Zirconocene−(μ-Organyl)borate Betaines Derived by Treatment of a (σ-Alkenyl)(σ-alkynyl)zirconocene Complex with Tris(pentafluorophenyl)borane☆

Wolfgang Ahlers, Gerhard Erker*, and Roland Fröhlich

Organisch-Chemisches Institut der Universität Münster,
Corrensstraße 40, D-48149 Münster, Germany
Fax: +49(0)251-83 36503
E-mail: erker@uni-muenster.de

Received January 7, 1998

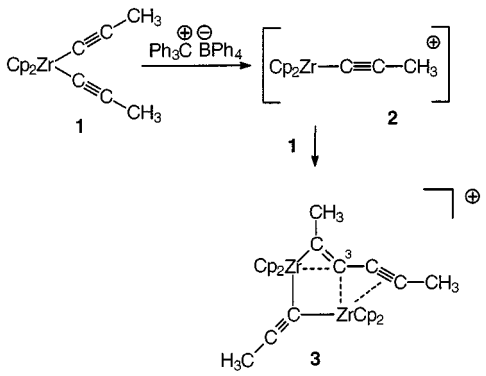
Keywords: Zirconocene / Metallocene cation / Isonitrile insertion / Isonitrile complex

Hydrozirconation of propyne followed by treatment with propynyllithium yields the (σ-propenyl)(σ-propynyl)zirconocene complex **11**. Its treatment with the organometallic Lewis acid $B(C_6F_5)_3$ results in transfer of the σ-propynyl group from zirconium to boron followed by insertion of the alkynylborate triple bond into the zirconium carbon bond of the remaining metallaallyl cation to furnish the zirconocene–(μ-hydrocarbyl)borate betaine complex **14**. This reacts with three molar equivalents of *tert*-butyl isocyanide to give **16**. Complex **16** contains a five-membered carbocyclic ring, formed by carbon-carbon coupling of the former propenyl and propynyl groups with the C≡N–R reagent, to which a (η^2-iminoacyl)(κ-*tert*-butyl isocyanide)zirconocene moiety is attached. Complex **16** was characterized by an X-ray crystal structure analysis.

Introduction

Allyl- and propargyl-conjugation effects are of great importance in organic chemistry. They greatly influence the chemistry of allylic and propargylic substrates due to the thermodynamic stabilization of the respective cations, radicals or anions.[1] Organometallic group 4 metallocene cations [$^{R}Cp_2Zr-R^+$] play a very important role as the active species of the homogeneous metallocene Ziegler catalysts.[2] It is therefore of interest to know about the electronic effects that influence and alter the properties of such cationic organometallic systems, i.e. whether allylic[3] or propargylic conjugation effects may lead to chemical consequences in such cations. We have recently investigated two potential synthetic entries into "metallapropargyl"-cation systems of the type [$^{R}Cp_2Zr-C\equiv C-R^+$].[4][5] Such species can be generated in situ, but they are extremely reactive. Their interesting chemical behavior has led to the development of a variety of rather simple synthetic pathways to a number of novel organometallic frameworks. Here are two representative examples: treatment of bis(propynyl)zirconocene (**1**) with trityltetraphenylborate[6] generated the reactive intermediate [$Cp_2Zr-C\equiv C-CH_3^+$] that instantaneously attacked an equivalent of the starting material **1** to form the CC-coupled product **3** which contains a planar-tetracoordinate carbon atom (C^3) at a bridgehead-position of the dimetallabicyclic framework.[3]

When **1** is treated with the strong organometallic Lewis acid tris(pentafluorophenyl)borane (**4**)[7] a propynyl anion equivalent is transferred[8] from zirconium to boron with generation of a 1,1-bis(cyclopentadienyl)zircona-propargyl cation intermediate (**5**). This then inserts the alkynyl moiety of the resulting anion to give the observed product **6**. The



metallocene (μ-hydrocarbyl)borate betaine **6** exhibits a unique reactivity. It seems to be in an (endothermic) equilibrium with its isomer **7**, formally obtained by an intramolecular alkyne insertion reaction into the Zr−C(sp^2) σ-bond, from which the stable corresponding methylenecyclopropene derivatives are obtained in high yield by treatment with suitable insertion reagents, e.g. isonitriles (see Scheme 1). Subsequent hydrolysis of **8** led to interesting novel organic three-membered ring systems.[5][9]

It would be interesting to know whether this chemistry of conjugated metallocene cations could be extended from metallapropargyl to metallaallyl systems.[3] Which of the two cations is preferrentially formed in a competitive situation? Do ring closure reactions of the **6** ⟹ **7** type require the presence of two acetylide-derived building blocks (i.e. to make cyclopropenylium product stabilization possible as in **8**) or would building blocks of lower unsaturation being tolerable in the chemistry depicted in Scheme 1? To address these and related questions experimentally we have pre-

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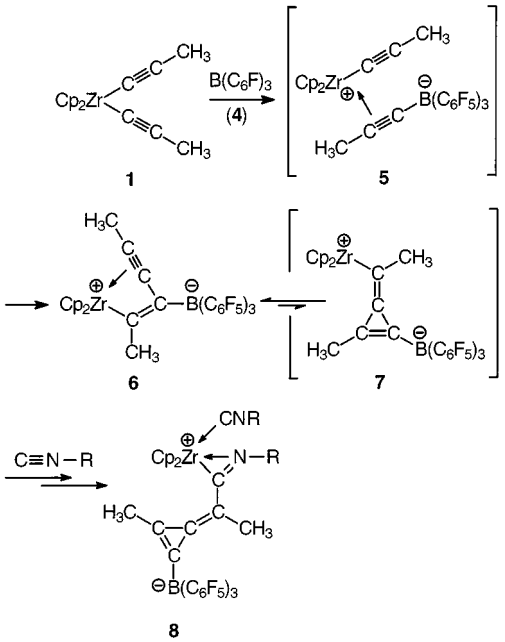
Scheme 1

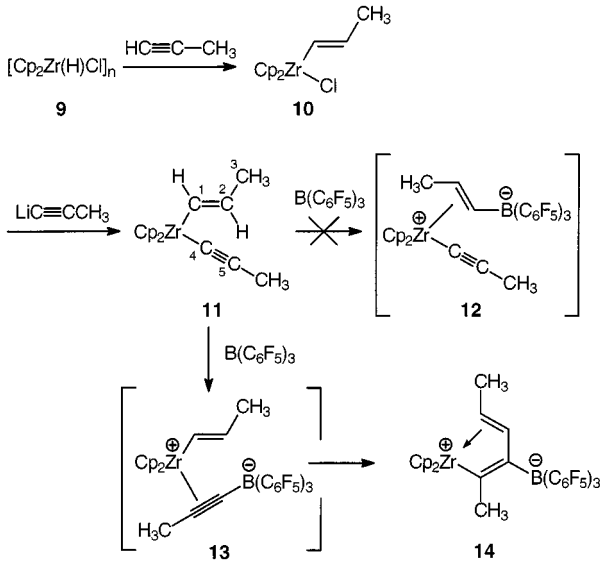


pared a "mixed" (σ-alkenyl)(σ-alkynyl)metallocene and investigated its metallocene cation chemistry initiated by treatment with $B(C_6F_5)_3$.

Results and Discussion

(σ-Propenyl)(σ-propynyl)zirconocene **11** was synthesized in the following way. Propyne was hydrozirconated by treatment with the oligomeric $[Cp_2Zr(H)Cl]_n$ reagent **9** in toluene at ambient temperature[10] to give the (*trans*-1-propenyl)zirconocene chloride complex **10** (74%). Subsequent treatment with propynyllithium in toluene furnished **11** in good yield (>90%). It shows the characteristic spectroscopic features of the *trans*-1-metallated alkene (^{1}H NMR: δ 6.98, 5.88, ^3J = 17.4 Hz; ^{13}C NMR: δ 182.2 (C1); IR: ν = 1635 cm^{-1}) and of the σ-alkynyl unit [IR: ν = 2086 cm^{-1}; ^{13}C NMR: δ 129.1, 118.1 ($C^4{\equiv}C^5$)].

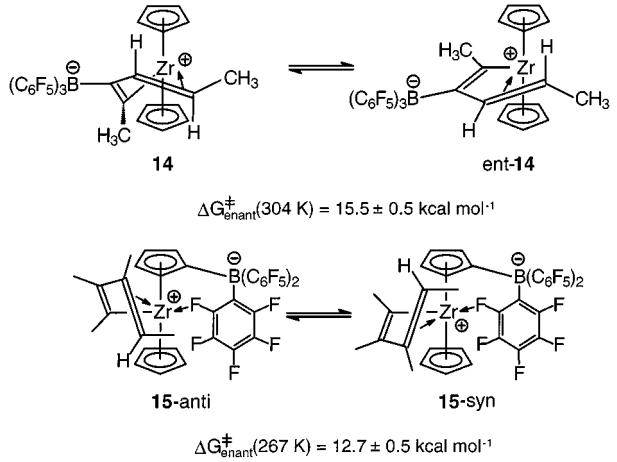
Scheme 2



Complex **11** reacts instantaneously with $B(C_6F_5)_3$ at room temperature. A mixture of products is formed containing a major component (**14**) that amounts to ca. 80%, but this product has turned out not to be very stable. In the course of several hours it decomposes unspecifically. Therefore, the product **14** was not isolated but only characterized spectroscopically from freshly prepared solutions (in [D_6]benzene, [D_8]toluene, or [D_5]bromobenzene). The NMR spectra clearly showed that carbon-carbon coupling of the two unsaturated σ-ligands at zirconium had occurred under the influence of the borane Lewis acid. The product exhibits the signals of a terminal *trans*-$H_3C^6-C^5H=C^4H$ moiety [233 K, [D_8]toluene: ^{1}H NMR: δ 7.40, 5.78, ^3J = 16 Hz; ^{13}C NMR: δ 158.8 (C4), 115.5 (C5)].

The C4=C5 double bond is probably coordinated to the electrophilic zirconium center, according to the corresponding ^{13}C-NMR chemical shifts and a comparison with typical reference data from the literature.[12a] Compound **14** at 233K in [D_8]toluene at 564 MHz exhibits a set of 15 ^{19}F NMR signals, which indicates hindered rotation about the C(sp^2)−B bonds. In addition, complex **14** exhibits a pair of diastereotopic cyclopentadienyl ligands (^{1}H-/^{13}C-NMR signals in [D_8]toluene at 233 K: δ 5.16, 5.02/112.8, 111.0). Raising the temperature results in a coalescence of the Cp-signals [T_{coal} (^{1}H NMR, 600 MHz) = 304 K], and a Gibbs activation energy of $\Delta G^{\ddagger}_{isom}$ (304 K) = 15.5 ± 0.5 kcal mol^{-1} for the dynamic exchange process.[11] This NMR behavior has precedence for substituted (1-butadienyl) ligand systems bonded to a cationic Cp_2M^+ unit: we assume a weak π-interaction of the $C^4=C^5$ double bond with the very electrophilic group 4 metallocene unit in **14**.[12] Conformational equilibration of the helically arranged C_4 unit in **14** may then occur by reversible cleavage of this weak π-complexation similarly as it was previously observed in the structurally and chemically related betaine system **15** (see Scheme 3).[13][14]

Scheme 3

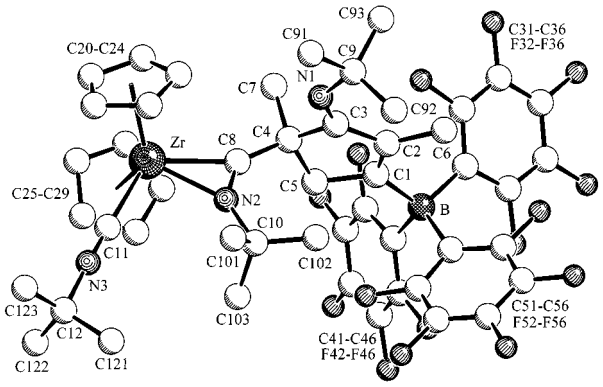


Complex **14** reacts readily with *tert*-butyl isocyanide (it consumes three equivalents of this reagent) to give an insertion/addition product **16**, that was isolated in >80% yield as a very pale yellow amorphous solid. Recrystallization from chloroform by slow evaporation of the solvent eventually

gave single crystals that were suited for an X-ray crystal structure analysis (see Figures 1 and 2). An overall view of the structure is given in Figure 1.

Figure 2 shows a projection of the central core of atoms of the newly formed product. This reveals that two equivalents of the isonitrile reagent were inserted. The first was used to couple the alkenyl- and alkynyl-derived moieties of the starting material together to form a five-membered carbocycle (C1−C5). The carbon framework $H_3C^6-C^2=C^1[B]-C^5H_2-C^4-C^7H_3$ of the product **16** corresponds exactly to the connectivity of the framework of its precursor **14**, only that the number of hydrogen atoms at carbon centers C5 and C4 does not correspond with the starting material.

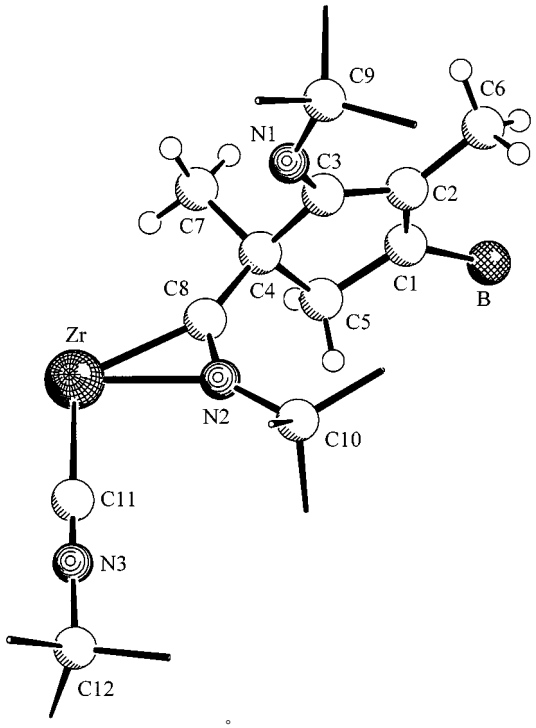
Figure 1. A view of the molecular structure of **16**



Unfortunately, we could not find any intermediate along the reaction pathway. Therefore, a detailed mechanistic picture of the **14**→**16** transformation must remain speculative at this time. A possible pathway is formulated in Scheme 4, starting with isonitrile insertion followed by electrophilic addition of the activated iminoacyl group at the C=C double bond to form the five-membered ring. We must assume a subsequent 1,2-hydride migration, potentially assisted by zirconium−carbon σ-bond formation to form the likely intermediate **19**. This is then trapped by insertion of an additional *tert*-butyl isocyanide insertion into the Zr−C σ-bond, followed by coordination of the third C≡NR molecule to give the observed stable reaction product.[15]

The X-ray crystal structure analysis of **16** shows the presence of the newly formed carbocyclic five-membered ring system (C1−C5) that contains the C1−C2 double bond [1.346(7) A] in conjugation to the ketimine functionality [C3−N1 1.266(7) A]. The bulky $-B(C_6F_5)_3$ substituent is attached to the sp^2-carbon atom C1 [C1−B 1.662(8) A]. Noteworthy is the presence of a η^2-iminoacyl group at the group 4 bent metallocene unit. The corresponding Zr−C8 bond length is 2.209(5) A, the Zr−N2 distance is 2.234(4) A. The angles inside the organometallic three-membered ring system are small [C8−Zr−N2 32.9(2)°, Zr−C8−N2 74.7(3)°, Zr−N2−C8 72.4(3)°]. The C8−N2 bond length is 1.258(6) A which is marginally shorter than the uncomplexed N1=C3 imino double bond at the adjacent five-membered ring (see above).

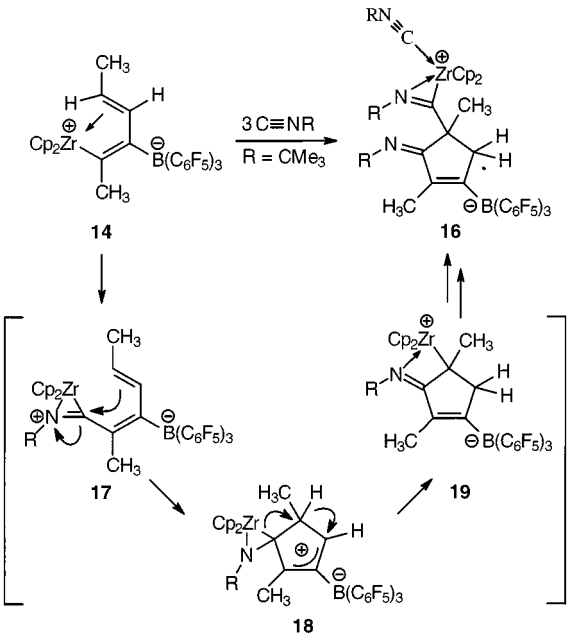
Figure 2. A view of the central atom framework of **16** with atom numbering scheme[a]



[a] Selected bond lengths [A] and angles [°]: Zr−C8 2.209(5), Zr−N2 2.234(4), Zr−C11 2.338(7), C11−N3 1.153(7), N3−C12 1.477(8), N2−C8 1.258(6), N2−C10 1.498(6), C8−C4 1.525(7), B−C1 1.662(8), C1−C2 1.346(7), C1−C5 1.517(7), C2−C3 1.500(7), C2−C6 1.503(7), C3−C4 1.545(7), C3−N1 1.266(7), N1−C9 1.471(7), C4−C5 1.548(7), C4−C7 1.537(7); Zr−C8−C4 148.8(4), Zr−C8−N2 74.7(3), Zr−N2−C8 72.4(3), Zr−N2−C10 148.5(3), Zr−C11−N3 175.5(5), C11−N3−C12 175.8(7), C11−Zr−N2 84.1(2), C11−Zr−C8 117.0(2), N2−Zr−C8 32.9(2), C8−N2−C10 139.0(5), N2−C8−C4 136.4(5), C8−C4−C5 111.8(4), C8−C4−C3 115.0(4), C8−C4−C7 108.4(4), B−C1−C2 126.3(5), B−C1−C5 122.4(5), C1−C2−C3 111.9(5), C1−C2−C6 123.1(5), C2−C3−C4 114.8(5), C2−C3−N1 140.1(5), C3−C4−C5 104.7(4), C3−C4−C7 106.6(4), C3−N1−C9 130.8(5), C5−C4−C7 110.2(4), C4−C5−C1 104.4(4); α(Zr,C8,N2)/(C1,C2,C3,C4,C5) 85.4.

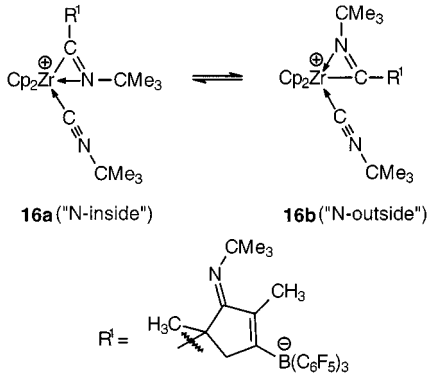
The complex framework of **16** corresponds to a zirconium−borate-betaine structure, which means that the zirconium center bears a partial positive charge. Its high electrophilicity and coordinative unsaturation has led to the complexation of the *tert*-butyl isocyanide ligand. In view of the special stereoelectronic features of the group 4 bent metallocene framework[16] it is likely that the metal−isonitrile coordination is dominated by ligand to metal σ-donation of electrons, without a significant π-backbonding contribution. This is confirmed by the bonding parameters of the Zr←C≡NR unit of **16** and its spectroscopic properties.[17] The C≡N bond length in the free isonitrile is 1.145 A. The C11−N3 distance of the coordinated *tert*-butyl isonitrile ligand in **16** is only marginally elongated at 1.153(7) A. The RN≡C→Zr unit is close to linear [angle N3−C11−Zr 175.5(3)°], and the Zr−C11 distance is 2.338(7) A. Thus the $Cp_2Zr^+\leftarrow C\equiv N-CMe_3$ unit in **16** shows very similar bonding features as found in the pure donor/acceptor adduct $[Cp_3Zr\leftarrow C\equiv N-CMe_3^+]$ (**20**)

Scheme 4



[Zr−C: 2.313(3) Å, C−N 1.145(4) (identical with the uncomplexed ligand); angle Zr−C−N 178.4(2)°].[18] The IR (C≡NR) band of **16** is at ν = 2197 cm^{-1} (**20**: 2209 cm^{-1}) which is above the free ligand value of ν = 2140 cm^{-1} as expected.[17]

The η^2-iminoacyl ligand and the isonitrile donor ligand are both oriented in the σ-ligand plane of the bent metallocene group, as expected. Therefore, two isomeric arrangements of these ligands are possible, which are characterized by central or lateral positioning of the iminoacyl nitrogen atom, respectively.[19] In the crystal we have only found the N-inside isomer (**16a**). But an investigation of the system in solution has revealed the presence of the other, the N-outside isomer (**16b**) and shown that the two stereoisomers **16a** and **16b** are interconverted on the NMR time scale.



In [D$_8$]THF solution complex **16** exhibits two complete sets of ^{1}H- and ^{13}C-NMR signals at 213 K in a ratio of 70:30 which correspond to the two isomers **16a** and **16b**. The chemical shifts of the sets of signals are mostly very similar, some of them are overlapping. The presence of the two isomers can clearly be monitored e.g. by observing six ^{13}C NMR signals of the $-C(CH_3)_3$ substituents at the nitrogen atoms (major isomer **16a**: δ 30.57, 26.61, 26.30; minor isomer **16b**: 30.66, 26.56, 25.58) or the narrowly separated Cp signals at δ 105.23/103.87 (**16a**) and δ 105.28/103.91 (**16b**). Two of the ^{1}H-NMR Cp resonances of the isomers are isochronous (δ 6.00), but the others are split into a 70:30 intensity pair of signals at 5.80 (**16a**) and 5.82 (**16b**). Upon increasing the temperature, coalescence of the two sets of spectra takes place to give an averaged single set of signals corresponding to the equilibrated chiral isomers (leading e.g. to a single pair of ^{1}H-NMR signals of the diastereotopic Cp-ligands at δ 5.94 and 5.75). From the temperature dependent ^{1}H NMR spectra the activation barrier of the **16a** ⟹ **16b** isomerization reaction was determined at $\Delta G^{\neq}_{isom}$ (273 K) = 14 ± 1 kcal mol^{-1} using the DNMR5 dynamic NMR simulation program.[20]

It is very clear that the dynamic process monitored by the temperature dependent ^{1}H- and ^{13}C-NMR spectra as described above corresponds to the iminoacyl N-inside ⟹ N-outside isomerization reaction and not from an equilibration process that solely involves the advent or disappearance of a persistent propeller conformation at the $-B(C_6F_5)_3$ borate group attached at the sp^2-C carbon atom C1 of the five-membered ring system. We are quite sure about this interpretation since we were able to observe this "freezing" of the chiral propeller-geometry at the boron center[5] independently by temperature dependent ^{19}F-NMR spectroscopy (at 564 MHz). As expected for this overall scenario we have observed a total of 30 ^{19}F-NMR resonances of the $B(C_6F_5)_3$ residues at 233 K in [D$_8$]THF, 15 arising from the major isomer **16a** (70% intensity) [δ −128.4, −130.2, −130.7, −133.3, −134.8, −135.6 (*ortho*), −164.6, −165.3, −165.6 (*para*), and −167.4, −168.3, −168.5, −168.6, −169.2, −169.3 (*meta*)] and 15 of lower intensity (30%) due to the minor isomer **16b** [δ −128.9, −130.5, −131.2, −133.2, −133.9, −135.3 (*ortho*), −164.9, −165.2, −165.9 (*para*), and −167.6, −167.8, −168.7, −169.2, −169.7, −169.9 (*meta*)]. Increasing the temperature results in massive line broadening which is first due to giving the (sp^2-C)−B rotation free and thus leading to individual equilibration of the six −*o*-F, three −*p*-F, and six −*m*-F signals for each of the isomers − which gives rise to the observation of a set of two *ortho*-F, two *meta*-F and two *para*-F resonances, each in a ca. 70:30 ratio. Raising the temperature further eventually leads to rapid **16a** ⟹ **16b** equilibration also on the ^{19}F-NMR time scale and thus gives rise to a very simple limiting high temperature spectrum showing only three remaining lines corresponding to the *o*-, *m*-, and *p*-F substituents at the $B(C_6F_5)_3$ unit under rapidly equilibrating conditions.

Conclusions

In principle, the reaction of the (σ-propenyl)(σ-propynyl)zirconocene complex **11** with the strong organometallic Lewis acid $B(C_6F_5)_3$ proceeds very similar to the reaction of bis(σ-propynyl)ZrCp_2 with tris(pentafluorophenyl)borane.[5][9] The propynyl ligand is transferred, followed by an insertion reaction with carbon-carbon coupling to give the group 4 metallocene−(μ-hydrocarbyl)borate betaine com-

plex **14**. The reaction of **11** with $B(C_6F_5)_3$ proceeds rather selectively. Within the limits of detection it is the σ-propynyl group that is transferred. The σ-propenyl ligand remains bonded to zirconium in the first step, it is only used subsequently as a reactive reagent in the insertion reaction. This pronounced selectivity might indicate an increased thermochemical stabilization of the 1,1-bis(cyclopentadienyl) "zircona-allyl" cation over the corresponding "zircona-propargyl" cation system, but this experimental result could also merely reflect the higher mobility of the σ-propynyl group in the transfer step. In any case the resulting "zircona-allyl" cation complex is extremely unstable and rapidly reacts with the in situ generated alkynyl-functionalized borate anion by insertion to yield the metallocene−betaine complex **14**. We conclude that metalla-allyl type reagents can readily be generated by the synthetic route applied in this study, but we must note that such systems seem to be very reactive. If there should be any thermodynamic stabilization at all it is certainly overruled by a very high kinetic reactivity of this organometallic cationic system.

The reaction of **14** with *tert*-butyl isocyanide yields the product **16** which is very interesting in view of its specific bonding features that are derived from the dipolar (i.e. betaine) structure of this metal complex. The connection of the borate anion part $[R-B(C_6F_5)_3^-]$ with the $Cp_2Zr(\eta^2$-iminoacyl) group by means of the bridging carbocyclic framework in fact creates a situation where the zirconocene unit effectively behaves like a metallocene cation that is completely separated from its anion.[21] This shows up in its property to serve as an organometallic Lewis acid strongly coordinating an isonitrile donor ligand. The structural and spectroscopic features of the resulting local $[Cp_2Zr(R')\leftarrow C\equiv NR^+]$ moiety are as expected for an (isonitrile)-zirconocene cation donor-acceptor adduct. This provides additional evidence that a variety of group 4 metallocene−(μ-organyl)borate betaines are very suited organometallic molecules to detect, study, and eventually use a typical metallocene cation reactivity in an overall *neutral* molecule.

Financial support from the *Fonds der Chemischen Industrie*, the *Bundesminister für Bildung, Wissenschaft, Forschung und Technologie (BMBF)*, the *Deutsche Forschungsgemeinschaft*, and the *Ministerium für Wissenschaft und Forschung des Landes Nordrhein-Westfalen* is gratefully acknowledged.

Experimental Section

All reactions were carried out in an inert atmosphere (argon) using Schlenk-type glassware or in a glovebox. Solvents, including deuterated solvents, were dried and distilled under argon prior to use. For additional general information, including a list of spectrometers used, see ref.[5] and ref.[9]. The reagents (hydrido)zirconocene chloride[10] and tris(pentafluorophenyl)borane[7] were prepared according to literature procedures.

Preparation of (1-Propenyl)zirconocene Chloride (**10**): (Hydrido)-zirconocene chloride (1.10 g, 4.32 mmol) was suspended in 10 ml of toluene. The Schlenk flask was evacuated and filled with propyne. The mixture was stirred and additional propyne was entered into the gasphase in ca. 20 min intervals. A clear solution was obtained after ca. 4 h. Solvent was removed in vacuo and the residue stirred with pentane (3 ×) to give 950 mg (74%) of **10** as a pale yellow solid, m. p. 78°C (decomp.). − ^{1}H NMR ([D$_6$]benzene): δ 6.88 (dq, ^3J = 17.2 Hz, ^4J = 1.5 Hz, 1 H, Zr-C^1*H*=), 5.89 (dq, ^3J = 17.2 Hz, 6.0 Hz, 1 H, =C^2*H*-), 5.81 (s, 10 H, Cp), 1.79 (dd, ^3J = 6.0 Hz, ^4J = 1.5 Hz, 3 H, CH_3). − ^{13}C NMR ($CDCl_3$): δ 177.2 (C1), 138.6 (C2), 112.8 (Cp), 23.8 (CH_3).

Preparation of (1-Propenyl)(1-propynyl)zirconocene (**11**): (Propenyl)zirconocene chloride **10** (1.00 g, 3.47 mmol) and propynyllithium (165 mg, 3.59 mmol) were mixed as solids. At −78°C 10 ml of cold toluene was added with stirring. The cooling bath was removed after 1 h and the mixture allowed to warm to room temperature. After stirring overnight a lithium chloride precipitate was removed by filtration and the solvent evaporated in vacuo from the filtrate. The oily residue was solidified by treatment with pentane (12 h stirring) and the product dried in vacuo to yield 956 mg (91%) of **11**, m.p. 129°C (decomp.). − ^{1}H NMR ([D$_6$]benzene): δ 6.98 (dq, ^3J = 17.4 Hz, ^4J = 1.2 Hz, 1 H, Zr-CH=), 5.95 (s, 10 H, Cp), 5.88 (dq, ^3J = 17.4 Hz, 5.8 Hz, 1 H, =CH-), 1.78 (s, 3 H, C=C-CH_3), 1.77 (dd, ^3J = 5.8 Hz, ^4J = 1.2 Hz, 3 H, =CH-C*H*$_3$). − ^{13}C NMR ([D$_6$]benzene): δ 182.2 (Zr-*C*H=), 135.6 (=CH-), 110.6 (Cp), 129.1, 118.1 (-C=C-), 23.9 (=CH-*C*H$_3$), 5.90 (=C-*C*H$_3$). − IR (KBr): ν = 2086 (C=C), 1635 (C=C). − $C_{16}H_{18}Zr$ (301.5): C 63.67, H 5.97; found: C 62.68, H 5.49%.

Reaction of **11** *with B(C$_6$F$_5$)$_3$: Generation of* **14**: 5 mg (16.6 μmol) of **11** and 8.5 mg (16.6 μmol) of $B(C_6F_5)_3$ were mixed as solids. 0.5 ml of the respective deuterated solvent (see below) was added and the clear orange colored solution characterized spectroscopically. The solutions were not stable for prolonged periods of time. They turned brownish and a dark colored oil precipitated. Spectroscopic characterization of **14**: ^{1}H NMR ([D$_8$]toluene, 600 MHz, 233 K): δ 7.40 (d, ^3J = 16.2 Hz, 1 H, 4-H), 5.78 (br. s, 1 H, 5-H), 5.16 (s, 5 H, Cp), 5.02 (s, 5 H, Cp), 1.86 (s, 3-H, 2-CH_3), 0.80 (d, ^3J = 6.0 Hz, 3 H, 5-CH_3). − ^{13}C NMR ([D$_8$]toluene, 150 MHz, 233 K): δ 158.8 (C4), 149.3 [$^1J_{CF}$ = 253 Hz, o-$B(C_6F_5)_3$], 115.5 (C5), 112.8 (Cp), 111.0 (Cp), 26.9 (2-CH_3), 19.1 (5-CH_3) [C2, C3, *m*-, *p*-, and *ipso*-C of $B(C_6F_5)_3$ not observed]; the spectral assignment was secured by GCOSY, GHSQC, and GHMBC-NMR experiments[22]. − ^{11}B NMR ([D$_6$]benzene): δ −13.2. − ^{19}F NMR ([D$_8$]toluene, 233K, 564 MHz): δ −128.7, −129.2, −129.8, −133.3, −133.8, −138.2 (*o*-), −160 to −164 (*p*-), −164.5, −164.7, −165.7, −167.0, −167.3, −168.3 [*m*-$B(C_6F_5)_3$]. From the temperature-dependent dynamic NMR spectra (^{1}H-NMR coalescence of the Cp-signals) a Gibbs activation energy of the enantiomerization process of **14** was derived at $\Delta G^{\neq}_{enant}$ (T_c = 304 K) = 15.5 ± 0.5 kcal mol^{-1} (Δν = 20.6 Hz, in [D$_8$]toluene) using the Gutowsky-Holm approximation.[11]

Reaction of **14** *with tert-Butyl Isocyanide: Preparation of* **16**: The betaine **14** was generated in situ by treatment of 200 mg (0.66 mmol) of **11** with 340 mg (0.66 mmol) of $B(C_6F_5)_3$ in 8 ml of toluene at −78°C. The mixture was stirred for 30 min at −78°C and then allowed to warm to 0°C during 1 h. 1 ml of *tert*-butyl isocyanide was added to the orange colored turbid solution. The reaction mixture was stirred overnight at ambient temperature. Volatiles were removed in vacuo and the residue washed twice with 5 ml of pentane. The resulting solid was dissolved in 5 ml of dichloromethane and the product precipitated by the addition of 10 ml of pentane, collected by filtration and dried in vacuo; yield of **16** 527 mg (81%). Single crystals of **16** suited for the X-ray crystal structure analysis were obtained from $CDCl_3$ by a slow evaporation of the solvent. Characterization of **16**: m.p. 141°C (decomp.). In solution two isomers **16a** and **16b** were detected in a 70:30 ratio. − ^{1}H NMR ([D$_8$]THF, 600 MHz, 213 K) major isomer (**16a**): δ 6.00 (s, 5 H, Cp), 5.80 (s, 5 H, Cp), 2.75, 2.68 (AB, ^2J = 16 Hz, each 1 H, 5-H,

5-H′), 1.86 (s, 3 H, 4-CH_3), 1.65 (s, 3 H, 2-CH_3), 1.75, 1.35, 1.30 [s, each 9 H, C(CH_3)$_3$]; minor isomer (**16b**): δ 6.00 (s, 5 H, Cp), 5.82 (s, 5 H, Cp), 2.78, 2.36 (AB, ^2J = 16 Hz, each 1 H, 5-H, 5-H′), 1.92 (s, 3 H, 4-CH_3), 1.88 (s, 3 H, 2-CH_3), 1.72, 1.30, 1.02 [s, each 9 H, C(CH_3)$_3$]. – ^{13}C NMR ([D$_8$]THF, 150 MHz, 213 K) major isomer (**16a**): δ 230.0 (Zr-C=N), 179.4 (C3), 147.8 (Zr←C≡NR), 146.2 ($^1J_{CF}$ = 246 Hz), 136.6 ($^1J_{CF}$ = 240 Hz), and 135.0 [$^1J_{CF}$ = 254 Hz, *o*-, *p*-, *m*-B(C_6F_5)$_3$], 133.2 (C2), 122 [*ipso*-C of B(C_6F_5)$_3$], 105.23 and 103.87 (Cp), 58.8, 58.1, and 51.9 (*ipso*-C of *tert*-butyl), 55.1 (C4), 48.9 (C5), 28.1 (4-CH_3), 30.57, 26.61, and 26.30 [C(CH_3)$_3$], 16.6 (2-CH_3), C1 not observed; minor isomer (**16b**): δ 230.0 (Zr-C=N), 179.4 (C3), 147.3 (Zr←C≡NR), 146.2 ($^1J_{CF}$ = 246 Hz), 136.6 ($^1J_{CF}$ = 254 Hz), and 135.0 [$^1J_{CF}$ = 240 Hz, *o*-, *p*-, *m*-B(C_6F_5)$_3$], 132.6 (C2), 122 [*ipso*-C of B(C_6F_5)$_3$], 105.28 and 103.91 (Cp), 58.3, 52.00 (*ipso*-C of *tert*-butyl, 1 signal not observed), 54.2 (C4), 48.3 (C5), 30.66, 26.56, and 25.58 [C(CH_3)$_3$], 29.4 (4-CH_3), 16.2 (2-CH_3), C1 not observed. – These assignments were supported by the results of GCOSY, GHSQC and GHMBC NOE-difference, and ROESY NMR experiments[22]. – ^{11}B NMR ($CDCl_3$): δ −15.1. – ^{19}F NMR ([D$_8$]THF, 564 MHz, 233 K) major isomer (**16a**): δ −128.4, −130.2, −130.7, −133.3, −134.8, −135.6 (*ortho*-), −164.6, −165.3, −165.6 (*para*-), −167.4, 168.3, −168.5, −168.6, −169.2, −169.3 [*meta*-B(C_6F_5)$_3$]; minor isomer (**16b**): δ −128.9, −130.5, −131.2, −133.2, −133.9, −135.3 (*ortho*-), −164.9, −165.2, −165.9 (*para*-), −167.6, −167.8, −169.2, −169.7, −169.9 [*meta*-B(C_6F_5)$_3$]. IR (KBr): ν = 2197 (N≡CR), 1611 (C=C). – UV/Vis (dichloromethane): λ_{max} = 306 nm (ε = 34500), 254 (ε = 36000), 233 (ε = 21700). – $C_{49}H_{45}BF_{15}N_3Zr$ (1062.9): C 55.37, H 4.27, N 3.97; found: C 55.41, H 4.50, N 4.26%.

X-ray Crystal Structure Analysis of **16**: Formula $C_{49}H_{45}BF_{15}N_3Zr \cdot 1.5\ CHCl_3$, M = 1241.96, 0.30 × 0.20 × 0.10 mm, a = 12.105(1), b = 13.146(1), c = 17.167(1) A, α = 88.97(1), β = 82.62(1), γ = 82.29(1)°, V = 2684.7(4) A^3, ρ_{calc} = 1.536 g cm^{-3}, μ = 5.19 cm^{-1}, empirical absorption correction via φ scan data (0.891 ≤ C ≤ 0.999), Z = 2, triclinic, space group P1bar (No. 2), λ = 0.71073 A, T = 223 K, ω/2θ scans, 9916 reflections collected (±h, +k, ±l), [(sinθ)/λ] = 0.59 A^{-1}, 9463 independent and 4891 observed reflections [$I \geq 2\ \sigma(I)$], 705 refined parameters, R = 0.061, wR^2 = 0.141, max. residual electron density 1.06 (−0.75) e A^{-3}, hydrogens calculated and refined as riding atoms.

Data set was collected with an Enraf Nonius MACH3 diffractometer. Programs used: data reduction MolEN, structure solution SHELXS-86, structure refinement SHELXL-93, graphics SCHAKAL-92.

Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-100939. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: int. code +44(1223)336-033, e-mail: deposit@ccdc.cam.ac.uk].

☆ Dedicated to Professor *Heinrich Nöth* on the occasion of his 70th birthday.

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[14] From the observed experimental data two slightly different stereochemical situations can be envisaged for the characterization of **14**. If the C(sp^2)-B(C_6F_5)$_3$ unit (under ″frozen″ static NMR conditions) contains a *chiral* borate propeller geometry, than two diastereomeric isomers of **14** would result. However, it could also be possible that the C(sp^2)-B(C_6F_5)$_3$ unit favours a *prochiral* conformation that only leads to 15 diastereotopic ^{19}F NMR signals due to the presence of the adjacent chiral metal complex framework (for a discussion of such an example see e.g. S. Döring, G. Erker, R. Fröhlich, O. Meyer, K. Bergander, *Organometallics*, in press.) In the case of **14** we cannot decide between these two alternative stereochemical interpretations at present because it was not possible to identify the minor components of the obtained product mixture.

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