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New Bimetallic Complexes (M^1=Ti,Zr; M^2=B) Containing Planar Tetracoordinate Carbon

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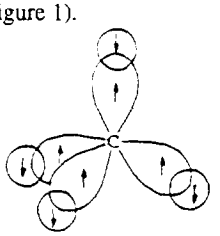
Abstract: *Bimetallic complexes of Zr/Ti and boron containing a planar tetracoordinate carbon atom have been prepared by reacting titanocene and zirconocene acetylene complexes with boron hydrides. The remarkable structural feature has been unequivocally proved by X-ray diffraction studies.*

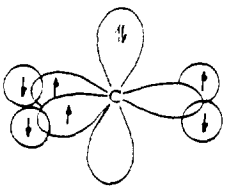
INTRODUCTION:

Since van't Hoff's and le Bell's imaginative thoughts developed in 1874 it is common knowledge that a tetracoordinate carbon atom exhibits a tetrahedral coordination geometry[1]. In 1970 R. Hoffmann described the electronic features of planar tetracoordinate carbon in methane[2]. In the following years a considerable number of papers appeared, dealing with the problem of stability of planar versus tetrahedral coordination geometry[3]. For planar coordination the central carbon atom is sp^2-hybridized thus possessing only three σ-orbitals for binding four substituents giving rise to an electron deficient σ-system with six electrons making a total four σ-bonds (two two-center two-electron bonds and one three-center two-electron bond) and a doubly occupied non-bonding π-orbital (figure 1).

Fig. 1:



J.H. van't Hoff, J.A. le Bell (1874)

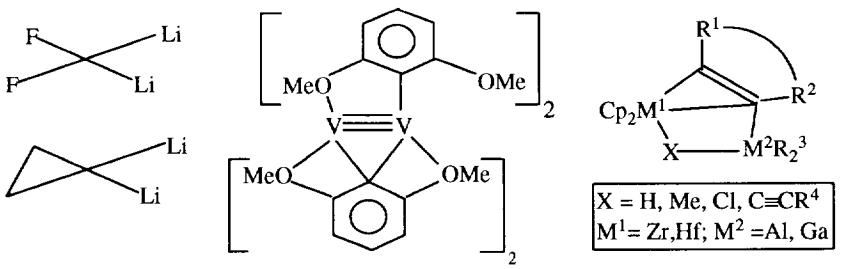


R.Hoffmann(1970)

Numerical calculations revealed that the configurational change from tetrahedral to planar methane affords a D_{4h}-symmetric species bearing an energy content of about 150 kcal/mol[3c,3d], which is 45 kcal/mol above the borderline of molecular existence posed by the magnitude of the C-H bond dissociation energy[4]. Despite this discouraging prognosis much effort went into trying to force all four σ-bonds to be coplanar by introduction of severe steric constraints by use of fenestranes, vespirenes and related compounds, but this "brute force method" was eventually unsuccessful[5]. The stability of the planar configuration is however

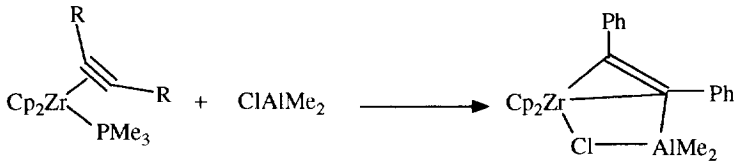
enhanced by the interaction between the two p-AO of the planar tetracoordinate carbon and π-MO's of appropriate ligands. The energy difference between planar and tetrahedral arrangement should be effectively reduced by ligands which combine reduced electron demand in σ-bonding with π-acceptor properties such as SiR_3, BR_2, Li or other metals[3f]. Li has been proposed to be especially effective in stabilizing planar tetracoordinate carbon. 1,1-dilithiocyclopropane or dilithio-difluoromethane were calculated to prefer a planar arrangement[3e]. Besides these theoretical considerations there exist an increasing number of synthetic results which realized this concept (figure 2). The first compound stabilizing the planar tetracoordinate carbon coordination geometry is the vanadium species V_2(2,6-dimethoxyphenyl)$_4$×2THF **1**[6a] . Other very special preparative examples followed[6]. The most variable synthetic approach known in this field leads to the bimetallic systems **2** containing a zirconium or hafnium and an aluminium or gallium center developed by Erker and co-workers[7].

Fig. 2:



P.v.R. Schleyer [3e] **1**: Cotton, Millar [6a] **2**: Erker [7]

Our original aim was to activate titanocene and zirconocene alkyne and alkene complexes with aluminium and boron organic compounds for catalytic processes. When reacting the trimethylphosphine stabilized zirkonocene tolane complex **3a** with dimethylaluminium chloride we did not obtain compounds with the desired catalytic activity, but we isolated the anti van't Hoff/le Bell compound **4** as a white microcrystalline solid, an analog to **2**[7], which was not described by Erker and co-workers:



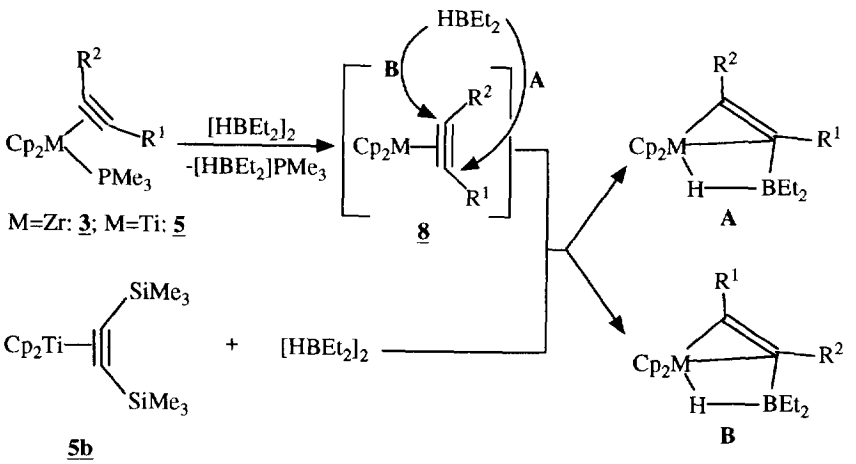
3a **4**

Following this new result and because the use of boron organic compounds for the synthesis of complexes with planar tetracoordinate carbon has not been investigated we focused our intention on this point[8]. Our investigations gave rise to a fruitful co-operation with Prof. Erker's group. The results obtained with dialkylboranes and 9-bis borabicyclo[3.3.1]nonane are reported herein.

RESULTS AND DISCUSSION:

The anti van't Hoff/le Bell-compounds **6** and **7** are obtained by reacting the trimethylphophine stabilized zirconocene and titanocene acetylene complexes **3** and **5** with tetraethyldiboran in pentane. The reactions are proposed to proceed via a two step reaction pathway. In the first step the trimethylphosphine ligand is removed from the starting complex giving the metallocene acetylene species **8**. This very reactive intermediate adds one equivalent of the Lewis acid to form the products **6** and **7**. If the starting complex contains an asymmetric substituted acetylene, mixtures of the two regioisomeric products are observed as is expected according to the outlined mechanism (scheme 1). A remarkable feature is provided by the fact that hydroboration reactions of the acetylenes by tetraethyldiborane which are known to be very fast even below 0°C have not been observed in any case. This remains true if the phophine free titanocene bis(trimethylsilyl)acetylene complex **5b** is used as starting complex. Furthermore the observation that the reaction of **5b** with tetraethyldiborane also gives the desired anti van't Hoff/le Bell compound is in agreement with our mechanistic proposal.

Scheme 1: Syntheses and mechanistic concept of the formation of the anti van't Hoff/le Bell compounds **6** and **7**

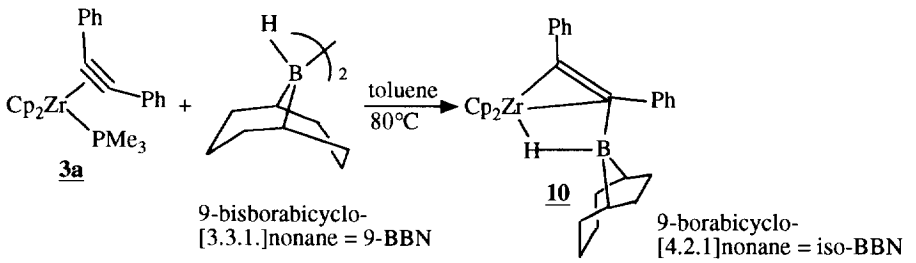


Zr: **6** Ti: **7**	R^1	R^2
a	Ph	Ph
b	$SiMe_3$	$SiMe_3$
6c^{A,B}	$SiMe_3$	Ph

The reactions are performed in pentane solution at ambient temperature. The zirconium compounds and **5b** are converted into the corresponding complexes **6a-c** and **7b** within several days in yields ranging from 70-88%, whereas the titanium complex **5a** reacts spontaneously with tetraethyldiborane to give **7a** in 94% yield. With a fourfold excess of

trimethylphosphine **7a** can be converted into **5a** again. The reaction of the trimethylphosphine stabilized bis(trimethyl)silyl zirconocene **3b** with $[HBEt_2]_2$ gives not only the anti van't Hoff/le Bell compound **6b** but also the dimeric species $\{Cp[\mu\text{-}(\eta^1{:}\eta^5\text{-}C_5H_4)]Zr(C(SiMe_3){=}C(H)(SiMe_3)\}_2$ **9** which was recently described by Rosenthal et al.[6c] as a side product. When heating the zirconium complex **3a** in toluene in the presence of 9-bis(borabicyclo[3.3.1]nonane) (BBN) to 80-90°C for eight hours, the complex **10** is formed in 83% yield. Besides the fact that **10** contains a square planar carbon atom this compound exhibits another remarkable feature. The borane unit shows a rearranged skeleton now being identified as 9-borabicyclo[4.2.1]nonane, the so-called iso-BBN (scheme 2).

Scheme 2:

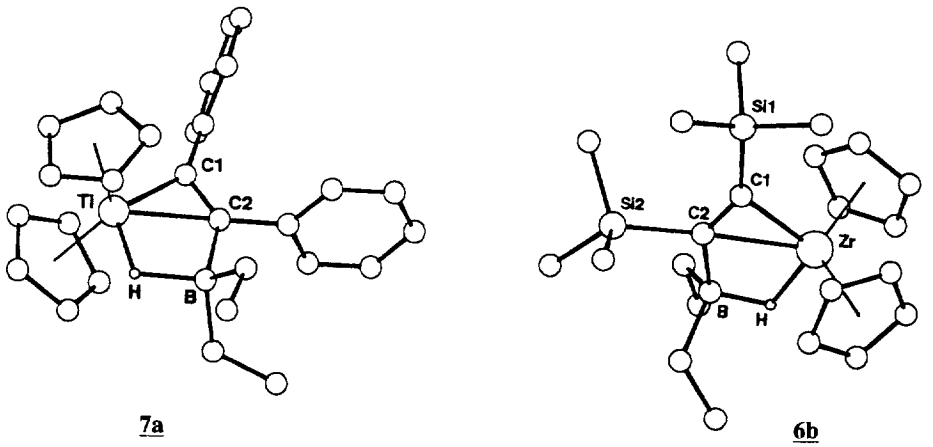


X-ray crystal structure analysis of dimetallic Zr or Ti and boron compounds:

It turned out that an unambigious characterization of the compounds **6,7** and **10** as anti van't Hoff/le Bell compounds cannot be revealed by nuclear magnetic resonance spectroscopy or by means of other routine spectroscopic methods. The extraordinary structural element, namely the square planar carbon coordination geometry does not cause any remarkable analytical features which allow resolution of the structure. This is why crystallographic investigations by means of X-ray diffraction techniques were performed whenever possible. **7a** was crystalized from a toluene solution by cooling to -20°C. Unfortunately the data obtained for **7a** are not suitable for publication due to strong disorder. The corresponding results are discussed only qualitatively showing the plot but providing no numerical information. Crystals of **6b** and **10** where obtained from pentane solutions by cooling to -78°C. The asymmetric units of the unit cells of **6b** and **10** contain two independent molecules. **10** and **10'** differ in the position of C21 (scheme 3) of the iso-BBN unit. This carbon atom can be arranged in an endo or exo like manner. **6b** and **6b'** show different distortion angles of the cyclopentadienyl rings. All these complexes exhibit a planar, bicyclic five-membered ring system consisting of Zr or Ti, the hydridic hydrogen H, B, C2 and C1 (figure 3 and scheme 2) which is lying in the plane bisecting the Cp-centroid metal Cp-centroid angle. The phenyl substituents of **10** and **7a** are oriented perpendicular to this framework thus excluding a stabilizing interaction of the aromatic π-system with the C1-C2-double bond. In all these complexes the boron atom exhibits a slightly distorted tetrahedral coordination geometry. The bond angle H-B-C2 is slightly smaller than the tetrahedral angle of 109.28° whereas the other

angles around boron are a bit larger. This structural feature is to be expected as there are three center two electron bonds between M, C2 and B and M, H and B[9]. The most remarkable structural feature is the coordination geometry of the carbon atom C2. C2 is bonded to C1, M, B and either the ipso carbon atom of the phenyl ring in **7a** and **10** or the Si-atom of the trimethylsilylgroup in **6b** with all four bonds lying perfectly in one plane. The values found for the distances from the metal atom to C2 (table 1) are slightly larger than those usually found for M-C-σ-bonds but they are still shorter than the average metal-C(Cp) distances (**7a**: 2.399Å, **6b**: 2.524Å **10**: 2.512Å). The C1-C2-bond distances are in the range of $C(sp^2)$-$C(sp^2)$ double bonds. The B-C2-bond length is about 0.1Å larger than the bond lengths from boron to the ethyl carbon atoms of the Et_2B-unit. This elongation is a typical feature for three center two electron bonds[9]. The boron-metal distances lie in the range that is known for such distances in two- and terdentate tetrahydroborate complexes of these metals[10].

Figure 3: Crystal structures of $Cp_2Ti(PhCCPh)(\mu\text{-}H)(BEt_2)$ **7a** and $Cp_2Zr(Me_3SiCCSiMe_3)(\mu\text{-}H)(BEt_2)$ **6b**



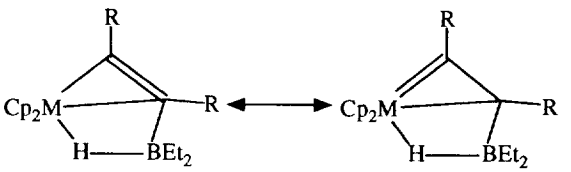
7a **6b**

Table 1: Selected bond distances and angles for **6b** and **10**

	atomic distances			bonding angles	
	10	**6b**		**10**	**6b**
M-B	2.589(4)	2.523(8)	B-H-M	112.4(2)	113.8(4)
M-C1	2.134(4)	2.196(6)	H-M-C2	64.4(1)	67.5(1)
M-C2	2.433(4)	2.386(6)	C2-M-C1	33.2(1)	33.4(2)
M-H	1.929(1)	1.771(1)	H-B-C2	108.5(3)	105.1(5)
B-C2	1.738(6)	1.73(1)	B-C2-M	74.7(2)	73.6(3)
B-H	1.142(4)	1.220(8)	C2-C1-M	85.8(2)	81.1(3)
C1-C2	1.335(5)	1.331(8)	C1-C2-M	61.0(2)	65.4(3)

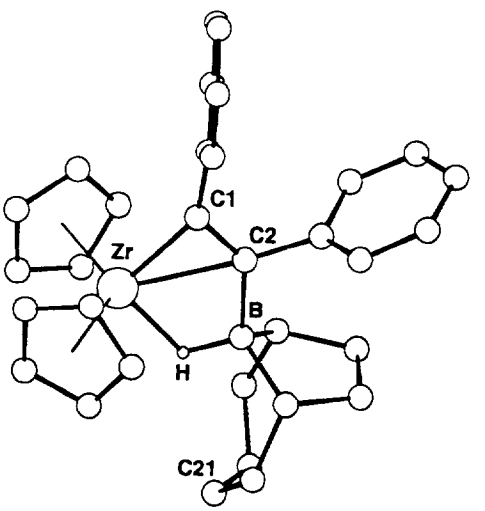
There is a striking difference between the zirconium compounds **6b** and **10** and the

titanium complex **7a** as far as the M-H and the B-H-distances are concerned. For **6b** and **10**[10] the corresponding values lie in the usual range. The B-H-distance in **7a** is extremely long whereas the Ti-H-bond adopts a very small value. Two points must be taken into consideration when trying to interprete this observation. The expressiveness of the crystallographic results of **7a** suffers from a disordered toluene molecule that had to be included in the refinement (R=0.080). Furthermore it is in general quite difficult to determine hydrogen positions with satisfactory accuracy by the methods of X-ray defraction techniques[9,11]. The distances between the transition metal and the carbon atom C1 are remarkably short. For the Zr-C1 bond lenghts values in the range of the Zr-C(sp) distance of $Cp_2Zr(CO)_2$[12] are found. The Ti-C1 bond length is exactly the same as that one found for a titanocene carbene complex prepared by P. Müller in our group[13]. For this reason we propose a metal alkylidene type resonance structure as a mesomeric description for such complexes[7]:



The complex **10** contains a borabicyclo[4.2.1]nonane unit instead of the expected [3.3.1]bicyclic system.

Scheme 3: Crystal structure of $Cp_2Zr(PhCCPh)(\mu\text{-}H)(BB[4.2.1]N)$ **10**

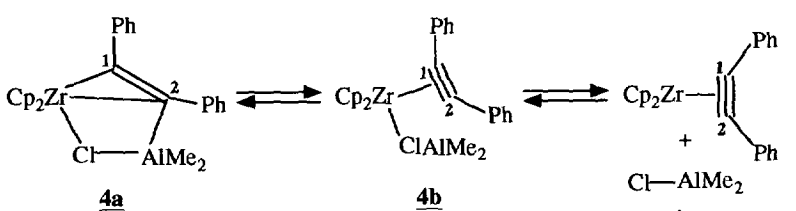


10

The ability of the BBN-system to undergo skeletal rearrangements by reversible de-hydroboration/hydroboration reactions at elevated temperatures has already been described[14]. The iso-BBN molecule can be stabilized by complexation with one equivalent of chinuclidin at 150°C. The aduct can be crystalized and has been characterized by crystal structure analyses. Although the iso-BBN system is well known from this report, the reactivity of this system has never been described possibly due to its instability even as a pure substance. At ambient temperature the thermodynamically more stable [3.3.1] bicyclic system is formed again by a renewed rearrangement reaction. It is not only the lower temperature that makes our synthesis remarkable but also the fact that the iso-BBN complex does not show any tendencies to undergo BBN-formation even after months of storing at room temperature. We expect it to be possible to perform further reactions with this stabilized iso-BBN molecule thus opening up a way to make this BBN-isomer easily accessible for organic synthesis. The geometric data found for the iso-BBN-unit are in accordance to what has already been published for the iso-BBN-unit of the crystallographically characterized iso-BBN chinuklidin adukt[14].

Spectroscopic data:

The discussion shall be started with compound **4**. The ^{1}H-NMR-signals are located in the expected spectral ranges. When looking at the carbon NMR-spectrum something very strange was observed. Instead of two different absorptions for the carbon atoms C1 and C2 only one singlett at δ=188.1ppm occurs at 29°C. When lowering the temperature to -78 and -110°C two resonance signals are obtained as originally expected. However instead of an olefinic resonance[7] and a signal at remarkably lower field the two carbon atoms feature two low field shifted signals:



T[°C]	δ[ppm](Mult.) C1	C2
29	188.1(s)	
-70	173.9(s)	189.5(s)
-100	173.8(s)	188.9(s)

The spectroscopic results can be explained satisfactory when an equilibrium between **4a**, **4b** and **4c** is presumed. **4c** seems to be the only detectable form at 29°C. The tolane ligand can rotate freely and the carbon atoms C1 and C2 as well as the phenyl carbon atoms become equivalent. When cooling the sample the equilibrium is shifted towards **4b** which is to be looked upon as an

aduct comparable to the starting complex with Cl_2AlMe_2 instead of PMe_3 and two different signals are detected for the carbon atoms of the tolane unit. **4a** is not observed in solution but we assume this to be the correct structure in solid state.

The most characteristic proton NMR-spectroscopic feature of the compounds **6**, **7** and **10** is the high field resonance of the bridging hydrido ligands. The resonance signals appear in the negative range of the spectrum (δ-scale) as broad singletts due to couppling to the neighbouring quadrupolar boron nucleus. The ^{13}C-resonances of the C1-carbon atoms are detected at lower field as the $\delta^{13}C$-values usually found for zirconocene and titanocene cyclopentene[15,16], cyclopentadiene[15] and cyclobutene[9,10c] complexes. This provides another hint for the π-interaction between the transition metal and C1, which was already discussed in connection with the crystallographic results. The carbon atoms C2 cause no extraordinary absorptions which allow an unequivocal identification as planar tetracoordinate carbon atoms. Their resonance signals appear in the region where the sp^2-hybridized carbon atoms of olefins and aromatic systems are ususally located. The titanium complex **7b** exhibits two cyclopentadienyl singletts. For a perfectly planar bicyclic metallacyclopentene system only one signal should appear. Obviously this complex shows a slight deviation from planarity possibly due to the steric hindrance caused by the bulky silyl substituents neighbouring the small transition metal.

Table 2: Selected NMR-spectroscopic data of **6**, **7** and **10**:

	δ[ppm](mult.)			
	^1H-NMR	^{13}C-NMR		^{11}B-NMR
	H[a)]	C1	C2	B[b)]
6a	-2.13(s)	212.2(s)	superposed	21.5
6b	-3.38(s)	228.7(s)	141.9(s)	28.9
6c^A	-2.64(s)	224.5(s)	144.1(s)	27.0
6c^B	-2.64(s)	220.1(s)	superposed	23.0
10	-1.90(s)	214.1(s)	superposed	21.3
7a	-4.06(s)	218.7(s)	110.6(s)	25.2
7b	-5.94(s)	234.9(s)	118.6(s)	24.8

a) broad signals, line width at half hight: 30-104Hz

b) broad signals, line width at half hight: 174-246Hz, no resolved fine structure

The boron nuclei show broad ^{11}B-resonances with line widths at half hight of 120-246 Hz. A resolved fine structure is not observed. The $\delta^{11}B$-values of the complexed boron fragments are very similar to those of the free diboranes of δ=27.8 ppm for $[HBEt_2]_2$ and δ=28.0 ppm for

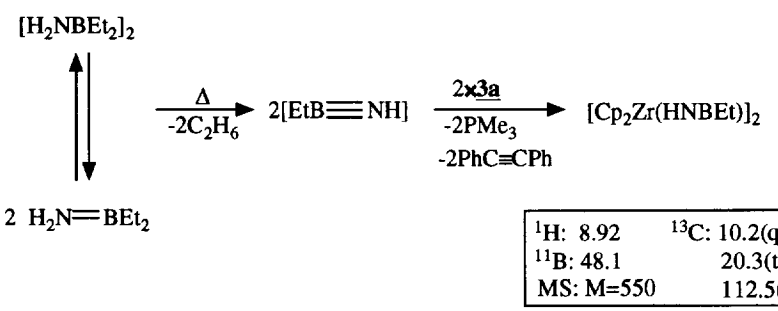
BBN[17]. ^{11}B-chemical shifts of tetracoordinate boron atoms mainly depend on charge density and on changes in symmetry[18]. The observed shift values (table 2) suggest that neither of these two features is strongly affected by complexation. The conclusions drawn from the NMR-spectroscopic charataristics confirm the crystallographic results.

The wave numbers for the B-H-M-bridge in the IR-spetra are locted in the range from 1605-1737 cm^{-1}. Compared to the spectral region from 1520 to 1610 cm^{-1} which is usually preserved for the antisymmetric streching vibration of the BH_2B bridge of diboranes[19] they are shifted to slightly larger wave numbers, now to be found in the typical region for $B\text{-}H_{bridge}$ streching frequencies of transition metal tetrahydroborato complexes with bidentate BH_4-ligands[9].

In the mass spectra no molecule peaks can be identified. The compounds release the borane unit or parts of it very easily, so that only the corresponding fragments can be detected.

PROSPECTS

In order to test the scope of the synthetic procedure for the preperation of anti van't Hoff/le Bell compounds with organoboranes we tried to react other substrates than boron hydrids with the acetylene complexes **3** and **5**. Our attempts to generate the corresponding compounds with boron halides failed. The reactions with amino boranes also did not give the desired complexes analogous to **6**, **7** or **10** but in this case we obtained new and unexpected compounds the analytical features of which are not yet satisfactory understood. **3a** reacts with aminodiethyl borane to yield a dimetallic complex with the composition $[Cp_2Zr(HNBEt)]_2$. The structure of this complex is not yet certain. We presume this compound to be formed by ligand exchange of the phosphine and the acetylene unit of **3a** versus in situ formed boron imines. The latter should arise from the amino borane by ethane elemination at elevated temperature:



As there are only very few examples for reactions of boron imines with metal complexes[20] this unexpected result is quite remarkable and we will focus our attention to the structure determination as well as to the synthesis of further examples of this new class of compounds.

ACKNOWLEDGMENT

This work was supported by the Fonds der Chemischen Industrie (stipend to F.S.).

EXPERIMENTAL SECTION:

Preparations and handling of the organometallic compounds were carried out in an inert argon atmosphere using Schlenk type glassware. Solvents were dried and distilled prior to use. The following instruments were used for product characterization: MP: Gallencamp Melting Point Apparatus, melting points uncorrected. NMR: Bruker AM 200FT (^{1}H), Bruker AC 200FT (^{1}H, ^{11}B), Bruker WM 300FT (^{1}H, ^{13}C). IR: Nicolet FT-IR spectrometer 7199. MS: Varian MAT 311 A/DF. X-Ray: Enraf Nonius CAD-4. Programs used for structure determination: solution: SHELX-86, refinement: SHELX 93, GFMLX; plot programm: ORTEP. Mass spectroscopic data refer to the most frequent isotopes: ^{1}H (99.985%), ^{11}B (80,45%), ^{12}C (98,9%), ^{31}P (100%), ^{48}Ti (73,8%), ^{90}Zr (51,5%), ^{28}Si (92.2%), ^{14}N (99.63%), ^{27}Al (100%), ^{35}Cl (75.8%).

Synthesis of $Cp_2Zr(PhCCPh)(\mu\text{-}Cl)(AlMe_2)$ (4): To a suspension of 1.0g (2.1mmol) **3a** in 45mL hexane 0.6g (0.9mL, 6.5mmol) dimethylaluminiumchloride are pipetted at room temperature. The reaction mixture is stirred for 21 hours at ambient temperature and the white precipitate of **4** is filtered off. Further product is obtained upon cooling the mother liquor to -78°C (yield: 1.0g, 2.0mmol, 95%), mp: 126°C (decomposition). Anal. calcd. for $C_{26}H_{26}ZrAlCl$ (490): C: 63.67, H: 5.31. Found C: 63.29, H: 5.38. ^{1}H-NMR ([D_8]-THF, 29°C, 300.1MHz) δ: -0.74 (s, 6H, $AlMe_2$), 5.86 (s, 10H, Cp), Ph: 6.86-7.10 (m, 10H), ^{13}C ([D_8]-THF, ***29°C***, 75.5MHz) δ[$^1J_{C,H}$]: 188.1 (s,2C: (PhC=CPh), -8.9 (q [123Hz], $AlMe_2$), 107.3 (d [170Hz], Cp), Ph: 150.3(s), 126.4(d), 128.3(d), 123.6(d); ^{13}C ([D_8]-THF, ***-78°C***, 75.5MHz) δ: 173.9 (s, Zr-C=), 189.5 (s, C_{planar}), -7.4 (q [112Hz], $AlMe_2$), 107.2 (d [170Hz], Cp), Ph: 157.8(s), 142.3(s), 122.8(d), 128.4(d), 128.5(d), 130.1(d), 121.5(d), 125.8(d); ^{13}C ([D_8]-THF, ***-110°C***, 75.5MHz) δ: 173.8 (s, Zr-C=), 188.9 (s, C_{planar}), -6.2 (q, $AlMe_2$), 107.1 (d, Cp), Ph: 158.2(s), 141.8(s), 122.6(d), 128.5(d), 128.6(d), 130.4(d), 121.4(d), 126.0(d). MS (70eV, 125°C) m/z, (intensity [%]): 220 (Cp_2Zr, [100]), 57 (Me_2Al, [94%]), 255 (Cp_2ZrCl, [89]), 180 (PhC(H)C(H)Ph, [60]), 290 (Cp_2ZrCl_2, [36]), 396 (M-Me_2AlCl, [36]), 434 (M-Me_2Al, [3]), 475 (M-Me, [3]).

Synthesis of $Cp_2Zr(PhCCPh)(\mu\text{-}H)(BEt_2)$ (6a): To a suspension of 1.4g (3.0mmol) **3a** in 30mL pentane, 0.7mL (6.1mmol $HBEt_2$) tetraethyldiborane as a solution in triethylborane (87.3% $[HBEt_2]_2$) are pipetted. The reaction mixture is stirred for 16 hours at ambient temperature. The white precipitate of **6a** is filtered off. Further **6a** is obtained by cooling the mother liquor to -78°C (yield: 1.0g, 2.1mmol, 88%), mp: 122°C (decomposition). Anal. Calcd for $C_{28}H_{31}ZrB$ (469): C: 71.62, H: 6.65; Found: C: 71.48, H: 6.68. ^{1}H-NMR ([D_8]-THF, 29°C, 300.1MHz) δ: 0.81-0.57 (m, 10H, BEt_2), 6.04 (s, 10H, Cp), Ph: 7.02 (t, 2H), 6.96 (t, 2H), 6.82 (t, 2H), 6.76 (d, 2H), 6.62 (d, 2H), -2.13 (br. s, 1H, μ-H); ^{13}C ([D_8]-THF, 29°C, 75.5MHz) δ [$^1J_{C,H}$]: 212.2 (s,Zr-C=), 18.7 (t [118Hz], CH_2), 13.2 (q [125Hz], CH_3), 109.7 (d [173Hz], Cp), Ph: 143.9

(s), 147.4 (s), 124.7 (d), 125.0 (d), 126.6 (d), 127.6 (d), 128.2 (d), 129.4 (d); C_{planar} cannot be detected. ^{11}B ([D_8]-THF, 27°C, 64.2MHz) δ: 21,5 ($H_{1/2}$=226±5Hz). IR (KBr): $\tilde{\nu}$=1675cm^{-1} (B-H-Zr). MS (70eV) m/z (intensity [%]): 220 (Cp_2Zr, [100]), 398 (M-Et_2BH, [27]), 440 (Cp_4Zr_2, [9]), 69 (Et_2B, [7]).

Synthesis of $Cp_2Zr(Me_3SiCCSiMe_3)(\mu\text{-}H)(BEt_2)$ (6b): To a suspension of 1.4g (3.0mmol) **3b** in 30mL pentane 0.7g (1.0mL, 5.0mmol) tetraethyldiborane are pipetted. The reaction mixture is stirred at room temperature. After 46h a clear, yellow solution is obtained from which a mixture of **6b** and **9** is isolated by cooling to -20°C. About half of the solvent is removed under reduced pressure and the mother liquor cooled to -78°C to give another crop of **6b** and **9** the latter being identified by comparison of the analytical data with an authentic sample[6c] (yield: 1.30g **6b**+**9**: 0.3g **9** (0.8mmol) and 1.0g **6b** (2.2mmol, 73%) estimated by ^{13}C), mp: 126°C, (decomposition). The two complexes can be seperated by fractional crystallisation from a pentane solution at -78°C. Anal. Calcd. for $C_{22}H_{39}ZrBSi_2$ (460): C: 57.39, H: 8.48, B: 2.39. Found: C: 57.72, H: 8.61, B: 2.41. ^{1}H-NMR ([D_8]-THF, 29°C, 300.1MHz) δ: 0.26 (s, 9H, $SiMe_3$), 0.44 (s, 9H, $SiMe_3$), 1.11 (m, 10H, BEt_2), 5.68 (s, 10H, Cp), -3.38 (br. s, 1H, μ-H). ^{13}C ([D_8]-THF, 29°C, 75.5MHz) δ [$^1J_{C,H}$]: 228.7 (s, Zr-C=), 141.9 (s, C_{planar}, $^1J_{C,Si}$=69.6±0.5Hz), 4.3 (q [118Hz], $SiMe_3$), 5.3 (q [118Hz], $SiMe_3$), 19.1 (t, B-CH_2), 14.5 (q [125Hz], B-CH_2-$\underline{C}H_3$), 107.7 (d [172Hz], Cp). ^{11}B ([D_8]-THF, 27°C, 64.2MHz) δ: 28.9 ($H_{1/2}$=174±5Hz). IR (KBr): $\tilde{\nu}$=1614cm^{-1} (B-H-Zr). MS (70eV, 80°C) m/z (intensity [%]): 220 (Cp_2Zr, [100]), 390 (M-Et_2BH, [30]), 431 (M-Et, [4]).

Synthesis of $Cp_2Zr(Me_3SiCCPh)(\mu\text{-}H)(BEt_2)$ ($6c^{A,B}$): To a solution of 1.3g (2.8mmol) **6c** in 65mL pentane 0.7mL (6.1mmol $HBEt_2$) of a solution of tetraethyldiborane in triethylborane (87.3% $[HBEt_2]_2$) is pipetted. The reaction mixture is stirred for 47h at room temperature. Suspended particles are removed by filtration over Celite^R. The filtrate is cooled to -78°C and solvent removed under reduced pressure until $\mathbf{6c}^{\mathbf{A,B}}$ begins to fall out as yellow precipitate. $\mathbf{6c}^{\mathbf{A,B}}$ is filtered off at -78°C. Further $\mathbf{6c}^{\mathbf{A,B}}$ is obtained upon storing the mother liquor at -78°C for three days. $\mathbf{6c}^{\mathbf{A,B}}$ is isolated in a total yield of 69% (0.9g, 1.9mmol), mp: 184°C (decomposition). Anal. Calcd. for $C_{25}H_{35}ZrBSi$ (464): C: 64.66, H: 7.54. Found: C: 63.88, H: 7.78. ^{1}H-NMR ([D_8]-THF, 29°C, 300.1MHz) δ: -0.13 (s, $SiMe_3$), -0.02 (s, $SiMe_3$), 0.73, 0.64, 0.57, 1.10 (m, B-CH_2), 1.16, 0.82 (m, B-CH_2-$C\underline{H}_3$), 5.77, 5.98 (s, Cp), -2.64 (br. s, μ-H). ^{13}C ([D_8]-THF, 29°C, 75.5MHz) δ: 224.5, 220.1 (s, Zr-C=), 144.1 (s, C_{planar}, the second planar tetracoordinate carbon cannot be detected) , 1.1, 4.3 (q [118, 119Hz], $SiMe_3$), 19.3 (t, 2xB-CH_2), 14.9, 13.2 (q [126,126Hz], B-CH_2-$\underline{C}H_3$), 109.0, 108.8 (d [173, 173Hz], Cp), Ph: 145.5(s), 151.1(s), 129.2(d), 124.0(d), 127.4(d), 128.5(d), 124.9(d), 124.4(d). ^{11}B ([D_8]-THF, 27°C, 64.2MHz) δ: 27.0, 23.0 ($H_{1/2}$ cannot be determined as the two resonances superpose each other). IR (KBr): $\tilde{\nu}$=1685cm^{-1}, 1605cm^{-1} (B-H-Zr). MS (70eV, 100°C) m/z (intensity [%]): 220 (Cp_2Zr, [100]), 394 (M-Et_2BH, [47]), 435 (M-Et, [2]).

Synthesis of $Cp_2Zr(PhCCPh)(\mu\text{-}H)(iso\text{-}BC_8H_{14})$ (10): A mixture of 3.1g (6.5mmol) **3a** and 2.3g (18.9mmol) 9-BBN in 50mL toluene is heated to 80-90°C for 8h. The solution

becomes dark green. The solvent is removed in vacuo and the residue suspended in 30mL diethylether. **10** can be filtered off as yellow precipitate. Further crystalisation by cooling the mother liquor to -78°C affords another crop of **10** (yield: 2.8g, 5.4mmol, 83%), mp: 196°C (decomposition). Anal. Calcd. for $C_{32}H_{35}ZrB$ (520): C: 73.70, H: 6.72, B: 2.12. Found: C: 73.42, H: 6.79, B: 2.22. ^{1}H-NMR ([D_8]-THF, 29°C, 300.1MHz) δ: 2.01-0.87 (m, 14H, iso-BBN), 6.11 (s, 10H, Cp), -1.9 (br.s, 1H, μ-H), Ph(10H): 6.71(d), 6.77(d), 6.83(t), 6.88(t), 6.96(t), 7.03(t). ^{13}C ([D_8]-THF, 29°C, 75.5MHz) δ: 214.1 (s, Zr-C=), C_{planar} cannot be detected, iso-BBN: 37.0(mult. superposed), 37.2(t [126Hz]), 38.0(t [122Hz]), 27.6(t [124Hz]), 109.9 (d [173Hz], Cp), Ph: 142.6(s), 147.4(s), 124.8(d), 125.0(d), 126.7(d), 127.6 (d), 128.1(d), 129.3(d). ^{11}B ([D_8]-THF, 27°C, 64.2MHz) δ: 21.3 ($H_{1/2}$= 233±5Hz). IR (KBr): $\tilde{\nu}$=1737cm^{-1}, 1711cm^{-1} (B-H-Zr). MS (70eV, 300°C) m/z (intensity [%]): 178 (PhCCPh, [100]), 220 (Cp_2Zr, [70]), 576 ($Cp_2Zr(PhCCPh)_2$, [23]), 398 (Cp_2Zr(PhCCPh), [16]).

Synthesis of $Cp_2Ti(PhCCPh)(\mu\text{-}H)(BEt_2)$ (7a): To a suspension of 1.5g (3.5mmol) **5a** in 35mL pentane 0.9mL (7.7mmol $HBEt_2$) tetraethyldiborane as a solution in triethylborane (87.3% $[HBEt_2]_2$) is pipetted at ambient temperature. The suspension spontaneously changes its colour from greenish yellow to orange. The reaction is completed after three minutes. **7a** is isolated by filtration as a voluminous orange powder. Upon cooling the filtrate to -20°C another sample of **7a** is isolated (yield: 1.4g, 3.3mmol, 94%), mp: 104°C (decomposition). Anal. calcd. for $C_{28}H_{31}TiB$ (426): C: 78.87, H: 7.28. Found: C: 79.89, H: 7.27. ^{1}H-NMR ([D_8]-THF, 29°C, 300.1MHz) δ: 0.87 (m, 4H, B-CH_2), 0.71 (m, 6H, B-CH_2-$C\underline{H}_3$), 5.94 (s, 10H, Cp), -4.06 (br.s, 1H, μ-H), 6.71-7.09(m, 10H, Ph). ^{13}C ([D_8]-THF, 29°C, 75.5MHz) δ: 218.7, (s, Zr-C=), 110.6 (s, C_{planar}), 110.3 (d [175Hz], Cp), 19.0 (t [117Hz], B-CH_2), 13.0 (mult. superposed, B-CH_2-$C\underline{H}_3$), Ph: 145.9(s), 143.1(s), 124.9(d), 125.9(d) , 127.5(d), 128.1 (d), 128.7(d), 129.6(d). ^{11}B ([D_8]-THF, 27°C, 64.2MHz) δ: 25.2 ($H_{1/2}$= 210±5Hz). IR (KBr): $\tilde{\nu}$=1685cm^{-1} (B-H-Zr). MS (70eV) m/z (intensity [%]): 178 (PhCCPh and Cp_2Ti [100]), 69 (BEt_2, [42]), 113 (CpTi, [17]), 248 ($Cp_2Ti(HBEt_2)$, [7]), 356 (Cp_2Ti(PhCCPh), [4]).

Synthesis of $Cp_2Ti(Me_3SiCCSiMe_3)(\mu\text{-}H)(BEt_2)$ (7b): To the dark green solution of 1.2g (3.4mmol) **5b** in 30mL pentane 0.5g (0.7mL, 3.6mmol) tetraethyldiborane is pipetted at room temperature. The solution is stirred at ambient temperature for 5 days. Upon cooling to -78°C a green precipitate forms which is filtered off (yield: 1.0g, 2.5mmol, 74%; mp: 134°C (decomposition). Attempts to isolate further product by evaporating small amounts of solvent and cooling the residue are unsuccessful. When the solvent is completely removed a green oil is obtained which contains **5b**, **7b**, and impurities. The good solubility of the product obviously prevents a complete isolation. Anal. calcd. for $C_{22}H_{39}TiBSi_2$ (418): C: 63.16, H: 9.33, B: 2.63. Found: C: 63.92, H: 9.41, B: 2.75. ^{1}H-NMR ([D_8]-THF, 27°C, 200.1MHz) δ: 0.28, 0.39 (s, 18H, 2×$SiMe_3$), 1.80 (m, 10H, BEt), 5.31,5.40 (s, 5H, 2×Cp), -5.94 (br.s, 1H, μ-H), ^{13}C ([D_8]-THF, 27°C, 50.3MHz) δ: 234.9 (s, Ti-C=), 118.6 (s, C_{planar}), 107.5, 106.9 (d [173, 173Hz], Cp), signal for B-CH_2 not observed, 14.7 (q [125Hz], B-CH_2-$\underline{C}H_3$), 4.6, 3.2 (q [123,121Hz], $SiMe_3$). ^{11}B ([D_8]-THF, 27°C, 64.2MHz) δ: 24.8 ($H_{1/2}$= 246±5Hz). IR (KBr): $\tilde{\nu}$=1530cm^{-1}, 1695cm^{-1}

(possible for B-H-Ti, an unequivocal determination is not possible). MS (70eV, 80°C) m/z (intensity [%]): 178 (PhCCPh and Cp_2Ti [100]), 73 ($SiMe_3$, [42]), 388 ($M-C_2H_6$, [0.1]); (CI, NH_3): 195 (Cp_2Ti+NH_3, [100]), 389 ($M-C_2H_5$, [18]).

References

1. a) van't Hoff, J.H.; Arch. Neerl. Sci. Exactes Nat., **1874**, 445; b) le Bell, J.A.; Soc, Chim. Fr., **1874**, *22*, 337.
2. Hoffmann, R.; Alder, R.W.; Wilcox jr., C.F.; J. Am. Chem. Soc., **1970**, *92*, 4992.
3. a) Olah, G.; Klopman, G.; Chem. Phys. Lett., **1971**, *11*, 604; b) Lathan, W.A.; Hehre, W.J.; Curtiss, L.A.; Pople, J.A.; J. Am. Chem. Soc., **1971**, *93*, 6377, c) Wiberg, K.B.; Ellison, G.B.; Tetrahedron **1974**, *30*, 1573, d) Wiberg, K.B.; Ellison, G.B.; J.J. Wendoloski, J. Am. Chem. Soc., **1976**, *98*, 1212, e) Collins, J.B.; Dill, J.D.; Jemmis, E.D.; Apeloig, Y.; Schleyer, P.v.R.; Seeger, R.; Pople, J.A.; J. Am. Chem. Soc., **1976**, *98*, 5419, f) Schleyer, P.v.R.; Boldyrev, A.I.; J. Chem. Soc. Chem. Commun., **1991**, 1536.
4. Golden, D.M.; Walsh, R.; Benson, S.W.; J. Am. Chem. Soc., **1965**, *87*, 4053.
5. a) R. Keese, R.; Nachr. Chem. Tech. Lab. **1982**, *30*, 844, b) Mulzer, J.; Altenbach, H.-J.; Braun, M.; Krohn, K.; Reissig, H.-U.; Organic Synthesis Highlights, Verlag Chemie, Weinheim New York, 1990, S.371-377.
6. a) Cotton F.A.; Millar, M.; J. Am. Chem. Soc., **1977**, *99*, 7886, b) Harder, S.; Boersma, J.; Brandsma, L.; van Heteren, A.; Kanters, J.A.; Bauer W.; Schleyer, P.v.R.; J. Am. Chem. Soc., **1988**, *110*, 7802, c) Rosenthal, U.; Ohff, A.; Michalik, M.; Görls, H.; Burlakov, V.V.; Shur, V.B.; Angew. Chem., **1993**, *105*, 1228; Angew. Chem. Int. Ed. Engl. **1993**, *32*, 1193, d) Horten, A.D.; Orpen, A.G.; Angew. Chem., **1992**, *104*, 912; Angew. Chem. Int. Ed. Engl., **1992**, *31*, 876, e) Cotton, F.A.; Schwotzer W.; Shamshoum, E.S.; Organometallics, **1985**, *4*, 461, f) Cayton, R.H.; Chacon, S.T.; Chisholm, M.H.; Hampden-Smith, M.J.; Huffman, J.C.; Folting, K.; Ellis, P.D.; Huggins, B.A.; Angew. Chem., **1989**, *101*, 1547; Angew. Chem. Int. Ed. Engl. **1989**, *28*, 1523; g) Smith, G.M., Sabat, M., Marks, T.J.; J. Am. Chem. Soc., **1987**, *109*, 1854.
7. a) Review: Erker, G.; Comments Inorg. Chem. **1992**, *13*, 111; b) Erker, G, Albrecht, M., Krüger, C., Werner, S., Organometallics, **1991**, *10*, 3793; c) Erker, G., Albrecht, M., Krüger, C., Werner, S., J. Am. Chem. Soc., **1992**, *114*, 8531; d) Albrecht, M., Erker, G., Nolte, M., Krüger, C., J. Organomet. Chem., **1992**, *427*, C21.
8. There is one Zr/B-compound reported in: Erker, G.; Albrecht, M.; Krüger, C.; Werner, S.; Binger, P.; Langhauser, F.; Organometallics, **1992**, *11*, 3517, but the reaction pathway by which this complex has been obtained was not suitable for the synthesis of more of these compounds.

9. Marks, T.J., J.R. Kolb, J.R., Chem. Rev. **1977**, *77*, 263.

10. a) Melmed, K.M., Coucouvanis, D., Lippard, S.J., Inorg. Chem., **1973**, *12*, 232. b) Jensen, J.A., Girolami, G.S., J. Chem. Soc. Chem. Commun. **1986**, 1160. c) Corazzo, F., Floriani, C., Chiesi-Villa, A., Guastini, C., Inorg. Chem., **1990**, *30*, 145. d) Jensen, J.A., Wilson, S.R., Schultz, A.J., Girolami, G.S., J. Am. Chem. Soc., **1987**, *109*, 8094. e) Kot, W.K., Edelstein, N.M., Zalkin, A., Inorg. Chem., **1987**, *26*, 1339. f) Erker, G., Hoffmann, U., Zwettler, R., Krüger, C., J.Organomet. Chem. **1989**, *367*, C15. g) Erker, G., Noe, R., Wingbergmühle, D., Petersen, J.L., Angew. Chem., **1993**, *105*, 1216; Angew. Chem. Int. Ed. Engl., **1993**, *32*, 1213.

11. a) Schunn, R.A., Fritchie jr., C.J., Prewitt, C.T., Inorg. Chem., **1966**, *5*, 892 . b) Frenz, B.A., Ibers, J.A., in Transition Metal Hydrids, Vol. 1, E.L. Mutterties (Herausgeber), Marcel Dekker, New York, 1971, S.35-37. c) W.C. Hamilton, J.A. Ibers, Hydrogen Bonding in Solids, W.A. Benjamin, New York, 1968, chapter 2.

12. Atwood, J.L., Rogers, R.D., Hunter, W.E., Floriani, C., Fachinetti, G., Chiesi-Villa, A., Inorg. Chem., **1980**, *19*, 3812.

13. Binger, P., Müller, P., Gabor, B., Mynott, R., Herrmann, A.T., Langhauser F., Krüger, C., Chem. Ber. **1992**, *125*, 2209.

14. Yalpani, M., Boese, R., Köster, R., Chem. Ber., **1988**, *121*, 287.

15. Review: Negishi, E., Takahashi, T., Synthesis, **1988**, 1; Buchwald, S.L., Nielsen, R.B., Chem. Rev., **1988**, *88*, 1047, and literature cited therein.

16. Binger, P., Müller, P., Langhauser, F., Sandmeyer, F., Phillips, P., Gabor, B., Mynott, R., Chem. Ber., **1993**, *126*, 1541.

17. Contreras, R., Wrackmeyer, B., Spectrochim. Acta, **1982**, *39A*, 941.

18. Kroner, J., Wrackmeyer, B., J. Chem. Soc. Faraday Trans. II, **1976**, *72*, 2283.

19. B. Wrackmeyer, R. Köster in: Houben Weyl, Methoden der organischen Chemie, Organobor-Verbindungen, Band XIII/3c, R.Köster (Herausgeber), G. Thieme-Verlag, Stuttgart New York, 1984, S.440 and literature cited in there.

20. Peatzold, P., Adv. Inorg. Chem., **1987**, *31*, 123.

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