

1,3-Diboraheterocycles as ligands in metal complexes involving *endo*-C–H bonds

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ABSTRACT

Pentaalkyl-2,3-dihydro-1,3-diboroles possess unique properties in $[L_nM(C_3B_2HR_5)]$ complexes because the neutral heterocycle functions as 4e donor toward metal complex fragments e.g. CpM (M = Co, Rh), (arene)Fe, and others. The specific feature of these complexes is its MeC–H group with methyl in the *exo*- and hydrogen in an *endo*-position, forming a bridging 3c,2e C–H–B or an axial M–C–H bonding. This reduces the strength of the C–H bond, and thus complexes of this type exhibit a high reactivity and synthetic potential. Various complexes with a MeC–H group between identical boron centers have been analyzed by X-ray diffraction and NMR studies regarding the bonding of the *endo*-C–H in bridging or in axial position. The bond lengths of *endo*-C–H and B–C, the NMR shifts as well as the coupling constant J_{C-H} give information about the bonding situation. In the CpCo(C₃B₂HMeEt₄) sandwich the *endo*-hydrogen could not be located, its ¹H NMR spectrum shows a high-field quartet at –8.8 ppm, and a low J_{C-H} = 81 Hz indicates a weakening of the bond strength. Deprotonation leads to the anion, used as building block for oligo-decker complexes. The complex Ni(C₃B₂H₂Me₄)₂ having two *endo*-C–H bonds, exhibits a unique reactivity in losing hydrogen at ambient temperature and forming 2,3,5-tricarba-hexaboranyl-nickel complexes. Only few complexes allowed to locate the *endo*-hydrogen in C–H–B position by X-ray diffraction studies, which is supported by calculations. The energy difference between bridging and axial positions is very small.

The surprising formation of the slipped 34 VE triple-decker $[(Cp^*Ru)_2(\mu-C_6B_4H_2Me_8)]$ as sideproduct was observed in the reaction of tetrameric (Cp^{*}RuCl) with C₃B₂HMe₅ and zinc dust to improve the synthesis of the violet sandwich Cp^{*}Ru(C₃B₂Me₅). The related chloro complex Cp^{*}Ru(C₃B₂ClMe₄) is a postulated intermediate, however, its transformation into the dinuclear species must include the uptake of two hydrogen atoms, which is not yet clarified. The yellow bis(pentamethylcyclopentadienyl-ruthenium)- $\mu, \eta^6: \eta^6$ -hexahydro-tetraboranaphthalene has an unprecedented framework with a bridge-head diborane(4) unit, two additional boron atoms and two MeC–H groups each located between two different boron centers. The *endo*-hydrogen atoms were not found in the X-ray diffraction analysis, DFT calculations indicate their location in axial positions. ¹H NMR data confirm the presence of two *endo*-H atoms (showing a quartet at –4.6 ppm), of which only one could be deprotonated by potassium.

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1. Introduction

Endo-C–H bonding is a very active terrain in organometallic chemistry. Numerous transition metal complexes with *agostic* interactions (i.e. three-center, two-electron C–H–M bonding) have been reviewed [1,2], a more general review covers “Agostic Interactions from a Computational Perspective: One Name, many Interpretations” [3]. This report focusses on *endo*-C–H bonding of 1,3-diboraheterocycles in metal complexes, which are related to carborane compounds containing methylene groups in their polyhedral framework [4]. The first carboranes having *endo*-C–H bonds were obtained from dicarba-*closo*-undecaboranes being degraded by dichromate in acetic acid solution [5]. The parent carborane



and its derivatives contain two B–H–B bonds and two methylene groups each having a C–H bond in axial position. The proposed structures of these dicarba-nona-boranes(13) were confirmed by an X-ray diffraction study, and MO calculations on C₂B₇H₁₃ suggested that the axial hydrogen atom of the methylene group is more positive than the equatorial hydrogen atom [6]. A recent DFT study reveals that the axial and equatorial C–H bond lengths are very similar (Fig. 1) [7]. The *nido*-carboranes C₂B₄H₈ and C₃B₃H₇ possess only one CH₂ group with an *endo*-C–H bond. The experimentally observed derivative C₂B₄H₂Et₆ was suggested to be a 2-carba-*nido*-pentaborane(8) [8], however, an analysis by the *ab initio*-GIAO/NMR method showed it to be a 2,4-dicarba-*nido*-hexaborane(8) [9]. Calculation on the *nido*-carborane C₂B₄H₂Me₆ support that the *endo*-hydrogen is in axial position. In

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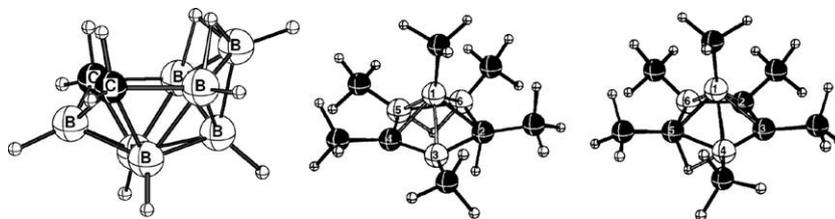


Fig. 1. Arachno- $C_2B_7H_{13}$, nido- $C_2B_4H_2Me_6$, and nido- $C_3B_3H_1Me_6$ carboranes.

the 1H NMR spectrum of $C_2B_4H_2Et_6$ a high-field multiplet is observed at -1.47 ppm indicating the special bonding of the *endo*-hydrogen, however, on the basis of the shift alone it is not possible to distinguish between an axial and a bridging position.

Its deprotonation with $Na[HBtEt_4]$ leads to the dimeric sodium hexaethyl-2,4-dicarba-*nido*-hexaborate(1-) shown in Fig. 2 [8]. Derivatives of the 2,3,5-tricarba-*nido*-hexaborane were first obtained from labile bis(2,3-dihydro-1,3-diborole)nickel complexes. In solution they slowly transform into mono and bis(2,3,5-tricarba-hexaboranyl)nickel complexes by capping of the C_3B_2 heterocycle with boranediyl (:B-Me) and stacking leads to oligo-decker complexes [10]. The structure of a bis(2,3,5-tricarba-hexaboranyl)nickel is depicted in Fig. 2 [11]. Designed routes to 2,3,5-tricarba-*nido*-hexaboranes (Fig. 1) start with 1,4-diborafulvenes and 4,5-bis(isopropylidene)-1,3-diborolanes, which are doubly hydroborated with $(HBtEt_2)_2$. Elimination of $BtEt_3$ yield oily tricarba-*nido*-hexaboranes [12], showing a high-field multiplet near -1.35 ppm. This 1H NMR shift is indicative of an *endo*-hydrogen, which according to calculation is in a C-H-B bridging position [9].

2. *Endo*-C-H bonding in 2,3-dihydro-1,3-diborole-metal complexes

Formal replacement of the *apex*-B-Me group in 2,3,5-tricarba-*nido*-hexaboranes(7) by an isolobal metal complex fragment **M** (Fig. 3) leads to metal-1,3-diborole complexes. The formation of a bridging C-H-B bond is accompanied by a second 3c,2e bonding between the σ -B-C bond and **M** (not shown in Fig. 3). This creates a B_2H_6 -like bridge-bonding which may also be described as a 4c,4e interaction. In an axial H-C-M bonding the *endo*-hydrogen does not interact with the neighboring boron centers. An entirely differ-

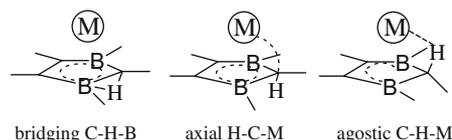


Fig. 3. *Endo*-C-H bonding in bridging, axial and agostic interactions.

ent bonding occurs when the heterocycle approaches the metal center via its C-H group which results an *agostic*-C-H-M 3c,2e interaction. In case the ligands at **M** are capable to stabilize a higher oxidation state of the metal, the *agostic* interaction may lead to an oxidative addition by cleavage of the C-H bond.

The complex $CpCo(C_3B_2HMeEt_4)$ having an *endo*-C-H bond was obtained by reacting $CpCo-(C_2H_4)_2$ with tetraethylmethyl-1,3-diborole [13]. Its NMR spectra exhibit an unusual high-field quartet at -8.8 ppm for $MeC-H$ and a small coupling constant $J_{C-H} = 81$ Hz, the latter indicates a reduced bond strength due to a 3c,2e interaction. Unfortunately, the *endo*-hydrogen atom could not be located in an X-ray diffraction study (Fig. 4) because of a crystallographic mirror plane. However, the C4-C5 bond [$1.632(2)$ Å] is significantly longer than that of the related $CpNi(C_3B_2MeEt_4)$ complex, which is indicative of a bridging C-H-B bond. The related (toluene)iron(1,3-diborole) complex obtained from $(C_7H_8)Fe(C_2H_4)_2$ and tetraethylmethyl-1,3-diborole, shows also a high-field quartet for *endo*-C-H (at -8.4 ppm). A combined X-ray/neutron diffraction analysis allowed to locate the *endo*-hydrogen atom in two independent positions [4]. The structural data for B1-H6a-C2 and C2-H6b-B3 (1.53, 1.13 and 1.14, 1.51 Å, respectively) prove the presence of bridging C-H-B bonds.

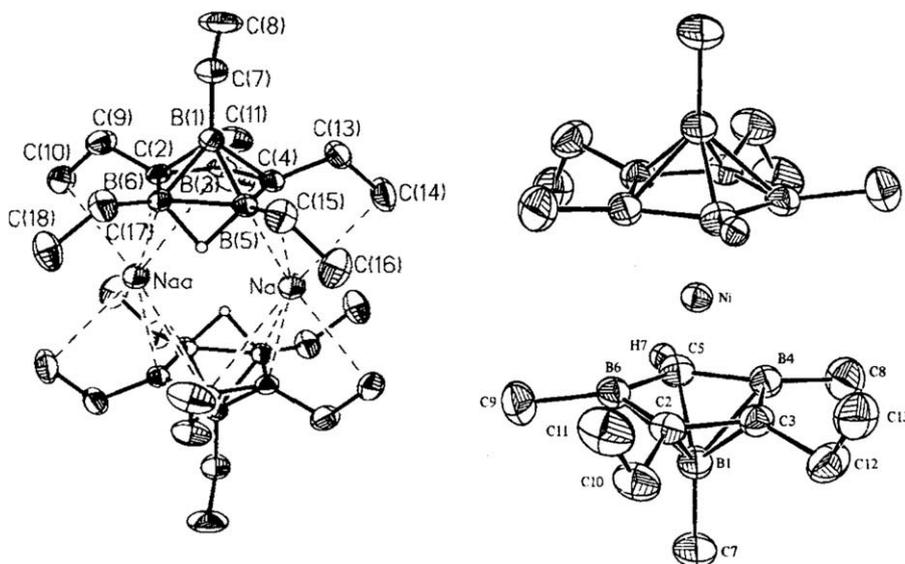


Fig. 2. Dimeric $[Na \text{ nido-}C_2B_4H_1Et_6]_2$ and the nickel complex $Ni(\text{nido-}C_3B_3H_1Me_3Et_2)_2$.

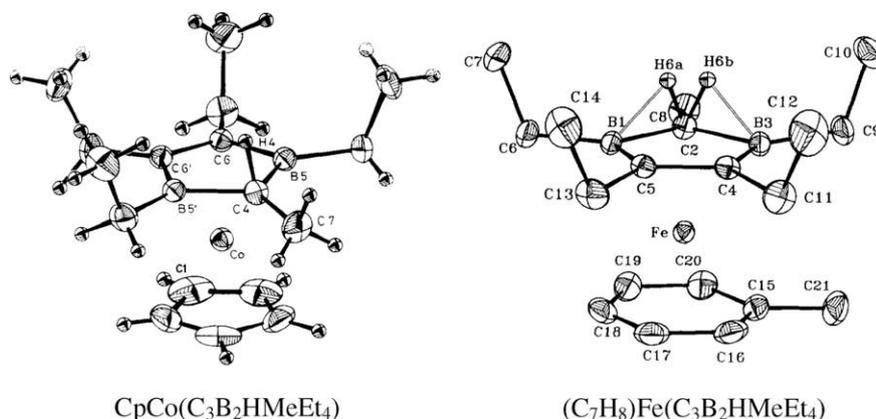


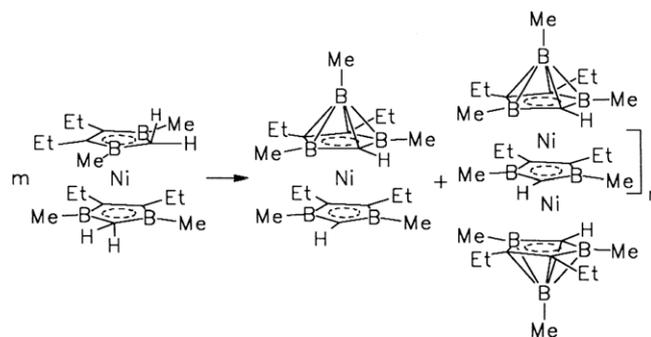
Fig. 4. Molecular structures of CpCo- and $(C_7H_8)Fe$ -1,3-diborole complexes with *endo*-C–H bonding.

In the X-ray structure analysis of the complex $CpCo\{(C_3H_6C)_2(BMe)_2CHMe\}$ [14] two independent molecules were found, which differ in the position of the *endo*-H1 atom. One molecule shows a typical C2–H1–B1 bridging bond (Fig. 5), whereas in the other the *endo*-C–H represents almost an axial C–H group (B1–H1 1.71, B3–H1 1.78 Å). This is evidence for a small energy difference between the two molecules, one having a bridging, the other an axial hydrogen atom. DFT calculations on the parent complex $(CH)_5Co(C_3B_2H_6)$ with the *endo*-H atom in the bridging or in the axial position yield a ΔE of 0.9 kcal/mol [15]. The nickel complex $(cod)Ni\{(C_3H_6C)_2(BMe)_2CHMe\}$ also contains an *endo*-hydrogen atom showing a high-field quartet at -1.56 ppm [14].

In the 1,3-diborole-rhodiumchloride-dimer $[ClRh(C_3B_2HMe_3tBu_2)]$ the bridging C–H–B bonding is identified by the following bond lengths: B1–C2 1.746(3), B3–C2 1.578(3), B1–H2 1.49(2), C2–H2 0.92(2) Å. The complex exhibits a high reactivity with respect to substitution of the chloro bridges. With CpNa the diborole complex $CpRh(C_3B_2HMe_3tBu_2)$ is formed, whereas with Cp^*Li the oxidative addition leads the diboroly complex $Cp^*RhH(C_3B_2Me_3tBu_2)$ [16]. In the former complex the *endo*-H atom could not be located, however, its 1H NMR spectrum exhibits a high-field signal at -6.7 (dq) ppm which is indicative of an *endo*-C–H. The formation of the oxidative addition product $Cp^*RhH(C_3B_2Me_3tBu_2)$ containing Rh(III) is proven by a high-field doublet at -11.9 ppm for the Rh–H group.

The most interesting class of compounds with *endo*-hydrogen atoms are the 18 VE bis(1,3-diborole)nickel complexes, obtained by reacting 1,3-diboroles with bis(allyl)nickel at low temperatures.

In the X-ray structure analysis of the $Ni(C_3B_2H_2Me_4)_2$ sandwich only the equatorial hydrogen of the CH_2 group was found. The chemical shift at -2.3 ppm is in agreement with the presence of the *endo*-H [10]. In solution at ambient temperature the complexes slowly lose hydrogen and the resulting 16 VE sandwich is capped by a boranediyl from another molecule to yield an 18 VE carboraanyl complex as shown in Scheme 1. A second capping leads to a di(2,3,5-tricarba-hexaboranyl)nickel complex [12] (Fig. 2). Besides capping also stacking occurs which results in the formation of



Scheme 1. Transformation of bis(1,3-diborole)nickel by elimination of hydrogen and capping of the formed bis(1,3-diboroly)nickel by boranediyl (B–Me) yields the 18 VE (1,3-diboroly)nickel(2,3,5-tricarba-hexaboranyl) complex. Combined capping and stacking reactions lead to the bis(2,3,5-tricarba-hexaboranyl)nickel(μ -1,3-diboroly) triple-decker ($n = 1$) and to oligo-decker complexes [4,10].

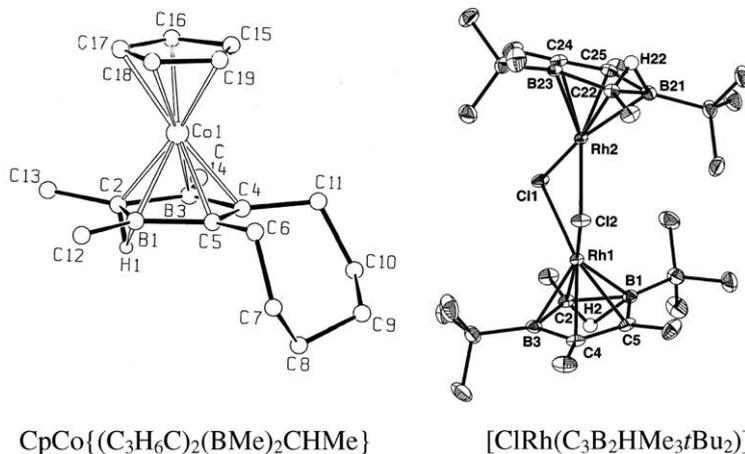


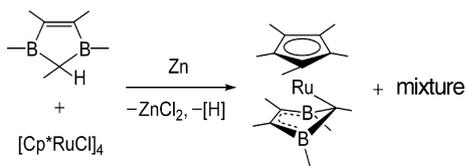
Fig. 5. Molecular structures of the complexes $CpCo\{(C_3H_6C)_2(BMe)_2CHMe\}$ and dimeric $[ClRh(C_3B_2HMe_3tBu_2)]$ having C–H–B bridges.

oligo-decker species, having 2,3,5-tricarba-hexaboranyl ligands in terminal positions.

3. Endo-C–H bonding in a μ -hexahydro-tetraboranaphthalene triple-decker complex

In an attempt to improve the synthesis of the violet (penta-methylcyclopentadienyl)ruthenium-(pentamethyl-1,3-diboroly) sandwich by reacting first $[\text{Cp}^*\text{RuCl}]_4$ with pentamethyl-1,3-diborole and then adding zinc dust, the expected sandwich with the strongly folded 1,3-diboroly heterocycle was formed [17] (Scheme 2). In addition a yellow-orange mixture of three dinuclear compounds was obtained, which could be separated by TLC. One of the triple-decker complexes in Fig. 6 is paramagnetic (29 VE), the other (30 VE) has an additional hydrogen atom which is detected by ^1H NMR. The yellow crystals of the third compound proved to be the unusual slipped triple-decker sandwich having the hexahydro-tetrabora-naphthalene in bridging position. According to NMR and MS data, the dinuclear ruthenium complex contains two MeC–H groups with an *endo*-hydrogen, which in the ^1H NMR spectrum yields a high-field quartet at -4.76 ppm.

The ten-membered bridging ligand in $[(\text{Cp}^*\text{Ru})_2(\mu\text{-C}_6\text{B}_4\text{H}_2\text{Me}_8)]$ is almost planar and contains two boron atoms in the bridge-head positions as well as two B–Me groups. The B–C–B bond lengths are different due to the different boron environment. The structural data regarding the position of the *endo*-hydrogen atoms did not give reliable information. DFT calculations [17] show that the *endo*-hydrogen atoms are in axial positions.



Scheme 2. Formation of the violet Ru sandwich (containing a strongly folded heterocycle) and a mixture of three dinuclear complexes (shown in Fig. 6).

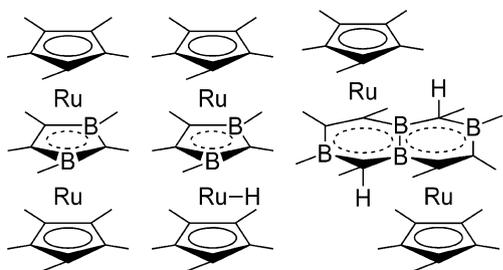


Fig. 6. Dinuclear ruthenium complexes obtained as sideproducts (Scheme 2) having 29, 30 and 34 VE. The *endo*-hydrogen atoms of the slipped triple-decker $[(\text{Cp}^*\text{Ru})_2(\mu\text{-C}_6\text{B}_4\text{H}_2\text{Me}_8)]$ were not found in the X-ray diffraction study.

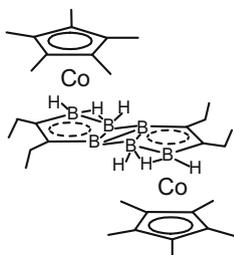


Fig. 7. The slipped triple-decker $[\text{Cp}^*\text{Co}(\text{Et}_2\text{C}_2\text{B}_3\text{H}_3)]_2$ with edge-fused carboranyl rings [19] is related to $[(\text{Cp}^*\text{Ru})_2(\mu\text{-C}_6\text{B}_4\text{H}_2\text{Me}_8)]$ having a ring-fused bridging ligand.

The unusual formation of the slipped triple-decker from the sandwich $\text{Cp}^*\text{Ru}(\text{C}_3\text{B}_2\text{Me}_5)$ under ambient condition is difficult to explain at this point as there are no experimental details available regarding a mechanism of the fusion process: A formal loss of a methyl group from a boron atom in $\text{Cp}^*\text{Ru}(\text{C}_3\text{B}_2\text{Me}_5)$ yields the radical $\text{Cp}^*\text{Ru}(\text{C}_3\text{B}_2\text{Me}_4)$ which has only 16 VE when the heterocycle is planar [18]. Its coupling and fusion of two complexed C_3B_2 rings give with uptake of two hydrogen atoms the 34 VE complex $[(\text{Cp}^*\text{Ru})_2(\mu\text{-C}_6\text{B}_4\text{H}_2\text{Me}_8)]$. As a possible intermediate the chloro-containing sandwich $\text{Cp}^*\text{Ru}(\text{C}_3\text{B}_2\text{ClMe}_4)$ is assumed to be coupled by zinc to yield an edge-fused dimer $[(\text{Cp}^*\text{Ru}(\text{C}_3\text{B}_2\text{Me}_4))_2]$ with a diamond-like linkage [17]. Its transformation with the uptake of two hydrogen could lead to the ring-fused dimer $[(\text{Cp}^*\text{Ru})_2(\mu\text{-C}_6\text{B}_4\text{H}_2\text{Me}_8)]$.

The first slipped triple-decker $[\text{Cp}^*\text{Co}(\text{Et}_2\text{C}_2\text{B}_3\text{H}_3)]_2$ with edge-fused carboranyl rings as bridging ligand [19] is shown in Fig. 7. Our dinuclear complex $[(\text{Cp}^*\text{Ru})_2(\mu\text{-C}_6\text{B}_4\text{H}_2\text{Me}_8)]$ is related to it having also 34 VE but a ring-fused hexahydro-tetraboranaphthalene ligand.

4. Conclusion

An analysis of metal complexes containing neutral 2,3-dihydro-1,3-diborole ligands has been carried out with respect to the involvement of the *endo*-hydrogen in the complex bonding. The preferred location of the *endo*-C–H bond in the solid state is the bridging position with one of the neighboring boron centers. The alternative, the axial position on the mirror plane is not favored, as it is a transition state between the equivalent boron atoms. In a complex having two independent molecules in the cell, one has a C–H–B bonding, whereas in the other almost an axial H–C–M situation is realized. The energy difference is very small. In contrast, the ring-fused dimer $[(\text{Cp}^*\text{Ru})_2(\mu\text{-C}_6\text{B}_4\text{H}_2\text{Me}_8)]$ in which two complexed C_3B_2 heterocycles have formed the hexahydro-tetraboranaphthalene ligand, both *endo*-hydrogen atoms are near the axial position, according to DFT calculation. However, the neighboring boron atoms are no longer equivalent.

Acknowledgements

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