Electron-Poor 2,3-Dihydro-1,3-diborolyl Complexes of Iron and Ruthenium: Synthesis, Reactivity, and Crystal and Electronic Structures of an Iron Sandwich Complex

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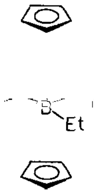
Dedicated to Professor Herbert Schumann on the occasion of his 60th birthday

Abstract: The addition product of sodium hydride and the 2,3-dihydro-1,3-diborole $(CiPr)_2(BEt)_2CHMe$ (**3c**) reacted with $[\{(C_5Me_5)FeCl\}_x]$ to produce the green sandwich complex $[(C_5Me_5)Fe\{\eta^5\text{-}(CiPr)_2(BEt)_2CMe\}]$ (**2c**), which formally contains 16 valence electrons (VE). Complex **2c** has unexpected structural properties in the solid state: the 1,3-diborolyl ring is extremely folded (41°), and the Fe–C2 distance is short (1.90 Å). Analogously, violet Ru complexes **4a,c,d** were obtained from **3a,c**, NaH or *t*BuLi, and $[\{(C_5Me_5)RuCl\}_4]$. With the less bulky heterocycles **3b,e** the new 30 VE triple-decker complexes $[(C_5Me_5)Ru\{\mu,\eta^5\text{-}(CR^1)_2(BR^2)_2CMe\}RuH(C_5Me_5)]$ (**5b,e**) were formed, which contain a Ru–H bond. Cyclic voltammetric studies revealed the existence of stable anions $\mathbf{2c}^-$ and $\mathbf{4d}^-$ formed by reversible one-electron reduction at −1.26 and −1.40 V, respectively (vs. SCE). The red-brown anions were further characterized by ESR spectroscopy following stepwise reduction of the neutral species with potassium in THF. Addition of CO to **4a** and **4d** led to formation of the monocarbonyl complexes $[(C_5Me_5)Ru(CO)\{\eta^5\text{-}(CR^1)_2(BR^2)_2CMe\}]$ (**6a,d**), and **6d** was characterized by X-ray structure analysis. The heterocycle in **6d** is less folded (19°) than in **2c**. Its CO ligand causes a 28.5° tilt of the cyclic ligands. Reaction of CO with **2c** yielded a red product of unknown structure. The electronic structure of **2** was studied by EH-MO theory, which revealed a unique bonding in the sandwich. The σ electron density of the B–C bonds participates in the bonding to the iron atom; this demonstrates that the number of bonding electrons is the same as in ferrocene. Thus, the complexes **2** actually have 18 VE.

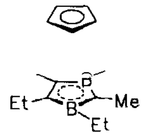
Keywords
boron compounds · diboroles · Group 8 complexes · sandwich complexes · semi-empirical calculations

There are few examples of organometallic complexes of the iron triad known that have less than 18 valence electrons.[1–3] Cocondensation of iron vapor and cyclooctadiene (cod) leads to the 16 VE species $[Fe(cod)_2]$, which is stable only below −40 °C.[1a] The 17 VE complexes $[(C_5H_5)Fe(cod)]$[2] and the more recently reported $[(C_5Me_5)Fe(C_2H_4)_2]$ and $[(C_5Me_5)Fe(cod)]$[3] are valuable sources of the $Fe(C_5H_5)$ and the $Fe(C_5Me_5)$ moieties, respectively. Low-coordinate iron complexes such as $[\{(\eta^1\text{-}2,4,6\text{-}Me_3C_6H_2)Fe(\mu,\eta^1\text{-}2,4,6\text{-}Me_3C_6H_2)\}_2]$[4a] and $[Fe(\eta^1\text{-}2,4,6\text{-}tBu_3C_6H_2)_2]$ are stabilized by the bulky substituents; in the latter complex the coordination number is two at the iron atom, which has a high-spin configuration.[4b] The 16 VE complexes $[\{(C_5Me_5)Ru(XR)\}_2]$ (X = O,S) have coordinatively unsaturated Ru atoms.[5–7] The sulfur compounds are active catalysts for the addition of thiols to polar alkynes.[8] Recently, 16 VE cationic complexes of $Ru(C_5Me_5)$ with a 2,2′-bipyridyl[9a] or a 1,4-diazabutadiene[9b] ligand have been prepared.

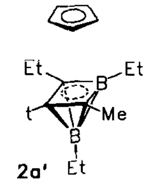
In the synthesis of the paramagnetic 29 VE triple-decker sandwich complex **1a**, we proposed that the diamagnetic double-decker sandwich **2a** is the intermediate, which was obtained in low yield and identified by its mass and ¹H NMR data.[10] However, the structure of the complex **2a** with formally 16 VE could not be determined. In the related 16 VE complex (η^3-cyclooctenyl)(η^5-1,3,4,5-tetraethyl-2-methyl-1,3-diborolyl)pla-



1a



2a



2a′

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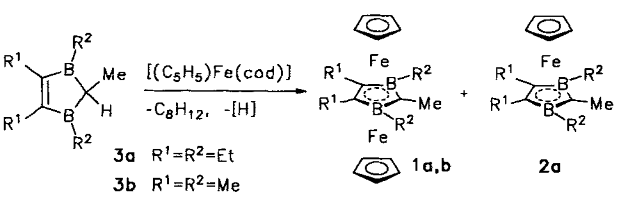
tinum, the heterocycle exhibits a considerable fold angle along the B–B vector (28°).[11] We speculated that **2a** could either contain a similarly folded heterocycle or even adopt the *closo* structure **2a'**. According to the cluster electron count[12] **2a'** has the required 14 framework electrons. The *nido* C_3B_2 ligand would supply five electrons yielding an 18 VE configuration.

Recently we unexpectedly obtained the iron sandwich $[(\eta^5\text{-}C_5Me_5)Fe(\eta^5\text{-}\{CiPr)_2(BEt)_2CMe\}]$ (**2c**); its formation and structure has been published in a preliminary communication.[13] In this paper we describe the synthesis and reactivity of electron-poor complexes of iron (**2**) and ruthenium (**4**), as well as their crystal and electronic structures.

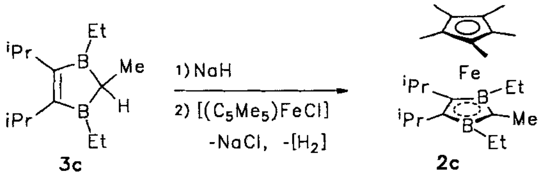
Results and Discussion

Synthesis and Reactivity: The reaction of the 2,3-dihydro-1,3-diborole derivative **3a** with $[(C_5H_5)Fe(cod)]$[2] in benzene at 60 °C led to the formation of a dark solution, from which the green diamagnetic sandwich **2a** (7%) and the blue paramagnetic triple-decker **1a** (36%) were separated by chromatography (Scheme 1). The mononuclear complex **2a** was found to be extremely sensitive to oxygen, and it partly decomposed on silica during chromatography to form **1a**. Because of the low yield, the reactivity of **2a** could not be studied further. The synthesis of **2a** was difficult to reproduce owing to the ease of formation of **1a**. Oily **2a** was only identified by its ¹H NMR and its mass spectrum, which also contained the molecular ion of **1a**. The reaction of 1,2,3,4,5-pentamethyl-1,3-diborole (**3b**) and $[(C_5H_5)Fe(cod)]$ at 0 °C yielded neither **2b** nor **1b**; however, the blue paramagnetic triple-decker **1b** was obtained in low yield by heating a solution of **3b** and $[\{(C_5H_5)Fe(cod)\}_2Zn]$[2] in decalin.[14]



Scheme 1.

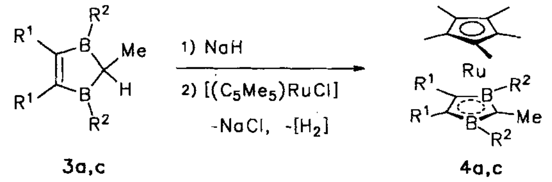
Rather surprisingly we observed the formation of the bulky diborole **3c** as a by-product in the hydroboration reaction of 1,3-diethyl-2-methyl-4,5-diisopropylidene-1,3-diborolane with $(HBEt_2)_2$ to give the corresponding 2,3,5-tricarbahexaborane.[13, 15] The mixture of the *nido* C_3B_3 carborane and **3c** was treated with NaH, and the resulting anionic species were treated with $[\{(C_5Me_5)FeCl\}_x]$ prepared in situ (Scheme 2).[16] A mixture of the green sandwich **2c** and the green ferracarborane [**2c**·BEt] was obtained by chromatography. Complex **2c** was separated by crystallization in 42% yield and identified by ¹H NMR, ¹¹B NMR, and mass spectrometry.



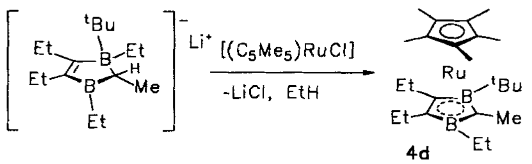
Scheme 2.

Although the ¹¹B NMR shift of **2c** ($\delta = 19$) lies up-field of those of related 1,3-diborolecobalt complexes ($\delta \approx 28$),[10, 17] a *closo* structure analogous to **2a'** can be ruled out since two high-field signals would then be expected. Surprisingly, the ¹¹B NMR shift of **2c** is similar to that of the 30 VE triple-decker complexes $[(\eta^5\text{-}C_5H_5)Fe\{\mu,\eta^5\text{-}3(-H)\}Co(\eta^5\text{-}C_5H_5)]$[17, 18] with pentacoordinated boron atoms. On the other hand, the ¹¹B NMR shift is very different to that of the (η^3-cyclooctenyl)(η^5-1,3,4,5-tetraethyl-2-methyl-1,3-diborolyl)platinum complex[11] ($\delta = 50$) with a folded 1,3-diborolyl ring (28° along the B–B vector). The X-ray structure analysis (see below) reveals that the heterocycle {**3c**(−H)} in **2c** is even more folded (41°) than in the platinum complex. The electronic reasons for this are discussed below.

In an analogous synthesis to that of **2c**, the products formed by reaction of **3a,c** and NaH were treated with $[\{(C_5Me_5)RuCl\}_4]$ to give the ruthenium complexes **4a,c** in moderate yields (Scheme 3). The violet, extremely air-sensitive liquids could be isolated by chromatography on alumina at low temperature. When **3a** was treated with *t*BuLi and then with $[\{(C_5Me_5)RuCl\}_4]$,[19] **4d** was obtained, in which the ethyl group at one boron atom is replaced by a *tert*-butyl group (Scheme 4). The ¹¹B NMR spectra of **4a,c,d** show one signal for each compound in the region of $\delta = 19-22$, which is also found for **2c**. This indicates that **2** and **4** have similar structures.

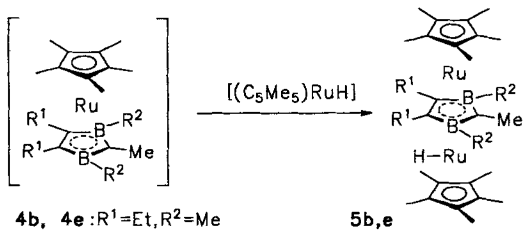


Scheme 3.



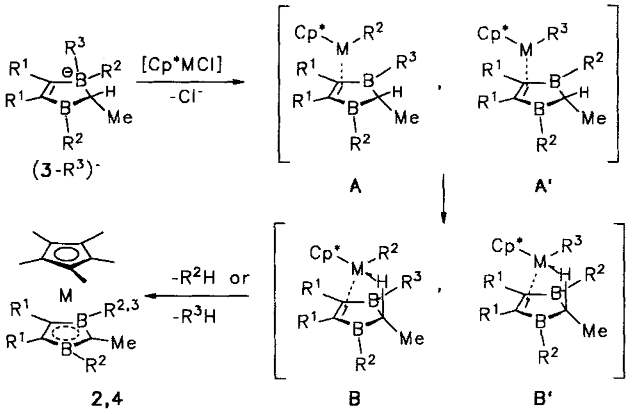
Scheme 4.

The reaction of the 1,2,3,4,5-pentamethyl- and the 1,2,3-trimethyl-4,5-diethyl-1,3-diborole derivatives **3b,e** with NaH and $[\{(C_5Me_5)RuCl\}_4]$ did not lead to formation of **4b,e**, but of the 30 VE triple-decker complexes **5b,e** with a hydrogen atom at one of the ruthenium atoms. Its formation may occur through stacking of the sandwich intermediates **4b,e** by attack of a $[(C_5Me_5)RuH]$ molecule (Scheme 5).



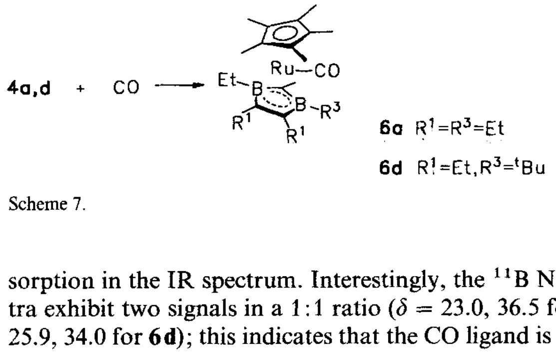
Scheme 5.

For the reaction of **3** with a nucleophile and $[\{(C_5Me_5)MCl\}_x]$ (M = Ru, $x = 4$;[19] M = Fe, x unknown[16]) we propose the following mechanism: **3** reacts with one equivalent of either NaH or *t*BuLi to form the 1,3-diborolate $(\mathbf{3}\text{-}R^3)^-$ (R^3 = H, *t*Bu; Scheme 6). It is likely that the metal of $[\{(C_5Me_5)MCl\}_x]$ interacts with the double bond of diborolate. This step is related to that reported for the interaction between $[\{(C_5Me_4Et)RuCl\}_4]$ and ethylene.[5] Transfer of alkyl anion or hydride may then take place from the 1,3-diborolate to the metal to yield **A**/**A′**, followed by an agostic bonding of the C–H groups with the metal to give the transient 18 VE complex **B**/**B′**. The final step is the elimination of H–R^2 (R^2 = Et) or H–R^3 (R^3 = H) with formation of the complexes **2** or **4**, respectively.



Scheme 6.

The reaction of violet **4a,d** with carbon monoxide led to the formation of the yellow monocarbonyl complexes **6a,d** (Scheme 7) as indicated by the mass spectra and a strong absorption in the IR spectrum. Interestingly, the ^{11}B NMR spectra exhibit two signals in a 1:1 ratio (δ = 23.0, 36.5 for **6a** and 25.9, 34.0 for **6d**); this indicates that the CO ligand is asymmetrically bound with respect to the heterocycle. In the X-ray structure analysis of **6d** we observe a relatively short B1–C17 distance (2.41 Å), which may indicate a weak interaction. The coordination of CO results in the formation of "classic" 18 VE complexes, which is accompanied by a decrease in the folding of the heterocycle. Attempts to obtain a monocarbonyl complex by reacting green **2c** with CO failed.[20] A red product of unknown structure was formed, presumably by insertion of CO into the heterocycle.



Scheme 7.

Crystal Structures: The structure of **2c** differs from other known 1,3-diborolyl sandwich structures[21] since the diborolyl ring is severely folded along the vector B1–B1′ by an angle of 41.3° with the carbon atoms closer to the iron atom (Fig. 1). The coordination of C2 deviates from that of an sp^2 carbon in a π complex, tending towards an sp^3 geometry with a small B1-C2-B1′ angle of 89.5° and a very short Fe1–C2 distance of (1.899(6) Å) (Table 1). In the 18 VE complex $[(C_5H_5)Ni\{\mathbf{3a}(-H)\}]$ the Ni–C2 bond length is 0.19 Å longer and Ni–B 0.07 Å shorter. The folding in the nickel compounds is only 10–12°.[21]

Complex **2c** can be compared with the 16 VE complex[11] $[(C_8H_{13})Pt\{\mathbf{3a}(-H)\}]$, which also shows a similar coordination of the diborolyl ring $\{\mathbf{3a}(-H)\}$ to the metal. The C2–Pt bond is shorter (2.09 Å) than the Pt–C4/5 bonds (2.30–2.33 Å), and the ring is folded along the B–B vector (28°). The folding is less than in **2c**; this reflects the greater tendency of Pt to form 16 VE complexes.

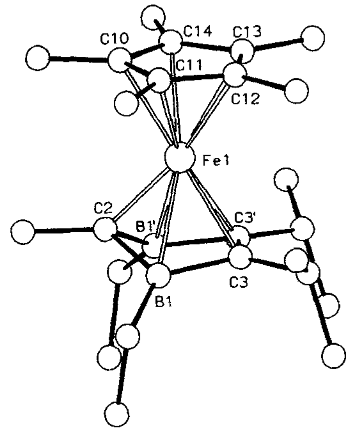


Fig. 1. The crystal structure of **2c**. Selected interatomic distances and angles are listed in Table 1.

Table 1. Some selected distances [Å] and angles [°] in **2c**.

Fe1–C10–14	2.054–2.118(5–7)	B1–C2	1.547(6)
Fe1–C2	1.899(6)	B1–C3	1.568(5)
Fe1–C3	2.116(3)	C3–C3′	1.412(6)
Fe1–B1	2.248(4)	C2–C6	1.516(9)
B1-C2-B1′	89.7(3)	C3′-C3-B1	104.2(6)
C3-B1-C2	110.1(3)	C6-C2-B1	126.1(3)

In **6d** the CO group tilts the two rings by an angle of 28.5° (between the best planes through all the atoms of the diborolyl and C_5Me_5 rings) (Fig. 2, Table 2). A relatively short distance between B1 and C17 (2.41 Å) and a deviation from linearity for the Ru–C≡O group (167°) are observed. A similar geometry is found for a bis(thiadiborole)ironcarbonyl complex, where the CO group is situated between two boron atoms

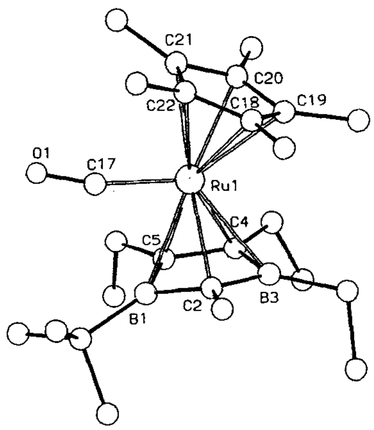


Fig. 2. The crystal structure of **6d**. Selected interatomic distances and angles are listed in Table 2.

Table 2. Some selected distances [Å] and angles [°] in **6d**.

Ru–C(C_5Me_5)	2.203–2.277(2)	Ru–C17	1.869(2)
Ru–C2	2.265(2)	B1–C2	1.522(3)
Ru–C4	2.293(2)	B3–C2	1.538(3)
Ru–C5	2.318(2)	B1–C5	1.556(3)
Ru–B1	2.456(2)	B3–C4	1.590(3)
Ru–B3	2.424(2)	C4–C5	1.418(3)
B1-C2-B3	107.1(2)	C4-C5-B1	109.6(2)
C4-B3-C2	104.4(2)	C5-C4-B3	109.1(2)
C5-B1-C2	106.1(2)		

belonging to separate rings, with B–CO distances of 2.41 and 2.42 Å, but with an almost linear Fe–C≡O group.[22] It is not obvious whether these distances can be interpreted in terms of weak bonding interactions. The diborolyl ring in **6d** is much less folded than in **2c**; the planes through B1-C2-B3 and B1-B3-C4-C5 form an angle of 19.0°. The distances and angles in the diborolyl ring do not deviate from those expected of diborolyl complexes, while the distances to the Ru atom show larger differences; the distances from Ru to B are significantly larger than those to C.

Electronic Structure and Bonding: We have performed extended Hückel (EH) calculations[23] for the model compounds **2** and **2'**, in which the substituents on both ligands were replaced by hydrogen atoms. In the case of **2'** we assumed a planar structure for the diborolyl ligand. The geometrical parameters of **2** were taken from the X-ray data of **2c**. Those used for the calculations on **2'** were deduced from the structures of related complexes having planar diborolyl ligands[17, 18] and from those of **2c**. The parameters used in the EH calculations as well as the most important geometrical parameters of **2** and **2'** are collected in Table 3. The EH calculations on **2** and **2'** were carried out under the C_s symmetry constraint.

Table 3. Extended Hückel parameters.

	Orb.	H_{ii} (eV)	ξ_1	ξ_2 [a]	c_1 [a]	c_2 [a]	Ref.
H	1s	−13.60	1.30				[23a]
B	2s	−15.20	1.30				[23b]
	2p	−8.50	1.30				
C	2s	−21.40	1.625				[23a]
	2p	−11.40	1.625				
Fe	4s	−9.10	1.90				[23c]
	4p	−5.32	1.90				
	3d	−12.60	5.35	2.00	0.5505	0.6260	

[a] Contraction coefficients in the double ξ expansion. Chosen distances [Å]: **2**: Fe–C(C_5H_5) 2.083; Fe–B1 2.248; Fe–C2 1.901; Fe–C3 2.115; B1–C2 1.542; B1–C3 1.568; C3–C4 1.406; **2'**: Fe–C(C_5H_5) 2.083; Fe–B1 2.125; Fe–C2 2.070; Fe–C3 2.111; B1–C2 1.580; B1–C3 1.570; C3–C4 1.412.

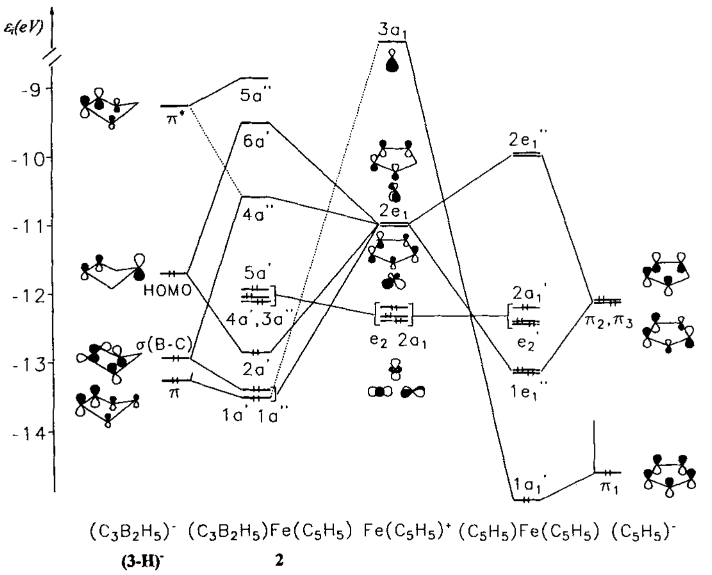


Fig. 3. Qualitative diagram showing the interactions between the valence MOs of molecular fragments to give the frontier MOs of **2** and ferrocene.

To elucidate the electronic structure of **2**, we will start by discussing briefly the electronic structure of the ferrocene molecule. Figure 3 (right) shows a simplified diagram of the interactions between the Cp^- ion (Cp = C_5H_5) and the $(FeCp)^+$ fragment to give [$FeCp_2$]. The frontier orbitals of both molecular units are well-known.[24] For the sake of clarity three doubly occupied valence orbitals of the $(FeCp)^+$ fragment describing the bonding between iron and the Cp ligand have been omitted from Figure 3. These levels do not change in character with the coordination of the second ligand and are not important for the discussion of the bonding between $(FeCp)^+$ and the second ligand.

The π_1, π_2, and π_3 MOs of Cp^- interact with the LUMO ($2e_1$) and the empty $3a_1$ MO of $(FeCp)^+$ to produce the bonding $1a_1'$ and $1e_1''$ levels of [$FeCp_2$]. The "t_{2g}"-like iron orbitals of $(FeCp)^+$ ($2a_1$ and e_2 MOs) are not involved in stabilizing interactions with the Cp^- ligand. In [$FeCp_2$] six electrons are stabilized in the $1a_1'$ and $1e_1''$ levels. These electrons together with six electrons from the "t_{2g}^6"-like iron levels and six Cp^- donor electrons involved in the metal–ligand bonding in $(FeCp)^+$ form the well-known stable 18 VE configuration of [$FeCp_2$]. Let us now move to Figure 3 (left) describing the orbital interactions in the complex **2**. An examination of the shapes of the frontier MOs shows that the LUMO and HOMO of the diborolyl anion correlate with the π_3 and π_2 levels of Cp^- and that the π double bond is similar to the π_1 level (Fig. 3). Thus in **2** the HOMO and the π level of the diborolyl anion are stabilized in the same manner as the π_2 and π_1 levels of Cp^- in [$FeCp_2$].

In contrast to the π_3 level of Cp^-, the LUMO of the diborolyl anion cannot participate in stabilizing donor interactions with $(FeCp)^+$, and **2** thus lacks two stabilizing electrons with respect to [$FeCp_2$]. However, the diborolyl ligand has a high-lying occupied σ (B–C) orbital, which is able to interact with the d_{xz}-like component of the LUMO of the $(FeCp)^+$ unit. In Figure 4 we show the calculated shapes of the $1a''$ MO of **2** and of the corresponding $1e_{1a}''$ component of [$FeCp_2$]. It can be seen that the character of the stabilizing interaction is essentially the same in both complexes.

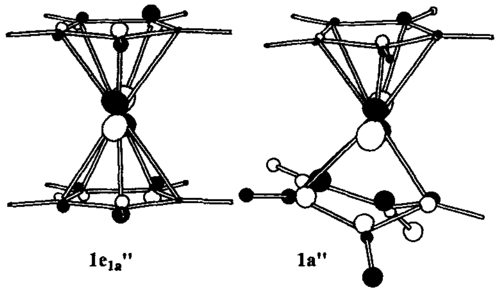


Fig. 4. MOs of the $1e_{1a}''$ level of of ferrocene (left) and the $1a''$ level of **2** (right).

Thus, in the interactions with $(FeCp)^+$, the high-lying σ (B–C) orbital of the diborolyl ligand plays the same role as the π_3 level of Cp^-, and six electrons are stabilized in the $1a'$, $1a''$, and $2a'$ MOs of **2**, as in [$FeCp_2$]. Although the formal electron count yields a total of 16 valence electrons for **2**, the number of stabilized electrons is the same as in ferrocene, and consequently the electronic structure of **2** shows the typical features of 18 VE complexes.

In order to further explore the electronic structure of **2** and to examine the influence of the geometrical structure of the diborolyl ligand on the stabilizing interactions, we performed the EH calculations on **2'** with the planar diborolyl ligand

$\{3'(-\mathrm{H})\}$. The calculations predict that the perturbation introduced by the folding of the diborolyl ligand destabilizes the free ligand by 12.2 kcal mol^{-1}. The reason is the destabilization of the σ (B–C) level in **3**, due to the tilting of the p components away from the B–C axis. Thus in **2** the σ (B–C) level of the diborolyl ligand is closer in energy and overlaps better with the LUMO of $(\mathrm{FeCp})^+$, and the stabilizing interactions are consequently stronger than in **2'**. In Figure 5 we compare the stabilization energy of the 1*a'*, 1*a''*, and 2*a'* MOs of **2** and **2'** with respect to the donor levels of the free ligands. The stabilizing interactions for all three levels are much stronger in **2** than in **2'**. The large stabilization of the 2*a'* MO of **2** is not surprising if one takes into account the short Fe–C2 distance (1.90 Å) in **2c**.

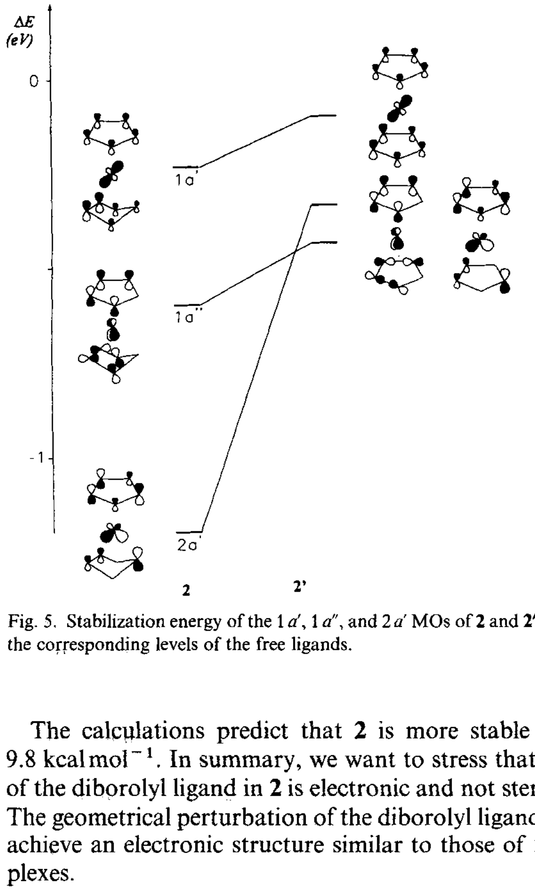


Fig. 5. Stabilization energy of the 1*a'*, 1*a''*, and 2*a'* MOs of **2** and **2'** with respect to the corresponding levels of the free ligands.

The calculations predict that **2** is more stable than **2'** by 9.8 kcal mol^{-1}. In summary, we want to stress that the folding of the diborolyl ligand in **2** is electronic and not steric in origin. The geometrical perturbation of the diborolyl ligand allows **2** to achieve an electronic structure similar to those of 18 VE complexes.

Electrochemistry: To evaluate the electrochemical behavior of the iron and ruthenium diborolyl complexes, cyclic voltammograms of **2c** and **4d** were recorded. The measurements were performed on 0.1 M $n\mathrm{Bu_4NPF_6}$/dimethoxyethane (DME) solutions with glassy carbon (GC) working electrodes.[16] The one-electron nature of the observed reversible redox processes was established by comparison with the one-electron standard $[\mathrm{Cp_2Fe}^{+/0}]$. Differences between cathodic and anodic peak potentials (ΔE_p) were measured and compared to the results for $[\mathrm{Cp_2Fe}]$ (70–100 mV for reversible waves at scan rates of 0.05–0.5 V s^{-1}). In DME we investigated a voltage range between +2.0 and −3.1 V vs. SCE (+2.6 to −2.2 V in $\mathrm{CH_2Cl_2}$) at a ground current sensitivity of 5 μA cm^{-1}.

The cyclic voltammograms of **2c** (Fig. 6A) and **4d** (Fig. 6B) both show reversible one-electron reductions to the monoanion (at −1.26 and −1.40 V, respectively). For **2c** this process is followed by an irreversible reduction at −2.57 V ($v = 0.1$ V s^{-1}). Both potentials are located well within the range of the reducing capacity of potassium. The behavior of **2c** with respect to oxidation is irreversible; the first one-electron oxidation at +0.18 V is followed by multi-electron processes at around +0.5 V (+0.72 V for **4d**). A very similar redox behavior is observed for **4d**, with a reversible formation of the monoanion at −1.40 V and a second irreversible reduction at −1.96 V. In accordance with the extended Hückel calculations, **2c** is easier to reduce than ferrocene. The LUMO of **2** is energetically lower than that of $[\mathrm{Cp_2Fe}]$.

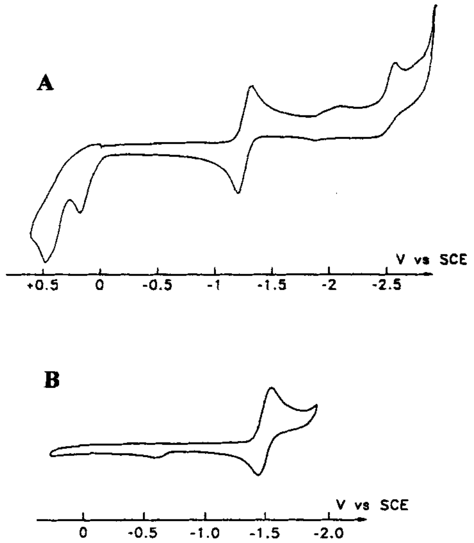


Fig. 6. Cyclic voltammograms of **2c** (A) and **4d** (B) in 0.1 M $\mathrm{Bu_4NPF_6}$/dimethoxyethane (DME, 298 K) recorded at glassy carbon (GC) electrodes vs. saturated calomel electrode (SCE), $v = 100$ V s^{-1}.

Ruthenocenes have been the subject of various electrochemical studies.[25] Compared to the cathodic waves of sandwich complexes of the type $[\mathrm{Cp_2Fe}]$, those of $[(\mathrm{arene})_2\mathrm{Fe}]$ and mixed-ligand complexes [CpFe(arene)] are either found at extremely low potentials[26] or, in most cases, are not observed.[25] The Ru analogues often exhibit a significantly lower stability.[27] The significant anodic shift of the reduction potentials of **2c** and **4d** provides further evidence for the fact that many mixed-ligand carborane complexes can stabilize transition metals in high oxidation states.[16, 28] In sandwich complexes with carbocyclic ligands[29, 30] only permethylated $\mathrm{C_5}$ and $\mathrm{C_6}$ rings lead to considerable stabilization of the 19 VE complexes.[29] Even for ruthenocene derivatives with an electron-withdrawing ligand as in $[(\mathrm{C_5Me_5})\mathrm{Ru}(\mathrm{C_5F_5})]$, cathodic waves are not observed within the accessible range of $\mathrm{CH_2Cl_2}$.[27]

ESR Spectroscopy: The radical anions $\mathbf{2c}^-$ and $\mathbf{4a}^-$ were generated by reduction of the neutral species in a sealed tube at a potassium mirror in THF. The stepwise reactions, during which a color change occurred from green (purple for **4a**) to red-brown, led to the formation of stable radicals, which were characterized by the ESR spectra (Fig. 7). The data are listed in Table 4. For both radical anions we found a rhombic *g* tensor showing no hyperfine splitting. Rhombic distortion of $\mathrm{Fe^I}$ in sandwich complexes gives rise to three *g* values close to 2 without hyperfine coupling due to spin–lattice relaxation.[29–31] The mean *g* value $\langle g \rangle$ for the Ru compound is higher; this confirms that spin–orbit coupling increases on moving to heavier elements. $\mathrm{Fe^{III}}$[32] and $\mathrm{M^{III}}$ complexes[33] are mainly characterized as being orbitally degenerate exhibiting *g* tensors of axial symmetry in their ESR spectra.[32, 33]

Our spectra bear resemblance to those observed for 19 VE $\mathrm{d^7}$ $\mathrm{Fe^I}$ sandwich compounds such as $[(\mathrm{C_5Me_5})\mathrm{Fe}(\mathrm{C_6Me_6})]$.[29]

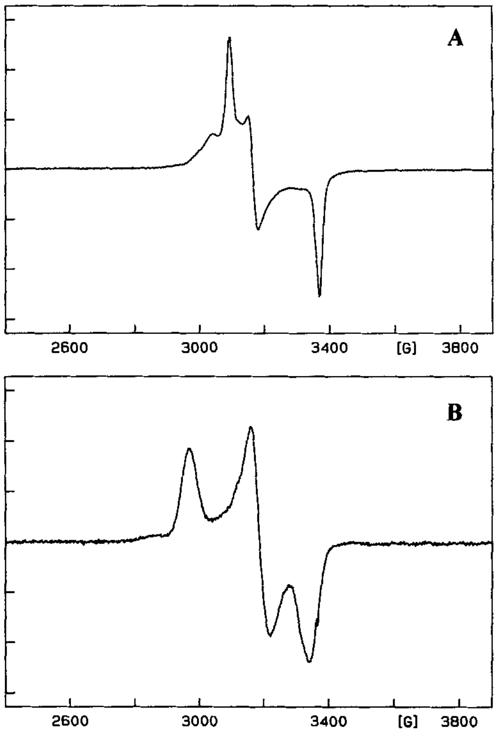


Fig. 7. X-band ESR spectra of $2c^-$ (A) and $4d^-$ (B) in THF glass at 110 K.

Table 4. X-band ESR data for $2c^-$, $4d^-$, and related complexes.

	g_1	g_2	g_3	T (K)	Solvent	Ref.
$2c^-$	2.182	2.132	2.002	110	THF	this work
$4d^-$	2.271	2.110	2.020	115	THF	this work
$[(C_5Me_5)Fe(C_6Me_6)]$	2.062	2.002	1.912	4	DME	[30]
$[(C_6H_5Me)Fe(C_2B_2S)]^-$	2.086	2.000	1.985	110	THF	[34a]
$[(C_6H_5Me)Fe(C_4B_2)]^-$	2.072	1.994	1.939	110	THF	[34b]

ESR data of structurally related Cp, arene, and mixed-ligand carboranyl Fe complexes are listed in Table 4. Based on calculations combined with ESR [31] and Mössbauer spectra,[29] one has to conclude that these sandwich complexes have a very similar electronic ground-state structure.

Conclusions

The addition of H^- or tBu$^-$ to certain 2,3-dihydro-1,3-diborole derivatives followed by reaction with $[\{(C_5Me_5)MCl\}_x]$ (M = Fe, Ru) leads to the new sandwich complexes **2c** and **4a,c,d**. These highly sensitive compounds are susceptible to reduction and oxidation. The steric requirements of the substituents in the diborolyl ring for the stabilization of **2** and **4** have been studied. If smaller groups are used, especially at C4 and C5, the sandwich complexes **2** and **4** are difficult to obtain because stacking reactions yield the triple-decker complexes **1** and **5**, respectively. This observation explains why the search for electron-poor sandwich complexes of the iron triad has been unsuccessful in the past.

Complexes **2** and **4** show interesting structural and bonding patterns in the 2,3-dihydro-1,3-diborolyl ring, including a strong folding of the ring and a very short Fe–C2 distance in **2c**. The EH MO calculations indicate that the folding is due to interaction of σ electron density of the boron–carbon bonds with the metal center.

Addition of CO to **4d** yields complex **6d** containing a bent CO ligand.

Experimental Section

General Techniques: Experiments were carried out under nitrogen or argon, which had been dried and purified before use. Solvents were dried by conventional methods and saturated with nitrogen. NMR spectra were recorded on Bruker AC-200 (^{1}H: 200.13 MHz, ^{13}C: 50.32 MHz, ^{11}B: 64.21 MHz) with C_6D_6 as solvent. Chemical shifts are relative to that of TMS and $BF_3 \cdot OEt_2$. The mass spectra were recorded on a Varian MATCH7 and a Finnigan MAT8230. Elemental analyses were performed in the Institut für Organische Chemie, Universität Heidelberg. Alumina used for chromatography was dried and deactivated by addition of 5% water. Voltammetric experiments were conducted as described elsewhere [16]. Potentials are given in volts vs. an SCE reference electrode. X-band ESR spectra were obtained on a Bruker ESP300E spectrometer equipped with a liquid N_2 variable-temperature unit. Calibration of field frequency relied on a microwave frequency counter and a Bruker Hall probe; the offset was checked with DPPH. The procedure for the preparation of THF solutions of radical anions by stepwise reduction using a potassium mirror has been reported [16].

(η^5-Cyclopentadienyl)(η^5-1,3,4,5-tetraethyl-2-methyl-2,3-dihydro-1,3-diborol-2-yl)iron (2a): A solution of [CpFe(cod)] (870 mg, 4.58 mmol) and **3a** (1.04 g, 4.54 mmol) in benzene (20 mL) was stirred at room temperature for 0.5 h. It was then heated to 60 °C for 2 h and then cooled to room temperature. The solvent was removed in vacuo, followed by some unreacted **3a**. The residue was dissolved in petroleum ether and chromatographed on SiO_2. The green fraction (200 mg after removal of solvent) contained the oily compound **2a**. This was followed by a blue fraction containing the triple-decker **1a**. Yield: 355 mg (36%) of **1a** after twofold recrystallization from petroleum ether. The crude **2a** was again chromatographed (SiO_2, petroleum ether) to remove some more **1a**. The product was then distilled at 60 °C/10^{-3} Torr to give **2a** (100 mg, 7%), which was still slightly contaminated with **1a**. ^{1}H NMR ([D$_8$]THF): $\delta = 0.53$ (br m, 10H, BCH_2CH_3)), 1.58 (t, 6H, CCH_2CH_3), 2.7 (s, 3H, CCH_3), 4.13 and 4.29 (m, 4H, CCH_2CH_3), 4.37 (s, 5H, Cp); m/z (%): 310 (84) [M^+], 281 (29) [$M^+ - C_2H_5$], 252 (48) [$M^+ - 2C_2H_5$]; **1a:** m.p. 210 °C; MS (EI): m/z (%): 431 (100) [M^+].

(η^5-Pentamethylcyclopentadienyl)(η^5-1,3-diethyl-4,5-diisopropyl-2-methyl-2,3-dihydro-1,3-diborol-2-yl)iron (2c): The diborole **3c** (0.218 g, 1.0 mmol) was added to a suspension of NaH (0.065 g, 2.7 mmol) in THF (10 mL) at −20 °C and then stirred at room temperature for 2 h. The solution was filtered (to remove excess NaH) directly into a solution of $[\{(C_5Me_5)FeCl\}_x]$ at −75 °C, prepared from C_5Me_5H (0.136 g, 1.0 mmol), MeLi solution, and $FeCl_2 \cdot 2THF$ [36] (0.27 g, 1.0 mmol). The reaction mixture was stirred for 20 h at room temperature, and the solvent (Et_2O/THF) was then removed under vacuum. The green residue was dissolved in a mixture of 0.5 mL toluene and 0.5 mL hexane and passed at −10 °C through a chromatography column packed with Al_2O_3 with hexane as eluant. The green fraction obtained contained **2c** and a small amount of $[(C_5Me_5)_2Fe]$. Complex **2c** crystallized at −30 °C after concentration of the solution. Yield: 0.17 g (42%); m.p. 216–218 °C (decomp.); ^{1}H NMR: $\delta = 0.42$ (br m, 4H, BCH_2CH_3), 0.53 (br t, 6H, ^3J(H,H) = 6 Hz, BCH_2CH_3), 1.26 (d, 6H, ^3J(H,H) = 6.5 Hz, $CCH(CH_3)_2$), 1.45 (s, 15H, C_5CH_3), 1.91 (d, 6H, ^3J(H,H) = 6.5 Hz, $CCH(CH_3)_2$), 2.77 (s, 3H, CCH_3), 4.21 (sept, 2H, ^3J(H,H) = 6.5 Hz, $CCH(CH_3)_2$); ^{11}B NMR: $\delta = 19.4$; ^{13}C NMR: $\delta = 5.7$ (BCH_2CH_3, br), 10.0 (BCH_2CH_3), 10.5 ($C_5(CH_3)_5$), 20.2 (CCH_3), 23.7, 24.3 ($CCH(CH_3)_2$), 33.6 ($CCH(CH_3)_2$), 80.3 ($C_5(CH_3)_5$), 132.5 ($CCH(CH_3)_2$, C2 (CCH_3) not observed; MS (EI): m/z (%): 408 (100) [M^+], 393 (4) [$M^+ - CH_3$], 379 (5) [$M^+ - C_2H_5$], 365 (10) [$M^+ - C_3H_7$]; $C_{24}H_{42}B_2Fe$ (408.06): calcd C 70.64, H 10.38, found C 70.04, H 10.37.

(η^5-Pentamethylcyclopentadienyl)(η^5-1,3,4,5-tetraethyl-2-methyl-2,3-dihydro-1,3-diborolyl)ruthenium (4a): same procedure as described for **2c**. From **3a** (0.19 g, 1.0 mmol), NaH (0.06 g, 2.5 mmol), and $[\{(C_5Me_5)RuCl\}_4]$ (0.272 g, 0.25 mmol) **4a** was obtained as a dark violet oil. Yield 139 mg (32%); b.p. 52 °C/10^{-3} Torr, ^{1}H NMR: $\delta = 0.6–0.9$ (m, 10H, BCH_2CH_3), 1.33 (t, 6H, ^3J(H,H) = 8.0 Hz, CH_2CH_3), 1.49 (s, 15H, $C_5(CH_3)_5$), 2.45 (m, 2H, CCH_2CH_3), 2.79 (s, 3H, CCH_3), 3.10 (m, 2H, CCH_2CH_3); ^{13}C NMR: $\delta = 6.9$ (BCH_2CH_3, br), 10.0 (BCH_2CH_3), 11.1 ($C_5(CH_3)_5$), 14.5 (CCH_2CH_3), 21.0 (CCH_3), 25.1 (CCH_2CH_3), 84.9 ($C_5(CH_3)_5$), 122.8 (CCH_2CH_3), C2 (CCH_3) not observed; ^{11}B NMR: $\delta = 20.2$; MS (EI): m/z (%): 426 (70) [M^+], 397 (100) [$M^+ - C_2H_5$], 368 (30) [$M^+ - 2C_2H_5$].

(η^5-Pentamethylcyclopentadienyl)(η^5-1,3-diethyl-4,5-diisopropyl-2-methyl-2,3-dihydro-1,3-diborolyl)ruthenium (4c): Same procedure as described for **4a**. From **3c** (0.22 g, 1.0 mmol), NaH (0.06 g, 2.5 mmol), and $[\{(C_5Me_5)RuCl\}_4]$ (0.272 g, 0.25 mmol) **4c** was obtained as a dark violet oil. Yield: 237 mg (52%); b.p. 60 °C/10^{-3} Torr, ^{1}H NMR: $\delta = 0.6–1.05$ (m, 10H, BCH_2CH_3), 1.10 (d, 6H, ^3J(H,H) =

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6.0 Hz, $\mathrm{CH(C}\mathit{H}_3)_2$), 1.48 (s, 15 H, $\mathrm{C_5(C}\mathit{H}_3)_5$), 1.58 (d, 6 H, ^3J(H,H) = 6.0 Hz, $\mathrm{CH(C}\mathit{H}_3)_2$), 2.75 (s, 3 H, $\mathrm{CC}\mathit{H}_3$), 3.45 (sept, 2 H, ^3J(H,H) = 6.0 Hz, $\mathrm{CH(CH_3)_2}$; ^{11}B NMR: δ = 17.7; ^{13}C NMR: δ = 6.5 ($\mathrm{B}\mathit{C}\mathrm{H_2CH_3}$, br), 10.0 ($\mathrm{BCH_2}\mathit{C}\mathrm{H_3}$), 11.0 ($\mathrm{C_5(}\mathit{C}\mathrm{H_3)_5}$), 20.8 ($\mathrm{C}\mathit{C}\mathrm{H_3}$), 23.4 and 24.0 ($\mathrm{CH(}\mathit{C}\mathrm{H_3)_2}$), 32.0 ($\mathit{CH}\mathrm{(CH_3)_2}$), 84.8 ($\mathit{C}_5\mathrm{(CH_3)_5}$), C2, C4, and C5 not observed; MS (EI): *m*/*z* (%): 453 (100) [M^+], 438 (20) [$M^+ - \mathrm{CH_3}$], 424 (22) [$M^+ - \mathrm{C_2H_5}$], 411 (38) [$M^+ - \mathrm{C_3H_7}$]. HRMS calcd for $\mathrm{C_{24}H_{42}B_2Ru}$: 454.2516, found: 454.2568.

(η^5-Pentamethylcyclopentadienyl)(η^5-1,4,5-triethyl-3-*tert*-butyl-2-methyl-2,3-dihydro-1,3-diborolyl)ruthenium (4d): *t*BuLi (1.5 M, 0.66 mL, 1 mmol) was added dropwise to a solution **3a** (120 mg) in THF (20 mL) at −50 °C. The reaction mixture was allowed to warm to room temperature and then transferred through a canula into a flask containing $[\{(\mathrm{C_5Me_5})\mathrm{RuCl}\}_4]$ (272 mg, 0.25 mmol). After the reaction mixture had been stirred for 12 h, the solvents were removed under vacuum. The violet residue was dissolved in 2 mL hexane and passed at −10 °C through a chromatography column packed with $\mathrm{Al_2O_3}$ with hexane as eluant. **4c** was isolated as a dark violet oil. Yield: 170 mg (37%); b.p. 85 °C/10^{-3} Torr; ^{1}H NMR: δ = 0.7–0.9 (m, 5 H, $\mathrm{BC}\mathit{H}_2\mathrm{C}\mathit{H}_3$), 0.92 (s, 9 H, $\mathrm{C(C}\mathit{H}_3)_3$, 1.34 (t, 6 H, ^3J(H,H) = 6.5 Hz, $\mathrm{CCH_2C}\mathit{H}_3$), 1.48 (s, 15 H, $\mathrm{C_5(C}\mathit{H}_3)_5$), 2.50 (m, 2 H, $\mathrm{CC}\mathit{H}_2\mathrm{CH_3}$), 2.9 (s, 3 H, $\mathrm{CC}\mathit{H}_3$), 3.15 (m, 2 H, $\mathrm{C}\mathit{H}_2\mathrm{CH_3}$); ^{13}C NMR: δ = 7.0 ($\mathrm{B}\mathit{C}\mathrm{H_2CH_3}$ and $\mathrm{B}\mathit{C}\mathrm{(CH_3)_3}$, br), 9.7 ($\mathrm{BCH_2}\mathit{C}\mathrm{H_3}$), 10.9 ($\mathrm{C_5(}\mathit{C}\mathrm{H_3)_5}$), 14.3 ($\mathrm{CCH_2}\mathit{C}\mathrm{H_3}$), 15.4 ($\mathrm{CCH_2}\mathit{C}\mathrm{H_3}$), 24.1 ($\mathrm{C}\mathit{C}\mathrm{H_3}$), 25.2 ($\mathrm{C}\mathit{C}\mathrm{H_2CH_3}$), 26.6 ($\mathrm{C}\mathit{C}\mathrm{H_2CH_3}$), 29.9 ($\mathrm{BC(}\mathit{C}\mathrm{H_3)_3}$), 84.9 ($\mathit{C}_5\mathrm{CH_3)_5}$), C2, C4, and C5 not observed; ^{11}B NMR: δ = 22.0; MS (EI): *m*/*z* (%): 454 (52) [M^+], 425 (30) [$M^+ - \mathrm{C_2H_5}$], 397 (71) [$M^+ - \mathrm{C_4H_9}$], 56 (100) [$\mathrm{C_4H_8^+}$]. HRMS calcd for $\mathrm{C_{24}H_{42}B_2Ru}$: 454.2516, found: 454.2489.

(η^5-Pentamethylcyclopentadienyl)(η^5-1,3,4,5-tetraethyl-2-methyl-2,3-dihydro-1,3-diborolyl)rutheniumcarbonyl (6a): Complex **4a** (0.15 g, 0.46 mmol) was dissolved in hexane (20 mL), and CO gas was bubbled through the solution for 3 min at a flow rate of 10 mL min^{-1}. The color changed from violet to yellow-orange. After distillation, **6a** was obtained as yellow oil. Yield: 0.083 g (52%), b.p. 81 °C/10^{-3} Torr, ^{1}H NMR: δ = 0.9 (m, 4 H, $\mathrm{BC}\mathit{H}_2\mathrm{CH_3}$), 1.09 (t, 6 H, ^3J(H,H) = 7.5 Hz, $\mathrm{BCH_2C}\mathit{H}_3$), 1.18 (t, 3 H, ^3J(H,H) = 7.5 Hz, $\mathrm{CCH_2C}\mathit{H}_3$), 1.37 (t, 3 H, ^3J(H,H) = 7.5 Hz, $\mathrm{CCH_2C}\mathit{H}_3$), 1.41 (s, 15 H, $\mathrm{C_5(C}\mathit{H}_3)_5$), 1.46 (s, 3 H, $\mathrm{CC}\mathit{H}_3$), 1.85 and 2.15 (m, 4 H, $\mathrm{CC}\mathit{H}_2\mathrm{CH_3}$); ^{13}C NMR: δ = 7.0 ($\mathrm{B}\mathit{C}\mathrm{H_2CH_3}$, br), 10.1 ($\mathrm{C_5(}\mathit{C}\mathrm{H_3)_5}$), 12.8 ($\mathrm{BCH_2}\mathit{C}\mathrm{H_3}$), 12.9 ($\mathrm{BCH_2}\mathit{C}\mathrm{H_3}$), 16.4 ($\mathrm{C}\mathit{C}\mathrm{H_3}$), 17.4 ($\mathrm{CCH_2}\mathit{C}\mathrm{H_3}$), 17.9 ($\mathrm{CCH_2}\mathit{C}\mathrm{H_3}$), 22.2 ($\mathrm{C}\mathit{C}\mathrm{H_2CH_3}$), 23.1 ($\mathrm{C}\mathit{C}\mathrm{H_2CH_3}$), 95.3 ($\mathit{C}_5\mathrm{(CH_3)_5}$), 215.2 ($\mathrm{Ru}\mathit{C}\mathrm{O}$), C2, C4, and C5 not observed; ^{11}B NMR: δ = 23.0 (1 B) and 36.5 (1 B); MS (EI): *m*/*z* (%): 454 (25) [M^+], 426 (60) [$M^+ - \mathrm{CO}$], 396 (100) [$M^+ - 2\,\mathrm{C_2H_5}$], FT-IR: $\tilde{\nu}_{\mathrm{co}}$ = 1933 cm^{-1}. HRMS calcd for $\mathrm{C_{22}H_{38}B_2Ru}$: 426.2203, found 426.2220.

(η^5-Pentamethylcyclopentadienyl)(η^5-1,4,5-triethyl-3-*tert*-butyl-2-methyl-2,3-dihydro-1,3-diborol-2-yl)rutheniumcarbonyl (6d): Same procedure as for **6a**; **4d** (0.135 g, 0.30 mmol) in 10 mL hexane, 10 mL min^{-1} CO for 3 min. After removal of a part of the solvent in vacuum **6d** crystallized at −20 °C. Yield 0.053 g (37%) after recrystallization, m.p. = 143 °C, subl. 81 °C/10^{-3} Torr. ^{1}H NMR: δ = 1.07 (m, 2 H, $\mathrm{BC}\mathit{H}_2\mathrm{CH_3}$), 1.08 (t, 3 H, ^3J(H,H) = 7.1 Hz, $\mathrm{BCH_2C}\mathit{H}_3$), 1.23 (t, 3 H, ^3J(H,H) = 7.6 Hz, $\mathrm{CCH_2C}\mathit{H}_3$), 1.33 (t, 3 H, ^3J(H,H) = 7.6 Hz, $\mathrm{CCH_2C}\mathit{H}_3$), 1.39 (s, 15 H, $\mathrm{C_5(C}\mathit{H}_3)_5$), 1.47 (s, 3 H, $\mathrm{CC}\mathit{H}_3$), 1.55 (s, 9 H, $\mathrm{BC(C}\mathit{H}_3)_3$), 1.73 and 2.38 (m, 4 H, $\mathrm{CC}\mathit{H}_2\mathrm{CH_3}$); ^{13}C NMR: δ = 6.9 ($\mathrm{B}\mathit{C}\mathrm{H_2CH_3}$ and $\mathrm{B}\mathit{C}\mathrm{(CH_3)_3}$, br), 9.0 ($\mathrm{C_5(}\mathit{C}\mathrm{H_3)_5}$), 11.5 ($\mathrm{BCH_2}\mathit{C}\mathrm{H_3}$), 16.9 ($\mathrm{CCH_2}\mathit{C}\mathrm{H_3}$ and $\mathrm{C}\mathit{C}\mathrm{H_3}$), 17.5 ($\mathrm{CCH_2}\mathit{C}\mathrm{H_3}$), 20.4 ($\mathrm{C}\mathit{C}\mathrm{H_2CH_3}$), 23.6 ($\mathrm{C}\mathit{C}\mathrm{H_2CH_3}$), 30.0 ($\mathrm{BC(}\mathit{C}\mathrm{H_3)_3}$), 94.1 ($\mathit{C}_5\mathrm{(CH_3)_5}$), 215.0 ($\mathit{C}\mathrm{O}$), C2, C4, and C5 not observed; ^{11}B NMR: δ = 25.9 (1 B), 34.0 (1 B), MS (EI): *m*/*z* (%): 482 (20) [M^+], 454 (42) [$M^+ - \mathrm{CO}$], 425 (40) [$M^+ - t\mathrm{Bu}$], 396 (100) [$M^+ - (t\mathrm{Bu} + \mathrm{Et})$]; FT-IR: $\tilde{\nu}_{\mathrm{co}}$ = 1927 cm^{-1}, for $\mathrm{C_{25}H_{42}B_2ORu}$ (481.30) calcd C 62.39 H 8.80; found C 61.90 H 9.03.

(μ,η^5-Pentamethyl-2,3-dihydro-1,3-diborolyl)(η^5-pentamethylcyclopentadienylruthenium)(η^5-pentamethylcyclopentadienylrutheniumhydride) (5b): Same procedure as described for **4a**; **3b** (0.134 g, 1.0 mmol), $[\{(\mathrm{C_5Me_5})\mathrm{RuCl}\}_4]$ (0.544 g, 0.5 mmol), NaH (0.06 g, 2.5 mmol), THF (20 mL). **5b** was obtained as red crystals. Yield: 0.11 g (19.2%), m.p. > 250 °C; ^{1}H NMR: δ = −8.27 (s, $\mathrm{Ru}\mathit{H}$), 1.21 (s, 6 H, $\mathrm{BC}\mathit{H}_3$), 1.42 (s, 15 H, $\mathrm{C_5(C}\mathit{H}_3)_5$), 1.70 (s, 15 H, $\mathrm{C_5(C}\mathit{H}_3)_5$), 1.78 (s, 3 H, $\mathrm{B_2CC}\mathit{H}_3$), 1.97 (s, 6 H, $\mathrm{CC}\mathit{H}_3$): ^{13}C NMR: δ = 9.9 ($\mathrm{C_5(}\mathit{C}\mathrm{H_3)_5}$), 10.7 ($\mathrm{C_5(}\mathit{C}\mathrm{H_3)_5}$), 14.7 ($\mathrm{C}\mathit{C}\mathrm{H_3}$), 16.9 ($\mathrm{B_2C}\mathit{C}\mathrm{H_3}$), 78.8 ($\mathit{C}_5\mathrm{(CH_3)_5}$), 90.2 ($\mathit{C}_5\mathrm{(CH_3)_5}$), C2, C4, C5, $\mathrm{B}\mathit{C}\mathrm{H_3}$ not observed; ^{11}B NMR: δ = 2.8; MS (EI): *m*/*z* (%): 607 (51) [M^+], 592 (100) [$M^+ - \mathrm{CH_3}\cdot$]; $\mathrm{C_{28}H_{46}B_2Ru_2}$ (606.43): calcd C 55.45, H 7.65, found C 54.99, H 7.65.

(μ,η^5-1,2,3-Trimethyl-4,5-diethyl-2,3-dihydro-1,3-diborolyl)(η^5-pentamethylcyclopentadienylruthenium)(η^5-pentamethylcyclopentadienylrutheniumhydride) (5e): Same procedure as described for **5b**. From **3e** (0.162 g, 1 mmol), and $[\{(\mathrm{C_5Me_5})\mathrm{RuCl}\}_4]$ (0.544 g, 0.5 mmol) in THF (20 mL) **5b** was obtained as red crystals. Yield: 0.230 g (36%), m.p. > 250 °C; ^{1}H NMR: δ = −8.43 (s, 1 H, $\mathrm{Ru}\mathit{H}$), 1.26 (s, 6 H, $\mathrm{BC}\mathit{H}_3$), 1.44 (s, 15 H, $\mathrm{C_5C(C}\mathit{H}_3)_5$), 1.47 (t, 6 H, ^3J(H,H) = 8.2 Hz, $\mathrm{CCH_2C}\mathit{H}_3$), 1.72 (s, 15 H, $\mathrm{C_5(C}\mathit{H}_3)_5$), 1.76 (s, 3 H, $\mathrm{B_2CC}\mathit{H}_3$), 2.12 and 2.34 (m, 4 H, $\mathrm{CC}\mathit{H}_2\mathrm{CH_3}$); ^{13}C NMR: δ = 9.9 ($\mathrm{C_5(}\mathit{C}\mathrm{H_3)_5}$), 10.3 ($\mathrm{CCH_2}\mathit{C}\mathrm{H_3}$), 10.8 ($\mathrm{C_5(}\mathit{C}\mathrm{H_3)_5}$), 16.9 ($\mathrm{B_2C}\mathit{C}\mathrm{H_3}$), 26.5 ($\mathrm{C}\mathit{C}\mathrm{H_2CH_3}$), 78.5 ($\mathit{C}_5\mathrm{(CH_3)_5}$), 90.3 ($\mathit{C}_5\mathrm{(CH_3)_5}$), C2, C4, C5, and $\mathrm{BCH_3}$ not observed; ^{11}B NMR: δ = 2.8; MS (EI): *m*/*z* (%): 635 (80) [M^+], 620 (100) [$M^+ - \mathrm{CH_3}$]; $\mathrm{C_{30}H_{50}B_2Ru_2}$ (634.49) calcd C 56.79 H 7.94; found C 56.20 H 8.02.

Crystal Structure Determinations for 2c and 6d [36]: Diffraction data were collected on a Siemens-Stoe AED 2 diffractometer ($\mathrm{Mo}_{K\alpha}$ radiation, graphite monochromator) in the ω-scan mode. Crystal data and details of the measurements are summarized in Table 5. The structures were solved by direct methods (SHELXS 86) and refined by full-matrix least-squares (SHELXL 93) based on F^2 using all reflections. Non-hydrogen atoms were refined anisotropically, hydrogen atoms were added in calculated positions.

Table 5. Crystal and collection parameters for compounds **2c** and **6d.**

Compound	**2c**	**6d**
formula	$\mathrm{C_{24}H_{42}B_2Fe}$	$\mathrm{C_{25}H_{42}B_2ORu}$
M_r	408.0	481.3
F_{000}	888	1016
crystal system	orthorhombic	monoclinic
space group	*Pbnm*	$P2_1/n$
a [Å]	10.752(5)	11.422(6)
b [Å]	14.481(7)	16.065(8)
c [Å]	15.565(8)	13.903(7)
β [°]		95.37(2)
V [Å^3]	2423	2540
Z	4	4
d_c [g cm^{-3}]	1.12	1.26
μ ($\mathrm{Mo}_{K\alpha}$) [mm^{-1}]	0.63	0.63
crystal size [mm]	0.4 × 0.5 × 0.5	0.3 × 0.5 × 0.6
collection T	ambient	−55 °C
$2\theta_{\max}$ [°]	55	50
h,k,l range	13,18,20	±13, +19, +16
reflns collected	3154	5739
unique	2886	4370 [R(int) = 0.018]
absorption correction	empirical	empirical
transmission	(0.72–0.80)	(0.71–0.84)
parameters refined	176	279
$R1$ [on F, $I > 2\sigma(I)$]	0.064	0.022
$wR2$ [on F^2, all reflns]	0.200	0.062

For **2c** there are two possible space groups, $Pbn2_1$ and *Pbnm*. In *Pbnm* the sandwich has a crystallographic mirror plane through Fe 1 and C 2. The $\mathrm{C_5Me_5}$ ring is disordered. The temperature factors of some atoms, especially the methyl carbon atoms of the $\mathrm{C_5Me_5}$ ring and at C 2, become strongly anisotropic. Refinements in $Pbn2_1$ with some restrictions regarding the diborolyl ring yields better R values, but the anisotropic temperature factor for the methyl carbon atoms of the $\mathrm{C_5Me_5}$ ring do not improve. Refinement with two rigid $\mathrm{C_5Me_5}$ rings was only possible with restrictions to the anisotropic temperature factors. The results of the refinements in *Pbnm* and $Pbn2_1$ are in good agreement for the geometry around the Fe atom and the diborolyl ring.

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