

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

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Received 1 June 2001; accepted 31 August 2001

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

Abstract

The reagent $[\text{butyl-B}(\text{C}_6\text{F}_5)_3]^- \text{Li}^+$ reacts with the complexes $\text{Cp}_2\text{ZrCl}(\text{N}=\text{CHR})$ (**6**) ($\text{R}=\text{CH}_3$ or *p*-tolyl) at ambient temperature by chloride abstraction. The resulting in situ formed $[\text{Cp}_2\text{Zr}(\text{N}=\text{CHR})]^+$ cations (**8**) dimerize under the reaction conditions. After removal of a stoichiometric amount of lithium chloride the corresponding μ -alkylideneamido-bridged dimeric $[\text{Cp}_2\text{Zr}(\text{N}=\text{CHR})]_2^{2+}$ dications **9a** ($\text{R}=\text{CH}_3$) and **9b** ($\text{R}=\textit{p}$ -tolyl) are isolated in yields of ca. 80% (with $[\text{butyl-B}(\text{C}_6\text{F}_5)_3]^-$ 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 $[\text{Cp}_2\text{Zr}(\text{N}=\text{CHR})\text{N}\equiv\text{C}-\text{CH}_3]^+ [\text{butyl-B}(\text{C}_6\text{F}_5)_3]^-$ (**16**). © 2002 Elsevier Science B.V. All rights reserved.

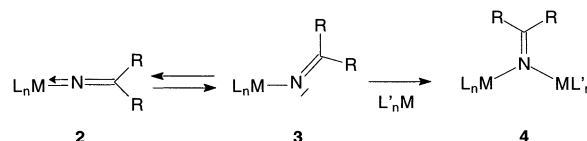
Keywords: Zirconocene cation complexes; Metallocenes; Dimerization; Bridging nitrogen-containing ligands

1. Introduction

Bis(alkylidene)ammonium ions $[\text{R}_2\text{C}=\text{N}=\text{CR}_2]^+$ (**1**) exhibit linear heteroallene-type structures around a central sp^2 -hybridized nitrogen atom [1]. The corresponding (alkylideneamido)metal complexes **2** also show near to linear metallaallene structures in cases where electron-deficient L_nM 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^2 -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].

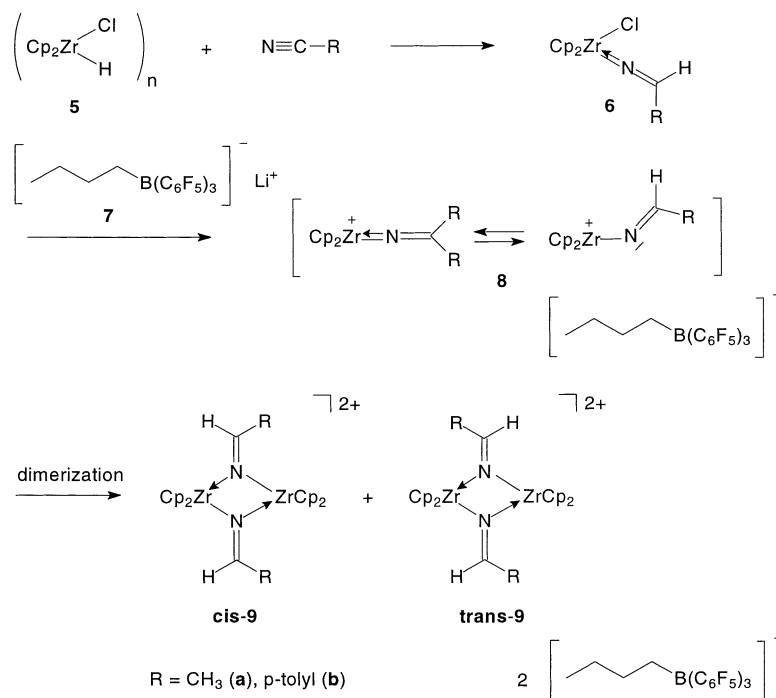


Scheme 1.

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¹ X-ray crystal structure analyses.



Scheme 2.

2. Results and discussion

Two neutral (alkylideneamido)zirconocene chlorides were used as the starting materials for our study, namely the complexes $\text{Cp}_2\text{ZrCl}(\text{N}=\text{CHR})$ **6a** ($\text{R} = \text{CH}_3$) and **6b** ($\text{R} = p\text{-tolyl}$). They were synthesized, as previously described by us [2a], by means of a hydrosilylation reaction of acetonitrile or 4-methylbenzonitrile, respectively, employing the oligomeric ‘Schwartz-reagent’ $(\text{Cp}_2\text{ZrHCl})_n$ (**5**) [9] suspended in toluene. These compounds were isolated in ca. 80% yield each. Complex **6a** shows a characteristic $\text{Zr}=\text{N}=\text{C}$ ^{13}C -NMR resonance at δ 167.5 ($^1J_{\text{CH}} = 168$ Hz). The related complex $\text{Cp}_2\text{Zr}=\text{N}=\text{CHPh}$ had been characterized by X-ray diffraction and shown to exhibit an almost linear $\text{Zr}=\text{N}=\text{C}$ framework (angle $\text{Zr}-\text{N}-\text{C}$: $170.5(5)^\circ$) [2a].

The (ethyldieneamido)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 unsatu-

rated (ethyldieneamido)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- $\text{B}(\text{C}_6\text{F}_5)_3$] $^-\text{Li}^+$ (**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 ($^1\text{H}/^{13}\text{C}$ -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(C₆F₅)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 Zr₂N₂ framework. The heavy atoms of the [(CH₃CH=N)₂Zr₂] framework are coplanar. The methyl substituents are located with C_i-symmetry at the periphery of the [(C=N)₂Zr₂] 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=CR₂M₂ 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

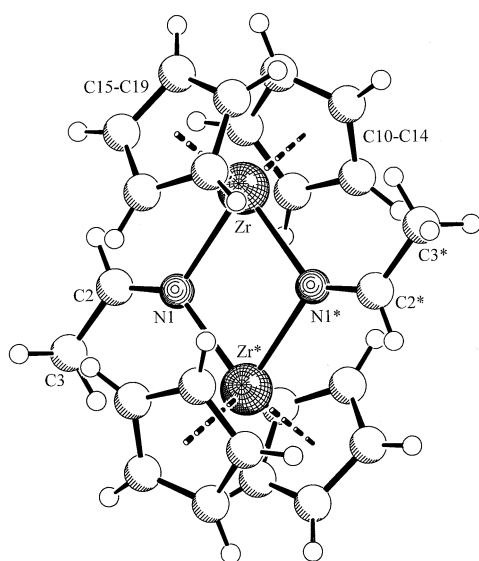


Fig. 1. Molecular structure of *trans*-**9a** (only the dication part is depicted). Selected bond lengths (Å) and angles (°): Zr–N1* 2.235(2), Zr–N1 2.255(2), N1–C2 1.281(4), C2–C3 1.482(4), B–C21 1.642(4), C21–C22 1.532(4), C22–C23 1.537(5), C23–C24 1.475(5), B–C31 1.669(4), B–C41 1.655(4), B–C51 1.666(4);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

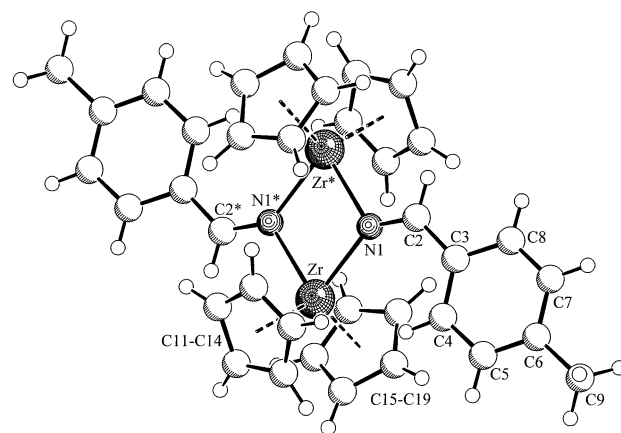
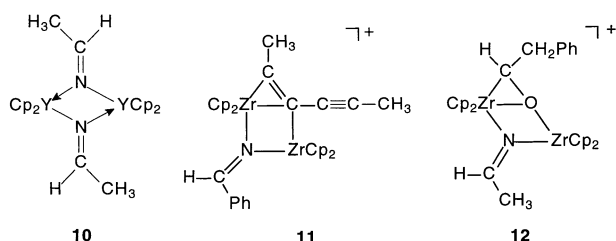


Fig. 2. A view of the *trans*-**9b** dication. Selected bond lengths (Å) and angles (°): Zr–N1* 2.272(4), Zr–N1 2.192(4), N1–C2 1.288(6), C2–C3 1.444(7), B–C21 1.658(8), C21–C22 1.509(8), C22–C23a 1.558(8), C22–C23b 1.555(8), C23–C24a 1.524(9), C23–C24b 1.535(10), B–C31 1.649(8), B–C41 1.655(8), B–C51 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).

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 η⁵-Cp ligands are arranged above and below the Zr₂N₂ plane with a Cp-(centroid)–Zr–Cp(centroid) angle of 129.6°.

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 Zr₂N₂ 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 ¹H-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 Cp₂ZrCH₃⁺ 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**.



Scheme 3.

The dication **9a** (*cis/trans*-mixture) was generated by treatment of the precursor **6a** with [butyl-B(C₆F₅)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 [Cp₂Zr(N=CHCH₃)·N≡CCH₃]⁺ (**15a**), with [butyl-B(C₆F₅)₃][−] counteranion. The product **15a** was isolated in close to 80% yield from the reaction mixture (Scheme 4). Complex **15a** shows a typical –N=CHCH₃ ¹³C-NMR resonance at δ 173.1.

Analogous treatment of the in situ generated *cis/trans*-**9a** mixture with *tert*-butylisocyanide gave the corresponding C≡N–CMe₃ 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, ¹³C-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 R¹-substituent with the stabilizing N≡C–R² ligand at the linear Cp₂Zr(N=CHR¹) framework as it is depicted in Scheme 4.

We conclude that [butyl-B(C₆F₅)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 [Cp₂Zr=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 μ – N=CHR units as active functional groups.

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(C₆F₅)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(C₆F₅)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.). ¹H-NMR: ([benzene-*d*₆, THF-*d*₈], 4:1, 200 MHz, 300 K): δ = 1.67 (br, 2H, B–CH₂), 1.53 (m, 2H, CH₂), 1.28 (br, 2H, CH₂), 0.93 (t, 3H, CH₃). ¹¹B{¹H}-NMR: ([benzene-*d*₆, THF-*d*₈], 4:1, 64.2 MHz, 300 K): δ = −12.6 (*w*_{1/2} = 225 Hz). ¹⁹F-NMR: ([benzene-*d*₆, THF-*d*₈], 4:1, 282.4 MHz, 300 K): δ = −167.9 (m, 6F, *m*-F), −165.5 (t, ³*J*_{FF} = 21 Hz, 3F, *p*-F), −131.7 (m, 6F, *o*-F). Anal. Calc. for C₂₂H₉BF₁₅Li (576.0): C, 45.87; H, 1.57. Found: C, 45.21; H, 2.52%. HRMS: Calc. for [C₂₂H₉BF₁₅][−]: 569.0558, found 569.0562.

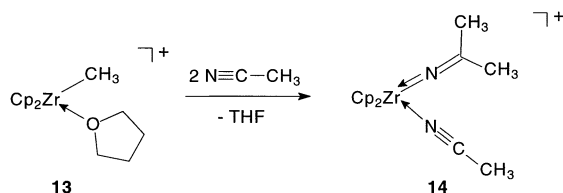
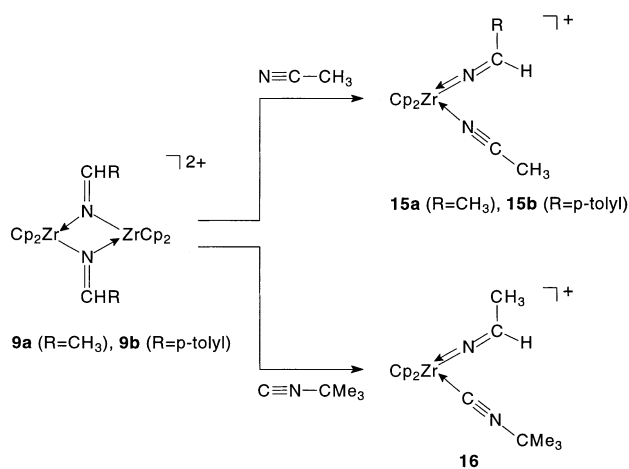


Chart 1.



all cations with [butylB(C₆F₅)₃][−] counteranion

Scheme 4.

3.2. Reaction of (alkylideneamido)zirconocene chlorides with [butyl-B(C₆F₅)₃][−]Li⁺ (**7**), preparation of the [Cp₂Zr(N=CHR)]₂⁺2[butyl-B(C₆F₅)₃][−] complexes **9**, general procedure

The respective Cp₂ZrCl(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 CH₂Cl₂ 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. ¹H-NMR (CD₂Cl₂, 200.1 MHz, 300 K): *trans*-**9a**: δ = 7.85 (q, 2H, ³J_{HH} = 4.7 Hz, CH(CH₃)), 6.83 (s, 20H, Cp-*H*), 1.77 (d, 6H, ³J_{HH} = 4.7 Hz, CH(CH₃)); *cis*-**9a**: 7.66 (q, 2H, ³J_{HH} = 4.7 Hz, CH(CH₃)), 6.84, 6.81 (each s, each 10H, Cp-*H*), 1.92 (d, 6H, ³J_{HH} = 4.7 Hz, CH(CH₃)); 1.21, 0.80 (each m, Σ 18H, [butyl-B(C₆F₅)₃][−]). ¹³C{¹H}-NMR (CD₂Cl₂, 50.3 MHz, 300 K): δ = 194.9 (N=C, *cis*- and *trans*-**9a**), 148.7 (dm, ¹J_{CF} = 242 Hz, B(C₆F₅)₃), 138.0 (dm, ¹J_{CF} = 242 Hz, B(C₆F₅)₃), 137.0 (dm, ¹J_{CF} = 243 Hz, B(C₆F₅)₃), 121.0, 117.8 (Cp-C, *cis*-**9a**), 119.5 (Cp-C, *trans*-**9a**), 67.1 (CH(CH₃)), 31.1, 27.3, 23.4 (br), 14.5 ([butyl-B(C₆F₅)₃][−]), *ipso*-C of C₆F₅ not observed. ¹¹B{¹H}-NMR (CD₂Cl₂, 64.2 MHz, 300 K): δ = −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 C₆₈H₄₆B₂F₃₀N₂Zr₂ (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 C₂₄H₂₈N₂Zr₂·2C₂₂H₉BF₁₅, *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, β = 90.90(1)°, *V* = 6348.7(7) Å³, ρ_{calc} = 1.742 g cm^{−3}, μ = 4.63 cm^{−1}, empirical absorption correction via SORTAV (0.874 ≤ *T* ≤ 0.913), *Z* = 4, monoclinic, space group *C*2/*c* (no. 15), λ = 0.71073 Å, *T* = 198 K, ω and φ scans, 19367 reflections collected (±*h*, ±*k*, ±*l*), [(sin θ)/λ] = 0.65 Å^{−1}, 7248 independent (*R*_{int} = 0.038) and 5730 observed reflections [*I* ≥ 2σ(*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 CH₂Cl₂ analogously as described above gave 337 mg (70%) of a 1:1.5 mixture of *cis*- and *trans*-**9b**, m.p. 140 °C. ¹H-NMR (CD₂Cl₂, 200.1 MHz, 300 K): δ = *trans*-**9b**: 8.89 (s, 3H, CH), 6.37 (s, 30H, Cp-*H*), 2.46 (s, 9H, tolyl-CH₃); *cis*-**9b**: 9.22 (s, 2H, CH), 6.77, 6.30 (each s, each 10H, Cp-*H*), 2.44 (s, 6H, tolyl-CH₃); 7.56–7.07 (m, 20H, tolyl-*H*), 1.22, 0.81 (each m, Σ 18H, [butyl-B(C₆F₅)₃][−]). ¹³C{¹H}-NMR (CD₂Cl₂, 50.3 MHz, 300 K): δ = 148.7 (dm, ¹J_{CF} = 242 Hz, B(C₆F₅)₃), 138.0 (dm, ¹J_{CF} = 242 Hz, B(C₆F₅)₃), 137.0 (dm, ¹J_{CF} = 243 Hz, B(C₆F₅)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-CH₃), 31.1, 27.3, 23.4 (br), 14.5 ([butyl-B(C₆F₅)₃][−]), one *ipso*-C of tolyl, *ipso*-C of B(C₆F₅)₃ and N=C carbon atoms not observed. ¹¹B{¹H}-NMR (CD₂Cl₂, 64.2 MHz, 300 K): δ = −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 C₈₀H₅₄B₂F₃₀N₂Zr₂ (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 C₃₆H₃₆N₂Zr₂·2C₂₂H₉BF₁₅, *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, β = 93.86(1)°, *V* = 3569.3(4) Å³, ρ_{calc} = 1.691 g cm^{−3}, μ = 4.20 cm^{−1}, empirical absorption correction via SORTAV (0.902 ≤ *T* ≤ 0.959), *Z* = 4, monoclinic, space group *P*2₁/*c* (no. 14), λ = 0.71073 Å, *T* = 198 K, ω and φ scans, 11777 reflections collected (±*h*, ±*k*, ±*l*), [(sin θ)/λ] = 0.62 Å^{−1}, 7080 independent (*R*_{int} = 0.056) and 3805 observed reflections [*I* ≥ 2σ(*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 $[Cp_2Zr(N=CHR^1)N\equiv CR^2]^+[butyl-B(C_6F_5)_3]^-$ complexes **15**, general procedure

The dications **9** were generated by treatment of 0.67 mmol of the respective $Cp_2ZrCl(N\equiv CHR^1)$ complex **6** with 0.65 mmol $[butyl-B(C_6F_5)_3]^-Li^+$ (**7**) in 50 ml of dichloromethane analogously as described above. Before workup one molar equivalent of the nitrile $N\equiv C-R^2$ 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 μ l (0.65 mmol) of acetonitrile analogously as described above gave 455 mg (78%) of **15a**, m.p. 189 °C (dec.). 1H -NMR ($CDCl_2$, 200.1 MHz, 300 K): δ = 8.55 (q, 1H, $^3J_{HH}$ = 5.1 Hz, CH), 6.19 (s, 10H, Cp-H), 1.88 (d, 3H, $^3J_{HH}$ = 5.1 Hz, CH_3), 2.22 (bs, 3H, nitrile- CH_3), 1.21, 0.80 (each m, Σ 9H, $[butyl-B(C_6F_5)_3]^-$). $^{13}C\{^1H\}$ -NMR (CD_2Cl_2 , 50.3 MHz, 300 K): δ = 173.1 (N=C), 148.7 (dm, $^1J_{CF}$ = 252 Hz, $B(C_6F_5)_3$), 137.3 (dm, $^1J_{CF}$ = 255 Hz, $B(C_6F_5)_3$), 137.0 (dm, $^1J_{CF}$ = 233 Hz, $B(C_6F_5)_3$), 110.1 (Cp-C), 27.7 (N=CH(CH_3)), 22.0 (nitrile- CH_3), 31.1, 27.5, 23.2 (br), 14.0 ($[butyl-B(C_6F_5)_3]^-$), N=C carbon atom and *ipso*-C of $-B(C_6F_5)_3$ not observed. $^{11}B\{^1H\}$ -NMR (CD_2Cl_2 , 64.2 MHz, 300 K): δ = -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 $C_{36}H_{26}BF_{15}N_2Zr$ (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 μ l (0.66 mmol) of acetonitrile as described above gave 432 mg (68%) of **15b** as a yellow solid, m.p. 187 °C (dec.). 1H -NMR (CD_2Cl_2 , 200.1 MHz, 300 K): δ = 9.07 (s, 1H, N=CH), 7.34–7.22 (m, 4H, tolyl-H), 6.26 (s, 10H, Cp-H), 2.42 (s, 3H, tolyl- CH_3), 2.29 (bs, 3H, nitrile- CH_3), 1.24, 0.81 (each m, Σ 9H, $[butyl-B(C_6F_5)_3]^-$). $^{13}C\{^1H\}$ -NMR (CD_2Cl_2 , 50.3 MHz, 300 K): δ = 170.1 (N=C), 149.7 (dm, $^1J_{CF}$ = 242 Hz, $B(C_6F_5)_3$), 138.3 (dm, $^1J_{CF}$ = 242 Hz, $B(C_6F_5)_3$), 137.5 (dm, $^1J_{CF}$ = 243 Hz, $B(C_6F_5)_3$), 131.1, 128.2 (*o*- and *p*-tolyl-C), 111.4 (Cp-C), 22.6 (nitrile- CH_3), 21.7 (tolyl- CH_3), 31.3, 27.4, 23.4

(br), 14.5 ($[butyl-B(C_6F_5)_3]^-$). The N=C carbon atom, *ipso*-C of tolyl and $-B(C_6F_5)_3$ were not observed. $^{11}B\{^1H\}$ -NMR (CD_2Cl_2 , 64.2 MHz, 300 K): δ = -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 $C_{43}H_{30}BF_{15}N_2Zr$ (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_2Cl_2 followed by treatment with 7.60 μ l (0.67 mmol) of $N\equiv C-CMe_3$ carried out according to the general procedure gave 490 mg (80%) of **16**, m.p. 123 °C (dec.). 1H -NMR (CD_2Cl_2 , 200.1 MHz, 300 K): δ = 8.45 (q, 1H, $^3J_{HH}$ = 5.1 Hz, CH), 6.14 (s, 10H, Cp-H), 1.87 (d, 3H, $^3J_{HH}$ = 5.1 Hz, CH_3), 1.58 (s, 9H, $C(CH_3)_3$), 1.21, 0.80 (each m, Σ 9H, $[butyl-B(C_6F_5)_3]^-$). $^{13}C\{^1H\}$ -NMR (CD_2Cl_2 , 50.3 MHz, 300 K): δ = 173.2 (N=C), 148.8 (dm, $^1J_{CF}$ = 253 Hz, $B(C_6F_5)_3$), 137.9 (dm, $^1J_{CF}$ = 257 Hz, $B(C_6F_5)_3$), 136.7 (dm, $^1J_{CF}$ = 227 Hz, $B(C_6F_5)_3$), 109.1 (Cp-C), 30.0 ($C(CH_3)_3$), 27.8 (N=CH(CH_3)), 22.8 ($C(CH_3)_3$), 31.3, 27.4, 22.8 (br), 14.6 ($[butyl-B(C_6F_5)_3]^-$), isonitrile $C\equiv N$ carbon and *ipso*-C of $-B(C_6F_5)_3$ not observed. $^{11}B\{^1H\}$ -NMR (CD_2Cl_2 , 64.2 MHz, 300 K): δ = -12.8 ($w_{1/2}$ = 38 Hz). IR (KBr): $\tilde{\nu}$ = 2961 (m), 2924 (m), 2874 (m), 2219 ($C\equiv N$, m), 1641 (m), 1512 (s), 1457 (vs), 1266 (m), 1080 (s), 972 (s), 806 (s), 677 (w) cm^{-1} . Anal. Calc. for $C_{39}H_{32}BF_{15}N_2Zr$ (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](http://www.ccdc.cam.ac.uk)).

Acknowledgements

Financial support from the Fonds der Chemischen Industrie and the Deutsche Forschungsgemeinschaft is gratefully acknowledged.

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