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Molecular and electronic structure of (η^5-pentaalkyl-2,3-dihydro-1,3-diborolyl) (η^5-pentamethylcyclopentadienyl)metal complexes, M = Fe, Ru

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Dedicated to Professor Mike Mingos.

Abstract

The X-ray diffraction study of the violet ruthenium sandwich derivative **2b** revealed a folding along the B···B vector of the 1,3-diborolyl heterocycle of 40.7°, which is very similar to that in the green iron complex **1b**. The molecular and electronic structure of the 1,3-diborolyl complexes of iron and ruthenium have been studied by density functional theory (DFT) with the B3LYP functional and extended triple-ζ basis sets. It is shown that the folding of the diborolyl ligand in the title complexes is due to electronic factors. The model complexes with a planar diborolyl ligand **1′** (M = Fe) and **2′** (M = Ru) are by 24.9 and 24.5 kcal/mol less stable than the equilibrium folded structures of **1** and **2**, respectively. The electronic structures of **1** and **2** show similarities to those of the 18 VE species due to the participation of the σ(B–C2) bonds in the stabilizing diborolyl–metal bonding. The electronic spectra of **1** and **2** have been studied with the time-dependent DFT method. The absorptions observed in the visible range in the electronic spectrum of the title complexes are assigned as spin-allowed d–d transition with an admixture of metal to diborolyl (π^*) charge transfer (MLCT).

Keywords: Boron; Heterocycle; Iron; Ruthenium; Complexes; DFT calculation

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1. Introduction

Electron-poor organometallic compounds of the iron triad have interesting electronic structures and reactivities. We have studied the formally 16 VE sandwich **1b** [1a,1b] [(η^5-C_5Me_5)Fe(η^5-($C^iPr)_2(BEt)_2$CMe)] and more recently, its analogous (η^5-pentaalkyl-2,3-dihydro-1,3-diborolyl)(η^5-pentamethylcyclopentadienyl)ruthenium complexes **2** [2]. The unique structural feature of the green iron complex **1b** is its severe folding of the diborolyl ring along the B···B vector (folding angle $\alpha = 41.3°$) as a result of a strong Fe–C2 bond (1.899 Å) and the additional interaction of the high-lying combination of σ(B–C) orbitals with the empty d_{xz} orbital of iron. This bonding pattern allows 5e of the (neutral) folded 1,3-diborolyl ring to interact with the metal, which is markedly different from less folded 1,3-diborolyl ligands functioning as 3e donors. According to spectroscopic data, the violet ruthenium analogs **2** [2] are assumed to have a similar bonding situation, however, the difficulty [3] in obtaining suitable crystals has hampered the determination of a detailed structure. Its reactivity e.g. the formation of classic 18 VE complexes with a decreased folding of the heterocycle has been studied by coordination of the donor molecules :CO and :CN–R at the Ru center which yields yellow complexes **3** with folding angles <20° along the B···B vector of the heterocycles [1b,2a]. Phosphanes and **2** also form donor–acceptor complexes **2** · PH_2R (R = H, Ph), whereas triorganylphosphane adducts **2** · PR_3 (R = Me, Ph) are

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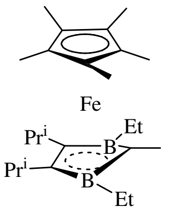
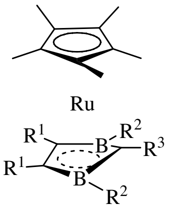
unstable. Terminal alkynes insert into one of the B–C–B bonds to give the novel 18 VE η^7-4-borataborepine complexes **4** in which the (anionic) seven-membered ring functions as 6e ligand [4]. With internal alkynes the formation of boratabenzene complexes occurs, and preliminary results have been communicated. Here we report on the details of the crystal and electronic structures of the violet sandwiches **2** in comparison to those of green **1**.



1b



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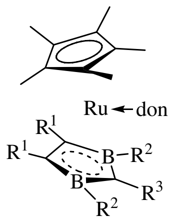

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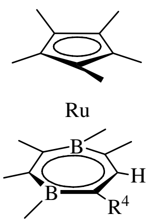

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2. Results and discussion

2.1. Crystal structure of the bis-trimethylsilylmethyl derivative *2b*

We have been trying for years to obtain the detailed structure of a derivative of (η^5-pentaalkyl-2,3-dihydro-1,3-diborolyl)(η^5-pentamethylcyclopentadienyl)ruthenium complexes **2** to further understand its unique properties. Finally, compound **2b** [2a], first isolated as a dark violet oil, on cooling in hexane gave suitable crystals for an X-ray structure analysis. Its structure (Fig. 1) confirms that the 1,3-diborolyl ring is folded by 40.7° along the B···B vector, very similar to its green iron analog **1b**. The Ru–C2 bond length (2.029, cf. Fe–C2 1.899 Å) is markedly shorter than the other Ru–C bond lengths to the heterocycle. Upon coordination of a donor ligand such as Me_3CNC the folding angle along the B···B vector is reduced to 16.2°/19.0° [1b,2a].

2.2. Electronic structures of the model complexes of iron *1* and ruthenium *2*

Some years ago the electronic structure of complex **1** was investigated with the help of semiempirical Extended-Hückel calculations [1b]. On the basis of the qualitative interaction diagrams and the comparison with bonding properties of the cyclopentadienyl ligand as well as the 18 VE rule it was possible to postulate that the folding of the diborolyl ligand of complex **1** is due to electronic factors. It is clear that a more accurate and quantitative description of the structural and electronic properties of complex **1** could not be achieved within the Extended-Hückel scheme. Nowadays, computational transition metal chemistry is dominated by density functional theory (DFT) approaches [5] which are able to provide good results not only for geometries and the energetics but also for spectroscopic properties of the investigated species. Up to now, alternative high level *ab initio* methods are either too costly for large molecules or not accurate enough.

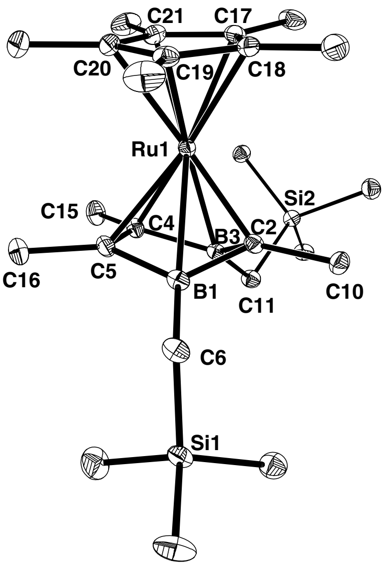

Fig. 1. Molecular structure of **2b**, hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and bond angles (°): Ru1–Cp* 2.139(2)–2.219(2), Ru1–C2 2.029(2), Ru1–B1 2.359(2), Ru1–C5 2.225(2), Ru1–C4 2.221(2), Ru1–B3 2.405(3), B1–C5 1.574(3), C4–C5 1.399(3), B3–C4 1.582(3), B3–C2 1.560(3), B1–C2 1.559(3) and C2–B1–C5 109.7(2), C4–C5–B1 105.8(2), C5– C4–B3 103.8(2), C2–B3–C4 109.6(2), B1–C2–B3 90.1(2).

The investigation has been continued on complex **2** as well as on **1** with the DFT/B3LYP method [6] as described in Section 4.2. We started with geometry optimizations for

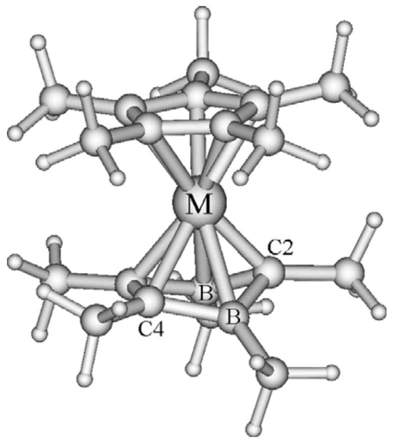

Fig. 2. Optimized structure of the decamethyl model complexes **1a** (M = Fe) and **2a** (M = Ru).