

# Synthesis, X-ray and Electronic Structure of Trinickel Tetradecker Sandwich Complexes $\{(\eta^5\text{-C}_5\text{H}_5)\text{Ni}[\mu, \eta^5\text{-(CR}^1)_2(\text{BR}^2)_2\text{CR}^3]\}_2\text{Ni}^{\star}$

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The reduction of the 18-VE complexes  $(\eta^5\text{-C}_5\text{H}_5)\text{Ni}[\eta^5\text{-(CR}^1)_2(\text{BR}^2)_2\text{CR}^3]$  (**2a**, **b**) with potassium in THF leads to the paramagnetic anions **2<sup>-</sup>**, which react with  $\text{NiBr}_2 \cdot \text{DME}$  to give the triple-decker complexes  $(\eta^5\text{-C}_5\text{H}_5)\text{Ni}[\mu, \eta^5\text{-(CR}^1)_2(\text{BR}^2)_2\text{CR}^3]\text{Ni}(\eta^5\text{-C}_5\text{H}_5)$  (**3a**, **b**) and the tetradecker  $\{(\eta^5\text{-C}_5\text{H}_5)\text{Ni}[\mu, \eta^5\text{-(CR}^1)_2(\text{BR}^2)_2\text{CR}^3]\}_2\text{Ni}$  (**4b**). Surprisingly, **4b** is also obtained by heating the double-decker complex **2b** and  $\text{H}_2\text{AlOCMe}_3$  in THF. The reaction between **2c** and  $\text{AlH}_3$  in  $\text{Et}_2\text{O}$  leads to the substitution of the ethoxy groups at the boron atoms and to the formation of the tetradecker **4d** with four B–H groups. Heating of the 1,3-benzodiborole ligand **1e** and  $[(\text{C}_5\text{H}_5)\text{Ni}(\text{CO})]_2$  in toluene yields small amounts of **2e** and **3e**,

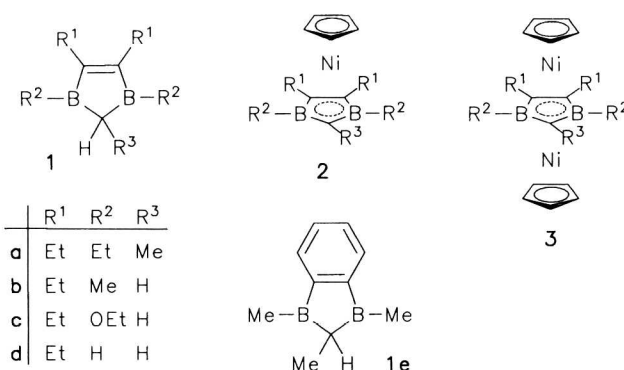
and the tetradecker **4e**. X-ray structure analyses were performed for **4d** and **4e**. Complex **4d** is centrosymmetric with relatively short nickel-to-bridging ligand distances (1.69, 1.70 Å). In the tetradecker **4e** the two bridging ligands adopt a synclinal conformation (rotating about 36° resp. 41° against each other). The Ni–Ni distance (3.42, 3.43) is slightly longer than in **4d** (3.39 Å). The electronic structures of the triple-decker cation **3<sup>+</sup>** (32 VE) and of the tetradecker **4** (46 VE) have been investigated by means of the Fenske-Hall method. The findings are in agreement with the experimental results that **3<sup>+</sup>** is a triplet species and **4** possesses a closed-shell electron configuration.

Alkyl derivatives of the 2,3-dihydro-1,3-diborole heterocycle **1** react with an excess of  $[(\eta^5\text{-C}_5\text{H}_5)\text{Ni}(\text{CO})]_2$  or  $[(\eta^5\text{-C}_5\text{H}_5)\text{Ni}(\eta^3\text{-C}_3\text{H}_5)]$  via the 18-valence electron (VE) sandwich **2** to give the paramagnetic, green triple-decker sandwich complexes **3**<sup>[1,2]</sup>. For the construction of the tetradecker **4** a formal insertion of the 13-VE ( $\eta^5$ -2,3-dihydro-1,3-diboroly)nickel stack  $[(\text{I-H})\text{Ni}]$  into the 33-VE triple-decker **3** is required. An early attempt to synthesize the trinickel tetradecker **4a** by the reaction of two sandwich anions **2a<sup>-</sup>** with  $\text{NiCl}_2$  gave only a very small amount of a green product; its mass spectrum indicated the formation of **4a**<sup>[3]</sup>. This result is in contrast to the high-yield synthesis of the tetradecker sandwich series  $\{(\eta^5\text{-C}_5\text{H}_5)\text{Co}[\mu, \eta^5\text{-(CR}^1)_2(\text{BR}^2)_2\text{CR}^3]\}_2\text{M}$  (M = Cr, Mn, Fe, Co, Ni, Cu, Zn)<sup>[2,4]</sup> from two 18-VE sandwich anions  $\{(\eta^5\text{-C}_5\text{H}_5)\text{Co}[\eta^5\text{-(CR}^1)_2(\text{BR}^2)_2\text{CR}^3]\}^-$  and  $\text{MX}_2$ . The bridging 1,3-diboroly ligands adopt an antiperiplanar configuration, the observed slip distortions depend on the central metal. EHMO calculations of these trinuclear complexes have been reported<sup>[5]</sup>.

Recently, Grimes et al. synthesized the first examples of two new classes of tetradecker sandwich complexes. The "hybrid" class of tetradecker has  $\text{C}_2\text{B}_3$  and  $\text{C}_3\text{B}_2$  bridging rings<sup>[6a]</sup>, and the  $\{(\text{C}_5\text{Me}_5)\text{Co}[(\text{CEt})_2(\text{BH})_2\text{BX}]\}_2\text{M}$  tetradecker complexes<sup>[6b]</sup> (M = Co, Ni; X = MeCO, Cl, Br) have two bridging  $\text{C}_2\text{B}_3$  carborane ligands.

A general approach to stacked (2,3-dihydro-1,3-diboroly)nickel compounds is provided by the reactions of 1,3-diboroles **1** with bis(allyl)nickel. The trinickel tetradecker compounds<sup>[7]</sup> bis[( $\eta^3$ -allyl)nickel( $\mu, \eta^5$ -2,3-dihydro-1,3-diboroly)]nickel,  $[(\eta^3\text{-C}_3\text{H}_5)\text{Ni}(\text{I-H})]_2\text{Ni}$  are obtained by using a 1:2 molar ratio. These 42-VE trinuclear complexes are diamagnetic, in contrast to isoelectronic  $\{(\eta^5\text{-C}_5\text{H}_5)\text{Co}[\mu, \eta^5\text{-(CR}^1)_2(\text{BR}^2)_2\text{CR}^3]\}_2\text{Fe}$  complexes, which possess an electronic high-spin configuration.

The bis( $\eta^5$ -2,3-dihydro-1,3-diborole)nickel sandwich complexes (**1**)<sub>2</sub>Ni, formed by the reaction of **1** with  $\text{Ni}(\eta^3\text{-C}_3\text{H}_5)_2$  in a 2:1 ratio, exhibit an unusual reactivity<sup>[8]</sup>. After elimination of hydrogen from the 2-position of the heterocycle, they undergo capping and stacking reactions, leading to the formation of a series of bis[( $\eta$ -2,3,5-tricarbahexaboranyl)-



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nickel] $(\mu, \eta^5-2,3\text{-dihydro-1,3-diboroly})$  complexes<sup>[8,9]</sup>  $[\eta^5-(\text{CR}^1)_2(\text{BR}^2)_3\text{CR}^3]\text{Ni}\{[\mu, \eta^5-(\text{CR}^1)_2(\text{BR}^2)_2\text{CR}^3]\text{Ni}\}_n[\eta^5-(\text{CR}^1)_2(\text{BR}^2)_3\text{CR}^3]$ ,  $n = 1, 2, 3$ .

These findings prove that stacking reactions with these nickel complexes occur even at room temperature; however, the capping reaction with the formation of the tricarbaboranyl ligand prevents the formation of polymeric 1,3-diborolynickel compounds. They are obtained by thermal condensation reactions of tris(allyl)dinickel- $\mu, \eta^5-1,3\text{-diboroly}$  triple-decker complexes<sup>[10]</sup>. To extend our knowledge of the formation and the electronic structure of tetradeccker species the possibility of connecting two 18-VE double-decker complexes **2** with nickel to yield **4** was investigated. Previously we have found that in the isovalence electronic NiPtNi tetradeccker **5a** the bridging ligands adopt a hitherto unknown synclinal conformation<sup>[11]</sup>. In this paper we report on the synthesis of the diamagnetic tetradeccker complexes **4b**, **4d** and **4e**, the X-ray structure analyses of **4d** and **4e**, and Fenske-Hall SCF MO calculations.

## Results and Discussion

### Formation of the Tetradeccker Sandwich Complexes **4b**, **4d** and **4e**

The reaction of the sandwich **2a** with potassium in THF results in a brown solution, which on treatment with  $\text{NiBr}_2 \cdot \text{DME}$  gives **2a** (30%) and the triple-decker **3a** (22%), however no tetradeccker **4a**. In contrast, treatment of the sandwich **2b** with potassium in THF yields a green solution; its reaction with  $\text{NiBr}_2 \cdot \text{DME}$  leads to **2b** (5%), **3b** (8%), and dark green **4b** (13%). In both reactions with potassium the 19-VE sandwich anions **2a<sup>-</sup>** and **2b<sup>-</sup>** are formed, identified by their ESR spectra. **2a<sup>-</sup>** exhibits a  $g$  value of 2.030.

An additional signal of an unknown compound is found at  $g = 2.070$ , its intensity increases when the sample is stored for several days at room temperature. **2b<sup>-</sup>** ( $g = 2.030$ ) is less stable.

the reaction mixture gives **2b** and **3b**. The residue is chromatographed to yield green **4b** (27%). The reaction of **2c** with  $\text{H}_2\text{AlOCCMe}_3$  in petroleum ether at room temperature gives a green solution, from which a mixture of **2c/2d** and **3d** (3.5%) is isolated. The use of the more reactive  $\text{AlH}_3$  in diethyl ether leads to the green triple-decker **3d** (5%) and to the dark green tetradeccker **4d** (16%).

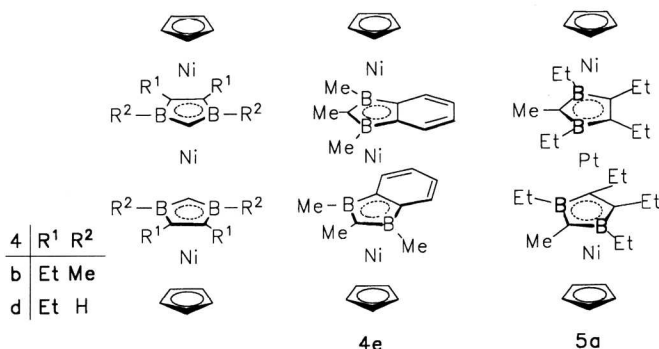
The formation of the tetradeccker **4d** indicates that not only substitution of the ethoxy group at the boron but also cleavage of the sandwich **2d** must occur to supply nickel atoms, required for the stacking of two sandwich complexes **2d** to give the tetradeccker **4d**. A related reaction sequence proceeds when the 1,3-benzodiborole **1e** and dimeric carbonyl(cyclopentadienyl)nickel are heated in toluene for two hours. From the reaction mixture a small amount of yellow **2e** and only traces of green **3e** as well as the green tetradeccker **4e** (20%) are separated by column chromatography. The formation of **4e** most likely occurs by complexation of a nickel atom by two sandwich units **2e** since it is known that  $[(\text{C}_5\text{H}_5)\text{Ni}(\text{CO})_2]_2$  decomposes above  $120^\circ\text{C}$  to give  $(\text{C}_5\text{H}_5)_2\text{Ni}$ , CO, and nickel. In **2e**, **3e**, and **4e** the ligand **1e**-H functions as a three-electron donor, two of the electrons are supplied by the benzo system.

The diamagnetic sandwich complexes **2** and the tetradeccker sandwich complexes **4** were identified by NMR and MS studies (see Experimental). The paramagnetic triple-deckers **3** were detected by their mass spectra. Diamagnetic 46-VE **4b**, **d**, **e** exhibit a singlet for  $\text{C}_5\text{H}_5$  ( $\delta = 4.94, 4.91, 3.02$ ), a singlet for CH [3.26, 3.7 (br), 2.33 ( $\text{CH}_3$ )], an  $\text{ABX}_3$  spin system for  $\text{C}_2\text{H}_5$  [1.9 (m), 1.27 (t); 1.8 (m), 1.56 (t)], and a singlet for  $\text{BCH}_3$  (0.67, 0.07). No signal is found for B-H in **4d**. The  $^{11}\text{B}$ -NMR signal ( $\delta = 6$ , br) for **4d** does not show B-H coupling, the shift is typical of compounds with bifacial coordination of the bridging 2,3-dihydro-1,3-diboroly ring<sup>[2,9]</sup>. The  $^{11}\text{B}$ -NMR signal for **4b** is shifted to  $\delta = 16.3$ .

### Crystal Structures of **4d** and **4e**

The tetradeccker molecule **4d** is centrosymmetric. The two bridging ligands are arranged antiperiplanar (Figure 1). The best planes through the 2,3-dihydro-1,3-diboroly ( $\pm 0.02 \text{ \AA}$ ) and the cyclopentadienyl ring ( $\pm 0.005 \text{ \AA}$ ) are almost parallel ( $2.4^\circ$ ). The Ni atoms lie above and below the centroids of the rings. The distances of the terminal and central Ni atoms to the  $\text{C}_2\text{B}_2\text{C}$  ring (1.69, 1.70  $\text{ \AA}$ ) are quite short compared to the distances in the corresponding tetradeccker<sup>[2]</sup> with the metal sequence Co Ni Co (1.76  $\text{ \AA}$ ), but slightly greater than in the sandwich **2a** (1.66  $\text{ \AA}$ )<sup>[13]</sup>.

In the asymmetric unit of **4e** two independent tetradeccker molecules were found, which show no significant differences. The two bridging 2,3-dihydro-1,3-benzodiboroly ligands (Figure 2) adopt a synclinal conformation (rotated about  $36^\circ$  resp.  $41^\circ$  against each other). The distances from the Ni atoms to the best planes through the heterocycle lie in the range 1.70 to 1.73  $\text{ \AA}$ , and to the planes through the cyclopentadienyl rings 1.74 and 1.75  $\text{ \AA}$ . The rings of the same molecule are almost parallel (angles  $< 3^\circ$ , the cyclopentadienyl rings showing somewhat larger deviations up to  $6^\circ$ ).



It is well-known<sup>[12]</sup> that the sandwich complexes ferrocene and cobaltocene react with alkali metal in donor solvents to form MCp fragments. We assume that an analogous reaction occurs with **2a**, **b** yielding a reactive  $[(1\text{-H})\text{Ni}]$  stacking fragment, which might form oligomeric or polymeric products. Surprisingly, the tetradeccker **4b** is obtained by heating orange **2b** and  $\text{H}_2\text{AlOCCMe}_3$  in THF to  $65^\circ\text{C}$ . A slow color change to green is observed, and distillation of

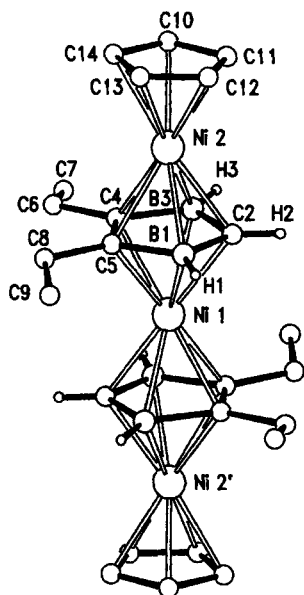


Figure 1. Molecular structure of **4d**; selected bond lengths [ $\text{\AA}$ ] and angles [ $^\circ$ ]: Ni1–Ni2 3.389(2), Ni1–B1 2.168(4), Ni1–B3 2.151(4), Ni1–C2 2.101(3), Ni1–C4 2.109(3), Ni1–C5 2.122(3), Ni2–B1 2.143(4), Ni2–B3 2.139(4), Ni2–C2 2.126(3), Ni2–C4 2.139(3), Ni2–C5 2.141(3); C2–B1–C5 104.4(3), B1–C2–B3 111.1(3), C2–B3–C4 103.8(3), B3–C4–C5 110.2(3), C4–C5–B1 110.4(3)

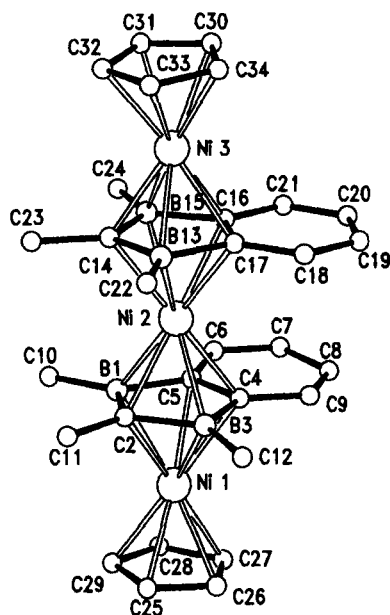


Figure 2. Molecular structure of **4e**; selected bond lengths [ $\text{\AA}$ ] and angles [ $^\circ$ ] (average values): Ni1(3)–Ni2 3.435(2), Ni1(3)–B 2.163(13), Ni1(3)–C2(14) 2.136(11), Ni1(3)–C4(5,16,17) 2.168(11), Ni2–B 2.186(13), Ni2–C2(14) 2.123(11), Ni2–C4(5,16,17) 2.157(11); C2–B1–C5 103.9(9), B1–C5–C4 110.2(8), C4–B3–C2 103.9(8), C5–C4–B3 110.4(8), B3–C2–B1 111.5(9)

The Ni–Ni distances (3.42–3.43  $\text{\AA}$ ) are slightly greater than in **4d** (3.39  $\text{\AA}$ ). In both structures the  $\text{C}_2\text{B}_2\text{C}$  ring is slightly bent along B1–B3 with the boron atoms closer to the terminal Ni atoms. The structures can be compared with that of the tetradecker **5a**, in which the central atom is platinum<sup>[11]</sup>. The NiPtNi tetradecker shows a similar syn-

clinal conformation ( $44^\circ$  rotation of the  $\text{C}_2\text{B}_2\text{C}$  rings against each other) as **4e**. As expected the distances to the central Pt atom are greater; however, the distances from the Ni atom to both rings have increased, too (Ni– $\text{C}_5\text{C}_5$  1.79, Ni– $\text{C}_2\text{B}_2\text{C}$  1.76  $\text{\AA}$ ). These elongations may be caused by the four ethyl groups on the diborolyl ring which point toward the cyclopentadienyl ring.

### Electronic Structure and Bonding

To obtain an insight into the electronic structure, the NiNi triple-decker sandwich complex cation  $\{(\eta^5\text{-C}_5\text{H}_5)\text{Ni}[\mu,\eta^5\text{-(CH)}_2\text{(BH)}_2\text{CH}]\text{Ni}(\eta^5\text{-C}_5\text{H}_5)\}^+$  (**3**<sup>+</sup>) and the NiNiNi tetradecker  $\{(\eta^5\text{-C}_5\text{H}_5)\text{Ni}[\mu,\eta^5\text{(CH)}_2\text{(BH)}_2\text{CH}]\}_2\text{Ni}$  (**4**) have been investigated by means of the Fenske-Hall method<sup>[14]</sup>. The oligodecker sandwich complexes can be viewed as being composed of several fragments whose electronic structures have been studied<sup>[15]</sup>. A Mulliken population analysis with respect to the molecular orbitals of the fragments provides the gross populations which are represented in Figures 3, 5 and 6 above or below the bars representing the energy level of the fragment orbitals.

### Sandwich Complex 2

The sandwich **2** can be viewed as being composed of the two fragments  $[\text{CpNi}]^+$  and  $(\text{C}_2\text{B}_2\text{C})^-$ . Since the rotation

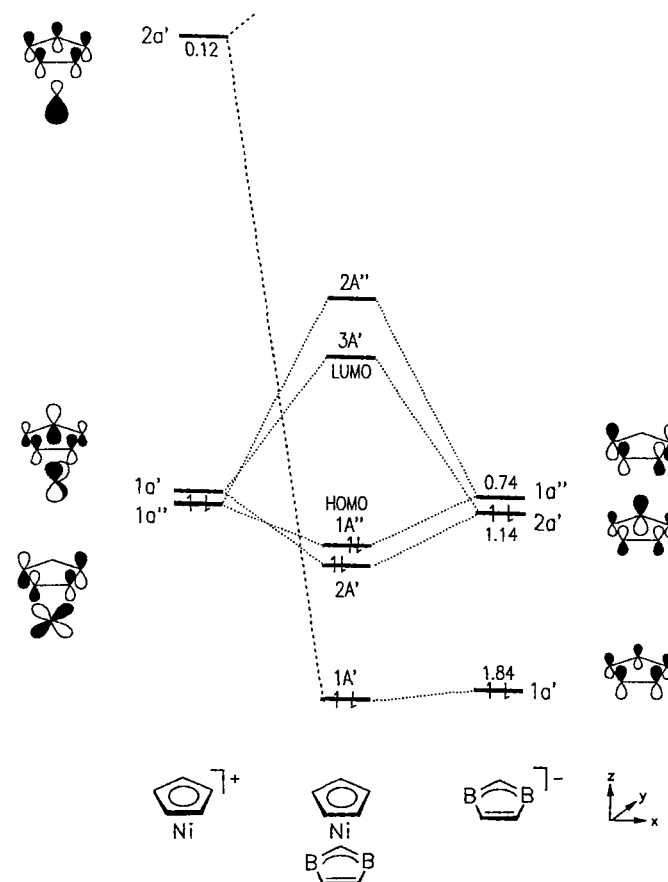


Figure 3. Simplified interaction diagram for the interaction of  $\text{CpNi}^+$  with  $(\text{C}_2\text{B}_2\text{C})^-$  fragments

around the metal-cyclopentadienyl axis is essentially unhindered, complex **2** displays  $C_s$  symmetry (mirror plane  $yz$ ).

The complexes **3** and **4** also have  $C_s$  symmetry. Figure 3 shows only a simplified interaction diagram displaying orbitals of the two fragments which interact strongly with each other. The most cylindrically occupied  $1a'$  orbital of the 1,3-diborolyli anion ( $C_2B_2C$ )<sup>-</sup> has the proper local symmetry to interact with the empty  $2a'$  orbital of  $[CpNi]^+$ ; likewise,  $2a'$  of ( $C_2B_2C$ )<sup>-</sup> overlaps strongly with the empty  $1a'$  of  $[CpNi]^+$ . Backdonation from the metal to the ligand occurs by the interaction of the filled  $1a''$  of  $[CpNi]^+$  into the empty  $1a''$  of ( $C_2B_2C$ )<sup>-</sup>. Six electrons are stabilized by these interactions. The other electrons are either non-bonding ( $6e$ ) in the formal " $t_{2g}$ " set of the metal or involved in the Cp  $\pi$  bonding ( $6e$ ). This yields a total of 18 VE, which corresponds to a stable situation equivalent to that of ferrocene.

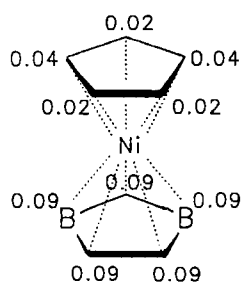


Figure 4. Total overlap population of the nickel with the carbon and boron centers

Figure 4 describes the total overlap population of the Ni with the carbon and boron centers of the two rings. It appears that the ( $C_2B_2C$ )<sup>-</sup> ring is more tightly bound to Ni than the Cp ring. This is due to the fact that the d orbitals of Ni are closer in energy to the  $\pi$  orbitals of the ( $C_2B_2C$ )<sup>-</sup> and that the overlap between the two fragments is also stronger (more diffuse orbitals on boron, larger size of the ring).

### Triple-decker Complex 3

The triple-decker **3**<sup>+</sup> can be analyzed in a similar manner. A convenient way to discuss the bonding is to view **3**<sup>+</sup> as being composed of  $CpNi(C_2B_2C)$  and the  $[CpNi]^+$  fragment. A simplified interaction diagram is shown in Figure 5. In this case also there is a good matching between occupied and empty orbitals of both fragments.  $1a'$  of  $CpNi(C_2B_2C)$  interacts with  $2a'$  of  $[CpNi]^+$  while  $2a'$  and  $3a'$  of  $CpNi(C_2B_2C)$  interact with  $1a'$  of  $[CpNi]^+$ . This gives rise to a bonding orbital ( $2A'$ ), a non-bonding one ( $3A'$ ), and an anti-bonding ( $4A'$ ). A similar orbital diagram arises from the  $a''$  orbitals. Eight electrons are stabilized in those interactions. The calculation shows that the non-bonding  $2A''$  and  $3A'$  are almost degenerate leading to a 32-VE paramagnetic system in agreement with the experiment and with the iso-electronic NiCo triple-decker<sup>[1]</sup>. This confirms the earlier studies by Hoffmann et al.<sup>[16]</sup> on triple-deckers. A 34-VE complex is less stable since two electrons are added to non-bonding orbitals.

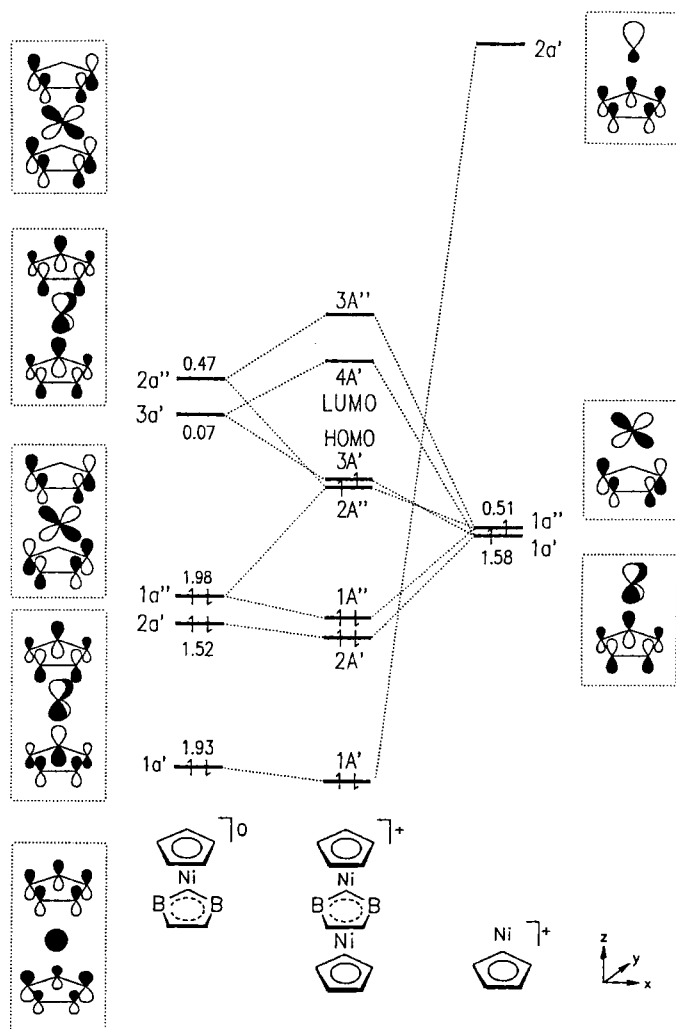


Figure 5. Simplified interaction diagram for the interaction of  $CpNi(C_2B_2C)$  with the  $CpNi^+$  fragment

### Tetradeccker Complex 4

A convenient way to analyze the bonding in the tetradeccker complex **4** is to build up the system from  $CpNi(C_2B_2C)$  and the  $[CpNi(C_2B_2C)Ni]$  fragment. A favorable interaction between frontier orbitals of the two fragments also occurs. A simplified interaction diagram (Figure 6) shows the interactions between the orbitals which are closer in energy. The system is diamagnetic for 46 VE. The data listed in Table 1 indicate that bonding between the central nickel atom ( $Ni_c$ ) and the two ( $C_2B_2C$ )<sup>-</sup> rings is weaker than that between the two terminal nickel atoms ( $Ni_t$ ) and the two bridging ( $C_2B_2C$ )<sup>-</sup> rings. This is in agreement with the experimental Ni-to- $(C_2B_2C)$  ring distances [ $Ni_c - (C_2B_2C) = 1.70 \text{ \AA}$ ,  $Ni_t - (C_2B_2C) = 1.69 \text{ \AA}$ ], although the difference is marginal. The orbitals of the  $CpNi$  fragment are more located on the Ni center than orbitals of the ( $C_2B_2C$ )Ni fragments. This is due to the fact that Ni d orbitals mix more strongly with the  $\pi$  orbitals of ( $C_2B_2C$ )<sup>-</sup> than with that of Cp [this is responsible for the stronger  $Ni(C_2B_2C)$  interaction]. As a consequence,  $Ni_t$ , which is bound to one Cp ring, interacts more strongly with ( $C_2B_2C$ )<sup>-</sup> than  $Ni_c$ , which

is bound to the other  $(C_2B_2C)^-$ . This accounts for the stronger  $Ni_1(C_2B_2C)$  interaction as compared with  $Ni_2(C_2B_2C)$ .

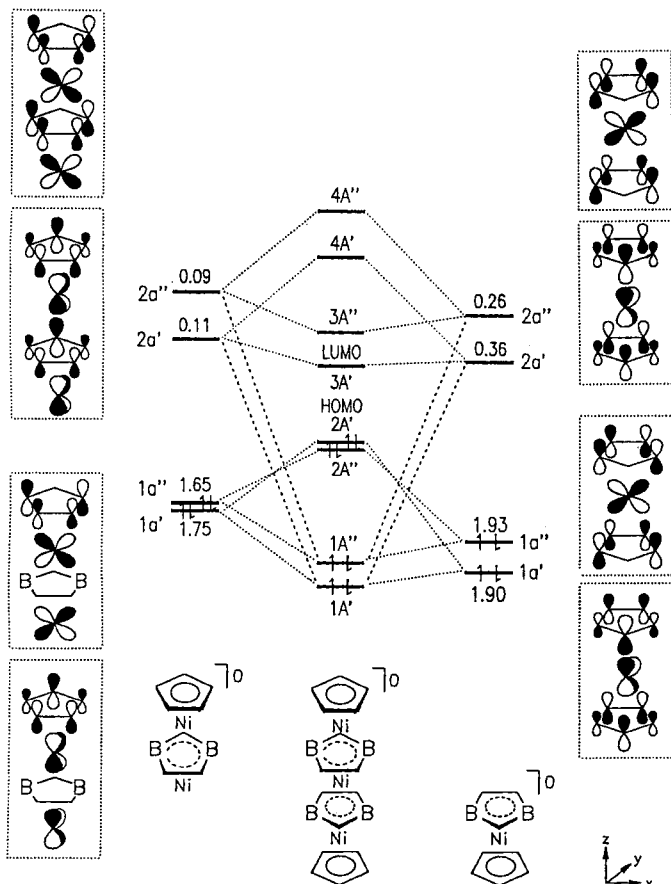


Figure 6. Simplified interaction diagram for the interaction of  $CpNi(C_2B_2C)$  with the  $CpNi(C_2B_2C)Ni$  fragment

Table 1. Total overlap population between the nickel atoms and the  $C_2B_2C$  ring in **4** ( $R^1 = R^2 = H$ )<sup>[a]</sup>

M	B1	C2	B3	C4	C5
$Ni_c$	0.028	0.040	0.035	0.040	0.035
$Ni_t$	0.065	0.062	0.067	0.050	0.049

<sup>[a]</sup>  $Ni_c$ : central nickel atom. —  $Ni_t$ : terminal nickel atom.

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## Experimental

All experiments were carried out under nitrogen, the solvents were dried according to standard procedures. — NMR: Bruker AC 200 ( $^1H$  at 200.1 MHz,  $^{13}C$  at 50.3 MHz), Jeol FX-90Q ( $^1H$  at 90

MHz,  $^{11}B$  at 28.75 MHz). — MS: MAT CH7 and VG Micromass 7070 H.

### Reaction of Sandwich Anions $2^-$ with $NiBr_2 \cdot DME$

a) To 30.0 mg (0.76 mmol) of a potassium mirror 200 mg (0.64 mmol) of **2a**<sup>[13]</sup> in 30 ml of THF was added, and the obtained mixture was stirred. Potassium reacted with **2a** to form a brown solution of the anion  $2a^-$ . Solid  $NiBr_2 \cdot DME$ <sup>[17]</sup> (300 mg, 0.97 mmol) was added, which resulted in a color change of the solution to deep green. After stirring for 12 h a black solid was filtered off, the solvent evaporated in vacuo, and the residue was dissolved in petroleum ether. Chromatography of the obtained solution on silica gel yielded 60.0 mg (30%) of orange **2a** and 30.0 mg (22%) of green **3a**.

b) To a potassium mirror (30.0 mg, 0.76 mmol) 200 mg (0.74 mmol) of **2b** in 30 ml of THF was added to afford a green solution. After the addition of 350 mg (1.13 mol) of  $NiBr_2 \cdot DME$  the color changed to deep green. The reaction mixture was stirred for 1 h, filtered, and the solvent was stripped off from the filtrate. Chromatography of the residue yielded 10.0 mg (5%) of **2b** and a mixture of **3b** and **4b** (identified by a mass spectral analysis). Distillation of the mixture gave 10.0 mg (8%) of **3b** (80–90°C/0.01 Torr) and at higher temperatures 30.0 mg (13%) of **4b**, m.p. 135–136°C. — EI MS,  $m/z$  (%): 600 (19), 598 (17) [ $M^+$ ], 393 (6) [ $3b^+$ ], 270 (100) [ $2b^+$ ].

**Tetradecker 4b from 2b and  $H_2AlOCMe_3$** : A solution of 300 mg (1.11 mmol) of **2b**<sup>[11]</sup> and 110 mg (1.08 mmol) of  $H_2AlOCMe_3$ <sup>[18]</sup> in 20 ml of THF was heated to 65°C for 2 h, whereby the solution turned green. After removal of the solvent, **2b** and **3b** were distilled (80–100°C/0.01 Torr), and the residue was chromatographed on silica gel with *n*-hexane to yield 60.0 mg (27%) of dark green **4b**, m.p. 135–136°C (from hexane). —  $^1H$  NMR ( $C_6D_6$ ):  $\delta$  = 4.90 (s, 10H), 3.26 (s, 2H), 1.9 (m, 8H), 1.27 (t, 12H), 0.67 (s, 12H). —  $^{11}B$  NMR ( $C_6D_6$ ):  $\delta$  = 16.3. —  $C_{28}H_{44}B_4Ni_3$  (600.0): calcd. C 55.15, H 7.36; found C 56.05, H 7.39.

**Tetradecker 4d from 2c and  $AlH_3$** : To a solution of 700 mg (2.12 mmol) of **2c**<sup>[19]</sup> in 20 ml of  $Et_2O$  at  $-60^\circ C$  freshly prepared  $AlH_3$ <sup>[20]</sup> (4.20 mmol) in  $Et_2O$  was added. An orange-brown solid formed which dissolved at room temp. A color change to deep green and the formation of a green-black solid occurred. After filtration the solvent was removed from the filtrate and the green triple-decker distilled at 90–100°C/0.01 Torr; yield: 20.0 mg (5%) of **3d**, m.p. 116–117°C. — EI MS,  $m/z$  (%): 365 (60) [ $M^+$ ], 297 (21), 281 (18), 266 (16), 242 (33) [ $2d^+$ ], 123 (38) [ $C_3H_5Ni^+$ ].

The black distillation residue was dissolved in petroleum ether (40–60°C) and chromatographed on silica gel. With petroleum ether/toluene a deep green fraction was obtained, from which black-green crystals of **4d** [60.0 mg (11%)] were isolated; m.p. 134–135°C. — FD MS,  $m/z$  (%): 544 (100), 542 (81) [ $M^+$ ]. — EI MS,  $m/z$  (%): 542 (2.4) [ $M^+$ ], 242 (12) [ $2d^+$ ], 167 (52), 149 (100). —  $^1H$  NMR ( $C_6D_6$ ):  $\delta$  = 4.94 (s, 10H), 1.84 (m, 8H), 1.56 (t, 12H); signals of  $B_2CH$  and  $BH$  not found. —  $^{11}B$  NMR ( $C_6D_6$ ):  $\delta$  = 5.6. — IR (Nujol):  $\tilde{\nu}$  = 2500  $cm^{-1}$  (B–H). —  $C_{24}H_{36}B_4Ni_3$  (543.9): calcd. C 53.00, H 6.67; found C 52.79, H 6.76.

**Tetradecker 4e from 1e and  $[(C_5H_5)Ni(CO)]_2$** : A solution of 0.18 g (0.60 mmol) of  $[(C_5H_5)NiCO]_2$ <sup>[21]</sup> and 0.27 g (1.70 mmol) of **1e** in 30 ml of toluene was heated for 2 h to 125°C, whereby the color changed from red-brown to deep green. Toluene was removed in vacuo and the residue dissolved in hexane. The obtained solution was chromatographed on silica to furnish 2 mg of yellow **2e**. Using toluene, we obtained a green fraction consisting of traces of **3e** and **4e**. 100 mg (10%) of **4e** was recrystallized from pentane (m.p. 160–161°C).

Table 2. Crystal data of **4d** and **4e**

	<b>4d</b>	<b>4e</b>
formula	C <sub>24</sub> H <sub>36</sub> B <sub>4</sub> Ni <sub>3</sub>	C <sub>30</sub> H <sub>36</sub> B <sub>4</sub> Ni <sub>3</sub>
mol wt	543.9	615.9
crystal system	monoclinic	monoclinic
Space group	P2 <sub>1</sub> /a	P2 <sub>1</sub> /n
a [Å]	11.098(2)	9.696(9)
b [Å]	12.223(1)	17.476(15)
c [Å]	9.600(1)	34.20(2)
β [°]	96.15(1)	92.22(7)
V [Å <sup>3</sup> ]	1294.7	5790
Z	2	8
D <sub>calc</sub> [gcm <sup>-3</sup> ]	1.40	1.41
μ [cm <sup>-1</sup> ]	20.8	18.7
cryst.dimens [mm]	0.3x0.5x0.6	0.1x0.3x0.5
transmission, min.max.	0.63-0.75	0.63-1.00
2θ <sub>max</sub> [°]	50	48
diffractometer	Stoe 2-circle (ω-scan, Mo Kα)	Stoe 4-circle (ω-scan, Mo Kα)
reflections		
measured	2336	9424
observed	2070 (I > σ <sub>I</sub> )	4191 (I > 2σ <sub>I</sub> )
hkl-range	14, 14, ± 13	± 11, 19, 38
refinement		
anisotropic	Ni, C, B	Ni
isotropic	H	C, B, H
no. of parameters	196	433
R	0.036	0.064
R <sub>w</sub>	0.041	0.059
max.residual electron density [e Å <sup>-3</sup> ]	0.3	0.5

**2e**: <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>): δ = 7.60–7.20 (m, 4H), 4.45 (s, 5H), 1.50 (s, 3H), 1.25 (s, 6H). – <sup>11</sup>B NMR (C<sub>6</sub>D<sub>6</sub>): δ = 37. – EI MS, m/z (%): 278 (100) [M<sup>+</sup>].

**3e**: EI MS, m/z (%): 401 (100) [M<sup>+</sup>], 335 (90) [M<sup>+</sup> – C<sub>5</sub>H<sub>6</sub>].

**4e**: <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>): δ = 7.1–6.9 (m, 8H), 3.02 (s, 10H), 2.33 (s, 6H), 0.07 (s, 12H). – C<sub>30</sub>H<sub>36</sub>B<sub>4</sub>Ni<sub>3</sub> (616.0): calcd. C 58.50, H 5.89; found C 58.76, H 5.93.

*X-Ray Structure Determination of 4d and 4e*<sup>[22]</sup>: Crystal data are given in Table 2. The structures were solved by Patterson and difference Fourier maps and refined by least-squares methods. For **4d** non-hydrogen atoms were refined anisotropically, the hydrogen atoms directly bound to the heterocycle and to the cyclopentadienyl ring were located in a difference Fourier map and refined isotropically, the hydrogen atoms of the ethyl groups were included in calculated positions or as part of a rigid group. For **4e** only the Ni atoms were refined anisotropically. The cyclopentadienyl rings were refined as rigid groups. Hydrogen atoms were included in calculated

positions or as part of a rigid group. SHELX76 and SHELXS86<sup>[23]</sup> were used for all calculations.

- \* Herrn Prof. Dr. Heinrich Nöth zum 65. Geburtstag gewidmet.
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[15/93]