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Structures and bonding of homoleptic bis(2,3-dihydro-1,3-diborole) complexes of nickel and platinum

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Dedicated to Russell N. Grimes on the occasion of his 80th birthday.

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ABSTRACT

Homoleptic metal complexes of the boron heterocycle 2,3-dihydro-1,3-diborole $\{(R^1C)_2(R^2B)_2R^3(H)C\}$ **1** are described. X-Ray crystal structure determinations of two nickel and platinum derivatives are presented. In the nickel complex $[Ni(\mathbf{1d})_2]$ **6d** ($R^1 = R^2 = R^3 = Et$) the essentially coplanar heterocycles attain a pentahapto coordination mode with a *gauche* orientation with respect to one another. An 18 VE count is attained. In contrast, in the 14 VE platinum complex $[Pt(\mathbf{1a})_2]$ **4a** ($R^1 = R^2 = Et$, $R^3 = Me$) the ligands are strongly folded and adopt a tetrahapto coordination. The molecule is centrosymmetric in the crystalline state. DFT MO calculations are presented to establish the relative stabilities of these coordination modes for nickel and platinum, respectively.

1. Introduction

Tetra- and penta-alkyl derivatives of the 2,3-dihydro-1,3-diborole heterocycle **1** and its closely related derivatives 2,3-dihydro-1,3-diborolyl ([**1** − H]) have unusual ligand properties [1]. Electron-donor capabilities of two to five electrons for bonding in metal complexes have been demonstrated. Four different coordination modes to transition metals are known, which represent distinct bonding patterns: **A** and **C** for **1**, and **B** and **D** for [**1** − H], respectively (Chart 1). In the complexes **A** − **D** the heterocycles function as 2, 3, 4, or 5 electron donors.

The majority of compounds belong to type **B**, having planar or slightly bent 2,3-dihydro-1,3-diborolyl derivatives [**1** − H] as 3e donors. In this form, they also function as bridging 3e ligands in a variety of multi-decker sandwich complexes [1]. However, in the less common structure **D** the heterocycle is highly folded towards the metal, supplying a total of 5 electrons (3 π electrons plus two more from the two B–C2 σ-bonds) [2–4].

Transition metal complexes with an intact ligand **1** are comparatively rare and fall into two distinct types, **A** and **C** (Chart 1). In the complexes **A** the C(R)H group bends away from the metal and the hydrogen substituent invariably occupies an *exo* position with respect to the metal. Two electrons only are donated to the metal by the *tetrahapto* bonded boron heterocycle.

A complex of type **A**, **2a**, was obtained along with its isomer **3a** from the reaction of bis(cyclooctadiene)platinum with **1a**. Both **2a** and **3a** were characterized by X-ray crystallography [5].

In structure **C** the C–H bond is also axial directed away from the metal, but the heterocycle is essentially planar. The most interesting feature of the complexes of type **C** is the pentacoordinated carbon atom C2, flanked by the two boron atoms, a situation which results in interesting spectroscopic properties, most notably a high field shift of the (C2)–H proton NMR resonance, and an enhanced chemical reactivity of the C2–H bond [6–10]. For example, this group is easily deprotonated to yield anions, which were used as building blocks for the construction of a large variety of stacked compounds ("multidecker sandwich" complexes) [1]. Two possible bonding situations were suggested, "*exo* axial" or C–H•••B

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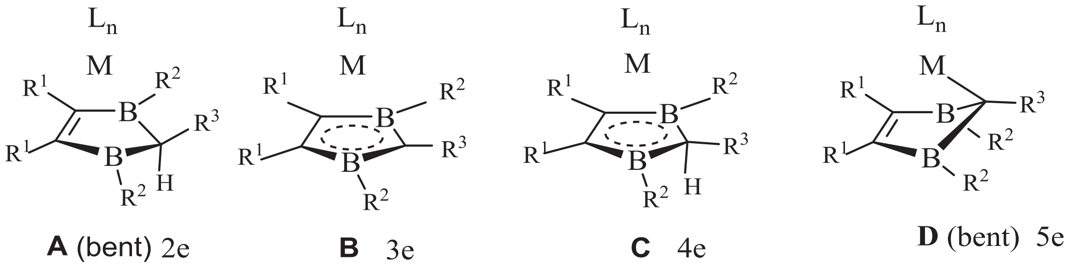
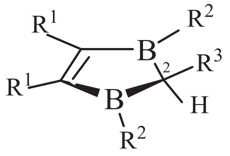
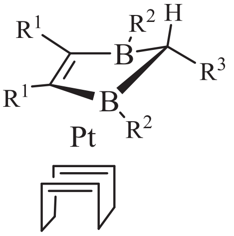


Chart 1.



1	R^1	R^2	R^3
a	Et	Et	Me
b	Et	Me	H
c	Me	Me	H
d	Et	Et	Et
e	Me	Me	Me



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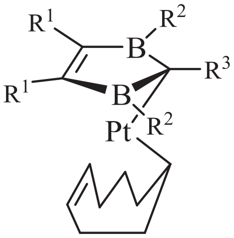

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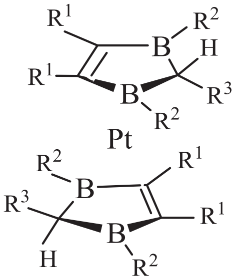
bridging (*vide infra*),[1] based on spectroscopic and semiempirical MO theoretical evidence [6]. In either case the two electrons of the C–H bond participate in bonding to the metal, resulting in a 4 electron donor ligand.

Although a (disordered) *endo* C2–H•••B bridge in **C** could be established by a combined X-Ray and neutron diffraction study of the complex [(η^6-toluene)Fe(**1a**)] [1,10], the alternative axial orientation of the C2–H group could not be completely ruled out in other cases [6,7].



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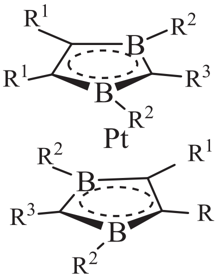

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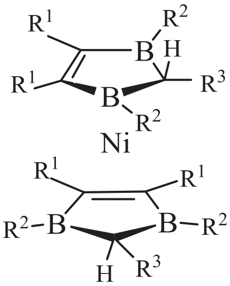

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Several decades ago we reported some reactions of [Pt($\mathbf{1a}$)$_2$] **4a** the structure of which could not be established beyond doubt at that time [12,13]. Smooth thermal conversion into the 16 VE sandwich complex **5a**, a useful building block for multidecker sandwich complexes [14], indicated an enhanced reactivity of the C2–H bond in **4a** [12,13].

Here we report more details and further studies of homoleptic bis(2,3-dihydro-1,3-diborole) complexes of nickel and platinum, giving new insight into the coordination geometry and bonding modes of this ligand.

2. Results and discussion

The first sandwich complex with the ligand [**1** − H] was the 18 VE complex [(η-C_5H_5)Ni(**1a** − H)], which was obtained from nickelocene and **1a** [15]. In this thermal reaction, only one of the two cyclopentadienyl ligands of nickelocene was replaced by the radical [**1a** − H]. In an attempt to generate a homoleptic 16 VE nickel sandwich [Ni(**1a**-H)$_2$] the boron heterocycle was reacted with $NiBr_2$ and $NaHBEt_3$ in DME. However, MS and NMR spectroscopic analysis of the product indicated the composition [Ni($\mathbf{1a}$)$_2$] **6a**, with intact 2,3-dihydro-1,3-diborole ligands. In particular, a high field quartet resonance for the R^3C–H proton was observed in the ^{1}H NMR spectra, characteristic of the *endo* C–H in complexes of type **C**. Two ^{11}B-NMR resonances indicated a rigid gauche arrangement of the

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[1] For such hydrogens the established nomenclatures for sandwich type metal complexes and carbaboranes are not consistent. Although *exo* with respect to the metal we choose to denote C–H•••B bridging hydrogens *endo* hydrogens, in line with what is commonly used for carbaboranes [11].