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Synthesis of dimetallic μ-alkylideneamido zirconocene dications by a thermodynamically favorable lithium chloride elimination pathway

Steve Döring, Gerhard Erker *, Roland Fröhlich [1]

Organisch-Chemisches Institut der Universität Münster, Corrensstrasse 40, D-48149 Münster, Germany

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Dedicated to Professor François Mathey on the occasion of his 60th birthday

Abstract

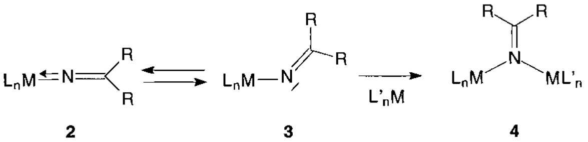
The reagent [butyl-B(C_6F_5)$_3$]$^-$Li$^+$ reacts with the complexes Cp$_2$ZrCl(N=CHR) (**6**) (R=CH$_3$ or *p*-tolyl) at ambient temperature by chloride abstraction. The resulting in situ formed [Cp$_2$Zr(N=CHR)]$^+$ cations (**8**) dimerize under the reaction conditions. After removal of a stoichiometric amount of lithium chloride the corresponding μ-alkylideneamido-bridged dimeric [Cp$_2$Zr(N=CHR)]$_2^{2+}$ dications **9a** (R = CH$_3$) and **9b** (R = *p*-tolyl) are isolated in yields of ca. 80% (with [butyl-B(C_6F_5)$_3$]$^-$ counteranion). The complexes **9a** and **9b** are each obtained as mixtures of *cis*- and *trans*-isomers. Crystallization from dichloromethane gave pure *trans*-**9a** and *trans*-**9b** samples. Both were characterized by X-ray crystal structure analyses. Treatment of the dications **9** with acetonitrile gave the respective mononuclear monocationic adduct complexes [Cp$_2$Zr(N=CHR^1)N≡C–CH$_3$]$^+$[butyl-B(C_6F_5)$_3$]$^-$ (**16**). © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Zirconocene cation complexes; Metallocenes; Dimerization; Bridging nitrogen-containing ligands

1. Introduction

Bis(alkylidene)ammonium ions [R$_2$C=N=CR$_2$]$^+$ (**1**) exhibit linear heteroallene-type structures around a central sp-hybridized nitrogen atom [1]. The corresponding (alkylideneamido)metal complexes **2** also show near to linear metallaallene structures in cases where electron-deficient L$_n$M moieties are employed [2–5]. In such substances a ligand to metal π-bonding component that makes use of the Schiff-base nitrogen lone pair often leads to a considerable stabilization of the linear structure around the sp-hybridized nitrogen [6]. However, in many such organometallic systems this π-component is often weaker than in the purely organic systems **1**, and, therefore, the bent isomers **3** are in an equilibrium situation with **2**, albeit mostly much less favored [2b]. In principle this endothermic equilibrium could be used to trap the bent isomer **3** by adding a suitable second electrophile to the aldimine nitrogen using the pronounced donor function of the sp^2-hybridized nitrogen center in the bent isomeric situation. This had been realized in a few instances, e.g. by using strongly electrophilic Group 3 metal centers [7].

We have now generated very electrophilic Group 4 metallocene alkylideneamido cations and found that they dimerized along the reaction path outlined in Scheme 1 to yield very stable dimetallic alkylideneamido-bridged bis(zirconocene) dications. Their structures and some of their chemical properties, probably originating from monomerization reactions, are described. For the preparation of the Group 4 metallocene alkylideneamido cation systems we have used a favorable LiCl salt elimination route [8].



Scheme 1.

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* Corresponding author. Tel.: +49-251-8333221; fax: +49-251-8336503.

E-mail address: erker@uni-muenster.de (G. Erker).

[1] X-ray crystal structure analyses.

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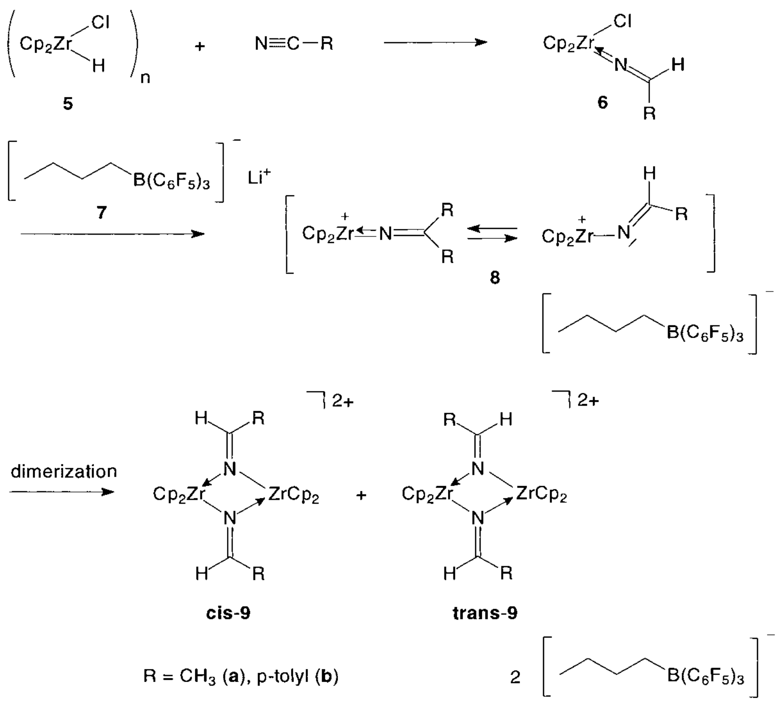


Scheme 2.

2. Results and discussion

Two neutral (alkylideneamido)zirconocene chlorides were used as the starting materials for our study, namely the complexes $Cp_2ZrCl(N{=}CHR)$ **6a** ($R = CH_3$) and **6b** ($R = p$-tolyl). They were synthesized, as previously described by us [2a], by means of a hydrozirconation reaction of acetonitrile or 4-methylbenzonitrile, respectively, employing the oligomeric 'Schwartz-reagent' $(Cp_2ZrHCl)_n$ (**5**) [9] suspended in toluene. These compounds were isolated in ca. 80% yield each. Complex **6a** shows a characteristic Zr=N=C ^{13}C-NMR resonance at δ 167.5 ($^1J_{CH} = 168$ Hz). The related complex $Cp_2Zr{=}N{=}CHPh$ had been characterized by X-ray diffraction and shown to exhibit an almost linear Zr=N=C framework (angle Zr–N–C: 170.5(5)°) [2a].

The (ethylideneamido)zirconocene chloride complex **6a** was treated with lithium[butyltris(pentafluorophenyl)borate] (**7**) in dichloromethane at room temperature. This results in an effective chloride abstraction from zirconium. Initially a clear solution of the reagents is obtained, from which after a short while at ambient temperature LiCl begins to precipitate. The reaction is essentially complete after 2 h stirring at room temperature. The LiCl precipitate is then removed by filtration and the resulting organometallic product (**9**) isolated in 70% yield from the solution.

The NMR spectra indicate that a 1:1 mixture of the dinuclear dication complexes *cis*- and *trans*-**9a** were formed, that have probably resulted from dimerization of the in situ generated reactive coordinatively unsaturated (ethylideneamido)zirconocene cations **8a** (Scheme 2).

The *cis*-dimer (*cis*-**9a**) exhibits a CH_3 signal in the ^1H-NMR spectrum in CD_2Cl_2 at δ 1.92, representing six hydrogen atoms and two ^1H-NMR Cp singlets at δ 6.84 and 6.81, each representing 10 H atoms. The corresponding ^{13}C-NMR Cp signals of *cis*-**9** are found at δ 121.0 and 117.8. In contrast, the C_i-symmetric isomer *trans*-**9a** exhibits a single ^1H-NMR Cp singlet (at δ 6.83) and a methyl resonance (at δ 1.77) in a 20:6 ratio. Both isomers show an identical chemical shift of the 'metalloaldimine'-carbon atom at δ 194.9 which is shifted markedly downfield from the neutral reference **6a**.

The aryl-substituted complex **6b** reacts analogously upon treatment with an equimolar quantity of the chloride abstractor $[butyl\text{-}B(C_6F_5)_3]^-Li^+$ (**7**). After removal of the LiCl precipitate a 1:1.5 mixture of the *cis*- and *trans*-**9b** dimers was isolated. They also show the characteristic symmetry-dependent appearance of the NMR spectra ($^1H/^{13}C$-NMR pairs of Cp signals of *cis*-**9b** at δ 6.70, 6.30/117.3, 114.0 and single Cp resonances of *trans*-**9b** at δ 6.37/112.6).

The favored formation of the dimeric bis[(alkylideneamido)zirconocene] dication complexes was also confirmed by the results of X-ray crystal structure analyses. Crystallization of the *cis*-/*trans*-**9a** mixture from dichloromethane gave single crystals of the pure *trans*-**9a** isomer that were suitable for the X-ray crystal structure analysis (Fig. 1).

In the crystal two [butyl-B(C_6F_5)$_3$]$^-$ anions were found that show typical tetraorganylborate structural features (averaged B–C(aryl): 1.663(4) Å, B–C(butyl): 1.642(4) Å). The anions are independent of the dication in the crystal. The dication shows a rhomboedric Zr_2N_2 framework. The heavy atoms of the [($CH_3CH{=}N$)$_2Zr_2$] framework are coplanar. The methyl substituents are located with C_i-symmetry at the periphery of the [(C=N)$_2Zr_2$] frame. The N–Zr–N* angles are rather small at 77.8(1)°. The corresponding Zr–N–Zr* angles are markedly larger at 102.2(1)°. The C2–N1 bond length in *trans*-**9a** amounts to 1.281(4) Å, which is in the typical range of a Schiff base C=N double bond [10]. Similar bonding features were observed previously for the typical examples of the neutral or mono-cationic μ-N=CR_2M_2 complexes **10** (C–N: 1.25(2) Å [7]), **11** (C–N: 1.266(13) Å [11]) and **12** (C–N: 1.235(19) Å [12]) (Scheme 3). In *trans*-**9a** the N1–C2–C3 angle is 126.2(3)° and the C3–C2–N1–Zr dihedral angle amounts to −179.0(3)°. The (*E*)-(Zr–N1) bond (2.255(2) Å) is slightly longer than the (*Z*)-(Zr*–N1) linkage (2.235(2) Å). The four η^5-Cp ligands are arranged above and below the Zr_2N_2 plane with a Cp-(centroid)–Zr–Cp(centroid) angle of 129.6°.

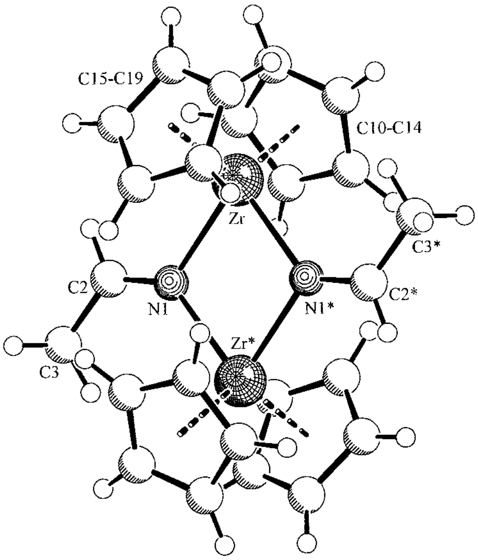
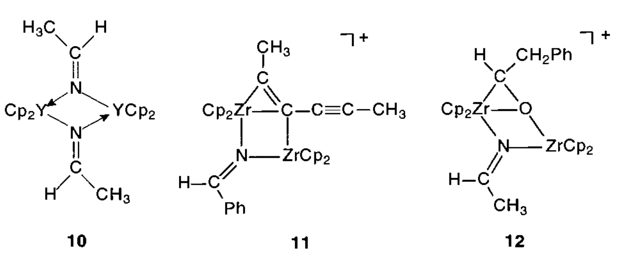


Fig. 1. Molecular structure of *trans*-**9a** (only the dication part is depicted). Selected bond lengths (Å) and angles (°): Zr–N1* 2.235(2), Zr–N1 2.255(2), N1–C2 1.281(4), C2–C3 1.482(4), B–C21 1.642(4), C21–C22 1.532(4), C22–C23 1.537(5), C23–C24 1.475(5), B–C31 1.669(4), B–C41 1.655(4), B–C51 1.666(4); N1*–Zr–N1 77.8(1), Zr–N1–Zr* 102.2(1), Zr–N1–C2 124.3(2), N1–C2–C3 126.2(3), C21–B–C31 115.4(2), C21–B–C41 105.7(2), C21–B–C51 109.7(2), C31–B–C41 111.8(2), C31–B–C51 102.1(2), C41–B–C51 112.2(2), B–C21–C22 115.9(2), C21–C22–C23 114.1(3), C22–C23–C24 114.8(3).



Scheme 3.

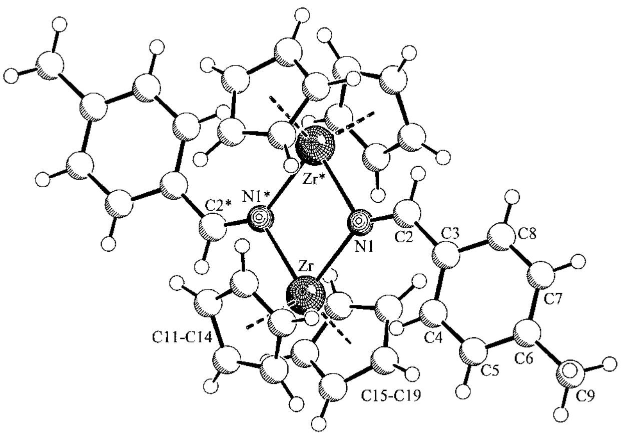


Fig. 2. A view of the *trans*-**9b** dication. Selected bond lengths (Å) and angles (°): Zr–N1* 2.272(4), Zr–N1 2.192(4), N1–C2 1.288(6), C2–C3 1.444(7), B–C21 1.658(8), C21–C22 1.509(8), C22–C23a 1.558(8), C22–C23b 1.555 (8), C23–C24a 1.524(9), C23–C24b 1.535(10), B–C31 1.649(8), B–C41 1.655(8), B–C51 1.648(8); N1*–Zr–N1 79.0(2), Zr–N1–Zr* 101.0(2), Zr–N1–C2 119.3(3), N1–C2–C3 129.8(5), C21–B–C31 110.5(5), C21–B–C41 115.9(4), C21–B–C51 103.8(4), C31–B–C41 102.0(4), C31–B–C51 113.6(4), C41–B–C51 111.4(4), B–C21–C22 116.1(5), C21–C22–C23a 121.3(7), C21–C22–C23b 97.9(9), C22–C23a–C24a 106.6(8), C22–C23b–C24b 108.5(9).

Single crystals of *trans*-**9b** were also obtained from dichloromethane. The molecular structure of the dication *trans*-**9b** in the crystal also shows the typical distorted Zr_2N_2 framework (N–Zr–N* angle: 79.0(2)°, Zr–N–Zr* 101.0(2)°). As expected, the conjugated aryl group exerts some influence on the coordination features of the C=N unit. In *trans*-**9b** the (*Z*)-(Zr–N1) bond (2.192(4) Å) is shorter than the (*E*)-(Zr*–N1) linkage (2.272(4) Å). The C2–N1 bond length is 1.288(6) Å. The aryl substituent at C2 is oriented close to coplanar with the central framework of the complex (dihedral angles Zr–N1–C2–C3 −1.3(9)°, N1–C2–C3–C4 −11.8(9)°) (Fig. 2).

The remaining solution from the crystallization of complex *trans*-**9a** was enriched in the isomer *cis*-**9a**. Monitoring by ^{1}H-NMR did not reveal reestablishment of the original 1:1 ratio during several hours at room temperature. From work reported by Jordan, Bochmann and others [13] it is well established that the formation of nitrile adducts of mononuclear monocations derived from (alkylideneamido)zirconocene systems are very stable and their formation, e.g. by treatment of $Cp_2ZrCH_3^+$ with acetonitrile proceeds readily (for an example see Chart 1). We, therefore, investigated whether the formation of such species could also be achieved starting from our readily available dimeric dication systems **9**.

The dication **9a** (*cis*/*trans*-mixture) was generated by treatment of the precursor **6a** with [butyl-B$(C_6F_5)_3]^-$ Li^+ (**7**) in dichloromethane (see above and the Section 3). Then one molar equivalent of acetonitrile–Zr was added. Workup after 1 h reaction time at room temperature revealed that the *cis*-/*trans*-**9a** dication mixture had been consumed with formation of the mononuclear zirconocene mono-cation product $[Cp_2Zr(N{=}CHCH_3)\cdot N{\equiv}CCH_3]^+$ (**15a**), with [butyl-B$(C_6F_5)_3]^-$ counteranion. The product **15a** was isolated in close to 80% yield from the reaction mixture (Scheme 4). Complex **15a** shows a typical $-N{=}CHCH_3$ ^{13}C-NMR resonance at δ 173.1.

Analogous treatment of the in situ generated *cis*-/*trans*-**9a** mixture with *tert*-butylisonitrile gave the corresponding $C{\equiv}N{-}CMe_3$ stabilized [(ethylideneamido)-zirconocene] mono-cation system **16** (80% isolated), and the reaction of the *cis*-/*trans*-**9b** dication mixture with acetonitrile furnished the corresponding system **15b** (68% isolated, ^{13}C-NMR $-N{=}CHR$ resonance at δ 170.1). In each case a single stereoisomer was obtained. We assume that this is characterized by coplanar (*E*)-arrangement of the R^1-substituent with the stabilizing $N{\equiv}C{-}R^2$ ligand at the linear $Cp_2Zr(N{=}CHR^1)$ framework as it is depicted in Scheme 4.

We conclude that [butyl-B$(C_6F_5)_3]^-Li^+$ (**7**) is a suitable reagent for facile chloride abstraction from Group 4 metallocene units and related systems. Treatment of the respective metallocene precursors with the sufficiently soluble reagent **7** provides a simple method for generating even very reactive metallocene based cations such as the elusive monomeric $[Cp_2Zr{=}N{=}CHR]^+$ cation. This cation is probably formed in situ under the reaction conditions but rapidly dimerizes to give the metallacyclic dications **9** in good yield. Whether the subsequently added nitrile reagents react directly with the strongly electrophilic dications **9** or trap the monomers (**8**) from an endothermic equilibration cannot be concluded with certainty so far. However, it is apparent that our halide abstraction method is able to make reactive metallocene cation systems easily available. We will investigate whether the system **9** can be used in organometallic syntheses for reactions that use the coordinated $\mu - N{=}CHR$ units as active functional groups.

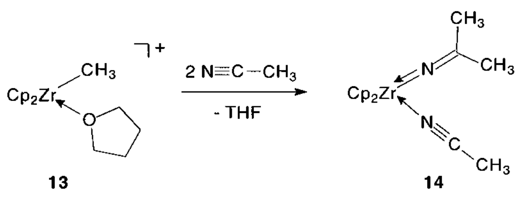
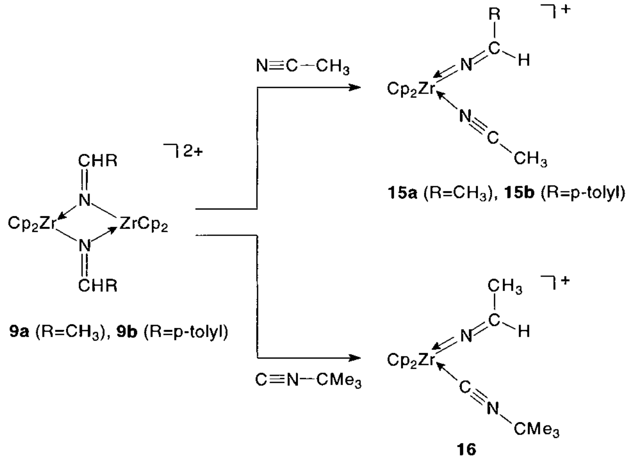


Chart 1.



all cations with [butylB$(C_6F_5)_3]^-$ counteranion

Scheme 4.

3. Experimental

Reactions were carried out under argon using Schlenk-type glassware or in a glovebox. Solvents were dried and distilled prior to use. The starting materials **6a** and **6b** were prepared analogously as described in the literature [2a]. [Butyl-B$(C_6F_5)_3]^-Li^+$ had previously been mentioned in the literature [14]. The preparation of the material (**7**) that was used in this study was synthesized as described below. For additional general information including a list of instrumentation used for the spectroscopic and physical characterization, see Ref. [15]. $B(C_6F_5)_3$ was prepared as described in the literature [16].

3.1. Synthesis of lithium[butyltris(pentafluorophenyl)borate] (7)

A 1.6 M solution of *n*-butyllithium in hexane (1.50 ml, 2.40 mmol) was added dropwise with stirring to a solution of trispentafluorophenylborane (1.00 g, 1.95 mmol) in 50 ml of pentane. The product **7** precipitated immediately. The mixture was stirred for 2 h to allow the reaction to go to completion. Then the product **7** was collected by filtration, washed with pentane (2 × 15 ml) and dried in vacuo [yield: 970 mg (86%)], m.p. 178 °C (dec.). ^{1}H-NMR: ([benzene-d_6, THF-d_8], 4:1, 200 MHz, 300 K): $\delta = 1.67$ (br, 2H, B–CH_2), 1.53 (m, 2H, CH_2), 1.28 (br, 2H, CH_2), 0.93 (t, 3H, CH_3). $^{11}B\{^1H\}$-NMR: ([benzene-d_6, THF-d_8], 4:1, 64.2 MHz, 300 K): $\delta = -12.6$ ($w_{1/2} = 225$ Hz). ^{19}F-NMR: ([benzene-d_6, THF-d_8], 4:1, 282.4 MHz, 300 K): $\delta = -167.9$ (m, 6F, *m*-F), -165.5 (t, $^3J_{FF} = 21$ Hz, 3F, *p*-F), -131.7 (m, 6F, *o*-F). Anal. Calc. for $C_{22}H_9BF_{15}Li$ (576.0): C, 45.87; H, 1.57. Found: C, 45.21; H, 2.52%. HRMS: Calc. for $[C_{22}H_9BF_{15}]^-$: 569.0558, found 569.0562.

*3.2. Reaction of (alkylideneamido)zirconocene chlorides with [butyl-B(C_6F_5)$_3$]$^-$ Li$^+$ (7), preparation of the [$Cp_2Zr(N=CHR)$]$_2^{2+}$ 2[butyl-B(C_6F_5)$_3$]$^-$ complexes **9**, general procedure*

The respective $Cp_2ZrCl(N{=}CHR)$ complex **6** and the reagent **7** were suspended in a 1:1 molar ratio in dichloromethane. The resulting clear yellowish solution was stirred at ambient temperature until a LiCl precipitate appeared (ca. 1 h). The mixture was stirred for additional 2 h to allow the reaction to go to completion. The LiCl precipitate was removed by filtration. Solvent was removed from the clear filtrate in vacuo. The solid was taken up with pentane and the product **9** collected by filtration. It was washed with pentane (2 × 20 ml) and dried in vacuo.

*3.3. Reaction of (ethanimido)zirconocene chloride **(6a)** with **7**: synthesis of cis/trans-**9a***

The reaction of **6a** (200 mg, 0.67 mmol) with 385 mg (0.67 mmol) of **7** in CH_2Cl_2 analogously as described above gave a 1:1 mixture of *cis*- and *trans*-**9a** in a combined yield of 407 mg (73%), m.p. 153 °C. ^{1}H-NMR (CD_2Cl_2, 200.1 MHz, 300 K): *trans*-**9a**: $\delta = 7.85$ (q, 2H, $^3J_{HH} = 4.7$ Hz, C*H*(CH_3)), 6.83 (s, 20H, Cp-*H*), 1.77 (d, 6H, $^3J_{HH} = 4.7$ Hz, CH(CH_3)); *cis*-**9a**: 7.66 (q, 2H, $^3J_{HH} = 4.7$ Hz, C*H*(CH_3)), 6.84, 6.81 (each s, each 10H, Cp-*H*), 1.92 (d, 6H, $^3J_{HH} = 4.7$ Hz, CH(CH_3)); 1.21, 0.80 (each m, Σ 18H, [butyl-B(C_6F_5)$_3$$^-$]). ^{13}C{^{1}H}-NMR ($CD_2Cl_2$, 50.3 MHz, 300 K): $\delta = 194.9$ (N=*C*, *cis*- and *trans*-**9a**), 148.7 (dm, $^1J_{CF} = 242$ Hz, B(C_6F_5)$_3$), 138.0 (dm, $^1J_{CF} = 242$ Hz, B(C_6F_5)$_3$), 137.0 (dm, $^1J_{CF} = 243$ Hz, B(C_6F_5)$_3$), 121.0, 117.8 (Cp-*C*, *cis*-**9a**), 119.5 (Cp-C, *trans*-**9a**), 67.1 (CH(CH_3)), 31.1, 27.3, 23.4 (br), 14.5 ([butyl-B(C_6F_5)$_3$$^-$]), *ipso*-C of C_6F_5 not observed. ^{11}B{^{1}H}-NMR (CD_2Cl_2, 64.2 MHz, 300 K): $\delta = -13.0$ ($w_{1/2} = 50$ Hz). IR (KBr): $\tilde{\nu} = 3380$ (w), 2964 (s), 2927 (m), 2855 (m), 1645 (m), 1512 (s), 1458 (vs), 1263 (vs), 1100 (s), 1019 (m), 970 (s), 795 (vs) cm^{-1}; m.p. 153 °C. Anal. Calc. for $C_{68}H_{46}B_2F_{30}N_2Zr_2$ (1665.1): C, 49.05; H, 2.78; N, 1.62. Found: C, 49.07; H, 3.49; N, 1.86%.

*3.3.1. X-ray crystal structure analysis of trans-**9a***

Single crystals were obtained from a solution of *cis*-/*trans*-**9a** in dichloromethane at −20 °C. Formula $C_{24}H_{28}N_2Zr_2 \cdot 2C_{22}H_9BF_{15}$, $M = 1665.1$, yellow crystal 0.30 × 0.20 × 0.20 mm, $a = 23.978(1)$, $b = 11.152(1)$, $c = 23.745(1)$ Å, $\beta = 90.90(1)°$, $V = 6348.7(7)$ Å^3, $\rho_{calc} = 1.742$ g cm^{-3}, $\mu = 4.63$ cm^{-1}, empirical absorption correction via SORTAV ($0.874 \le T \le 0.913$), $Z = 4$, monoclinic, space group $C2/c$ (no. 15), $\lambda = 0.71073$ Å, $T = 198$ K, ω and φ scans, 19367 reflections collected ($\pm h$, $\pm k$, $\pm l$), [$(\sin\theta)/\lambda$] = 0.65 Å^{-1}, 7248 independent ($R_{int} = 0.038$) and 5730 observed reflections [$I \ge 2\sigma(I)$], 471 refined parameters, $R = 0.043$, $wR^2 = 0.099$, max. residual electron density 1.09 (−0.52) e Å^{-3} around C23, refinement of split positions for C24 did not improve the model, hydrogens calculated and refined as riding atoms.

*3.4. Reaction of (p-tolylmethanimido)zirconocene chloride **(6b)** with **7**: synthesis of cis/trans-**9b***

Reaction of **6a** (200 mg, 0.53 mmol) with **7** (307 mg, 0.53 mmol) in CH_2Cl_2 analogously as described above gave 337 mg (70%) of a 1:1.5 mixture of *cis*- and *trans*-**9b**, m.p. 140 °C. ^{1}H-NMR (CD_2Cl_2, 200.1 MHz, 300 K): $\delta =$ *trans*-**9b**: 8.89 (s, 3H, C*H*), 6.37 (s, 30H, Cp-*H*), 2.46 (s, 9H, tolyl-CH_3); *cis*-**9b**: 9.22 (s, 2H, C*H*), 6.77, 6.30 (each s, each 10H, Cp-*H*), 2.44 (s, 6H, tolyl-CH_3); 7.56–7.07 (m, 20H, tolyl-*H*), 1.22, 0.81 (each m, Σ 18H, [butyl-B(C_6F_5)$_3$]$^-$). ^{13}C{^{1}H}-NMR (CD_2Cl_2, 50.3 MHz, 300 K): $\delta = 148.7$ (dm, $^1J_{CF} = 242$ Hz, B(C_6F_5)$_3$), 138.0 (dm, $^1J_{CF} = 242$ Hz, B(C_6F_5)$_3$), 137.0 (dm, $^1J_{CF} = 243$ Hz, B(C_6F_5)$_3$), 132.0 (*ipso*-tolyl-*C*), 129.5, 128.0 (*o*- and *p*-tolyl-*C*), 121.0, 117.8 (Cp-*C*, *cis*-**9b**), 119.5 (Cp-*C*, *trans*-**9b**), 21.1 (tolyl-CH_3), 31.1, 27.3, 23.4 (br), 14.5 ([butyl-B(C_6F_5)$_3^-$]), one *ipso*-C of tolyl, *ipso*-C of B(C_6F_5)$_3$ and N=C carbon atoms not observed. ^{11}B{^{1}H}-NMR (CD_2Cl_2, 64.2 MHz, 300 K): $\delta = -13.2$ ($w_{1/2} = 47$ Hz). IR (KBr): $\tilde{\nu} = 3020$ (m), 2964 (m), 2802 (m), 1632 (m), 1510 (vs), 1453 (vs), 1280 (vs), 1120 (s), 1019 (m), 975 (s), 795 (vs), 486 (m) cm^{-1}; Anal. Calc. for $C_{80}H_{54}B_2F_{30}N_2Zr_2$ (1817.3): C, 52.87; H, 3.00; N, 1.54. Found: C, 51.92; H, 3.70; N, 1.64%.

*3.4.1. X-ray crystal structure analysis of trans-**9b***

Single crystals were obtained from a solution of the *cis*/*trans*-**9b** mixture in dichloromethane at −20 °C. Formula $C_{36}H_{36}N_2Zr_2 \cdot 2C_{22}H_9BF_{15}$, $M = 1817.3$, yellow crystal 0.25 × 0.20 × 0.10 mm, $a = 10.524(1)$, $b = 16.288(1)$, $c = 20.870(1)$ Å, $\beta = 93.86(1)°$, $V = 3569.3(4)$ Å^3, $\rho_{calc} = 1.691$ g cm^{-3}, $\mu = 4.20$ cm^{-1}, empirical absorption correction via SORTAV ($0.902 \le T \le 0.959$), $Z = 4$, monoclinic, space group $P2_1/c$ (no. 14), $\lambda = 0.71073$ Å, $T = 198$ K, ω and φ scans, 11777 reflections collected ($\pm h$, $\pm k$, $\pm l$), [$(\sin\theta)/\lambda$] = 0.62 Å^{-1}, 7080 independent ($R_{int} = 0.056$) and 3805 observed reflections [$I \ge 2\ \sigma(I)$], 543 refined parameters, $R = 0.064$, $wR^2 = 0.119$, max. residual electron density 0.39 (−0.36) e Å^{-3}, positional disorder of C24 in the *n*-butyl-group, refined with split positions in the ratio 0.63:0.37(1), thermal displacement parameters of the Cp-carbon atoms indicate some disorder, not refined, hydrogens calculated and refined as riding atoms.

Data sets were collected with a Nonius KappaCCD diffractometer, equipped with a rotating anode generator Nonius FR591. Programs used: data collection COLLECT [17a], data reduction DENZO-SMN [17b], absorption correction SORTAV [17c,17d], structure solution SHELXS-97 [17e], structure refinement SHELXL-97 [17f], graphics SCHAKAL [17g].

3.5. Reaction of dications **9** *with nitriles: formation of the* [Cp$_2$Zr(N=CHR^1)N≡CR^2]$^+$[butyl-B(C$_6$F$_5$)$_3$]$^-$ *complexes* **15***, general procedure*

The dications **9** were generated by treatment of 0.67 mmol of the respective Cp$_2$ZrCl(N≡CHR^1) complex **6** with 0.65 mmol [butyl-B(C$_6$F$_5$)$_3$]$^-$Li$^+$ (**7**) in 50 ml of dichloromethane analogously as described above. Before workup one molar equivalent of the nitrile N≡C–R^2 was added via syringe. The reaction mixture was then stirred for 1 h at room temperature (r.t.). The LiCl precipitate was removed by filtration. Solvent was removed in vacuo to give the complexes **15** as yellow solids.

3.6. Treatment of **9a** *with acetonitrile, formation of* **15a**

The reaction of (ethanimido)zirconocene chloride (**6a**, 200 mg, 0.67 mmol) with 385 mg (0.67 mmol) of **7** in dichloromethane followed by treatment with 3.50 μl (0.65 mmol) of acetonitrile analogously as described above gave 455 mg (78%) of **15a**, m.p. 189 °C (dec.). ^{1}H-NMR (CDCl$_2$, 200.1 MHz, 300 K): $\delta = 8.55$ (q, 1H, $^3J_{HH} = 5.1$ Hz, C*H*), 6.19 (s, 10H, Cp-*H*), 1.88 (d, 3H, $^3J_{HH} = 5.1$ Hz, C*H*$_3$), 2.22 (bs, 3H, nitrile-C*H*$_3$), 1.21, 0.80 (each m, Σ 9H, [butyl-B(C$_6$F$_5$)$_3^-$]). ^{13}C{^{1}H}-NMR (CD$_2$Cl$_2$, 50.3 MHz, 300 K): $\delta = 173.1$ (N=*C*), 148.7 (dm, $^1J_{CF} = 252$ Hz, B(*C*$_6$F$_5$)$_3$), 137.3 (dm, $^1J_{CF} = 255$ Hz, B(*C*$_6$F$_5$)$_3$), 137.0 (dm, $^1J_{CF} = 233$ Hz, B(C$_6$F$_5$)$_3$), 110.1 (Cp-*C*), 27.7 (N=CH(*C*H$_3$)), 22.0 (nitrile-*C*H$_3$), 31.1, 27.5, 23.2 (br), 14.0 ([butyl-B(C$_6$F$_5$)$_3^-$]), N=C carbon atom and *ipso*-C of –B(C$_6$F$_5$)$_3$ not observed. ^{11}B{^{1}H}-NMR (CD$_2$Cl$_2$, 64.2 MHz, 300 K): $\delta = -13.4$ ($w_{1/2} = 38$ Hz). IR (KBr): $\tilde{\nu} = 2955$ (s), 3015 (s), 2910 (s), 2856 (m), 2310 (N≡C, s), 1640 (m), 1513 (s), 1456 (vs), 1443 (s), 1375 (m), 1080 (s), 965 (s), 802 (s) cm^{-1}. Anal. Calc. for C$_{36}$H$_{26}$BF$_{15}$N$_2$Zr (873.6): C, 49.49; H, 3.00; N, 3.21. Found: C, 49.90; H, 3.57; N, 2.59%.

3.7. Reaction of **9b** *with acetonitrile, formation of* **15b**

The dication **9b** was generated by treatment of 250 mg (0.66 mmol) of **6b** with 380 mg (0.66 mmol) of **7** in dichloromethane. Subsequent reaction with 2.80 μl (0.66 mmol) of acetonitrile as described above gave 432 mg (68%) of **15b** as a yellow solid, m.p. 187 °C (dec.). ^{1}H-NMR (CD$_2$Cl$_2$, 200.1 MHz, 300 K): $\delta = 9.07$ (s, 1H, N=C*H*), 7.34–7.22 (m, 4H, tolyl-*H*), 6.26 (s, 10H, Cp-*H*), 2.42 (s, 3H, tolyl-C*H*$_3$), 2.29 (bs, 3H, nitrile-C*H*$_3$), 1.24, 0.81 (each m, Σ 9H, [butyl-B(C$_6$F$_5$)$_3^-$]). ^{13}C{^{1}H}-NMR (CD$_2$Cl$_2$, 50.3 MHz, 300 K): $\delta = 170.1$ (N=C), 149.7 (dm, $^1J_{CF} = 242$ Hz, B(C$_6$F$_5$)$_3$), 138.3 (dm, $^1J_{CF} = 242$ Hz, B(C$_6$F$_5$)$_3$), 137.5 (dm, $^1J_{CF} = 243$ Hz, B(C$_6$F$_5$)$_3$), 131.1, 128.2 (*o*- and *p*-tolyl-C), 111.4 (Cp-C), 22.6 (nitrile-*C*H$_3$), 21.7 (tolyl-*C*H$_3$), 31.3, 27.4, 23.4 (br), 14.5 ([butyl-B(C$_6$F$_5$)$_3^-$]). The N≡C carbon atom, *ipso*-C of tolyl and –B(C$_6$F$_5$)$_3$ were not observed. ^{11}B{^{1}H}-NMR (CD$_2$Cl$_2$, 64.2 MHz, 300 K): $\delta = -12.6$ ($w_{1/2} = 32$ Hz). IR (KBr): $\tilde{\nu} = 2957$ (m), 2922 (m), 2849 (m), 2304 (N≡C, m), 1642 (m), 1604 (m), 1512 (s), 1458 (vs), 1265 (m), 1078 (vs), 972 (vs), 806 (vs), 733 (s), 680 (m) cm^{-1}. Anal. Calc. for C$_{43}$H$_{30}$BF$_{15}$N$_2$Zr (961.7): C, 53.70; H, 3.14; N, 2.91. Found: C, 53.08; H, 4.13; N, 2.32%.

3.8. Reaction of **9a** *with tert-butylisonitrile, formation of* **16**

The reaction of 200 mg (0.67 mmol) of **6a** with 385 mg (0.67 mmol) of **7** in CH$_2$Cl$_2$ followed by treatment with 7.60 μl (0.67 mmol) of N≡C–CMe$_3$ carried out according to the general procedure gave 490 mg (80%) of **16**, m.p. 123 °C (dec.). ^{1}H-NMR (CD$_2$Cl$_2$, 200.1 MHz, 300 K): $\delta = 8.45$ (q, 1H, $^3J_{HH} = 5.1$ Hz, C*H*), 6.14 (s, 10H, Cp-*H*), 1.87 (d, 3H, $^3J_{HH} = 5.1$ Hz, C*H*$_3$), 1.58 (s, 9H, C(C*H*$_3$)$_3$), 1.21, 0.80 (each m, Σ 9H, [butyl-B(C$_6$F$_5$)$_3^-$]). ^{13}C{^{1}H}-NMR (CD$_2$Cl$_2$, 50.3 MHz, 300 K): $\delta = 173.2$ (N=*C*), 148.8 (dm, $^1J_{CF} = 253$ Hz, B(C$_6$F$_5$)$_3$), 137.9 (dm, $^1J_{CF} = 257$ Hz, B(C$_6$F$_5$)$_3$), 136.7 (dm, $^1J_{CF} = 227$ Hz, B(C$_6$F$_5$)$_3$), 109.1 (Cp-*C*), 30.0 (C(*C*H$_3$)$_3$), 27.8 (N=CH(*C*H$_3$)), 22.8 (*C*(CH$_3$)$_3$), 31.3, 27.4, 22.8 (br), 14.6 ([butyl-B(C$_6$F$_5$)$_3^-$]), isonitrile C≡N carbon and *ipso*-C of $-$B(C$_6$F$_5$)$_3$ not observed. ^{11}B{^{1}H}-NMR (CD$_2$Cl$_2$, 64.2 MHz, 300 K): $\delta = -12.8$ ($w_{1/2} = 38$ Hz). IR (KBr): $\tilde{\nu} = 2961$ (m), 2924 (m), 2874 (m), 2219 (C≡N, m), 1641 (m), 1512 (s), 1457 (vs), 1266 (m), 1080 (s), 972 (s), 806 (s), 677 (w) cm^{-1}. Anal. Calc. for C$_{39}$H$_{32}$BF$_{15}$N$_2$Zr (915.7): C, 51.15; H, 3.52; N, 3.06. Found: C, 49.80; H, 3.91; N, 2.83%.

4. Supplementary material

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with Cambridge Crystallographic Data Centre as supplementary publications nos. CCDC 162645 and 162646. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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