OH) = 3200.

Reaction of 2b with MeI. A solution of **2b** (1.54 g, 4.15 mmol) and MeI (1.77 g, 12.45 mmol) in hexane (250 mL) was kept at 50 °C for 10 h. After filtration all volatiles were removed in vacuo. The residue contained a mixture of four isomeric methylation products **3a–6a** (total 0.48 g, 30%; ratio 62:7:<1:31, by ^{1}H NMR) and bis(1-phenylboratabenzene)iron (**7**) (0.08 g, 11%) which could be separated by chromatography on alumina with hexane.

Mixture of 3a–6a. Anal. Calcd for $C_{24}H_{31}BFe$: C, 74.65; H, 8.09. Found: C, 74.59; H, 7.91. MS (100 °C): m/z (I_{rel}) 386 (10, M$^+$), 371 (68, M$^+$ − Me), 209 (93, Fe(C_5H_5BPh)$^+$), 147 (100, $C_{11}H_{15}^+$).

3a. Mp: 109 °C, 120 °C dec. ^{1}H NMR (C_6D_6): δ 7.91 (m, 2 H_o), 7.43 (m, 2H_m + H_p), 5.38 (dd, $^3J_{23}$ = 7.6, $^3J_{34}$ = 4.5 Hz, 3-H), 3.44 (t, 4-H), 2.68 (d, ^3J = 7.6 Hz, 2-H), 2.13 (t, $^3J_{45} \approx {^3J_{56}}$ = 7.5 Hz, 5-H), 1.70 (s and m, HMB + 6-*endo*-H), 0.69 (d, ^3J = 6.8 Hz, 6-*exo*-Me). ^{13}C NMR (C_6D_6): δ 134.8 (dt, ^1J = 154, ^3J = 7 Hz, 2C_o), C_m + C_p hidden by solvent, 88.4 (dd, ^1J = 161, ^3J = 7 Hz, C3), 80.5 (d, ^1J = 163 Hz, C4), 64.8 (d br, ^1J = 130 Hz, C2), 55.0

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(d, ^1J = 149 Hz, C5), 24.2 (q, ^1J = 127 Hz, Me), 92.7 (s, C_6Me$_6$), 21.1 (q, ^1J = 127 Hz, C$_6$*Me*$_6$), C$_6$ and C$_i$ could not be observed because of $^{(10)11}$B quadrupole broadening. ^{11}B NMR (C_6D_6): δ 17.7. CV (DMF, TBAH, Ag/AgCl, v = 100 mV/s): E_p^a = −0.11 V (irreversible).

4a. Mp: 178 °C, 190 °C dec. ^{1}H NMR (C_6D_6): δ 8.26 (m, 2H$_o$), 7.48 (m, 2H$_m$ + H$_p$), 2.99 (d, $^3J_{23}$ = 8.2 Hz, H2/6), 2.51 (m, 3-/5-H + 4-*endo*-H), 0.52 (d, ^3J = 6.0 Hz, 4-*exo*-Me), 1.66 (s, HMB). ^{13}C NMR (C_6D_6): δ 134.2 (dt, ^1J = 154, ^3J = 7 Hz, 2C$_o$), C$_m$ + C$_p$ hidden by solvent, 77.0 (d br, ^1J = 150 Hz, C2/6), 54.4 (d, ^1J = 154 Hz, C3/5), 34.5 (d, ^1J = 132 Hz, C4), 25.6 (q, ^1J = 127 Hz, 4-*exo*-Me), 94.2 (s, C_6Me$_6$), 15.8 (q, ^1J = 127 Hz, C$_6$*Me*$_6$). ^{11}B NMR (C_6D_6): δ 16.0. CV (CH_2Cl_2, TBAH, SCE, v = 100 mV/s): E_p^a = +0.19 V (irreversible).

5a. Not isolated. ^{1}H NMR (C_6D_6), recorded of a mixture of **4a** and **5a**: δ 7.95 (m, 2H$_o$), 7.35 (m, 2H$_m$ + H$_p$), 5.07 (d, $^3J_{23}$ = 8.3 Hz, 2-H), 3.80 (t, $^3J_{23} \approx {}^3J_{34} \approx$ 8.0 Hz, 3-H), 1.68 (s, HMB), 0.53 (d, ^3J = 6.0 Hz, 5-*exo*-Me), remaining protons hidden by signals of **4a**.

6a. Mp: 46 °C, 120 °C dec. 1H NMR (C_6D_6): δ 8.15 (m, 2H$_o$), 7.45 (m, 2H$_m$ + H$_p$), 4.88 (m, 3-/5-H + 4-H), 4.40 (dd, $^3J_{23}$ = 8.5, $^4J_{24}$ = 1.5 Hz, 2-/6-H), 2.04 (s, 3-Me), 1.43 (s, 2-/6-Me), 1.16 (s, 6-*endo*-Me), 1.04 (s, 1-/5-Me), −0.25 (s, 6-*exo*-Me). ^{13}C NMR (C_6D_6): δ 134.0 (dt, ^1J = 154, ^3J = 7 Hz, 2C$_o$), C$_m$ + C$_p$ hidden by solvent, 97.4 (dd, ^1J = 170, ^3J = 7 Hz, C3/5), 84.8 (d, ^1J = 165 Hz, C4), 84.0 (d br, ^1J = 140 Hz, C2/6); cyclohexadienyl ligand δ 90.9 (s, C3), 90.3 (s, C2/4), 48.4 (s, C1/5), 39.3 (s, C6), 27.8 (q, ^1J = 125 Hz, Me), 25.5 (q, ^1J = 124 Hz, 2Me), 15.8 (q, ^1J = 127 Hz, Me), 15.6 (q, ^1J = 126 Hz, 3Me, 2 overlapping signals). ^{11}B NMR (C_6D_6): δ 17.3. CV (DMF, TBAH, Ag/AgCl, v = 100 mV/s): $E_{1/2}^1$ = +0.222 V (reversible), $E_{1/2}^2$ = −2.44 V (quasireversible).

Reaction of [(C_5H_5BPh)Fe(HMB)]$^+$ with NaBH$_4$. A suspension of **2b·I** (0.44 g, 0.88 mmol) and NaBH$_4$ (0.10 g, 2.60 mmol) in 15 mL of MeCN was stirred for 4 h at room temperature. After removal of the volatiles in vacuo the residue was extracted with hexane (100 mL). The hexane solution was filtered through alumina (2 cm) and then evaporated to dryness in vacuo to give a red powder (0.30 g, 93%). This contained three isomers **3b**, **4b**, and **6b** (ratio 8:17:75, by ^{1}H NMR) which were separated by chromatography on alumina with hexane as eluent. Anal. Calcd for $C_{23}H_{29}$BFe: C, 74.23; H, 7.81. Found: C, 74.05; H, 7.80. MS (100 °C): m/z (I_{rel}) 372 (89, M$^+$), 371 (100, M$^+$ − H), 209 (88, Fe(C_5H_5BPh)$^+$), 147 (94, $C_{11}H_{15}^+$).

3b. Mp: 154 °C, 175 °C dec. ^{1}H NMR (C_6D_6): δ 7.92 (m, 2H$_o$), 7.41 (m, 2H$_m$ + H$_p$), 5.50 (dd, $^3J_{23}$ = 7.3, $^3J_{34}$ = 4.5 Hz, 3-H), 3.53 (t, 4-H), 2.66 (d, 2-H), 1.71 (m, 5-H + 6-*endo*-H), 0.76 (d, ^2J = 14.1 Hz, 6-*exo*-H), 1.70 (s, HMB). ^{13}C NMR (C_6D_6/C_6H_6): δ 134.8 (dt, ^1J = 154, ^3J = 7 Hz, 2C$_o$), C$_m$ + C$_p$ hidden by solvent, 88.4 (dd, ^1J = 161, ^3J = 6 Hz, C3), 82.1 (d, ^1J = 161 Hz, C4), 65.5 (d br, ^1J = 132 Hz, C2), 46.6 (d, ^1J = 155 Hz, C5), 11.4 (t br, ^1J = 120 Hz, C6), 92.6 (s, C_6Me$_6$), 16.0 (q, ^1J = 127 Hz, C$_6$*Me*$_6$). ^{11}B NMR (C_6D_6): δ 18.0. IR (KBr, cm^{-1}): ν(CH$_{exo}$) = 2760 (s).

4b. Mp: 164 °C dec. ^{1}H NMR (C_6D_6): δ 8.31 (m, 2H$_o$), 7.53 (m, 2H$_m$ + H$_p$), 3.14 (d, $^3J_{23}$ = 8.4 Hz, 2-/6-H), 2.59 (dt, $^3J_{3,4endo}$ = 6.3 Hz, 4-*endo*-H), 2.05 (t, 3-/5-H), 1.81 (d, ^2J = 13.0 Hz, 4-*exo*-H), 1.66 (s, HMB). ^{13}C NMR (C_6D_6): δ 134.4 (dt, ^1J = 154, ^3J = 7 Hz, 2C$_o$), C$_m$ + C$_p$ hidden by solvent, 44.2 (d, ^1J = 154 Hz, C3/5), 30.1 (t, ^1J = 132 Hz, C4), 94.3 (s, C_6Me$_6$), 15.8 (q, ^1J = 127 Hz, C$_6$*Me*$_6$), C2/6 could not be observed because of $^{(10)11}$B quadrupole broadening. ^{11}B NMR (C_6D_6): δ 16.3. IR (KBr, cm^{-1}): ν(CH$_{exo}$) = 2772 (s).

6b. Mp: 115 °C, 140 °C dec. ^{1}H NMR (C_6D_6): δ 8.15 (m, 2H$_o$), 7.44 (m, 2H$_m$ + H$_p$), 4.83 (m, 3-/5-H + 4-H), 4.44 (d, $^3J_{23}$ = 8.9 Hz, 2-/6-H), 2.08 (s, 3-Me), 1.41 (s, 2-/4-Me), 0.94 (s, 1-/5-Me), 1.04 (m, 6-*endo*-Me + 6-*exo*-H). ^{13}C NMR (C_6D_6): δ 143.0 (br, C$_i$), 134.2 (dt, ^1J = 154, ^3J = 7 Hz, 2C$_o$), C$_m$ + C$_p$ hidden by solvent, 97.6 (dd, ^1J = 160, ^3J = 7 Hz, C3/5), 84.8 (d, ^1J = 166 Hz, C4), 84.0 (br, C2/6); cyclohexadienyl ligand δ 92.3 (s, C2/4), 91.0 (s, C3), 40.6 (s, C1/5), 36.9 (d, ^1J = 124 Hz, C6); signals of Me groups at δ 16.9–15.3, partially overlapping. ^{11}B NMR (C_6D_6): δ 16.4. IR (KBr, cm^{-1}): ν(CH$_{exo}$) = 2796 (m).

Table I. Crystallographic Data, Data Collection Parameters, and Refinement Parameters for 2a and 2a·PF$_6$

	2a	2a·PF$_6$
	Crystal Data	
formula	$C_{18}H_{26}$BFe	$C_{18}H_{26}$BFePF$_6$
fw	309.07	454.03
cryst system	monoclinic	orthorhombic
space group	$P2_1/n$ (No. 14)	$Cmc2_1$ (No. 36)
a, pm	1121.8(4)	933.06(9)
b, pm	1066.5(4)	1349.15(9)
c, pm	1358.1(7)	1587.4(2)
β, deg	90.28(5)	
V, nm^3	1.624(2)	1.9982(6)
d_{calcd}, g/cm^3	1.263	1.509
Z	4	4
F(000)	660.0	936.0
μ, cm^{-1}	9.14	8.85
cryst dimens, mm	0.8 × 0.6 × 0.5	0.4 × 0.4 × 0.6
	Data Collection	
radiation (λ, pm)	Mo Kα (70.93)	Mo Kα (70.93)
monochromator	graphite	graphite
T, K	293	293
scan mode	ω	ω
θ range, deg	$3 \le \theta \le 24$	$3 \le \theta \le 29$
	Refinement	
total data	3469	2220
unique obsd data ($I > 1\sigma(I)$)	2369	1299
no. of variables	181	135
R	0.036	0.044
R_w	0.049	0.056
weighting factor, w	$1/\sigma^2(F_o)$	$1/\sigma^2(F_o)$
GOF	2.482	1.933
10^{-6}(max resid density), e pm^{-3}	0.361 (89 pm from C13)	0.550 (112 pm from F1)

X-ray Structure Determination of Complexes 2a and 2a·PF$_6$. Crystals of Fe(C_5H_5BMe)(HMB) (**2a**) were obtained from toluene/hexane (1:10) at −30 °C. Crystals of [Fe(C_5H_5BMe)(HMB)]PF$_6$ (**2a·PF$_6$**) were grown by slow diffusion of ether into an acetone solution of the salt at room temperature. Geometry and intensity data were obtained on an ENRAF-Nonius CAD4 diffractometer. Pertinent crystallographic data for the two compounds are collected in Table I. Corrections for Lorentz polarization and an empirical absorption correction on the basis of ψ-scans[18] were applied. Only unique reflections with intensities $I > 1\sigma(I)$ were used in the structure solution and refinement.[19] Both structures were solved by Patterson and subsequent difference Fourier syntheses. In the final full-matrix least squares refinement, non-hydrogen atoms were refined with anisotropic displacement parameters, and hydrogen atoms were included isotropically as riding atoms [C–H = 98 pm, $B_{iso} = 1.3B_{eq}$(C)] in structure factor calculations.

Results and Discussion

(Boratabenzene)(hexamethylbenzene)iron Complexes. CpFe(HMB) (**1a**) reacts with dihaloboranes RBX$_2$ (MeBBr$_2$, PhBCl$_2$, Et$_2$NBCl$_2$) in toluene to produce yellow salts **1a·X** (X = Cl, Br) and black solutions containing the paramagnetic boratabenzene complexes (C_5H_5BR)Fe(HMB) (**2a–c**) (Scheme II) which can be isolated as black, crystalline solids.

The complexes **2** are extremely air-sensitive and do not survive attempted chromatography on alumina (7% H_2O, hexane, −30 °C). At room temperature they undergo very

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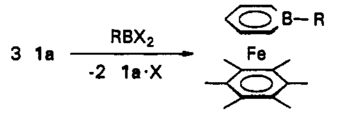
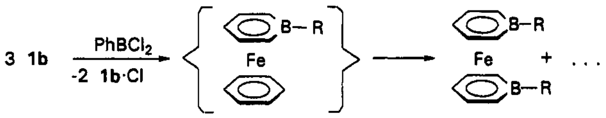
(19) Frenz, B. A. The ENRAF-Nonius CAD4 SDP—a real-time system for concurrent X-ray data collection and crystal structure determination. In computing in Crystallography; Schenk, H., Olthof-Hazekamp, R., van Koningsveld, H., Bassi, G. C., Eds.; Delft University Press: Delft, The Netherlands, 1978. Also SDP-PLUS, Version 1.1 (1984), and VAXSDP, Version 2.2 (1985).

Scheme II

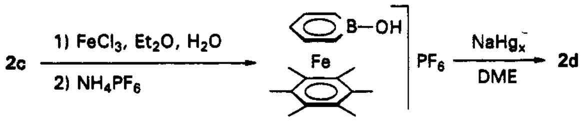


2a (R = Me)
2b (R = Ph)
2c (R = NEt_2)

Scheme III



Scheme IV



2d·PF_6

slow decomplexation of the arene, thereby forming known, robust bis(boratabenzene)iron compounds (Scheme III).[20] In contrast to this behavior, the analogous cyclopentadienyl compound **1a** is more stable and can be sublimed at 70 °C.[21] As shown below, the greater lability of the borabenzene complexes **2** as compared to **1a** corresponds to a markedly lengthened Fe–ring distance in **2a**. When we treated the parent complex $CpFe(C_6H_6)$ (**1b**) with $PhBCl_2$, we obtained bis(1-phenylboratabenzene)iron and **1b**·Cl as the only products. It seems plausible at this instance that the expected arene complex $(C_5H_5BPh)Fe(C_6H_6)$ acts as a labile intermediate that rapidly decomposes to form the observed complex $Fe(C_5H_5BPh)_2$.

Air-stable (boratabenzene)(hexamethylbenzene)iron salts **2a,b**·PF_6 are obtained on oxidation of the neutral complexes with $[FeCp_2]PF_6$ in CH_2Cl_2. If $FeCl_3·6H_2O$ in the two phase system Et_2O/H_2O is used as oxidant, the desired products **2a,b** (R = Me, Ph) are contaminated with small amounts of $[CpFe(HMB)]^+$. This observation is not surprising, as cationic boratabenzene complexes generally tend to undergo oxidative ring contraction to the corresponding cationic cyclopentadienyl complexes.[10,22] Under the same conditions the diethylamino derivative **2c** produces the hydroxo cation $[(C_5H_5BOH)Fe(HMB)]^+$ (**2d**$^+$). This in turn can be reduced to the neutral compound **2d** (Scheme IV).

Structure of $(C_5H_5BMe)Fe(HMB)$ (2a) and of $[(C_5H_5BMe)Fe(HMB)]PF_6$ (2a·PF_6). The molecular structure of **2a** is shown in Figure 1; that of **2a**$^+$, in Figure 2. Atomic coordinates and selected bond lengths and angles are listed in Tables II and III for **2a** and in Tables IV and V for **2a**·PF_6. **2a**·PF_6 possesses crystallographic mirror symmetry.

Both complexes **2a** and **2a**$^+$ show typical sandwich structures with two nearly coplanar ring ligands. Metal–ring distances are collected in Table VI. The conformation of the two rings is approximately staggered in **2a** while in **2a**·PF_6 it is precisely staggered and fixed by crystallographic symmetry.

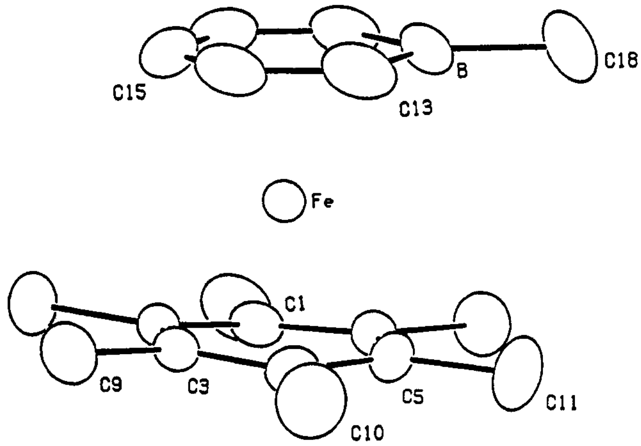


Figure 1. Molecular structure of $(C_5H_5BMe)Fe(HMB)$ (**2a**) (ORTEP plot at the 30% probability level).

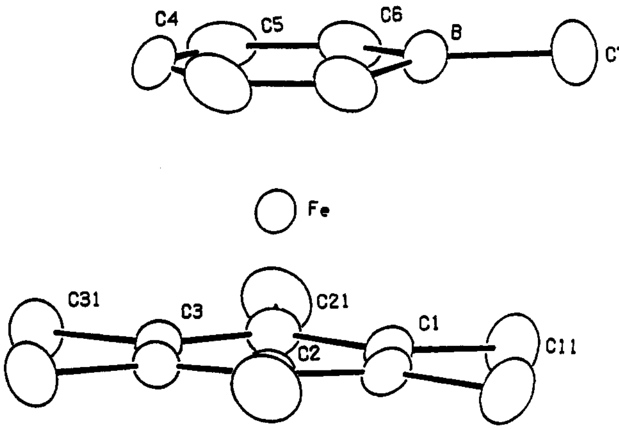


Figure 2. Molecular structure of the cation $[(C_5H_5BMe)Fe(HMB)]^+$ of **2a**·PF_6 (ORTEP plot at the 30% probability level).

Table II. Atomic Coordinates of Non-Hydrogen Atoms for 2a

atom	*x*	*y*	*z*	B_{eq}[a]
Fe	0.01843(3)	0.16279(3)	0.23757(2)	2.979(6)
C1	–0.1116(2)	0.2650(2)	0.1489(2)	3.71(5)
C2	–0.0303(2)	0.3467(2)	0.1945(2)	3.41(5)
C3	–0.0136(2)	0.3435(2)	0.2986(2)	3.43(5)
C4	–0.0788(2)	0.2577(3)	0.3555(2)	4.13(5)
C5	–0.1504(2)	0.1672(2)	0.3092(2)	4.21(6)
C6	–0.1674(2)	0.1707(2)	0.2049(2)	3.94(5)
C7	–0.1355(3)	0.2744(3)	0.0391(2)	6.30(8)
C8	0.0395(3)	0.4407(3)	0.1341(2)	5.63(7)
C9	0.0718(3)	0.4348(3)	0.3464(2)	5.75(7)
C10	–0.0643(4)	0.2575(4)	0.4677(2)	7.5(1)
C11	–0.2143(3)	0.0706(3)	0.3712(3)	7.75(9)
C12	–0.2492(3)	0.0759(3)	0.1554(3)	6.53(8)
C13	0.1194(3)	0.0176(3)	0.3187(2)	6.28(7)
C14	0.1913(2)	0.1253(3)	0.2983(3)	6.24(7)
C15	0.2003(3)	0.1691(3)	0.2028(3)	6.03(8)
C16	0.1470(3)	0.1131(3)	0.1247(3)	6.34(8)
C17	0.0781(3)	0.0103(3)	0.1374(2)	5.65(7)
B	0.0568(3)	–0.0499(3)	0.2344(3)	5.26(8)
C18	–0.0240(4)	–0.1718(3)	0.2489(4)	10.5(2)

[a] The anisotropic thermal parameters are given in the form of their isotropic equivalents, in 10^4 pm^2.

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(21) Astruc, D.; Hamon, J. R.; Althoff, G.; Roman, E.; Batail, P.; Michaud, P.; Mariot, J. P.; Varret, F.; Cozak, D. *J. Am. Chem. Soc.* **1979**, *101*, 5445.
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(23) Hamon, J. R.; Saillard, J. Y.; Le Beuze, A.; McGlinchey, M. J.; Astruc, D. *J. Am. Chem. Soc.* **1982**, *104*, 7549.

Table III. Selected Bond Distances and Bond Angles for 2a

(a) Bond Distances (pm)			
Fe–C1	217.9(1)	C1–C2	140.3(2)
Fe–C2	211.8(1)	C2–C3	142.7(3)
Fe–C3	212.9(2)	C3–C4	140.5(2)
Fe–C4	219.1(2)	C4–C5	140.3(3)
Fe–C5	213.4(2)	C5–C6	142.8(3)
Fe–C6	213.1(2)	C6–C1	141.0(2)
Fe–C13	220.9(2)	C13–C14	143.2(3)
Fe–C14	214.1(2)	C14–C15	138.2(3)
Fe–C15	209.8(2)	C15–C16	135.4(3)
Fe–C16	217.5(2)	C16–C17	135.2(3)
Fe–C17	222.5(2)	B–C13	152.2(3)
Fe–B	231.0(2)	B–C17	148.5(3)
		B–C18	159.8(4)
(b) Bond Angles (deg)			
C13–C14–C15	119.8(2)	C14–C13–B	119.5(2)
C14–C15–C16	123.5(2)	C16–C17–B	123.9(2)
C15–C16–C17	120.5(2)	C13–B–C18	123.5(3)
C13–B–C17	112.7(2)	C17–B–C18	123.8(3)

Table IV. Atomic Coordinates of Non-Hydrogen Atoms for 2a·PF$_6$

atom	x	y	z	B_{eq}[a]
Fe	0.000	0.91592(5)	0.480	3.08(1)
P	–0.500	1.0442(2)	0.2238(2)	4.90(4)
F1	–0.500	1.1441(4)	0.1712(4)	8.9(2)
F2	–0.500	1.0953(7)	0.3026(6)	20.5(6)
F3	–0.500	0.9933(8)	0.1312(6)	15.2(3)
F4	–0.500	0.9428(5)	0.2706(6)	12.0(2)
F5	–0.3392(4)	1.0358(4)	0.2139(4)	14.4(2)
C1	–0.0750(4)	0.8231(3)	0.3808(3)	3.80(7)
C11	–0.1566(7)	0.8421(5)	0.3005(3)	6.2(1)
C2	–0.1507(4)	0.8048(3)	0.4578(3)	3.83(8)
C21	–0.3126(5)	0.8116(4)	0.4590(4)	6.0(1)
C3	–0.0747(5)	0.7805(3)	0.5319(3)	3.65(7)
C31	–0.1579(6)	0.7559(4)	0.6119(3)	6.2(1)
C4	0.000	1.0034(7)	0.5862(5)	11.7(4)
C5	–0.1317(8)	1.0163(4)	0.5431(4)	8.7(1)
C6	–0.1347(6)	1.0426(3)	0.4589(4)	5.5(1)
B	0.000	1.0647(5)	0.4104(4)	3.9(1)
C7	0.000	1.0989(6)	0.3144(5)	6.1(2)

[a] See footnote *a* in Table I.

Table V. Selected Bond Distances and Bond Angles for 2a·PF$_6$

(a) Bond Distances (pm)			
Fe–C1	213.0(3)	C1–C1′	139.9(7)
Fe–C2	208.5(3)	C1–C2	143.3(5)
Fe–C3	212.2(3)	C2–C3	141.3(5)
		C3–C3′	139.4(7)
Fe–C4	205.7(7)	C4–C5	141.7(9)
Fe–C5	208.4(4)	C5–C6	138.2(8)
Fe–C6	214.8(4)	C6–B	150.4(6)
Fe–B	229.1(6)	B–C7	159.2(8)
(b) Bond Angles (deg)			
C1′–C1–C2	119.6(2)	C5–C4–C5′	120.2(6)
C1–C2–C3	120.2(3)	C4–C5–C6	121.1(6)
C2–C3–C3′	120.1(2)	C5–C6–B	121.9(6)
		C6–B–C6′	113.4(5)

Table VI. Metal Ring Distances (pm) in 2a, 2a·PF$_6$, 1a, and [CpFe(C$_6$Et$_6$)]PF$_6$

complex [LM(arene)]$^{0/+}$	M–L	M–arene	ref
(C$_5$H$_5$BMe)Fe(HMB) (**2a**)	166.88(3)	161.77(3)	this work
[(C$_5$H$_5$BMe)Fe(HMB)]$^+$ (**2a$^+$**)	157.97(6)	156.95(6)	this work
CpFe(HMB) (**1a**)	179.1	158.1	9
[CpFe(C$_6$Et$_6$)]$^+$	168.0	155.0	23

The geometry of the (borabenzene)iron fragments (Figure 3) essentially conforms to the previously established pattern.[10] **2a$^+$** is the first 18e sandwich species with a borabenzene ligand to be characterized by crystallography and shows a rather short distance Fe–C$_5$H$_5$B. While the C$_5$ skeleton forms a good plane (largest vertical displacement from the best plane 0.4 pm), the BMe group is bent away from the metal by 6°. Thus only the distance Fe–B of 229.1(6) pm is still somewhat long [cf. Fe–B 231(1) for [Fe(μ-CO)(CO)(C$_5$H$_5$BMe)]$_2$ (Fe–Fe),[24] 228.6(2) for Fe(CO)$_3$(C$_4$H$_4$BPh),[25] and to quote a sandwich species, 215.1(4) pm for CpFeH(Me$_4$C$_4$BPh)].[26] For the 19e species **2a** the borabenzene ring is planar (largest vertical displacement from the best plane 0.9 pm for C14) and no bending away of the BMe group is observed. The distance Fe–C$_5$H$_5$B is increased considerably due to the antibonding character of the excess electron (see Table VI).[27] We note that this effect is not very pronounced for the atoms in the (approximate) mirror plane (ΔFe–B 2 pm for B, ΔFe–C 4 pm for C15) and very marked (ΔFe–C 7–8 pm) for the remaining C atoms.

The distances Fe–HMB in **2a$^+$** and **2a** demonstrate again the labilizing effect of the excess electron. In addition, the arene ligands show considerable deviations from planarity (Figure 4). In **2a** the arene exhibits an inverted boat conformation, with C1 and C4 less tightly bonded than the remaining four C atoms [ΔFe–C (average) 5.7 pm]. In **2a$^+$** the arene shows a boat conformation with atoms C2 and C2′ somewhat closer to the metal than the remaining four C atoms [ΔFe–C (average) 4.1 pm].

The observed distortions of the HMB ligands can readily be understood on the basis of a qualitative MO consideration. In ferrocene-type complexes the main contribution to the bonding is the interaction between the e$_1$ ligand orbitals and e$_1$* metal orbitals.[28,29] In the borabenzene complexes the presence of the boron atom removes the degeneracy. In going from **1a** to **2a** the e$_1$(Cp) set is replaced with the a″(π_2) and the a′(π_3) levels of the borabenzene ligand with the antisymmetric level at lower energy (Figure 5). As a consequence of orbital interaction the e$_1$* set of essentially 3d metal character splits into a′(3d$_{xz}$*) and a″(3d$_{yz}$*) components, the e$_1$(HMB) set splits into a″(π_2) and the a′(π_3) levels of the HMB ligand, and the antisymmetric split level is at a lower energy in each case. Furthermore the bonding interaction between the arene and the Fe(C$_5$H$_5$BMe) fragment in **2a$^+$** is stronger for the a″ component than for the a′ component; this results in the observed shorter distances Fe–C for C2 and C2′ and the observed boat conformation of the arene.

The case of the 19e complex **2a** is closely related to the bonding situation in CpFe(HMB) (**1a**). There the excess electron is mainly in the e$_1$* set[21] and, due to its antibonding character, causes a lengthening of the Fe–ring distances, especially for the Fe–Cp bond. In **2a** the excess electron will mainly occupy the 3d$_{yz}$* split level which is at a lower energy. Hence its labilizing effect acts preferentially on the borabenzene carbon atoms close to the *yz* plane (i.e. C13/C17 and C14/C16), which show the most pronounced lengthening of the Fe–C distances, and on the HMB carbon

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(27) Cf. the distances M–Cp in metallocenes: Haaland, A. *Acc. Chem. Res.* **1979**, *12*, 415.
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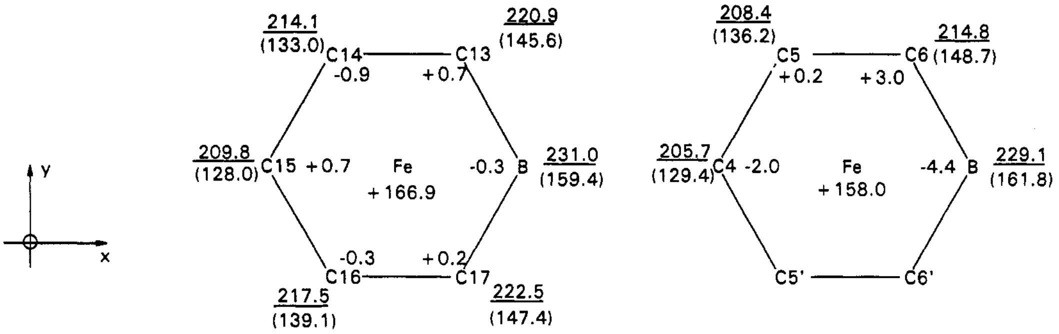
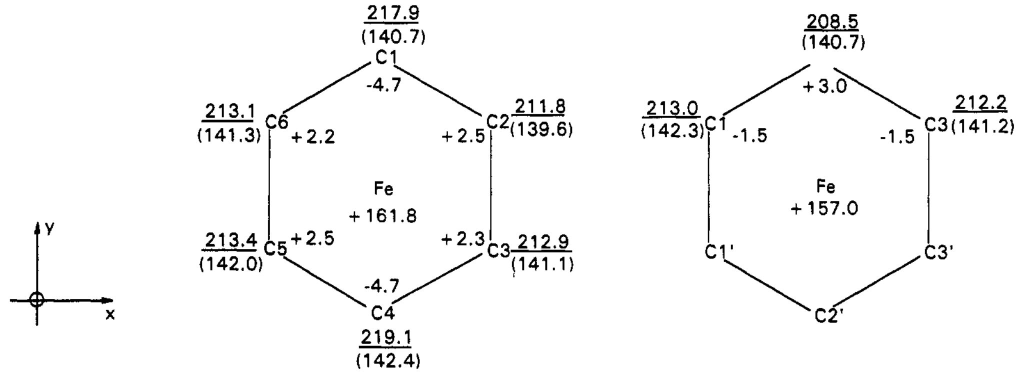
(29) e$_1$ with respect to C_{5v} symmetry for FeCp or to C_{6v} symmetry for Fe(C$_6$H$_6$).



2a 2a$^+$

Figure 3. $Fe(C_5H_5B)$ fragments with vertical displacements (pm) from the best plane through the ring skeleton. Underlined numbers are Fe–C and Fe–B distances (pm). Numbers in parentheses denote the lengths of Fe–C and Fe–B projections (pm) onto the ligand plane.



2a 2a$^+$

Figure 4. Fe(HMB) fragments with vertical displacements (pm) from the best plane through the ring skeleton. Underlined numbers are Fe–C distances (pm). Numbers in parentheses denote the lengths of Fe–C projections (pm) onto the ligand plane.

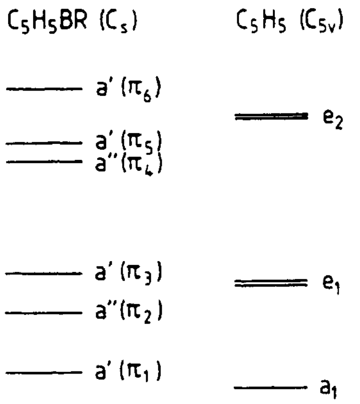


Figure 5. Qualitative energy level diagram for Cp and borabenzene (C_5H_5BR).

atoms in the *yz* plane (i.e. on C1 and C4), thereby enforcing the observed static distortion of the arene ring.

NMR Spectra. The diamagnetic cations show ^1H, ^{11}B, and ^{13}C NMR spectra which fit established patterns.[10] In the ^1H NMR spectra a complex ABB′CC′ type spectrum appears for the boratabenzene ligand,[10] and the $\delta(^{11}B)$ chemical shift values are in the usual range for sandwich type complexes with metal–boron bonding.[10,30]

The paramagnetic complexes **2a–d** give at least partial ^1H NMR spectra (see Experimental Section). All complexes **2a–d** show an intense resonance at about $\delta = -3$, which can be assigned to the coordinated HMB ligand; in **1a** this signal is found at $\delta = -6.8$. For the borabenzene ring of **2a,b** only two signals with intensities 2:1 could be found. For the heterosubstituted species **2c,d** however, no signals for the borabenzene ring could be detected and the HMB signal is significantly broadened. The explanation for this behavior can be found in different proton and electron relaxation times. The paramagnetic complexes give EPR signals only at low temperatures (see below). This behavior indicates rapid electron relaxation. As a consequence proton relaxation remains relatively slow,[31] allowing the observation of ^1H NMR spectra. For **2c,d** the more broadened HMB signal and the failure to find borabenzene ring protons indicate more rapid proton relaxation in comparison to **2a,b**.

EPR Studies. EPR spectra for the complexes **2a–d** could be observed at very low temperatures in frozen toluene, demonstrating a rhombic *g*-tensor (Figure 6, Table VII). Only for **2c,d** could isotropic spectra be observed which were recorded in liquid toluene at low temperature. These observations indicate very rapid electron spin relaxation for **2a,b** and somewhat slower electron relaxation for **2c,d**. A comparison with the cyclopentadienyl analogues **1a** and $CpFe(C_6Et_6)$ is illuminating.[9a] (Arene)(cyclopentadienyl)iron complexes should have an orbitally degenerate ground state in axial symmetry, with the excess electron in the e_1* orbital set of predominant metal character ($3d_{xy}$, $3d_{yz}$), and hence undergo a Jahn–Teller

(30) (a) Nöth, H.; Wrackmeyer, B. In *NMR Basic Principles and Progress*: Diehl, P., Fluck, E., Kosfeld, R., Eds.; Springer Verlag: Berlin, 1978; Vol. 14. (b) Wrackmeyer, B. *Annu. Rep. NMR Spectrosc.* **1988**, *20*, 61.

(31) Rettig, M. F. In *NMR of Paramagnetic Molecules, Principles and Applications*; La Mar, G. N., Horrocks, W. D., Jr., Holm, R. H., Eds.; Academic Press: New York, 1973; p 218 ff.

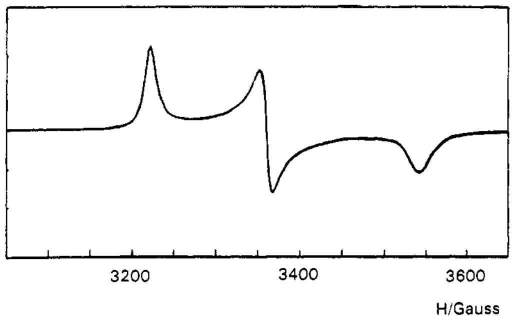


Figure 6. EPR spectrum of **2b** (≈10^{-4} M) in frozen toluene at 104 K.

Table VII. EPR Data for 2a–d and CpFe(HMB) (1a)

	matrix/T (K)	g_1	g_2	g_3
1a[9a]	DME/77	1.864	2.000	2.063
2a	toluene/104	1.896	1.999	2.083
2b	toluene/105	1.898	1.999	2.085
2c	toluene/104	1.913	2.002	2.084
2d	toluene/117	1.909	2.001	2.084
2c	toluene/200		g_e = 2.004	
2d	toluene/200		g_e = 2.000	

distortion.[32] Indeed, **1a** and CpFe(C_6Et_6) possess a rhombic (not an axial) g-tensor, the g values very much depend on the matrix, and the electron spin relaxation is very fast due to the near degeneracy of the system.[9a,33] In **2a–d** the orbital degeneracy is removed because of the intrinsically lower symmetry of the borabenzene ring. Going from an axially symmetric system to a complex **2** may be considered as a perturbation which will be less pronounced for **2a,b** and stronger for **2c,d**. Accordingly, the electron spin relaxation is still fast for complexes **2**, for **2a,b** more so than for **2c,d**. So all aspects of the EPR spectra are consistent with the notion that the complexes **2** are d^7 systems, very closely related to **1a**, with the excess electron having predominantly 3d metal character.

Cyclic Voltammetry. One of the very characteristic reactions of 19e sandwich species is their oxidation to the corresponding 18e cations. In some cases, as, *e.g.*, $CoCp_2$,[34] they can also be reduced to give 20e sandwich anions. Electrochemical parameters for the reduction of the 18e cations **2a–d**$^+$ are collected in Table VIII. A representative example of a cyclic voltammogram is shown in Figure 7. All cations show two reduction peaks corresponding to a +/0 and at 0/− transition. The first one is reversible, as evidenced by its peak current ratio close to 1. The second wave can only be measured in rigorously purified dimethoxyethane. For **2a,b** the corresponding second electron transfer (cf. Figure 7) is chemically not fully reversible, as indicated by a peak current ratio <1 (*e.g.* for **2b** i_p^a/i_p^c = 0.87 at a scan rate of 100 mV/s and 0.96 at 200 mV/s). The peak current separation is not significantly larger than in the first reduction step. This observation militates against a major structural reorganization during electron transfer and the anions 2^- so formed are most likely 20e sandwhich species. For the complexes **2c,d** with heteroatom substituents the reduction is irreversible. But even in these cases, the second wave is of equal height to the first one.

Table VIII. Electrochemical Parameters for the Reduction of 2a–d⁺ (DME, 0.1 M TBAH, vs SCE, 20 °C, ν = 100 mV s⁻¹)

Reduction +/0			
	$E_{1/2}$(V)	i_p^a/i_p^c	$E_{1/2}$(**1a**) − $E_{1/2}$(**2**)^a
2a·PF_6	−1.043	0.95	547
2b·PF_6	−1.014	0.97	566
2c·PF_6	−1.199	0.97	391
2d·PF_6	−1.145	0.96	435

Reduction 0/−				
	E_p^a(V)	E_p^c(V)	$E_{1/2}$(V)	i_p^a/i_p^c
2a	−2.06	−2.115	−2.088	0.80
2b	−2.045	−2.145	−2.095	0.87
2c		−2.40^b		
2d		−2.10^b		

^{a} Borininato shift; see text. ^{b} Irreversible.

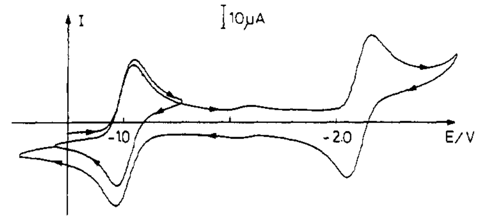
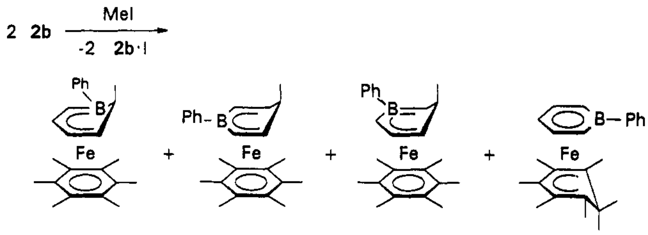


Figure 7. Cyclic voltammogram of **2b**·PF_6 measured at room temperature in DME (0.1 M TBAH, vs SCE, v = 100 MV s^{-1}).

Scheme V



3a (62%) 4a (7%) 5 (<1%) 6a (31%)

The data show that complexes of type **2**$^+$ are more easily reduced than those of type **1**$^+$. This observation can be quantified as anodic shift Δ = $E_{1/2}$ (**1a**) − $E_{1/2}$ (**2**) or the "borininato shift"[35] and amounts to ca. 500 mV in the present case. The reduction potential depends on the substituent R attached to the boron. For R = NEt_2 (**2c**) and OH (**2d**) the potentials are shifted cathodically in comparison to the methyl and phenyl compounds **2a,b**$^+$. The heterosubstituents of **2c,d** give rise to a π-interaction with the boron center and hence reduce the electron withdrawing character of the borabenzene ring. The same effect operates in the series of bis(borole)nickel complexes $Ni(C_4H_4BR)_2$.[36]

Reaction of (C_5H_5BPh)Fe(HMB) (2b) with Iodomethane. The 19e complexes **2a–d** are slightly stronger reductants than cobaltocene ($E_{1/2}$ = −0.95 V).[34] Therefore they were expected to react with organic halides in the same manner as cobaltocene or **1a**. We pesent one example for this reaction. When the phenyl derivative **2b** was treated with iodomethane in hexane at 50 °C, 0.5 equiv of the cation **2b**$^+$ and four isomeric neutral methylation products **3a–6a** were obtained (Scheme V, with isomer distribution). In the main products **3a** and **6a** methyl addition had occurred to the α-position of the borabenzene

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(33) (a) Rajasekharan, M. V.; Giezynski, S.; Ammeter, J. H.; Oswald, N.; Michaud, P.; Hamon, J. R.; Astruc, D. *J. Am. Chem. Soc.* **1982**, *104*, 2400. (b) Michaud, D.; Astruc, D.; Ammeter, J. H. *J. Am. Chem. Soc.* **1982**, *104*, 3755. (c) Ammeter, J. H. *J. Magn. Reson.* **1978**, *30*, 299.
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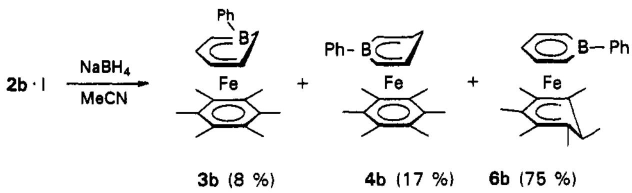
Scheme VI



ring and to the HMB ring. The isomers **3a**, **4a**, and **6a** could be separated by column chromatography on Al_2O_3 while the trace isomer **5a** could only be characterized by ^{1}H NMR. The methylation products are orange-red solids which, with the exception of **6a**, are rather air-sensitive.

The constitution of the methylation products **3a–6a** was determined on the basis of their ^{1}H and ^{13}C NMR data and with reference to related complexes of Co and Rh.[22] The isomers **3a** and **4a** possess bora-2,4-cyclohexadiene and bora-2,5-cyclohexadiene ligands, respectively, which already appeared in our earlier work.[11,22,37] Isomer **5a** with a bora-3-cyclohexene-2,6-diyl ligand is without precedent.

Hydride Addition to [(C_5H_5BPh)Fe(HMB)]$^+$ (2b$^+$). An alternative route to complexes with boracyclohexadiene ligands is the nucleophilic addition[38] of hydride to cationic boratabenzene complexes.[22] Treatment of **2b**$^+$ with $NaBH_4$ in acetonitrile gives three isomeric hydride addition products **3b**, **4b**, and **6b** in near quantitative total yield (Scheme VI, with isomer distribution). In the main product **6b** hydride addition had occurred at the HMB ring. The isomers could readily be separated by column chromatography on Al_2O_3; an isomer corresponding to **5a** was not found. All these complexes are air-sensitive (**6b** < **4b** < **3b**) orange-red solids.

The constitution of the new complexes **3b**, **4b**, and **6b** was deduced from their ^{1}H and ^{13}C NMR spectra. In their IR spectra they show a strong ν(CH) absorption at low frequencies (<2800 cm^{-1}); this band is diagnostic for the presence of an *exo*-C–H bond in ligands with a single sp^3 ring member (as, *e.g.*, cyclohexadienyl, but not cyclopentenyl).[39] This band is not present in the corresponding complexes **3a–6a** where the *exo* position is occupied by the methyl group.

Concluding Remarks

In this paper we have added a new class of 19e sandwich complexes to the small family of stable electron excess complexes. The (boratabenzene)(HMB) iron complexes **2a–d** are closely related to the well-known (arene)(cyclopentadienyl)iron complexes 1, as evidenced by their structure and their EPR spectra. The excess electron resides mainly in the antiboding a″(3d_{xz}) orbital of predominant metal character.

We have also demonstrated that the chemistry of the new boratabenzene complexes follows closely the paradigmatic patterns that have been established for cobaltocene and later for CpFe(HMB) (**1a**). Complex **1a** reacts with iodomethane to give two regioisomers, as expected (Scheme I). We had hoped that the reaction of **1a** with dihaloboranes would also give products of both regiochemistries. The preferred regiochemistry, with attack at the cyclopentadienyl ring, afforded the products of type 2. The alternative attack at the arene ligand should lead to complexes CpFe(Me_6C_6BR) with borepin ligands. However, we have not been able to trace compounds of this type.[40]

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Supplementary Material Available: Tables of atomic coordinates, thermal parameters, and bond distances and angles (11 pages). Ordering information is given on any current masthead page.

OM9300888

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