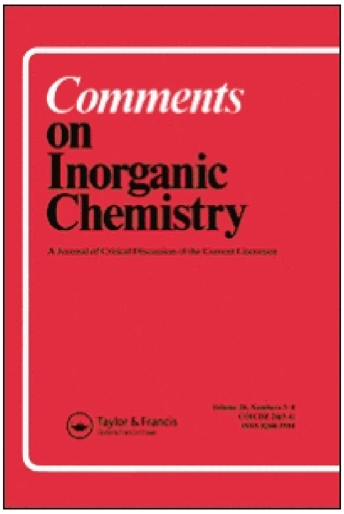

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BN-Perturbed Metallocenes

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BN-Perturbed Metallocenes

1,2-azaborolinyl systems (Ab) are derived from the well-known C_5H_5 ring (Cp) by substitution of two C atoms by the isoelectronic BN group. Like Cp, the Ab rings form a variety of sandwich compounds with transition metals. The BN-perturbation causes various structural consequences in the complexes. Due to the prochiral character of the C_3BN ring, diastereoisomers are formed. Depending on the electron configuration of the metal, slip distortions are observed. Electron-rich metals such as Co or Ni avoid contact with the donor atom N, electron-poor elements like Ti or V avoid contact with the acceptor B. 1,2-azaborolinyl sandwich complexes can therefore act as model compounds to study the metal behavior in sandwich structures depending on the electron configuration.

INTRODUCTION

Electron counting in the metallocene series $(\eta^5\text{-}C_5H_5)_2M$, (Cp_2M), with M = V, Cr, Mn, Fe, Co, and Ni results in 15–20 electrons for the metals. The ideal 18-electron configuration is only found when M = Fe. Nevertheless, all of these sandwich complexes (with the exception of the polymeric Cp_2Mn) possess essentially the same structure and can differ only in the staggered or eclipsed arrangement of the Cp rings.[1-6] However, the metal atoms are all considered to be located directly between the rings. This seems to be reasonable for the 15–18 electron complexes, but the question arises why Co and Ni do not avoid the 19 and 20 electron configuration by a slip distortion. This question has been investigated frequently. The increasing metal–ring distances and the decreasing metal–ligand bond

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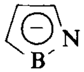
dissociation energies, on going from ferrocene to nickelocene, are due to the filling of the antibonding e_{1g}^* orbitals.[7,8] This causes a reduced covalent character of the M–Cp bond and favors the pentahapto arrangement of the rings, compared with a slip distortion.

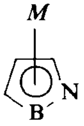
Substitution of a C_2 unit in a Cp ring by the isoelectronic BN group leads to the so-called 1,2-azaborolinyl ring systems. They usually are utilized as lithium salts to prepare 1,2-azaborolinyl sandwich and half-sandwich complexes.

cyclopentadienyl anion



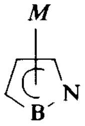
1,2-azaborolinyl anion

The replacement of two carbon atoms by BN necessarily disturbs the electronic standards, as the difference in electronegativity between N (3.0) and B (2.0) avoids a complete delocalisation of the π electrons: the 1,2-azaborolinyl rings therefore possess a donor atom (N), an acceptor atom (B), and a π allyl part. The coordination of an 1,2-azaborolinyl ring to a metal atom allows this atom to select the best position corresponding to its electron configuration:



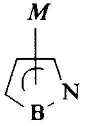
η^5

1



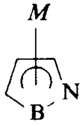
η^4

2



η^3

3



η^4

4

In the pentahapto arrangement **1**, the C, N, and B atoms all interact with the metal atom to the same extent. The influence of the transition metal makes the difference between B and N indistinct, i.e., the aromatic character of the ring is mainly preserved, despite the BN substitution. Here, the azaborolinyl ring really acts as an isoelectronic and isosteric analog of the cyclopentadienyl ligand. In **2** and **3** the

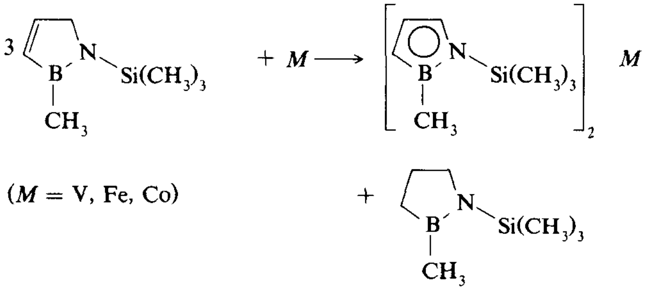
N atoms avoid contact with the metal. This is to be expected when electron-rich metals are used. **4** symbolizes a complex type where only the allyl part and the N atom interact with the metal, whereas the acceptor atom B does not participate in the ligand–metal bonding. Extremely electron-poor transition metals should prefer this variant. **1–4** of course symbolize extreme cases but document the versatility of the 1,2-azaborolinyl system. They should give us much more information about the electronic requirements of transition metals than the classical metallocenes do.

SYNTHESES

Two different methods have been used to synthesize 1,2-azaborolinyl sandwich complexes (Ab_2M):

1. Metal Atom Synthesis

Neutral 1,2-azaborolines react with transition metal atoms at $-130\,°C$ and 10^{-4} Torr in methylcyclohexane to give Ab_2M complexes[9]:

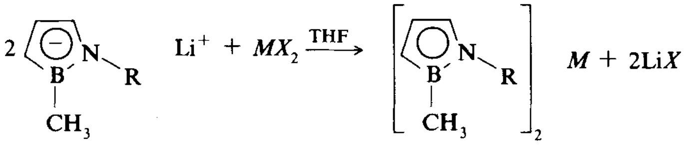


(1)

As can be seen from Eq. (1), the hydrogen, removed from two neutral 1,2-azaboroline molecules, hydrogenates another azaboroline molecule to form the saturated 1,2-azaborolidine. The reactions occur quantitatively with respect to the 1,2-azaborolines, but isolation by sublimation or chromatography reduces the yields to 10–20%.

2. From LiAb and MX_n

A more common method consists in the reaction of 1,2-azaborolinyllithium salts with transition metal halides[10–13]:

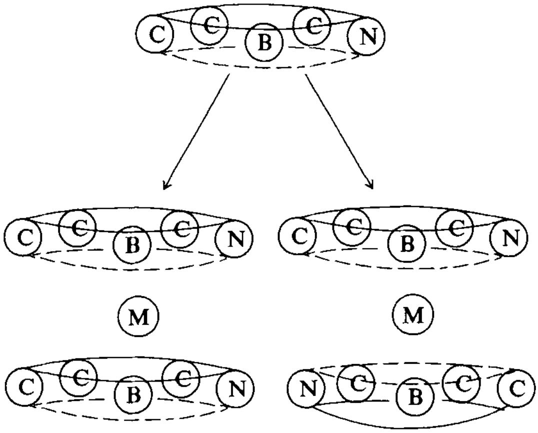

(2)

(M=V, Cr, Mn, Fe, Co, Ni, Ru, Os)

By this method the 3*d* elements from vanadium to nickel as well as the 4*d* and 5*d* elements ruthenium and osmium could be used successfully. The yields vary from 10 to 80%. Reactions with TiX_4 (X = Cl, Br) and VCl_3 result in the halogeno complexes Ab_2TiX_2 and Ab_2VCl.[14] It is to be expected that metals other than those tested up to now may generate sandwich complexes.

STRUCTURE AND BONDING

The most striking change on going from the C_5 to the C_3BN systems is, ignoring electronic factors, the loss of the fivefold symmetry. This results in important consequences for the geometry of the sandwich compounds. The prochiral character of the azaborolinyl rings leads to diastereoisomers, for the rings can be coordinated by equivalent or by different sides: In (a) below the rings use different sides for the coordination, leading to the atomic sequence BN/BN in both ligands. In (b) the equivalent faces interact with the metal and cause the BN/NB sequence. If there are no major differences in energy between the BN/BN and the BN/NB isomers, both should be generated with the same probability. Indeed, the diastereoisomers are formed in an approximate 1 : 1 ratio.



BN/BN

(a)

BN/NB

(b)

Further variations in structure are to be expected if we consider the orientations of the rings to each other. Each of the diastereoisomers can in principle form five eclipsed and five staggered conformers, respectively. All together up to 20 different structures could exist. The experimental results however show that each diastereoisomer forms either one staggered or one eclipsed conformational isomer.*

Besides the symmetry of the C_3BN ring framework, the differences in electronegativity between B and N play another structure-determining role. In the following, the structures of some selected 1,2-azaborolinyl sandwich complexes shall be discussed to demonstrate the structural specialities, compared with the metallocenes. In Fig. 1 the molecular structures of the two dark-red isomers of bis(2-methyl–1-trimethylsilyl–η^5–1,2-azaborolinyl)iron[11] are shown in side view and looking through the rings. Both in the BN/BN (a) and in the BN/NB isomer (b), the rings are coordinated in a pentahapto manner to the central Fe atom, following the structure type **1**. The

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*The prochiral character of the 1,2-azaborolinyl rings also plays an important role in half-sandwich complexes AbML_n which are not discussed here. Instead of diastereoisomers, pairs of enantiomers are formed. They are observed in the crystal structures of all investigated compounds.[15,16]

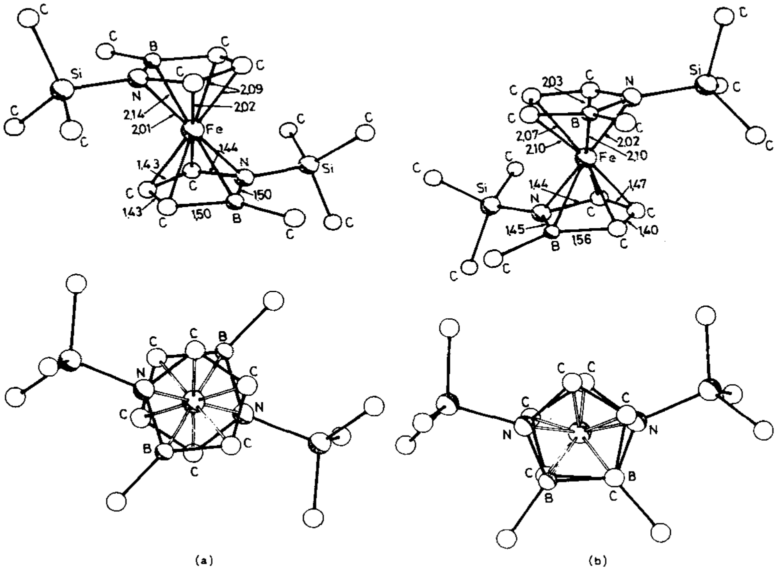


FIGURE 1 The molecular structure of the diastereoisomers of bis(2-methyl-1-trimethylsilyl-η^5-1,2-azaborolinyl)iron in side view and looking through the rings. (a) BN/BN isomer, (b) BN/NB isomer.

difference in the Fe–B and Fe–N bond lengths corresponds to the atomic radii of B and N.

Isomer (a) is one of the five possible staggered conformers with opposite positions of the ring ligands. This could lead to the presumption that steric effects may influence the stability of the conformers. This question cannot however be answered at present because other examples of azaborolinyl sandwich complexes show different structural behavior. Isomer (b) with the BN/NB sequence shows an eclipsed arrangement of the rings. Again only one conformer is found in the solid state although five forms could be possible.

The ^{1}H NMR spectra of both the BN/BN and the BN/NB isomer show three characteristic signals for the three ring protons[11] so that in the original solutions the existence of only two different isomers can be proven. If there is any ring motion in solution, this cannot be established by NMR spectroscopy, as the spectra do not change their pattern at low temperatures (−90 °C). It is assumed that the rings do rotate, but when crystallizing only one conformer is realized.

The results of the ^{11}B NMR measurements of the Ab_2Fe complexes are in agreement with the pentahapto arrangement of the azaborolinyl rings.[17,18] In the sense of a frequently confirmed concept, describing the interaction of BN groups with transition metals,[19,20] the ^{11}B signals of Ab_2Fe sandwich complexes show a characteristic high-field shift of about 15 ppm going from the uncoordinated state (in LiAb) to the π complex. This high-field shift is explained in all comparable cases by the metal–boron interaction, leading to a better electronic shielding of the B atoms, compared with the uncoordinated state (see below).

The x-ray structure investigations of the paramagnetic, green bis(2-methyl-1-trimethylsilyl–η^5–1,2-azaborolinyl)cobalt[11] again prove the existence of two isomers having BN/BN and BN/NB atomic sequences. As in Ab_2Fe, the BN/BN isomer has a staggered and the BN/NB isomer an eclipsed arrangement of the rings.

Let us now consider the structure aspects in bis(1-*tert*-butyl–2-methyl–η^5–1,2-azaborolinyl)cobalt[21] in Fig. 2. In agreement with the complexes discussed above, we again find a pair of diastereoisomers with BN/BN (a) and BN/NB (b) sequences, respectively; but, in contrast to the aforementioned cases, the BN/NB isomer (b) has not eclipsed but rather staggered rings, although the B–CH_3 groups are relatively close together. As already discussed, the reasons for the formation of special conformers in the solid state are still not clear, whereas the existence of the diastereoisomers can be regarded as a consequence of the prochiral character of the rings.

All the cobalt complexes investigated up to now show a typical structural property, compared with the iron and also with the vanadium sandwich complexes: the rings are slipped and the Co atoms are shifted by about 0.2 Å from the centers of the rings in a direction that reduces the distance to the N atom. By doing this, the Co–B and Co–N distances become almost identical, though the Co–B bond distances should be longer due to the larger atomic radius of the B atom. This signifies an elongation of the Co–N bond. From Fig. 4 this slip distortion clearly can be seen.[12] Thus, Ab_2Co sandwich complexes are related to the structure type **2**, even if the pure η^4 coordination is not established.

In Fig. 3 the molecular structure of the BN/BN isomer of bis(1-*tert*-butyl–2-methyl–η^3–1,2-azaborolinyl)nickel[12] is shown. We recognize such a strong slip distortion (0.45 Å) that the complex is to

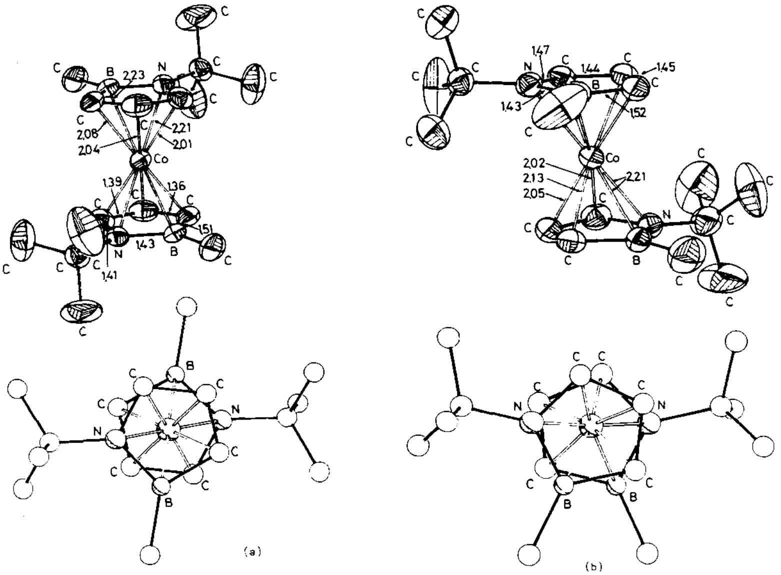


FIGURE 2 The molecular structure of the diastereoisomers of bis(1-*tert*-butyl-2-methyl-η^5-1,2-azaborolinyl)cobalt in side view and looking through the rings. (a) BN/BN isomer, (b) BN/NB isomer.

be formulated as an η^3 allyl complex. The side view in Fig. 4 demonstrates this extreme slip in an impressive manner. The bond lengths again best explain the situation. The Ni atom tries to avoid contact with the N atom completely, leading to a Ni–N distance which is longer than the Ni–B distance. Nevertheless, the Ni–B distance indicates no concrete interaction. The BN group just acts as a clasp for the π allyl group. These structural results are again supported by the ^{11}B NMR data. Due to the lack of any notable B–Ni interaction, the ^{11}B signal remains constant (27 ppm) compared with that in LiAb, as the B atom is not influenced by the metal. Hence, structure type **3** is present in this case.

As a last example of Ab_2M compounds, a ruthenium complex[13] will be mentioned. The molecular structure of the BN/BN isomer is shown in Fig. 5. As in Ab_2Fe, the metal atom is positioned above and below the ring centers, but the rings have lost their coplanar arrangement to form an interplanar angle of 8.6°. This must be due to the repulsion of the N-*tert*-butyl group in one ring and the B–CH_3 group in the other. A parallel arrangement of the rings would

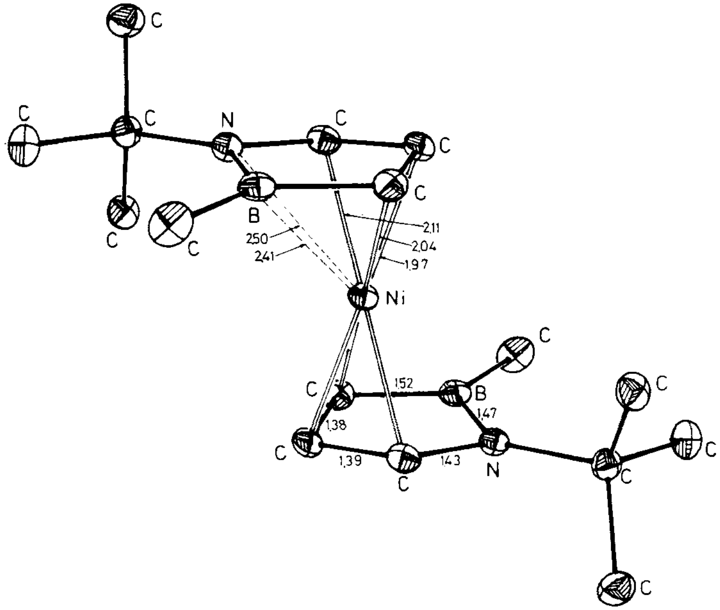


FIGURE 3 The molecular structure of bis(1-*tert*-butyl-2-methyl-η^3-1,2-azaborolinyl)nickel.

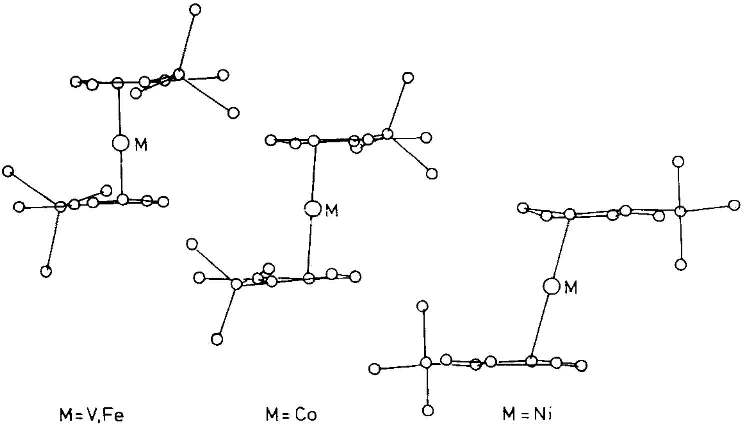


FIGURE 4 The side view of some bis(1,2-azaborolinyl)transition metal sandwich complexes showing the slip distortions.

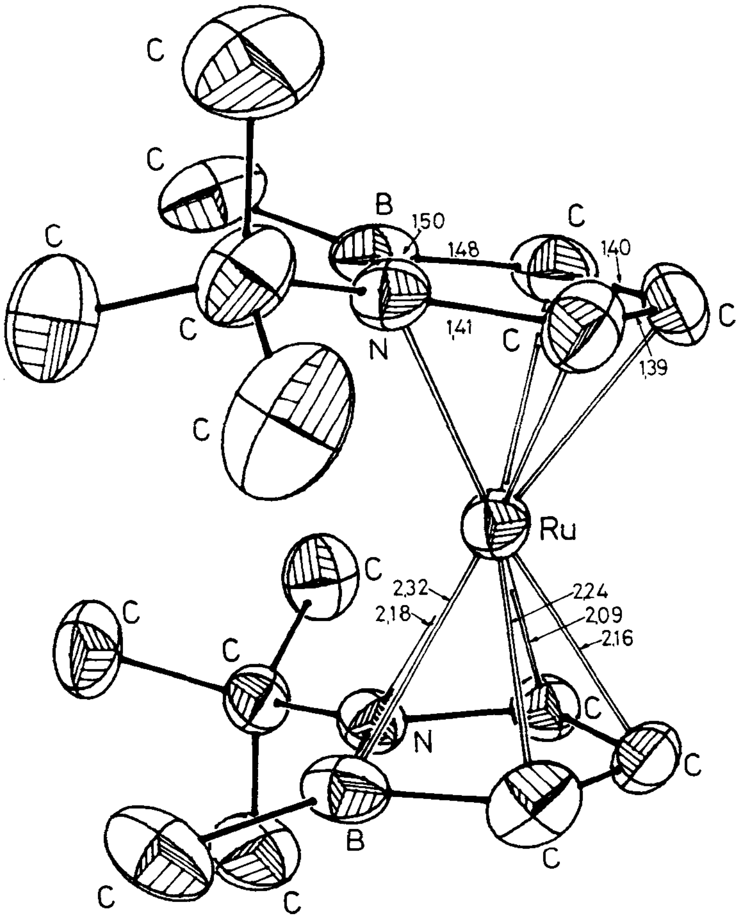


FIGURE 5 The molecular structure of bis(1-*tert*-butyl-2-methyl-η^5-1,2-azaborolinyl)ruthenium.

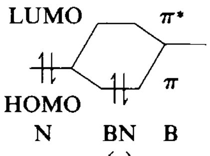
force H · · · H distances shorter than the sum of the van der Waals radii. The question of why the rings do not prefer another arrangement to avoid the ligand repulsion like in Ab_2Fe or Ab_2Co is unanswered at present. It seems as if electronic effects should play a dominant role here. Further investigations should clear up the problem.

In the Introduction we asked why the 19 and 20 electron complexes

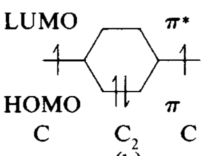
Cp_2Co and Cp_2Ni do not avoid the unfavorable electron configuration by shearing. The BN derivatives are able to do this very easily, as we have seen. The perturbation by the BN group, consisting of an electronegative and an electropositive element, allows the metal to differentiate and to find the best position between the rings.

Slip distortions are also observed in metallocarboranes, such as $[(C_2B_9H_{11})_2M]^{n-}$. Metals with more than 7d electrons cause a slip, bringing the metal away from the carbon atoms.[22,23] Recently Dunitz and Seiler performed an x-ray structure of nickelocene at 101 K and found different Ni–C distances, though the Cp rings are completely planar.[6] These differences in bond length are due to a displacement of the Ni atom of 0.03 Å from the centers of the rings. This is only about a tenth of the slip in Ab_2Ni, but is nevertheless of great interest. Crystal packing effects favor the higher symmetry of the molecule. Therefore the distortion is believed to be even more extensive in the gas phase.[6] The small dimension of the distortion in nickelocene is understandable. A larger slip extension would disturb the aromatic character. Naturally this is easier in azaborolinyl rings as they are disturbed aromatic systems. Nevertheless, the loss of aromaticity in Cp rings has been observed occasionally, e.g., in $Cp_2Mo(W)(CO)_2$,[24] having an η^5 and an η^3 Cp ring. The reason for this is believed to be found in a greater degree of covalent character of the M–Cp bond, compared with Cp_2Co or Cp_2Ni. This seems to be a questionable argument. It is more likely that the distortion of the sandwich by the CO ligands could be responsible for the behavior observed.

Finally, two 1,2-azaborolinyl complexes which have gained importance to support the bonding model generally used to describe transition metal–BN complexes will be discussed. Isoelectronic and isosteric behavior of the BN group in coordinated boron–nitrogen compounds, compared with the C_2 unit, demands a corresponding donor–acceptor relationship. In contrast to carbon systems where donor and acceptor capabilities are equivalent for the C atoms, these can be separated in BN systems. A very simple description of the π MO's in BN and in carbon systems elucidates the situations best:



(a)



(b)

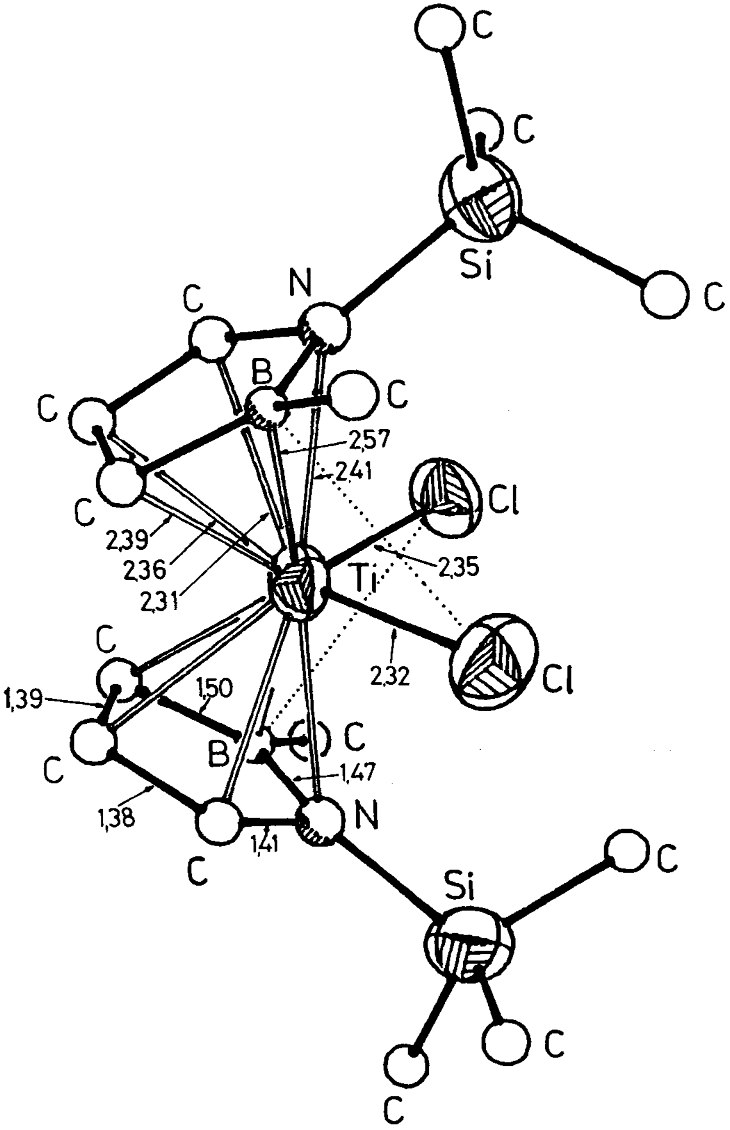


FIGURE 6 The molecular structure of bis(2-methyl–1-trimethylsilyl–η^5–1,2-azaborolinyl)titaniumdichloride.

The difference in electronegativity between B and N gives the occupied π MO more N character, but the empty π^* MO more B character. In other words, donor (HOMO) and acceptor (LUMO) character are considerably distributed to nitrogen and boron. In (b) the carbon atoms possess equivalent parts of HOMO and LUMO properties. Therefore, back-bonding capacities of transition metals will influence mainly the acceptor atom B. If the back-bonding is strong, the B atom will get a higher electron density and *vice versa*. These relationships can easily be observed by ^{11}B NMR spectroscopy. In the case of strong back-bonding, the ^{11}B signal will get a high-field shift, a low-field shift should occur if the metal is electron poor and not capable for good back-donation. In all sandwich complexes discussed up to now, a high-field shift has been registered.

The 1,2-azaborolinyl complexes Ab_2TiCl_2 and Ab_2VCl formally contain d^0 and d^2 metals. Indeed, the ^{11}B NMR spectra support the bonding model. Bis(2-methyl-1-trimethylsilyl-η^5-1,2-azaborolinyl)titaniumdichloride shows an ^{11}B signal at ~41 ppm, the corresponding Ab_2VCl complex even at 57 ppm. This signifies low-field shifts of about 14 and 30 ppm, respectively. A further peculiarity is observed in the x-ray structures of both compounds (Figs. 6 and 7). In both cases the rings have such an arrangement that the boron atoms can make contact with the *M*-bonded chlorine ligands. This helps the B atoms to increase their electronic shielding and to partially equalize the lack of considerable metal–ligand back-bonding. In spite of these B · · · Cl contacts, the electronic saturation of the B atoms is smaller than in LiAb.

An additional effect demonstrates the unfavorable B–*M* interactions: in both molecules the rings are folded in a way to lengthen the B–*M* contacts. These conditions are reminiscent of structure type **4**.

CONCLUSIONS

The present results in 1,2-azaborolinyl sandwich complex chemistry can be summarized by the following six points:

1. The substitution of C_2 units by BN groups in metallocenes allows the formation of diastereoisomers, due to the prochiral character of the C_3BN ring framework.

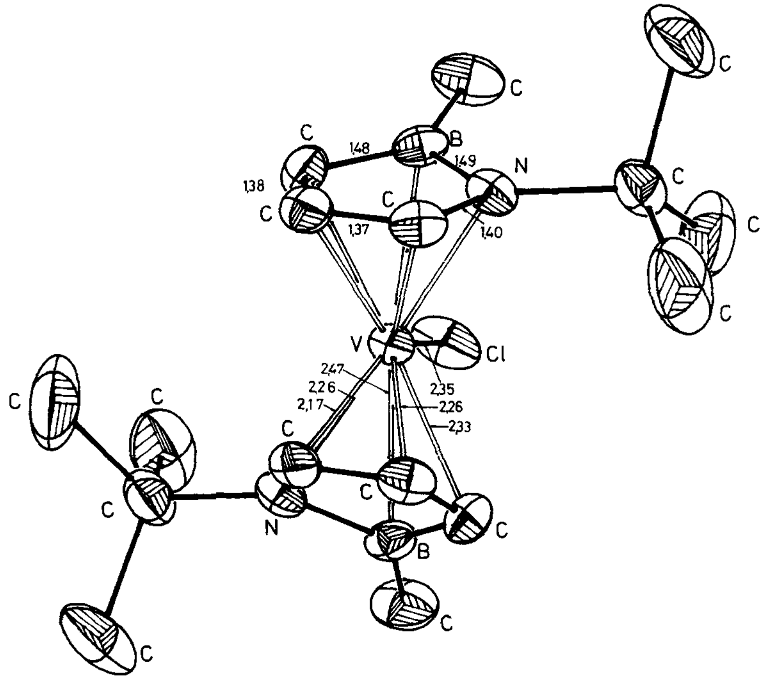


FIGURE 7 The molecular structure of bis(1-*tert*-butyl-2-methyl-η^5-1,2-azaborolinyl)vanadiumchloride.

2. Each isomer forms only one conformer in the solid state. The reasons for the formation of either one eclipsed or one staggered conformer are still not clear. Not only crystal packing but also electronic effects may be responsible.

3. The differences in electronegativity between N and B enable the metal atoms to select optimal positions between the rings depending on their electron configuration. Therefore, slip distortions are observed in Ab_2Co and Ab_2Ni.

4. In agreement with bonding models proposed in earlier work, the B atoms in η^5 coordinated rings are better shielded than in the uncoordinated ligands.

5. Metals which are incapable of considerable back-bonding, e.g., V(II) or Ti(IV), cause an opposite effect. The lack of electron density

in Ab_2TiCl_2 and Ab_2VCl leads to B · · · Cl interactions to partially increase the electron density of boron.

6. 1,2-azaborolinyl sandwich complexes prove to be excellent objects to study metal behavior in sandwich compounds. In contrast to classical metallocenes, 1,2-azaborolinyl rings can offer the metal atoms "individual" conditions.

Acknowledgments

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