Borabenzene Derivatives, 31[‡]

Enantiomerically Pure Complexes of Manganese, Iron, and Zirconium with Pinene-Fused Boratabenzene Ligands – Structures of *exo*-FeCp*($C_{13}H_{17}BNMe_2$) and *exo*,*exo*-$ZrCl_2(C_{13}H_{17}BNMe_2)_2$

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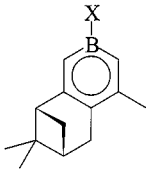
Complexes of pinene-fused boratabenzene ligands [(1*R*,9*R*)-6,10,10-trimethyl-4-boratatricyclo[7.1.1.$0^{2,7}$]undeca-2,4,6-trienes] $C_{13}H_{17}BX$ (with **a**: X = NMe_2; **b**: X = OMe; **c**: X = Me) are described. The lithium salt Li($C_{13}H_{17}BNMe_2$) [Li(**1a**)] reacts with [Cp*Fe(NCMe)$_3$]PF_6 and with $Mn(CO)_3Br(py)_2$ to give diastereomeric mixtures FeCp*($C_{13}H_{17}BNMe_2$) (**4a**) and $Mn(CO)_3(C_{13}H_{17}BNMe_2)$ (**7**). The mixture **4a** undergoes solvolysis in methanol to produce methoxy compounds **4b**, which in turn react with LiMe in Et_2O to give methyl derivatives **4c**. The lithium salts Li($C_{13}H_{17}BX$) [Li(**1a**–**c**)] react with $ZrCl_4$ in toluene or Et_2O to give *exo*,*exo*-$ZrCl_2(C_{13}H_{17}BX)_2$ complexes (**8a**–**c**). The dimethyl derivative *exo*,*exo*-$ZrMe_2(C_{13}H_{17}BNMe_2)_2$ (**9**) can also be prepared from **8a**/LiMe in Et_2O. NOE difference spectra have been analyzed to determine the configurations of the diastereomers and to establish a chemical shift criterion for assessing the configuration of the metal–ligand coordination. An independent confirmation of the product stereochemistries has been obtained by single-crystal X-ray structure determinations of *exo*-**4a** and **8a**.

Introduction

In previous work, we developed a synthetic route to enantiomerically pure, pinene-fused lithium boratabenzenes Li(**1a**–**c**).[1] In this paper, we describe the first transition metal complexes of the ligands **1a**–**c**.



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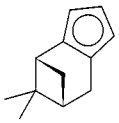
a: X = NMe_2
b: X = OMe
c: X = Me

The motivation for this research stems from analogous cyclopentadienyl chemistry. Chiral metallocenes[2] have been employed as catalyst precursors in stereoregular olefin polymerization,[3] in enantioselective synthesis,[4] and as auxiliary ligands in asymmetric catalysis.[5,6]

The chirality of a metallocene may have different origins.[7] Annulated chiral cyclopentadienyl ligands derived from the chiral pool are of particular interest. They promise well-defined asymmetry and stereocontrol. Using enantiomerically pure starting materials, enantiomerically pure complexes are obtained. Early and important examples are the camphor-derived CamCp ligand (**2**)[8] and the pinene-derived PinCp (**3**).[9] Finally, it should be noted that the ligands **2** and **3** as well as **1a**–**c** possess diastereotopic faces, the more crowded *endo* face with the dimethylmethylene bridge, and the less crowded *exo* face with an ethylene bridge in the case of **2** and a methylene bridge in the case of **1** and **3**. As a consequence, complex formation with these ligands will usually produce mixtures of *exo* and *endo* diastereomers.



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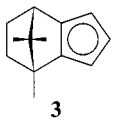

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Results and Discussion

(Pentamethylcyclopentadienyl)iron Complexes

First we describe complexes of the ligands **1a**–**c** with the FeCp* fragment. The simpler 1-methylboratabenzene derivative Fe(C_5H_5BMe)Cp*[10] has previously been synthesized in near quantitative yield from [Cp*Fe(NCMe)$_3$]PF_6[11] and Li(C_5H_5BMe).[12] Using the same general method,[13] [Cp*Fe(NCMe)$_3$]PF_6 was treated with the 4-dimethylamino compound Li(**1a**) in the form of its TMEDA adduct[1b] to give a mixture of the two diastereomers *exo*-FeCp*(**1a**) [≡ *exo*-**4a**] and *endo*-FeCp*(**1a**) [≡ *endo*-**4a**] as a deep-red crystalline solid in near quantitative yield (97%). The *exo* isomer was invariably formed preferentially, along with 10–25% of the *endo* isomer. Pure *exo* isomer *exo*-**4a** could be obtained by fractional crystallization from hexane in acceptable yield (50%). In methanol solution, the diastereomeric mixture **4a** slowly underwent solvolysis (60 °C, 24 h) to give, after workup, a corresponding mixture of the methoxy compounds **4b** as a red oil (100%). Treatment of **4b** with

[‡] Part 30: G. E. Herberich, X. Zheng, J. Rosenplänter, U. Englert, *Organometallics* **1999**, *18*, 4747-4752.

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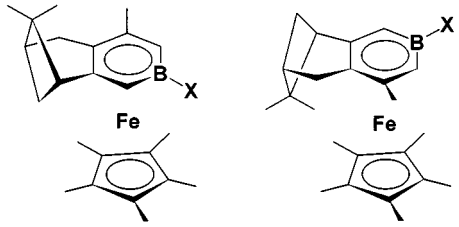
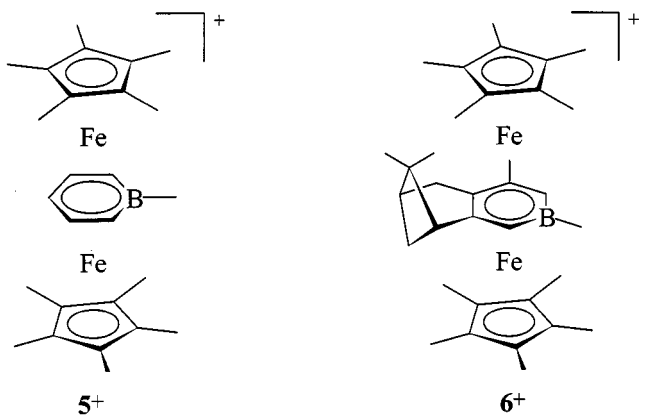


LiMe in Et_2O led to a smooth substitution to afford a mixture of the methyl compounds **4c** as a slowly solidifying deep-red oil (97%).

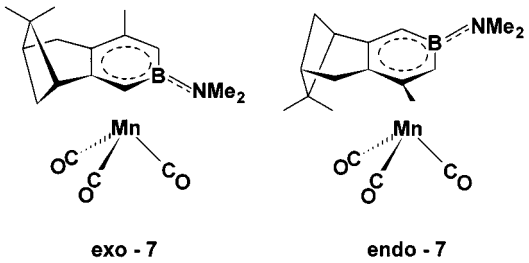
Careful analysis of the NMR spectra in combination with NOE difference spectra led to the conclusion that the major isomer in these mixtures **4a**–**c** was the *exo* diastereomer. This assignment was later confirmed by an X-ray structure determination of *exo*-**4a** (see below).

A fully satisfying preparative-scale separation of the diastereomers could not be achieved in any of the three cases. However, in the case of **4c**, which has an unreactive substituent at boron, a catalyzed isomerization could be observed. In an NMR tube, the diastereomeric mixture **4c** was dissolved in [D_6]acetone and treated with a catalytic amount of [Cp*Fe(NCMe)$_3$]PF_6 at ambient temperature; within a few hours complete isomerization to the clearly more stable *exo*-**4c** isomer had occurred. This observation can readily be explained. The sterically less crowded Fe(C_5H_5BMe)Cp* reacts with [Cp*Fe(NCMe)$_3$]PF_6 in dichloromethane with reversible formation of the triple-decker complex [Cp*Fe(μ-C_5H_5BMe)FeCp*]PF_6 [≡ (**5**)PF_6].[10] With the bulkier pinene-fused boratabenzene ligand **1c**, the corresponding triple-decker species $\mathbf{6}^+$ should be highly destabilized. The equilibrium of the triple-decker formation will be shifted to the left and the concentration of the triple-decker cation will be too low for its detection by NMR. On the other hand, we may assume that $\mathbf{6}^+$ is still energetically accessible, thus providing a low-energy isomerization pathway. This type of equilibration of diastereomers was first established by ourselves in the case of the diastereomeric isodicyclopentadienyl (Idcp) complexes *endo*- and *exo*-Ru(Icdp)Cp*.[14]



A Tricarbonylmanganese Complex

The tricarbonylmanganese complex Mn(CO)$_3$(**1a**) [≡ **7**] was chosen as a further example of a late transition metal complex. In reactions with *C*-unsubstituted lithium 1-aminoboratabenzenes, the complex [Mn(CO)$_3$(NCMe)$_3$]PF_6[15] has been successfully used as a source of the Mn(CO)$_3$ fragment.[16] However, treatment of the presumably much more basic[17] Li(TMEDA)(**1a**) with [Mn(CO)$_3$(NCMe)$_3$]PF_6 in THF led to protonation of $\mathbf{1a}^-$ and the pinene-fused dihydroborinine H(**1a**) (with the proton added at C-5)[1b] was isolated in near quantitative yield. We then used MnBr(CO)$_3$(py)$_2$[18] (see Experimental Section for an improved preparation); reaction with Li(**1a**) gave mixtures of the two diastereomers *exo*-**7** and *endo*-**7** as orange, light-sensitive oils.



A systematic variation of the reaction conditions[19] showed that nonpolar solvents favor the formation of *exo*-**7** (in hexane, 65 °C, 72 h; diastereomeric ratio *exo*/*endo* = 76:24), whereas in THF *endo*-**7** is obtained preferentially (65 °C, 2 h; *exo*/*endo* = 36:64). Pure *exo*-**7** could readily be obtained from mixtures **7** with high *exo*/*endo* ratios as a yellow, light-sensitive solid by two fractional crystallizations from hexane. In contrast, pure isomer *endo*-**7** could not be isolated.

Zirconium Complexes

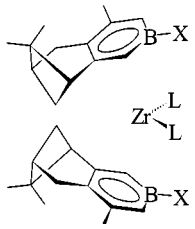
The synthesis of enantiomerically pure bis(ligand) complexes of zirconium seemed to be a particularly interesting goal. A number of simple achiral bis(boratabenzene)dichlorozirconium complexes,[20,21,22a] achiral *ansa*-,[22a] as well as some chiral *ansa*-compounds[22b] have been described. In combination with MAO, these complexes are active catalysts for olefin polymerization.[21,22]

The reaction of freshly sublimed $ZrCl_4$ with the lithium boratabenzene Li(**1a**) in toluene or diethyl ether produces the bis(ligand) complex **8a** as a blue to purple solid in a crude yield of 55%. The main by-product (20–30%) results from protonation of $\mathbf{1a}^-$ and is in fact the pinene-fused dihydroborinine H(**1a**) mentioned above. In THF, the protonation of $\mathbf{1a}^-$ becomes almost entirely predominant.

For a bis(ligand) complex, three diastereomers with *exo*,*exo*, *exo*,*endo*, and *endo*,*endo* coordination may be expected, but only the *exo*,*exo* diastereomer is found experimentally. This result is in accord with similar findings made for the analogous reaction with Paquette's pinene-fused lithium cyclopentadienide.[23]

The methoxy compound Li(**1b**) and the methyl compound Li(**1c**) also give bis(ligand) complexes, i.e. the orange compounds **8b** and **8c**, both of which also have the *exo*,*exo* configuration according to their spectral data. Loss of starting material by protonation is less significant in these cases [ca. 10% of Li(**1b**), negligible in the synthesis of **8c**], presumably because of the lower basicities of the corresponding anions.

The bis(boratabenzene)zirconium complex $ZrCl_2(C_5H_5BNiPr_2)_2$ can readily be methylated with LiMe in Et_2O to give the corresponding dimethyl derivative $ZrMe_2(C_5H_5BNiPr_2)_2$.[21a] Analogously, a solution of **8a** can be titrated with LiMe in Et_2O. The end of the titration is indicated by a color change from purple to deep-red; the dimethyl derivative **9** thus obtained can be crystallized from toluene to give small red crystals.



8: L = Cl; **a**: X = NMe_2, **b**: X = OMe, **c**: X = Me
9: L = Me, X = NMe_2

NMR Spectroscopic Distinction of Diastereomers

In the preceding paper on pinene-fused boratabenzenes, we discussed the characteristic spectroscopic features of these compounds and the assignment techniques used.[1a] In the present work, the only additional point of interest with regard to the NMR characterization is the distinction of the diastereomers and the assignment of *exo* and *endo* configurations, respectively. Selected ^{1}H-NMR data are presented in Table 1. In the case of the diastereomeric FeCp* complexes *exo*-**4a**–**c** and *endo*-**4a**–**c**, NOE difference spectra for the proton signals of the Cp* ligand and for the protons 10-Me_{endo}, and 11-H_{endo} (and to a lesser extent also 8-H_{endo} and 8-H_{exo}), respectively, can be used to assign these signals and to determine the configuration of the complex in question.

For the pairs of diastereomers of **4a**–**c**, chemical shift patterns emerge that show an unambiguous correlation with the configuration of the metal–ligand bond. The pair of manganese complexes *exo*-**7** and *endo*-**7** (for which the NOE assignment technique is not applicable) also conform to this pattern. In the case of the zirconium complexes **8a**–**c** and **9**, where only one diastereomer is found, the data (especially for the pair of methyl groups 10-Me_{exo}/10-Me_{endo} and the relatively high chemical shift values for 11-H_{endo}) indicate an *exo* configuration of the metal–ligand bond, and hence an *exo*,*exo* configuration of the complexes. These conclusions are in agreement with the results of the structure determinations described below.

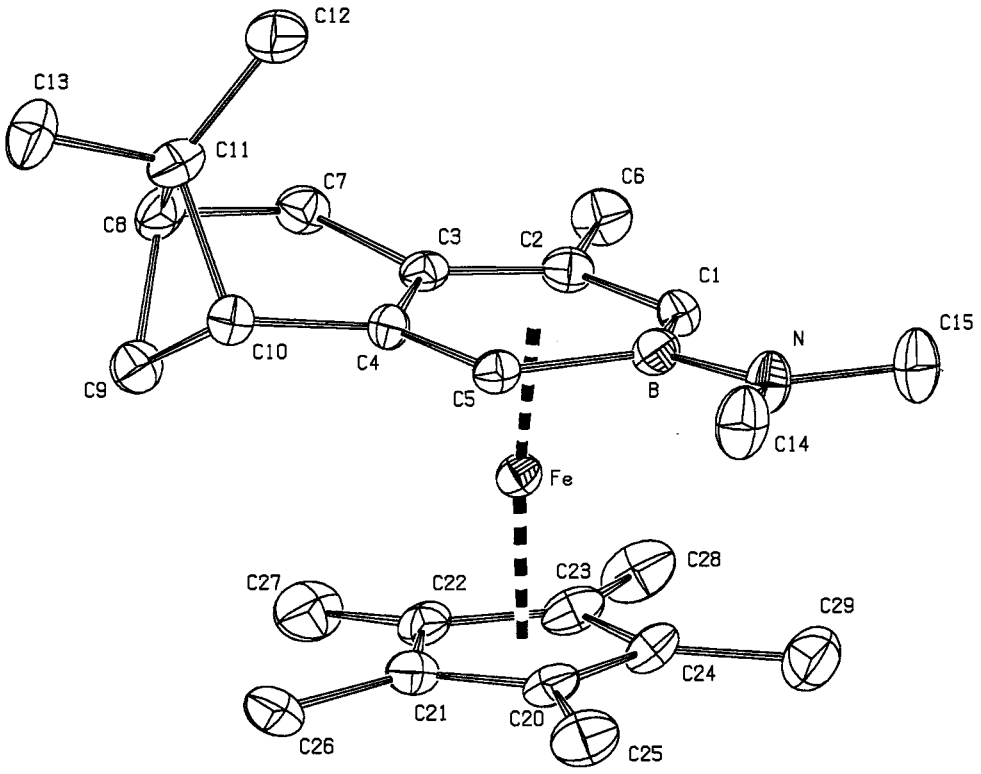


Figure 1. Molecular structure (PLATON plot, see ref.[25], at a 30% probability level) of *exo*-**4a** in the crystal; selected bond lengths [Å] for *exo*-**4a**: Fe–C1 2.121(5), Fe–C2 2.088(4), Fe–C3 2.114(4), Fe–C5 2.134(4), Fe–B 2.352(6), Fe–C(Cp*) 2.072 (av.), B–N 1.438(7), C1–B 1.519(7), C1–C2 1.409(6), C2–C3 1.413(6), C3–C4 1.435(5), C4–C5 1.397(6), C5–B 1.525(7), Fe–Cp* 1.6815(6), Fe–(C_5B) 1.5931(6)

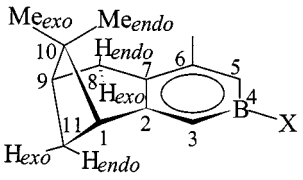


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Table 1. Selected ^{1}H-NMR chemical shift data

Compound[a]	10-Me$_{exo}$	10-Me$_{endo}$	11-H$_{exo}$	11-H$_{endo}$	8-H$_{exo}$	8-H$_{endo}$
exo-**4a**	1.32	0.60	2.58	2.10	2.63	2.25
exo-**4b**	1.29	0.56	2.56	2.04	2.59	2.20
exo-**4c**	1.28	0.51	2.56	2.04	2.62	2.20
endo-**4a**	1.30	1.66	2.39	0.75	2.24[b]	2.57[b]
endo-**4b**	1.28	1.60	2.37	0.71	2.12[b]	2.51[b]
endo-**4c**	1.28	1.60	2.35	0.66	–[c]	2.53
exo-**7**[b]	1.11	0.56	2.39	1.84	2.48	2.24
endo-**7**[b]	1.09	1.35	2.32	0.88	2.20	2.51
8a	1.33	0.56	2.37	1.83	3.30	2.65
8b	1.35	0.55	2.49	1.73	3.26	2.69
8c	1.35	0.48	2.49	1.69	3.25	2.68
9	1.35	0.67	2.33	1.22	2.97	2.79

[a] Measured in C_6D_6 for the Fe and Mn complexes and in CD_2Cl_2 for the Zr compounds. – [b] Assignments are not confirmed by NOE difference spectra. – [c] Signal obscured.

Structure of the Iron Complex *exo*-4a

A sample of pure *exo*-**4a** was recrystallized from hexane at –30 °C to give deep-red crystals of good quality. Complex *exo*-**4a** crystallizes in the chiral orthorhombic space group $P2_12_12_1$. The structure determination confirmed the *exo* configuration of *exo*-**4a** (Figure 1).

The molecule shows a typical sandwich structure. The atoms C1C5 are essentially coplanar [maximum vertical displacement of 0.021(4) Å for C3], but the aminoboranediyl group is bent away from the metal and the boron atom resides 0.191(5) Å above the C1C5 plane. There are several indications of transannular repulsive interactions. The ring–ring conformation places the methylene group between two methyl groups of the Cp* ligand and the same is true for the B–NMe_2 group. There is a marked bending of the sandwich, which results in an increased distance between the Cp* ligand and the *endo*-methylene bridge; the angle between the best Cp* plane and the best C_5B plane amounts to 5.0(1)°. The slip distortion[25] of the boratabenzene ring amounts to 0.11 Å and is smaller than that in Fe(C_5H_5BMe)Cp* (0.15 Å).[10] This detail may seem surprising, but an increase in the slip distortion would be counteracted by an increase in the transannular repulsion of the *endo*-methylene bridge. Finally, we note the relatively long Fe–B distance of 2.352(6) Å and the relatively short B–N distance of 1.438(7) Å. These features demonstrate the often documented π-interaction between the boron p_z orbital and the nitrogen lone pair.

Structure of the Bis(ligand) Zirconium Complex 8a

Crystals suitable for X-ray crystallographic analysis were obtained by crystallization of **8a** from toluene at –30 °C. Complex **8a** crystallizes in the chiral orthorhombic space group $P2_12_12_1$ and displays a bent-sandwich structure with a bending angle of 131.65(14)° (Figure 2 and 3). The front view illustrates the approximate C_2-symmetry of this complex.

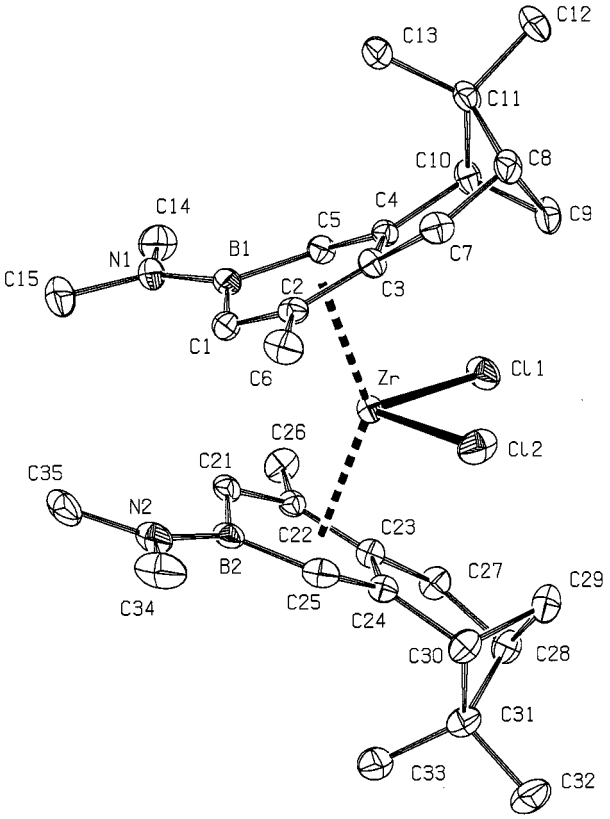

Figure 2. Side view of the molecular structure (PLATON plot, see ref.[25]) of **8a** in the crystal; selected bond lengths [A] and angles [°] for **8a**: Zr–Cl1 2.437(1), Zr–Cl2 2.428(1), Zr–C1 2.642(3), Zr–C2 2.615(3), Zr–C3 2.628(3), Zr–C4 2.627(3), Zr–C5 2.622(3), Zr–B1 2.901(4), Zr–C21 2.593(3), Zr–C22 2.599(3), Zr–C23 2.641(3), Zr–C24 2.685(3), Zr–C25 2.656(3), Zr–B2 2.860(4); Cl1–Zr–Cl2 94.85(3)

The planes C1C5 and C21C25 of the boratabenzene ligands are good planes [with a maximum vertical displacement of 0.017(3) Å]; the aminoboranediyl groups are bent away from the metal with vertical displacements of 0.271(4) Å for B1 and 0.229(4) Å for B2. The average Zr–B distance of 2.88 Å is comparable with the corresponding distances in $ZrCl_2(C_5H_5BMe)_2$ (2.81 Å),[20] $ZrCl_2$(4-Bu*t*$C_5H_4BPh)_2$ (2.80 Å),[21a] $ZrCl_2(C_5H_5BOEt)_2$ (2.83 Å),[21c] and $ZrCl_2(C_5H_5BNiPr_2)_2$ [2.98 Å; B–N 1.396(6) Å].[21a] The average B–N bond length amounts to 1.419 Å and indicates considerable π-interaction between the boron and the exocyclic substituent. This weakens the Zr–B interaction and as a consequence markedly lengthened Zr–B distances are found. A more subtle question is why this situation results in a shorter Zr–B distance and a longer B–N bond length in **8a** as compared to the values in $ZrCl_2(C_5H_5BNiPr_2)_2$.[21a] We suggest that this difference is due to steric effects. The

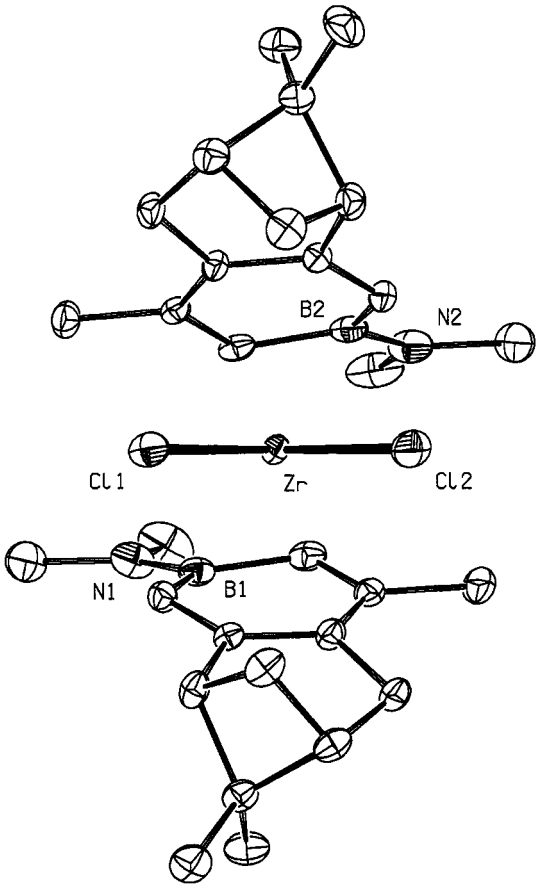

Figure 3. Front view of the molecular structure (PLATON plot, see ref.[25]) of **8a** in the crystal

bulky pinene part of the ligand in **8a** shifts the Zr atom towards the boron (as explained above in the case of *exo*-**4a**) and this results in shorter Zr–B distances and remarkably small slip distortions of just 0.12 and 0.15 Å for the two ligands. The bulky N*i*Pr$_2$ group in ZrCl$_2$(C$_5$H$_5$BN*i*Pr$_2$)$_2$ can be expected to have the opposite effect, resulting in particularly long Zr–B distances and particularly short B–N bond lengths.

Concluding Remarks

In this paper we have described the first transition metal complexes of pinene-fused boratabenzene ligands. With complex fragments incorporating late d-metals, complex formation gives diastereomeric mixtures in most cases, with a marked preference for the the sterically less congested *exo* diastereomers. In contrast, the bis(ligand)zirconium complexes are formed exclusively as *exo*,*exo* isomeric products. Parallels with earlier work by Paquette's group on complexes of the pinene-fused cyclopentadienyl ligand are evident. The pinene-fused Cp also shows a pronounced preference for coordination of the metal at the less hindered *exo* face.[9] Considering the data presented here, this preference seems to be less strong for the pinene-fused boratabenzenes.

Experimental Section

General Remarks: Reactions were carried out under an atmosphere of dinitrogen by employing conventional Schlenk techniques. Hexane was distilled from potassium, toluene from sodium, THF and Et$_2$O from sodium benzophenone ketyl, and CH$_2$Cl$_2$ from CaH$_2$. Electron-impact mass spectra were recorded on a Finnigan MAT-95 spectrometer with a nominal electron energy of 70 eV. Elemental analyses were performed by the Analytische Laboratorien Prof. Dr. H. Malissa und G. Reuter GmbH, D-51789 Lindlar. Melting points were determined in sealed capillaries on a Büchi 510 melting point apparatus and are uncorrected. NMR spectra were recorded on a Varian Unity 500 (^{1}H, 500 MHz; ^{13}C{^{1}H}, 125.7 MHz; ^{11}B{^{1}H}, 160.4 MHz), a Varian VXR 300 (^{1}H, 300 MHz; ^{13}C{^{1}H}, 75.4 MHz), or a Rototec/Picinotti Mini-FID spectrometer (^{11}B{^{1}H}, 29 MHz). Chemical shifts, measured at ambient temperature, are quoted relative to internal TMS for ^{1}H and ^{13}C, and relative to external BF$_3$·Et$_2$O for ^{11}B.

FeCp*(C$_{13}$H$_{17}$BNMe$_2$) (4a): A solution of Li(TMEDA)(**1a**) (1.23 g, 3.50 mmol) in THF (20 mL) was added to [Cp*Fe(NCMe)$_3$]PF$_6$ (1.56 g, 3.40 mmol) in acetonitrile (20 mL). The mixture immediately turned red and was left at ambient temperature for 12 h. After careful removal of the volatiles, the resulting residue was triturated with hexane. Filtration through a frit covered with kieselguhr and concentration of the filtrate in vacuo left a red oil, which was purified by chromatography on alumina (deactivated with 5% H$_2$O, 5 cm layer) using pentane containing 1% triethylamine as eluent. Removal of the solvents gave **4a** (1.38 g, 97%) as a red oil; the diastereomeric ratio *exo*/*endo* was found to vary between 3:1 and 9:1. Pure *exo* isomer *exo*-**4a** could be obtained from hexane at –30 °C as deep-red crystals in 50% yield; barely air-sensitive, soluble in hexane, benzene, THF, and CH$_2$Cl$_2$; m.p. 116 °C.

***exo*-4a**: ^{1}H NMR (500 MHz, C$_6$D$_6$): δ = 3.10 (d, *J* = 2.1 Hz, 5-H), 2.98 (d, *J* = 2.1 Hz, 3-H), 2.98 (br. s, NMe), 2.96 (br. s, NMe), 2.63 (dd, *J* = 15.7, 2.4 Hz, 8-H$_{exo}$), 2.58 (dddd, *J* = 9.2, 5.8, 5.8, 1.5 Hz, 11-H$_{exo}$), 2.25 (ddd, *J* = 15.7, 2.5, 1.5 Hz, 8-H$_{endo}$), 2.18 (dd, *J* = 5.8, 5.5 Hz, 1-H), 2.17 (dddd, *J* = 5.8, 5.5, 2.5, 2.4 Hz, 9-H), 2.10 (d, *J* = 9.2 Hz, 11-H$_{endo}$), 1.81 (s, 6-Me), 1.59 (s, Cp*), 1.32 (s, 10-Me$_{exo}$), 0.60 (s, 10-Me$_{endo}$). – ^{13}C{^{1}H} NMR (126 MHz, C$_6$D$_6$): δ = 113.7 (C-2), 98.3 (C-6), 80.8 (*C*$_5$Me$_5$), 79.5 (C-7), 66.3 (br., C-5), 64.8 (br., C-3), 48.4 (C-1), 41.3 (C-9), 39.9 (br., NMe$_2$), 39.4 (C-10), 33.7 (C-11), 29.4 (C-8), 26.8 (10-Me$_{exo}$), 21.3 (10-Me$_{endo}$), 20.9 (6-Me), 10.5 (C$_5$*Me*$_5$). – ^{11}B{^{1}H} NMR (160 MHz, C$_6$D$_6$): δ = 20. – MS: *m*/*z* (%) = 419 (100) [M$^+$], 364 (13) [M$^+$ – NMe$_2$]. – C$_{25}$H$_{38}$BFeN (419.3): calcd. C 71.62, H 9.14, N 3.34; found C 71.41, H 9.25, N 3.38.

***endo*-4a**: ^{1}H NMR (300 MHz, C$_6$D$_6$): δ = 3.08 (d, *J* = 2.0 Hz, 5-H), 2.96 (br. s, NMe$_2$), 2.84 (d, *J* = 2.0 Hz, 3-H), 2.57 and 2.24 (dm, *J* = 16.8 Hz, 1 H each, 8-H$_{exo}$, 8-H$_{endo}$), 2.39 (ddd, *J* = 9.1, 5.4, 5.4 Hz, 11-H$_{exo}$), 2.30 (dd, *J* = 5.7, 5.4 Hz, 1-H), 2.10 (m, 9-H), 1.87 (s, 6-Me), 1.66 (s, 10-Me$_{endo}$), 1.59 (s, Cp*), 1.30 (s, 10-Me$_{exo}$), 0.75 (d, *J* = 9.1 Hz, 11-H$_{endo}$). – ^{13}C{^{1}H} NMR (75 MHz, C$_6$D$_6$): δ = 118.0 (C-2), 97.9 (C-6), 80.4 (*C*$_5$Me$_5$), 79.8 (C-7), 67–64 (br., C-3 and C-5), 49.5 (C-1), 41.1 (C-9), 40.1 (br., NMe$_2$), 38.8 (C-10), 35.1 (C-11), 28.9 (C-8), 27.4 (10-Me$_{exo}$), 23.8 (10-Me$_{endo}$), 21.4 (6-Me), 10.9 (C$_5$*Me*$_5$). – ^{11}B{^{1}H} NMR (29 MHz, C$_6$D$_6$): δ = 20.

FeCp*(C$_{13}$H$_{17}$BOMe) (4b): A solution of **4a** (356 mg, 0.85 mmol) in methanol (10 mL) was kept at 60 °C for 24 h. Removal of the solvent in vacuo left **4b** (344 mg, 100%) as a red oil; isomer distri-

bution unchanged; barely air-sensitive, readily soluble in hexane, benzene, diethyl ether, and methanol. – MS: *m*/*z* (%) = 406 (3) [M^+], 56 (100). – $C_{24}H_{35}BFeO$ (406.2): calcd. C 70.97, H 8.69; found C 69.86, H 8.84.

***exo*-4b**: ^{1}H NMR (500 MHz, C_6D_6): δ = 3.84 (s, OMe), 3.46 (d, *J* = 2.1 Hz, 5-H), 3.34 (d, *J* = 2.1 Hz, 3-H), 2.59 (dd, *J* = 15.9, 2.7 Hz, 8-H$_{exo}$), 2.56 (dddd, *J* = 9.2, 6.1, 5.8, 1.2 Hz, 11-H$_{exo}$), 2.20 (ddd, *J* = 15.9, 2.4, 1.2 Hz, 8-H$_{endo}$), 2.16 (dd, *J* = 5.8, 5.5 Hz, 1-H), 2.13 (dddd, *J* = 6.1, 5.5, 2.7, 2.4 Hz, 9-H), 2.04 (d, *J* = 9.2 Hz, 11-H$_{endo}$), 1.76 (s, 6-Me), 1.60 (s, Cp*), 1.29 (s, 10-Me$_{exo}$), 0.56 (s, 10-Me$_{endo}$). – ^{13}C{^{1}H} NMR (126 MHz, C_6D_6): δ = 114.7 (C-2), 99.6 (C-6), 80.8 (C_5Me_5), 80.4 (C-7), 71.2 (br., C-5), 69.5 (br., C-3), 53.6 (OMe), 48.2 (C-1), 41.2 (C-9), 39.2 (C-10), 33.6 (C-11), 29.4 (C-8), 26.7 (10-Me$_{exo}$), 21.2 (10-Me$_{endo}$), 20.5 (6-Me), 10.3 (C_5Me_5). – ^{11}B{^{1}H} NMR (29 MHz, C_6D_6): δ = 25.

***endo*-4b**: ^{1}H NMR (500 MHz, C_6D_6): δ = 3.86 (s, OMe), 3.49 (d, *J* = 1.8 Hz, 5-H), 3.26 (d, *J* = 1.8 Hz, 3-H), 2.51 (dd, *J* = 16.2, 2.4 Hz, 8-H$_{endo}$), 2.37 (ddd, *J* = 9.2, 6.1, 5.8 Hz, 11-H$_{exo}$), 2.31 (dd, *J* = 5.8, 5.5 Hz, 1-H), 2.13 (dddd, *J* = 6.1, 5.5, 2.7, 2.4 Hz, 9-H), 2.12 (m, 8-H$_{exo}$), 1.82 (s, 6-Me), 1.61 (s, Cp*), 1.60 (s, 10-Me$_{endo}$), 1.28 (s, 10-Me$_{exo}$), 0.71 (d, *J* = 9.2 Hz, 11-H$_{endo}$). – ^{13}C{^{1}H} NMR (126 MHz, C_6D_6): δ = 119.3 (C-2), 99.3 (C-6), 81.0 (C-7), 80.4 (C_5Me_5), 71.4 (br., C-5), 64.4 (br., C-3), 53.6 (OMe), 49.4 (C-1), 40.9 (C-9), 38.6 (C-10), 34.9 (C-11), 28.8 (C-8), 27.2 (10-Me$_{exo}$), 23.6 (10-Me$_{endo}$), 21.0 (6-Me), 10.6 (C_5Me_5). – ^{11}B{^{1}H} NMR (29 MHz, C_6D_6): δ = 25.

FeCp*($C_{13}H_{17}$BMe) (4c): A solution of **4b** (215 mg, 0.53 mmol) in diethyl ether (4 mL) was cooled to –50 °C. LiMe (0.4 mL, 1.6 M in diethyl ether, 0.64 mmol) was added and the mixture was allowed to warm to room temperature overnight. After the addition of a small amount of alumina at –50 °C, the solution was filtered through alumina (deactivated with 5% H_2O, 5 cm layer) using pentane as eluent. Removal of the volatiles in vacuo left **4c** (206 mg, 100%) as a red, slowly solidifying oil; isomer distribution unchanged; barely air-sensitive, readily soluble in hexane, benzene, diethyl ether, and acetone. – MS: *m*/*z* (%) = 390 (100) [M^+]. – $C_{24}H_{35}BFe$ (390.2): calcd. C 73.88, H 9.04; found C 73.68, H 9.25.

***exo*-4c**: ^{1}H NMR (500 MHz, C_6D_6): δ = 3.80 (d, *J* = 1.2 Hz, 5-H), 3.70 (d, *J* = 1.2 Hz, 3-H), 2.62 (dd, *J* = 15.9, 2.8 Hz, 8-H$_{exo}$), 2.56 (m, 11-H$_{exo}$), 2.20 (m, 8-H$_{endo}$), 2.19 (dd, *J* = 5.8, 5.5 Hz, 1-H), 2.13 (m, 9-H), 2.04 (d, *J* = 9.2 Hz, 11-H$_{endo}$), 1.77 (s, 6-Me), 1.53 (s, Cp*), 1.28 (s, 10-Me$_{exo}$), 1.14 (s, BMe), 0.51 (s, 10-Me$_{endo}$). – ^{13}C{^{1}H} NMR (126 MHz, C_6D_6): δ = 114.1 (C-2), 98.8 (C-6), 82.9 (C-7), 80.4 (C_5Me_5), 84.9 and 83.5 (br., C-3 and C-5), 48.1 (C-1), 41.1 (C-9), 39.2 (C-10), 33.3 (C-11), 29.4 (C-8), 26.6 (10-Me$_{exo}$), 21.1 (10-Me$_{endo}$), 20.4 (6-Me), 10.1 (C_5Me_5), 1.3 (BMe). – ^{11}B{^{1}H} NMR (160 MHz, C_6D_6): δ = 20.

***endo*-4c**: ^{1}H NMR (500 MHz, C_6D_6): δ = 3.80 (d, *J* = 1.2 Hz, 5-H), 3.68 (d, *J* = 1.2 Hz, 3-H), 2.53 (m, 8-H$_{endo}$), 2.35 (m, 2 H, 1-H and 11-H$_{exo}$), 2.01 (m, 9-H), 1.84 (s, 6-Me), 1.60 (s, 10-Me$_{endo}$), 1.54 (s, Cp*), 1.26 (s, 10-Me$_{exo}$), 1.20 (s, BMe), 0.66 (d, *J* = 8.2 Hz, 11-H$_{endo}$). – ^{13}C{^{1}H} NMR (126 MHz, C_6D_6): δ = 79.9 (C_5Me_5), 49.5 (C-1), 40.9 (C-9), 38.4 (C-10), 34.8 (C-11), 28.9 (C-8), 27.2 (10-Me$_{exo}$), 23.8 (10-Me$_{endo}$), 20.9 (6-Me), 10.6 (C_5Me_5). – ^{11}B{^{1}H} NMR (160 MHz, C_6D_6): δ = 20. – Signals due to 8-H$_{exo}$, C-2, C-3, BMe, C-5, C-6, and C-7 could not be located; note that many signals are almost superimposed by those of the *exo* isomer.

MnBr(CO)$_3$(py)$_2$: Pyridine (20 mL) was added with stirring to MnBr(CO)$_5$,[18b] which resulted in rapid gas evolution (CO). As far as possible, light was excluded during the subsequent steps. When the gas evolution had subsided, the mixture was warmed to 80 °C for 1 h, then slowly allowed to cool to ambient temperature. Hexane (60 mL) was added and the deposited orange solid was collected on a frit. It was then washed through the frit by dissolving it in CH_2Cl_2. Removal of the solvent in vacuo left the orange-red crystalline product (9.65 g, 98%); light-sensitive, insoluble in hexane and toluene, soluble in pyridine, THF, and CH_2Cl_2. – ^{1}H NMR (250 MHz, CD_2Cl_2): δ = 8.74 (m, 2-/6-H), 7.61 (m, 4-H), 7.31 (m, 3-/5-H). – IR (CD_2Cl_2): $\tilde{\nu}$ = 2030 (s), 1944 (s), 1910 cm^{-1} (m).

Mn(CO)$_3$($C_{13}H_{17}$BNMe$_2$) (7): A solution of Li(**1a**) (873 mg, containing a known amount of THF, 3.10 mmol) in hexane (20 mL) was added to a suspension of MnBr(CO)$_3$(C_5H_5N)$_2$ (1.13 g, 3.00 mmol) in hexane (75 mL) at 65 °C by means of a cannula. The mixture was kept at 65 °C for 72 h and then filtered through a frit covered with kieselguhr. Removal of the volatiles left **7** (1.00 g, 91%) as an orange oil; the diastereomeric ratio *exo*/*endo* was found to be 3:1. The pure *exo* isomer was isolated as a yellow-orange shiny solid by fractional crystallization from hexane at –30 °C; m.p. 87 °C; soluble in hexane, benzene, THF, and diethyl ether; light-sensitive. When the same reaction was carried out in THF for 2 h at 65 °C, an orange oil with a diastereomeric ratio *exo*/*endo* of 1:2 in favour of the *endo* isomer was obtained.

***exo*-7**: ^{1}H NMR (500 MHz, C_6D_6): δ = 3.54 (d, *J* = 2.5 Hz, 5-H), 3.32 (d, *J* = 2.5 Hz, 3-H), 2.69 (br. s, NMe), 2.62 (br. s, NMe), 2.48 (dd, *J* = 16.3, 3.1 Hz, 8-H$_{exo}$), 2.39 (dddd, *J* = 9.8, 6.1, 5.5, 1.5 Hz, 11-H$_{exo}$), 2.24 (ddd, *J* = 16.3, 2.8, 1.5 Hz, 8-H$_{endo}$), 2.08 (dd, *J* = 5.5, 5.5 Hz, 1-H), 1.87 (dddd, *J* = 6.1, 5.5, 3.1, 2.8 Hz, 9-H), 1.84 (d, *J* = 9.8 Hz, 11-H$_{endo}$), 1.74 (s, 6-Me), 1.11 (s, 10-Me$_{exo}$), 0.56 (s, 10-Me$_{endo}$). – ^{13}C{^{1}H} NMR (126 MHz, C_6D_6): δ = 223.2 (CO), 134.7 (C-2), 120.0 (C-6), 91.0 (C-7), 78.6 (br., C-5), 72.4 (br., C-3), 49.6 (C-1), 40.9 (C-9), 38.8 (C-10), 38.5 (NMe$_2$), 33.2 (C-11), 30.1 (C-8), 26.3 (10-Me$_{exo}$), 21.3 (6-Me), 21.1 (10-Me$_{endo}$). – ^{11}B{^{1}H} NMR (160 MHz, C_6D_6): δ = 23. – MS: *m*/*z* (%) = 367 (14) [M^+], 311 (9) [M^+ – 2 CO], 283 (100) [M^+ – 3 CO], 228 (2) [M^+ – Mn(CO)$_3$], 55 (5) [Mn^+]. – $C_{18}H_{23}BMnNO_3$ (367.1): calcd. C 58.89, H 6.31, N 3.82; found C 60.08, H 6.04, N 3.82.

***endo*-7**: ^{1}H NMR (500 MHz, C_6D_6): δ = 3.64 (d, *J* = 2.5 Hz, 5-H), 3.09 (d, *J* = 2.5 Hz, 3-H), 2.75 (br. s, NMe), 2.62 (br. s, NMe), 2.51 (dd, *J* = 16.6, 2.4 Hz, 8-H$_{endo}$), 2.32 (ddd, *J* = 9.5, 5.8, 5.5 Hz, 11-H$_{exo}$), 2.20 (dd, *J* = 16.6, 3.6 Hz, 8-H$_{exo}$), 2.13 (dd, *J* = 5.5, 5.5 Hz, 1-H), 1.87 (dddd, *J* = 5.8, 5.5, 3.6, 2.4 Hz, 9-H), 1.70 (s, 6-Me), 1.35 (s, 10-Me$_{endo}$), 1.09 (s, 10-Me$_{exo}$), 0.88 (d, *J* = 9.5 Hz, 11-H$_{endo}$). – ^{13}C{^{1}H} NMR (126 MHz, C_6D_6): δ = 223.2 (CO), 134.2 (C-2), 119.9 (C-6), 93.0 (C-7), 79.6 (br., C-5), 65.9 (br., C-3), 49.6 (C-1), 41.1 (C-9), 39.9 (C-10), 38.5 (NMe$_2$), 34.4 (C-11), 29.8 (C-8), 27.2 (10-Me$_{exo}$), 23.5 (10-Me$_{endo}$), 21.3 (6-Me). – ^{11}B{^{1}H} NMR (160 MHz, C_6D_6): δ = 23.

***exo*,*exo*-ZrCl$_2$($C_{13}H_{17}$BNMe$_2$)$_2$ (8a):** A suspension of $ZrCl_4$ (743 mg, 3.19 mmol) in diethyl ether (20 mL) was cooled to –50 °C. Li(**1a**) (1.60 g, containing a known amount of THF, 6.32 mmol) in diethyl ether (30 mL) was then added dropwise through a cannula. The mixture was allowed to warm to room temperature and then stirred for 50 h. After removal of the volatiles, the residue was triturated with hexane (30 mL) and the resulting deep-purple suspension was cooled to –78 °C. The blue-purple solid was collected on a G4-frit at this temperature, washed with cold hexane (2 × 5 mL), and finally extracted from the frit with dichloromethane. Removal of the solvent left **8a** (1.08 g, 55%) as a fine microcrystalline powder. The product could be crystallized by dissolving it in hot toluene and cooling the solution to –30 °C (yield 50%); m.p. (dec.) 150 °C; slightly soluble in hexane and diethyl ether, soluble in benzene,

very soluble in CH_2Cl_2. – ^{1}H NMR (500 MHz, CD_2Cl_2): δ = 5.67 (d, *J* = 3.4 Hz, 5-H), 4.79 (d, *J* = 3.4 Hz, 3-H), 3.30 (dd, *J* = 16.5, 3.1 Hz, 8-H$_{exo}$), 3.01 (s, NMe), 2.74 (s, NMe), 2.65 (ddd, *J* = 16.5, 3.1, 1.2 Hz, 8-H$_{endo}$), 2.47 (dd, *J* = 5.8, 5.5 Hz, 1-H), 2.37 (dddd, *J* = 9.8, 6.1, 5.5, 1.2 Hz, 11-H$_{exo}$), 2.21 (dddd, *J* = 6.1, 5.8, 3.1, 3.1 Hz, 9-H), 1.83 (d, *J* = 9.8 Hz, 11-H$_{endo}$), 1.81 (s, 6-Me), 1.33 (s, 10-Me$_{exo}$), 0.56 (s, 10-Me$_{endo}$). – ^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2): δ = 163.0 (C-2), 148.3 (C-6), 121.9 (C-7), 116.8 (br., C-5), 108.0 (br., C-3), 53.2 (C-1), 40.6 (C-9), 39.3 (C-10), 39.3 (NMe), 38.4 (NMe), 31.7 (C-8), 31.1 (C-11), 26.2 (10-Me$_{exo}$), 24.2 (6-Me), 21.2 (10-Me$_{endo}$). – ^{11}B{^{1}H} NMR (160 MHz, CD_2Cl_2): δ = 34. – MS: *m*/*z* (%) = 618 (6) [M^+], 574 (4) [M^+ – NMe_2], 390 (100) [M^+ – $C_{13}H_{17}BNMe_2$], 229 (57) [$C_{13}H_{18}BNMe_2^+$]. – $C_{30}H_{46}B_2Cl_2N_2Zr$ (618.5): calcd. C 58.26, H 7.50, N 4.53; found C 58.32, H 7.47, N 4.67.

***exo*,*exo*-ZrCl$_2$(C$_{13}$H$_{17}$BOMe)$_2$ (8b):** A suspension of $ZrCl_4$ (116 mg, 0.50 mmol) in diethyl ether (3 mL) was cooled to –50 °C. Li(**1b**) (255 mg, containing a known amount of THF, 0.98 mmol) in diethyl ether (3 mL) was then added dropwise through a cannula. The mixture was allowed to warm to room temperature and stirring was continued for 72 h. Filtration of the red-orange suspension through a frit covered with kieselguhr and concentration of the filtrate in vacuo left an orange solid. Trituration with hot toluene and filtration gave a clear solution, from which **8b** (60 mg, 20%) could be obtained at –30 °C as an impure orange powder; soluble in benzene, diethyl ether, and CH_2Cl_2. – ^{1}H NMR (500 MHz, CD_2Cl_2): δ = 5.80 (d, *J* = 3.4 Hz, 5-H), 4.77 (d, *J* = 3.4 Hz, 3-H), 3.77 (s, OMe), 3.26 (dd, *J* = 16.5, 2.8 Hz, 8-H$_{exo}$), 2.69 (ddd, *J* = 16.5, 2.8, 1.2 Hz, 8-H$_{endo}$), 2.55 (dd, *J* = 5.5, 5.5 Hz, 1-H), 2.49 (dddd, *J* = 10.1, 6.1, 5.5, 1.2 Hz, 11-H$_{exo}$), 2.23 (dddd, *J* = 6.1, 5.8, 3.1, 2.8 Hz, 9-H), 1.97 (s, 6-Me), 1.75 (d, *J* = 10.1 Hz, 11-H$_{endo}$), 1.35 (s, 10-Me$_{exo}$), 0.55 (s, 10-Me$_{endo}$). – ^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2): δ = 167.7 (C-2), 153.7 (C-6), 125.9 (C-7), 119.9 (br., C-5), 107.1 (br., C-3), 53.4 (C-1), 52.8 (OMe), 40.2 (C-9), 39.0 (C-10), 32.4 (C-8), 32.0 (C-11), 26.1 (10-Me$_{exo}$), 24.6 (6-Me), 21.2 (10-Me$_{endo}$). – ^{11}B{^{1}H} NMR (160 MHz, CD_2Cl_2): δ = 38. – $C_{28}H_{40}B_2Cl_2O_2Zr$ (592.4): calcd. C 56.77, H 6.81; found C 56.69, H 6.73.

***exo*,*exo*-ZrCl$_2$(C$_{13}$H$_{17}$BMe)$_2$ (8c):** A suspension of $ZrCl_4$ (232 mg, 1.00 mmol) in diethyl ether (3 mL) was cooled to –60 °C. Li(**1c**) (416 mg, 2.02 mmol) in diethyl ether (6 mL) was then added dropwise through a cannula. The mixture was allowed to warm to room temperature and stirring was continued for one week. Filtration of the red-orange suspension through a frit covered with kieselguhr and concentration of the filtrate in vacuo left **8c** (560 mg, 100%) as an impure orange powder; moderately soluble in hexane, soluble in benzene, diethyl ether, THF, and CH_2Cl_2. – ^{1}H NMR (500 MHz, CD_2Cl_2): δ = 6.42 (d, *J* = 2.7 Hz, 5-H), 5.47 (d, *J* = 2.7 Hz, 3-H), 3.25 (dd, *J* = 17.1, 3.1 Hz, 8-H$_{exo}$), 2.68 (ddd, *J* = 17.1, 2.8, 1.2 Hz, 8-H$_{endo}$), 2.58 (dd, *J* = 5.8, 5.5 Hz, 1-H), 2.49 (dddd, *J* = 10.1, 6.1, 5.5, 1.2 Hz, 11-H$_{exo}$), 2.24 (dddd, *J* = 6.1, 5.8, 3.1, 2.8 Hz, 9-H), 1.93 (s, 6-Me), 1.69 (d, *J* = 10.1 Hz, 11-H$_{endo}$), 1.35 (s, 10-Me$_{exo}$), 0.92 (s, BMe), 0.48 (s, 10-Me$_{endo}$). – ^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2): δ = 165.2 (C-2), 150.8 (C-6), 133.2 (br., C-5), 131.3 (C-7), 124.9 (br., C-3), 53.0 (C-1), 40.2 (C-9), 39.0 (C-10), 32.8 (C-8), 31.6 (C-11), 26.1 (10-Me$_{exo}$), 23.6 (6-Me), 21.1 (10-Me$_{endo}$), 6.9 (br., BMe). – ^{11}B{^{1}H} NMR (160 MHz, CD_2Cl_2): δ = 43. – MS: *m*/*z* (%): 560 (5) [M^+], 361 (70) [M^+ – $C_{13}H_{17}BMe$].

***exo*,*exo*-ZrMe$_2$(C$_{13}$H$_{17}$BNMe$_2$)$_2$ (9):** A solution of LiMe (0.80 mL, 1.6 M in diethyl ether, 1.28 mmol) was added to **8a** (380 mg, 0.61 mmol) in diethyl ether (20 mL). After the addition of 2 equivalents, the mixture had turned red. Stirring was continued for 5 min. Filtration and removal of the solvent in vacuo gave **9** (331 mg, 93%) as a red oil. Crystallization from THF at –30 °C gave small red crystals (60%); m.p. (dec.) 160 °C; slightly soluble in hexane, soluble in benzene, diethyl ether, and THF, very soluble in CH_2Cl_2. – ^{1}H NMR (500 MHz, CD_2Cl_2): δ = 5.20 (d, *J* = 3.4 Hz, 5-H), 4.74 (d, *J* = 3.4 Hz, 3-H), 2.97 (dd, *J* = 15.9, 3.1 Hz, 8-H$_{exo}$), 2.79 (ddd, *J* = 15.9, 2.7, 1.2 Hz, 8-H$_{endo}$), 2.67 (br. s, NMe_2), 2.41 (dd, *J* = 5.8, 5.5 Hz, 1-H), 2.33 (dddd, *J* = 9.8, 6.1, 5.5, 1.2 Hz, 11-H$_{exo}$), 2.23 (dddd, *J* = 6.1, 5.8, 3.1, 2.7 Hz, 9-H), 1.96 (s, 6-Me), 1.35 (s, 10-Me$_{exo}$), 1.22 (d, *J* = 9.8 Hz, 11-H$_{endo}$), 0.67 (s, 10-Me$_{endo}$), –0.42 (s, ZrMe). – ^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2): δ = 156.3 (C-2), 146.0 (C-6), 116.3 (br., C-5), 111.9 (C-7), 107.9 (br., C-3), 52.8 (C-1), 42.9 (ZrMe), 40.7 (C-9), 39.9 (C-10), 38.7 (NMe), 38.7 (NMe), 31.3 (C-8), 30.3 (C-11), 26.3 (10-Me$_{exo}$), 23.9 (6-Me), 21.0 (10-Me$_{endo}$). – ^{11}B{^{1}H} NMR (160 MHz, CD_2Cl_2): δ = 32. – MS: *m*/*z* (%) = 348 (1) [M^+ – $C_{13}H_{17}BNMe_2$], 333 (1) [348$^+$ – Me]. – $C_{32}H_{52}B_2N_2Zr$ (577.6): calcd. C 66.54, H 9.07, N 4.85; found C 66.77, H 9.30, N 4.81.

X-ray Structure Determination of *exo*-4a: $C_{25}H_{38}BFeN$; formula mass 419.25 g·mol^{-1}, orthorhombic space group $P2_12_12_1$ (no. 19); *a* = 7.974(4), *b* = 16.783(4), *c* = 17.128(7) Å, *V* = 2292(3) Å^3, *Z* = 4, $d_{calcd.}$ = 1.21 g·cm^{-3}, μ_{lin} = 0.67 mm^{-1}. Enraf–Nonius CAD4 diffractometer; Mo-K_α radiation (λ = 0.71073 Å); graphite monochromator. Data collection at 223 K on a red crystal of dimensions ca. 0.50 × 0.40 × 0.35 mm^3 using ω/2θ scans in the diffraction range 3 < θ < 26° yielded 4798 reflections, which were corrected for Lorentz and polarization effects; no absorption correction was applied. After merging symmetry-equivalent data, 4478 unique reflections remained for structure solution by direct methods[26] and subsequent Fourier difference syntheses. Least-squares refinement on structure factors[27] was performed with anisotropic displacement parameters for all non-hydrogen atoms and with isotropic displacement parameters for all hydrogen atoms. Convergence was obtained for 405 variables, 3811 unique observations with $I > 1.0\ \sigma(I)$ at $R = 0.058$, $R_w = 0.050$, GoF = 1.079. A final difference Fourier map showed fluctuations of less than 0.50 e·Å^{-3}.[28]

X-ray Structure Determination of 8a: $C_{30}H_{46}B_2Cl_2N_2Zr$; formula mass 618.46 g·mol^{-1}, orthorhombic space group $P2_12_12_1$ (no. 19); *a* = 9.162(3), *b* = 17.777(3), *c* = 18.841(5) Å, *V* = 3069(1) Å^3, *Z* = 4, $d_{calcd.}$ = 1.34 g·cm^{-3}, μ_{lin} = 0.55 mm^{-1}. Enraf–Nonius CAD4 diffractometer; Mo-K_α radiation (λ = 0.71073 Å); graphite monochromator. Data collection at 203 K on a blue translucent platelet of dimensions ca. 0.50 × 0.50 × 0.20 mm^3 using ω/2θ scans in the diffraction range 2 < θ < 28° yielded 9358 reflections. The data were corrected for Lorentz and polarization effects, and an empirical absorption correction based on azimuthal scans[29] (min. rel. trans. 0.861, max. rel. trans. 1.000) was applied. After merging symmetry-equivalent data, 6869 unique reflections remained for structure solution by direct methods[26] and subsequent Fourier difference syntheses. Least-squares refinement on structure factors[27] was performed with anisotropic displacement parameters for all non-hydrogen atoms and with hydrogen atoms in calculated positions [C–H = 0.98 Å, U_{iso}(H) = 1.3 U_{eq}(C)]. Convergence was obtained for 334 variables, 6228 unique observations with $I > 1.0\ \sigma(I)$ at $R = 0.040$, $R_w = 0.041$, GoF = 1.095. A final difference Fourier map showed fluctuations of less than 0.62 eÅ^{-3}.[28]

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