

# Formation and Structure of a Bis(cyclopentadienyl)(formamidinato)zirconium Cation Complex

Carsten Cornelißen, Gerhard Erker, Gerald Kehr, and Roland Fröhlich

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

Reprint requests to Prof. Dr. G. Erker. E-mail: erker@uni-muenster.de

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Dedicated to Professor Hubert Schmidbaur on the occasion of his 70<sup>th</sup> birthday

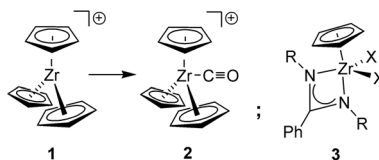
Deprotonation of *N,N'*-dicyclohexylformamidine with methyl lithium yields dicyclohexylformamidinyl lithium (**8a**). The X-ray crystal structure analysis of **8a** shows an unsymmetrically formamidinato-bridged THF-stabilized dimer in the crystal. Treatment of diphenylformamidinyl lithium (**8b**) with  $\text{Cp}_2\text{ZrCl}_2$  gives the  $(\kappa^2N,N'$ -diphenylformamidinato) $\text{Cp}_2\text{ZrCl}$  complex **6b** which was also characterized by X-ray diffraction, as was  $(\kappa^2N,N'$ -dicyclohexylformamidinato) $\text{Cp}_2\text{ZrCH}_3$  (**7a**). Treatment of  $(\kappa^2N,N'$ -diphenylformamidinato) $\text{Cp}_2\text{ZrCH}_3$  (**7b**) with  $[\text{Bu}_3\text{NH}^+][\text{BPh}_4^-]$  gave the salt  $[(\kappa^2N,N'$ -diphenylformamidinato) $\text{Cp}_2\text{Zr}^+][\text{BPh}_4^-]$  (**9b**). Its X-ray crystal structure analysis revealed a symmetrical bonding of the formamidinato ligand to the zirconium metal center.

**Key words:** Zirconium, Metallocene Cations, Formamidinato Ligands

## Introduction

Tris(cyclopentadienyl)zirconium cation (**1**) is a remarkable molecule. It contains three  $\eta^5$ -coordinated Cp-ligands in planar three-coordinate geometry. Although this might formally imply a saturated 18-electron count at the central *d*-metal, the cation **1** readily adds a variety of donor molecules such as THF, carbon monoxide, isonitriles etc to form the stable adducts **2** (see Scheme 1). This reactivity is due to the fact that in **1** an electron pair occupies a ligand centered molecular orbital and, thus,  $\text{Cp}_3\text{Zr}^+$  chemically behaves as a coordinatively unsaturated 16-electron fragment [1, 2].

There are a number of Group 4 metal complexes in which a  $\kappa^2N,N$ -bonded amidinato ligand [3] has formally replaced a  $\eta^5$ -Cp-ring [4–6]. The *e.g.*  $\text{Cp}(\text{benzamidinato})\text{ZrX}_2$  complexes (**3**) and related systems bear quite some similarity to the  $\text{Cp}_2\text{ZrX}_2$  systems, and have thus been extensively used in metallocene-like homogeneous Ziegler-Natta catalysis [7]. It was tempting to formally replace a Cp-ring in the  $\text{Cp}_3\text{Zr}$ -systems by a suitable amidinato ligand and see whether the resulting  $\text{Cp}_2(\text{amidinato})\text{Zr}$  systems would just be functionalized bent metallocenes or if they would rather bear some similarity to the tris( $\eta^5$ -cyclopentadienyl)zirconium derivatives. We have, therefore, synthesized a variety of neutral

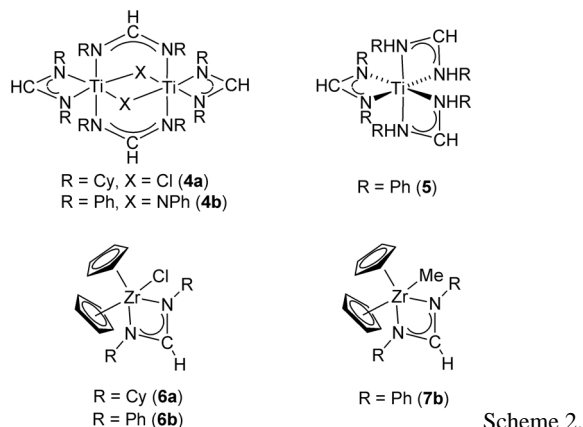


Scheme 1.

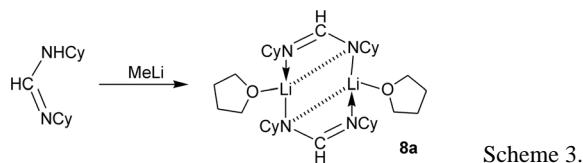
$\text{Cp}_2(\text{formamidinato})\text{ZrX}$  complexes and used them to generate the corresponding cation complexes from them.

## Results and Discussion

Although examples of *C*-substituted amidinato metal complexes are abundant in the literature, to our knowledge only rather few corresponding parent formamidinato complexes of the Group 4 metals have been described so far. S. Gambarotta *et al.* prepared the dinuclear  $\text{Ti}_2$  complex **4a** that contains bridging dicyclohexylformamidinato ligands [8]. A similar system (**4b**) was published by Cotton *et al.* [9]. In the same paper the tris(diphenylformamidinato)Ti complex **5** was described (see Scheme 2). Floriani *et al.* used the hydrozirconation reaction of diphenyl- or dicyclohexylcarbodiimide to prepare the neutral  $\text{Cp}_2(\text{formamidinato})\text{ZrCl}$  complexes **6(a,b)** [10]. The (dicyclohexylformamidinato)zirconocene chloride complex **6a** was characterized by X-ray diffrac-



Scheme 2.



Scheme 3.

tion. The corresponding (diphenylformamidinato) methylzirconocene (**7b**) was synthesized by treatment of  $\text{Cp}_2\text{ZrMe}_2$  with the  $\text{PhNH-CH=N-Ph}$  reagent. Complex **7b** was also characterized by X-ray diffraction [11].

For this study we have used the dicyclohexyl- or diphenylformamidinyl lithium reagents (**8a**, **8b**, Scheme 4) to attach these ligands to the zirconium complexes. The reagents, in turn, were prepared by deprotonation of the corresponding  $N,N'$ -disubstituted formamidines with methyl lithium (Scheme 3). Recrystallization from tetrahydrofuran gave single crystals of the THF-adduct of dicyclohexylformamidinyl lithium for the X-ray crystal structure determination of **8a**.

As depicted in Fig. 1 compound **8a** crystallizes as a THF-stabilized dimer. The dicyclohexylformamidinato ligand is unsymmetrically bridging between two lithium atoms. There is a tricoordinate nitrogen center (N3) that forms a very short bond to a single lithium atom (N3-Li : 2.016(7) Å). The other nitrogen interacts with both lithium atoms, although rather unsymmetrically. The N1-Li\* bond is short at 2.036(7) Å, the N1-Li linkage is markedly longer at 2.200(8) Å. The nitrogen atom N1 is pseudotetrahedrally coordinated (sum of the bonding angles: 653.2°). The angle between the C2-N1-C11 and Li-N1-Li\* planes was found at 131.3°. The N1-C11 bond (1.461(4) Å) is much longer than the N1-C2 linkage (1.326(4) Å). The

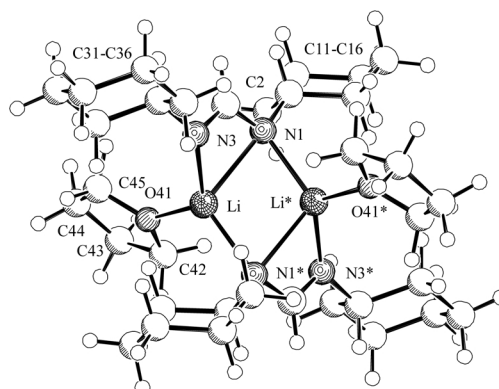
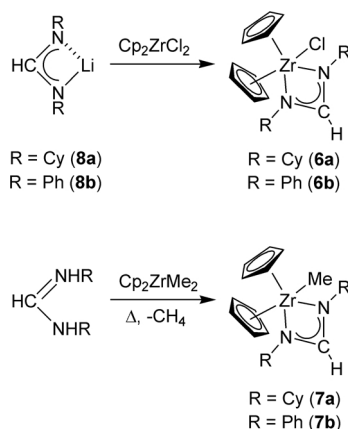


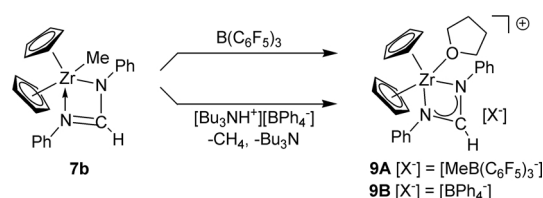
Fig. 1. Molecular structure of the THF-stabilized dicyclohexylformamidinyl lithium dimer (**8a**). Selected bond lengths (Å) and angles (°): Li-Li\* 2.501(14), Li-N1 2.200(8), Li-N1\* 2.036(7), Li-C2 2.339(8), Li-N3 2.016(7), Li-O41 1.929(8), N1-C2 1.326(4), N1-C11 1.461(4), C2-N3 1.304(4), N3-C31 1.461(4); Li-N1-Li\* 72.3(3), Li-N1-C2 78.9(3), Li-N1-C11 147.5(3), Li-N3-C2 86.8(3), Li-N3-C31 147.8(3), N1-Li-N1\* 107.7(3), N1-Li-N3 66.0(2), N1\*-Li-N3 122.9(4), N1-Li-O41 112.2(4), N1-Li-O41\* 112.7(4), N3-Li-O41 122.1(4), C11-N1-C2 116.6(3), N1-C2-N3 122.0(3), C2-N3-C31 117.3(3).



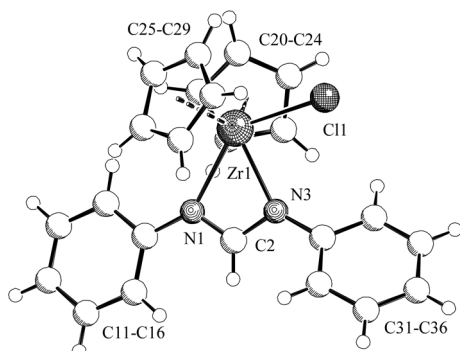
Scheme 4.

N1-C2-N3 angle at the “formamidinato-carbon” C2 is typical (122.0(3)°). It is noteworthy that the N3-C2 bond (1.304(4) Å) is shorter than the N1-C2 bond by  $\Delta d \sim 0.02$  Å which may indicate some contribution of the mesomeric imine coordination form (see Scheme 3). Consequently, the nitrogen center N3 is close to planar-tricoordinate (sum of the bonding angles: 351.9°). Inside this rigid framework the Li...Li\* separation is short at 2.501(14) Å. Each lithium atom inside the dimeric structure of **8a** has a single THF molecule coordinated (Li-O41: 1.929(8) Å) that stabilizes the bridged dinuclear structure.

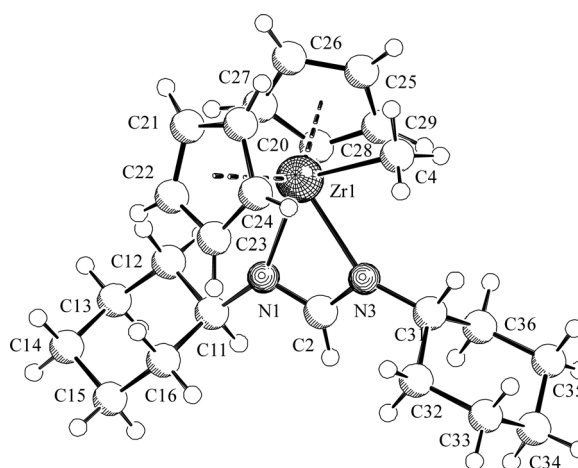
Compd.	<b>6a</b>	<b>6b</b>	<b>7a</b>	<b>7b</b>	<b>9</b>
R	Cy	Ph	Cy	Ph	Ph
X	Cl	Cl	CH <sub>3</sub>	CH <sub>3</sub>	THF
Zr-X	2.589(2) 2.551(2)	2.548(1) 2.547(1)	2.335(2) 2.336(2)	2.314(8) 2.341(5)	2.356(2)
Zr-N1	2.298(4) 2.310(5)	2.348(2) 2.346(2)	2.316(1) 2.362(1)	2.367(4) 2.356(4)	2.294(3)
Zr-N3	2.252(4) 2.275(5)	2.302(2) 2.285(2)	2.278(1) 2.264(1)	2.324(4) 2.343(4)	2.296(2)
C2-N1	1.309(6) 1.305(6)	1.312(3) 1.311(3)	1.312(2) 1.308(2)	1.320(8) 1.312(1)	1.321(4)
C2-N3	1.328(6) 1.329(8)	1.327(3) 1.321(3)	1.323(2) 1.321(2)	1.309(6) 1.321(1)	1.321(4)
Cp-Zr-Cp	130.4(2) 127.6(3)	129.03 128.39	129.80 128.26	129.1(3) 128.8(3)	127.88
N1-Zr-N3	58.1(2) 57.6(2)	56.88(7) 56.95(6)	57.39(4) 57.45(4)	56.4(1) 56.6(1)	57.82(9)
N1-C2-N3	113.8(5) 113.9(5)	114.2(2) 114.1(2)	113.7(1) 115.6(1)	114.9(5) 115.6(4)	114.3(3)
ref	[10]	<sup>a</sup>	<sup>a</sup>	[11]	<sup>a</sup>

Table 1. Selected structural data of the Cp<sub>2</sub>(RNCHNR)ZrX complexes.<sup>a</sup> This work.

Scheme 5.

Fig. 2. Molecular structure of complex **6b**.

We have prepared the bis(cyclopentadienyl)(formamidinato)ZrCl complexes **6a** (R = cyclohexyl) and **6b** (R = phenyl) in a different way than reported in the literature (see above [10]), namely by treatment of Cp<sub>2</sub>ZrCl<sub>2</sub> with the lithiated formamidinato reagents **8a** and **8b**, respectively (Scheme 4). The corresponding zirconocene chloride complexes **6** were each isolated in > 60% yield. Single crystals of **6b** (R = Ph) for the X-ray crystal structure determination (see below) were obtained from toluene. The complexes **7a** and **7b** were

Fig. 3. Molecular structure of complex **7a**.

prepared by treatment of Cp<sub>2</sub>ZrMe<sub>2</sub> with the neutral formamidine reagents, similarly as it was previously described for the synthesis of **7b** (R = Ph). Single crystals of **7a** (R = cyclohexyl) were again obtained from toluene.

The methyl(diphenylformamidinato)zirconocene complex (**7b**) was treated with methyl anion abstraction reagents [12]. The reaction with B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> was carried out in tetrahydrofuran. After 2 h the reaction was complete and the organometallic salt (**9A**, anion: [MeB(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>]<sup>−</sup>) was isolated in almost quantitative yield. Similarly, the methyl anion abstraction from **7b** was carried out by treatment with the mild Brønsted acid tributylammonium tetraphenylborate [13] to yield **9B** (with [BPh<sub>4</sub>]<sup>−</sup> anion). Both the THF-adducts of

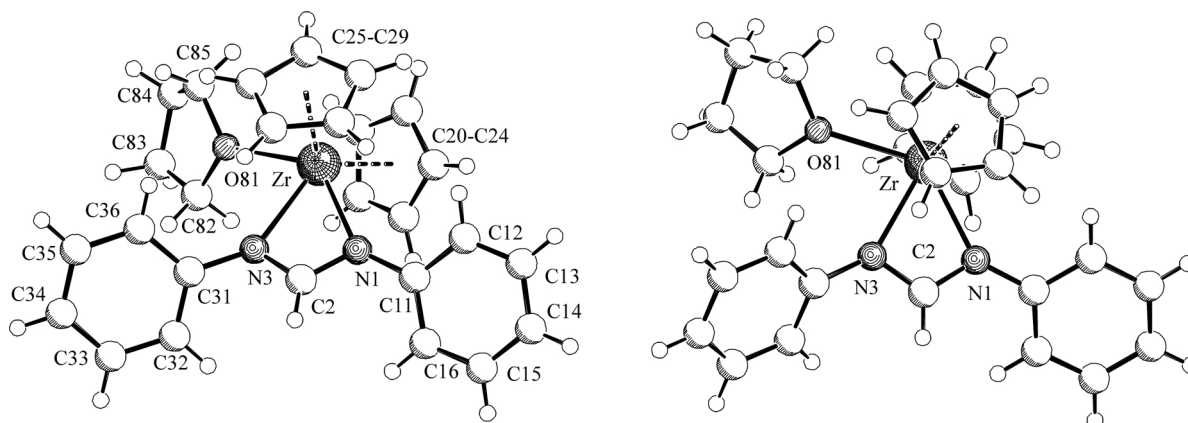


Fig. 4. Two views of the molecular structure of the cationic complex **9** [ $\text{BPh}_4^-$ ] anion not shown).

**9** appear as rapidly equilibrating systems in solution. Thus complex **9B** features only one set of N-aryl  $^{13}\text{C}$  NMR resonances in  $[\text{D}_2]$ -dichloromethane at 298 K ( $\delta = 147.2, 130.2, 125.2$ , and  $121.0$ : i-, m-, p-, o- $\text{C}_6\text{H}_5$ ). Single crystals of **9B** were obtained from the filtrate of the reaction mixture at  $-30^\circ\text{C}$ .

In the course of this study we have characterized the neutral complexes **6b** and **7a** by X-ray diffraction and the cationic complex **9** (with  $[\text{BPh}_4^-]$  counteranion). The structures of the remaining pair of complexes (**6a**, **7b**) had previously been reported in the literature [10, 11].

In all these complexes the formamidinato ligand is oriented coplanar with the  $\sigma$ -ligand plane of the bent metallocene unit and binds through both nitrogens. It appears that the neutral complexes **6** and **7** favour an unsymmetrical bonding arrangement of the  $\kappa^2\text{N},\text{N}$ -(RNCHNR) ligand to the  $d^0$ -transition metal center. Mostly a situation is found where the central Zr-N3 bond is markedly shorter than the lateral Zr-N1 linkage. For the complex **6b** this difference amounts to *ca.*  $\Delta d \approx 0.06$  Å. Consistently, the N3-C2 bond in most of these complexes is slightly longer than the N1-C2 linkage (**6b**:  $\Delta d \approx 0.01$  Å, see Table 1). This may indicate a participation of an unsymmetrical “imino-type” formamidinato coordination similarly as it is schematically characterized by the mesomeric form of **7b** depicted in Scheme 5.

The bonding situation of the Zr(diphenylformamidinato) moiety in the cation **9** is much more symmetrical, despite the presence of the stabilizing THF ligand. As seen from Table 1 and Fig. 4 both the Zr-N1 and Zr-N3 bonds in the cation **9** are almost identical in length (*ca.* 2.295 Å) as is the pair of

N1/N3-C2 bonds (1.321(4) Å) inside the  $\text{ZrN}_2\text{C}$  four-membered ring. This may perhaps indicate that the here described  $[\text{Cp}_2(\kappa^2\text{N},\text{N}-\text{PhNCHNPh})\text{Zr}^+]$  system bears some structural and chemical relation to the unique  $[\text{Cp}_3\text{Zr}^+]$  cation system. We will see whether the bis(cyclopentadienyl)(formamidinato) $\text{Zr}^+$  system will also strongly coordinate *e.g.* carbon monoxide in a purely  $\sigma$ -donor fashion, as it was observed for the mono-carbonyl complex of tris( $\eta^5$ -cyclopentadienyl)zirconium cation.

## Experimental Section

Reactions with organometallic compounds and reagents were carried out under argon using Schlenk-type glassware or in a glove-box. Solvents, including deuterated solvents used for NMR spectroscopy, were dried and distilled under argon prior to use. For additional general information, including a list of equipment used for the physical characterization of the compounds, see [1].

Data sets were collected with a Nonius KappaCCD diffractometer, equipped with a rotating anode generator Nonius FR591. Programs used: data collection COLLECT (Nonius B.V., 1998), data reduction Denzo-SMN (Z. Otwinowski, W. Minor, *Methods in Enzymology*, **276**, 307 (1997)), absorption correction data SORTAV (R. H. Blessing, *Acta Crystallogr.* **A51**, 33 (1995); R. H. Blessing, *J. Appl. Crystallogr.* **30**, 421 (1997)), structure solution SHELXS-97 (G. M. Sheldrick, *Acta Crystallogr.* **A46**, 467 (1990)), structure refinement SHELXL-97 (G. M. Sheldrick, Universität Göttingen, (1997)), graphics SCHAKAL (E. Keller (1997)).

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication CCDC-244882 (**6b**), 244883 (**7a**), 244884 (**8a**), 244885 (**9B**). Copies of the data can be ob-

tained 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].

#### Preparation of *N,N'*-dicyclohexylformamidinyl lithium (**8a**)

A 1.6 M solution of methyl lithium in diethylether (12.4 ml, 19.9 mmol) was added dropwise with stirring at 0 °C to a solution of 4.15 g (19.9 mmol) of *N,N'*-dicyclohexylformamidine [14] in 100 ml of ether. The mixture was warmed to room temperature and stirred for 2 h. The resulting white precipitate of **8a** was collected by filtration, washed with pentane and dried *in vacuo*. An additional fraction of the product was obtained upon concentration of the filtrate and stirring it at +6 °C for several days. Combined yield of **8a**: 3.25 g (76%). – <sup>1</sup>H NMR (200.13 MHz, [D<sub>8</sub>]-THF): δ = 7.81 (s, 1 H, CH), 2.70 (br, 2 H, 1-H), 1.63 (m, 10 H, C<sub>6</sub>H<sub>11</sub>), 1.26 (m, 10 H, C<sub>6</sub>H<sub>11</sub>). – <sup>13</sup>C{<sup>1</sup>H} NMR (50.32 MHz, [D<sub>8</sub>]-THF): δ = 167.3 (CH), 63.4 (C-1), 38.7 (C-2), 27.0 (C-4), 26.8 (C-3).

Single crystals of **8a** were obtained by a slow evaporation of solvent from a THF solution. X-ray crystal structure analysis of **8a**: formula C<sub>13</sub>H<sub>23</sub>LiN<sub>2</sub> × C<sub>4</sub>H<sub>8</sub>O, *M* = 286.38, colourless crystal 0.15 × 0.15 × 0.05 mm, *a* = 9.185(1), *b* = 10.251(1), *c* = 11.603(1) Å, α = 73.26(1), β = 67.51(1), γ = 63.91(1)°, *V* = 897.1(2) Å<sup>3</sup>, ρ<sub>calc</sub> = 1.060 g cm<sup>−3</sup>, μ = 0.64 cm<sup>−1</sup>, no absorption correction (0.990 ≤ *T* ≤ 0.997), *Z* = 2, triclinic, space group *P*1 bar (No. 2), λ = 0.71073 Å, *T* = 198 K, ω and φ scans, 5261 reflections collected (±*h*, ±*k*, ±*l*), [(sin θ)/λ] = 0.60 Å<sup>−1</sup>, 3143 independent (*R*<sub>int</sub> = 0.039) and 1728 observed reflections [*I* ≥ 2σ(*I*)], 191 refined parameters, *R* = 0.080, *wR*<sup>2</sup> = 0.197, max. residual electron density 0.53 (−0.28) e Å<sup>−3</sup>, hydrogen atoms calculated and refined as riding atoms.

#### Preparation of *N,N'*-diphenylformamidinyl lithium (**8b**)

Analogously as described above *N,N'*-diphenylformamidine (10.39 g, 52.9 mmol) in 100 ml of ether was reacted with methyl lithium (33.1 ml of a 1.6 M solution in ether, 52.9 mmol). After 2 h at room temperature the solvent was removed *in vacuo* to yield 5.77 g (54%) of **8b** that was used for further reactions without purification. <sup>1</sup>H NMR (200.13 MHz, [D<sub>8</sub>]-THF): δ = 8.76 (s, 1 H, CH), 7.05 (m, 4 H, C<sub>6</sub>H<sub>5</sub>), 6.90 (m, 4 H, C<sub>6</sub>H<sub>5</sub>), 6.66 (m, 2 H, C<sub>6</sub>H<sub>5</sub>). – <sup>13</sup>C{<sup>1</sup>H} NMR (50.32 MHz, [D<sub>8</sub>]-THF): δ = 162.7 (CH), 155.1 (*i*-C<sub>6</sub>H<sub>5</sub>), 129.2, 120.5, 119.6 (C<sub>6</sub>H<sub>5</sub>).

#### Synthesis of bis(η<sup>5</sup>-cyclopentadienyl)(*N,N'*-dicyclohexylformamidinato)zirconium chloride (**6a**)

This compound had previously been prepared by the hydrazirconation route [10]. We have synthesized compound **6a** by the following alternative procedure: A mixture of 2.16 g

(10.1 mmol) of the reagent **8a** and 2.95 g (10.1 mmol) of Cp<sub>2</sub>ZrCl<sub>2</sub> was dissolved in 60 ml of toluene plus 3 drops of THF. The mixture was stirred for 3 h at room temperature. The suspension was filtered through celite and the volume reduced to 1/4 *in vacuo*. After 5 d at −30 °C the precipitated product was collected by filtration, washed with pentane and dried *in vacuo* to yield 3.22 g (69%) of **6a**. <sup>1</sup>H NMR (200.13 MHz, [D<sub>8</sub>]-THF/[D<sub>8</sub>]-toluene): δ = 7.91 (s, 1 H, CH), 6.05 (s, 10 H, C<sub>5</sub>H<sub>5</sub>), 3.40 (m, 1 H, 1-H), 3.90 (m, 1 H, 7-H), 1.97–1.06 (m, 20 H, C<sub>6</sub>H<sub>11</sub>). – <sup>13</sup>C{<sup>1</sup>H} NMR (300.14 MHz, [D<sub>8</sub>]-THF/[D<sub>8</sub>]-toluene): δ = 160.1 (CH), 112.9 (C<sub>5</sub>H<sub>5</sub>), 59.4, 59.3 (C-1 and C-7), 36.3, 35.6 (C-2, C-6 and C-8, C-12), 27.3, 27.2 (C-3, C-5 and C-9, C-11), 26.9, 26.8 (C-4 and C-10).

#### Synthesis of bis(η<sup>5</sup>-cyclopentadienyl)(*N,N'*-diphenylformamidinato)zirconium chloride (**6b**)

A mixture of 6.18 g (30.7 mmol) of the reagent **8b** was reacted with 8.97 g (30.7 mmol) of Cp<sub>2</sub>ZrCl<sub>2</sub> in 60 ml of toluene. The reaction mixture was stirred for 2.5 h at ambient temperature. The suspension was filtered through Celite and the solvent reduced to 1/4 *in vacuo*. The product was collected by filtration, washed with pentane and dried *in vacuo* to yield 8.76 g (63%) of **6b**. M.p. 117 °C. – <sup>1</sup>H NMR 200.13 MHz, ([D<sub>8</sub>]-toluene): δ = 7.78 (s, 1 H, CH), 7.15 (m, 4 H, C<sub>6</sub>H<sub>5</sub>), 6.98 (m, 4 H, C<sub>6</sub>H<sub>5</sub>), 6.64 (m, 2 H, C<sub>6</sub>H<sub>5</sub>), 5.86 (s, 10 H, C<sub>5</sub>H<sub>5</sub>). – <sup>13</sup>C{<sup>1</sup>H} NMR (50.32 MHz, [D<sub>8</sub>]-toluene): δ = 158.5 (CH), 129.7, 128.4, 124.5, 124.1, 123.1, 119.6 (C<sub>6</sub>H<sub>5</sub>), 113.0 (C<sub>5</sub>H<sub>5</sub>); the ipso-<sup>13</sup>C<sub>Ph</sub> resonances were not observed. – C<sub>23</sub>H<sub>21</sub>N<sub>2</sub>ClZr (452.1): calcd. C 61.10, H 4.68, N 6.20; found C 61.09, H 4.69, N 6.25.

Single crystals were obtained by slow evaporation of solvent from a toluene solution. X-ray crystal structure analysis of **6b**: formula C<sub>23</sub>H<sub>21</sub>ClN<sub>2</sub>Zr × 0.5 C<sub>7</sub>H<sub>8</sub>, *M* = 498.16, colourless crystal 0.50 × 0.35 × 0.10 mm, *a* = 11.543(1), *b* = 19.120(1), *c* = 20.674(1) Å, *V* = 4562.8(5) Å<sup>3</sup>, ρ<sub>calc</sub> = 1.450 g cm<sup>−3</sup>, μ = 6.15 cm<sup>−1</sup>, empirical absorption correction (0.749 ≤ *T* ≤ 0.941), *Z* = 8, orthorhombic, space group *P*2<sub>1</sub>2<sub>1</sub>2<sub>1</sub> (No. 19), λ = 0.71073 Å, *T* = 198 K, ω and φ scans, 34307 reflections collected (±*h*, ±*k*, ±*l*), [(sin θ)/λ] = 0.66 Å<sup>−1</sup>, 10717 independent (*R*<sub>int</sub> = 0.036) and 9386 observed reflections [*I* ≥ 2σ(*I*)], 551 refined parameters, *R* = 0.030, *wR*<sup>2</sup> = 0.056, Flack parameter −0.06(2), max. residual electron density 0.25 (−0.37) e Å<sup>−3</sup>, hydrogens calculated and refined as riding atoms, contains two almost identically molecules in the asymmetric unit.

#### Synthesis of bis(η<sup>5</sup>-cyclopentadienyl)(*N,N'*-dicyclohexylformamidinato)methyl-zirconium (**7a**)

A solution of 2.50 g (9.93 mmol) of dimethylzirconocene and 2.07 g (9.93 mmol) *N,N'*-dicyclohexylformamidine in

60 ml of toluene was stirred under reflux for 4 d. Then the solvent was removed *in vacuo* and the precipitate stirred up in 20 ml of pentane. After keeping it at  $-30\text{ }^{\circ}\text{C}$  the precipitate was collected by filtration and dried *in vacuo*. An additional fraction of **7a** was obtained by concentration of the filtrate to *ca.* 25% of its volume and addition of 14 ml of perfluoromethylcyclohexane. The mixture was stirred for 3 d and the product collected by filtration and dried *in vacuo*. Combined yield of **7a**: 3.65 g (83%). M.p.  $61\text{ }^{\circ}\text{C}$ . –  $^1\text{H}$  NMR (599.11 MHz,  $[\text{D}_8]$ -toluene):  $\delta = 7.81$  (s, 1 H, CH), 5.63 (s, 10 H,  $\text{C}_5\text{H}_5$ ), 2.78 (tt,  $J = 11.8\text{ Hz}$ ,  $J = 3.6\text{ Hz}$ , 1 H, 1-H), 2.64 (tt,  $J = 11.4\text{ Hz}$ ,  $J = 3.7\text{ Hz}$ , 1 H, 7-H), 2.06–1.50 (m, 10 H,  $\text{C}_6\text{H}_{11}$ ), 1.19–0.97 (m, 10 H,  $\text{C}_6\text{H}_{11}$ ), 0.01 (s, 3 H,  $\text{CH}_3$ ). –  $^{13}\text{C}\{^1\text{H}\}$  NMR (150.67 MHz,  $[\text{D}_8]$ -toluene):  $\delta = 161.6$  ( $^1J_{\text{CH}} = 158\text{ Hz}$ , CH), 108.9 ( $^1J_{\text{CH}} = 170.4\text{ Hz}$ ,  $\text{C}_5\text{H}_5$ ), 59.7 (C-7), 55.7 (s, C-1), 35.7, 35.6 (s, C-2, C-6 and C-8, C-12), 27.6 ( $^1J_{\text{CH}} = 119.2\text{ Hz}$ ,  $\text{CH}_3$ ), 26.8, 26.6 (C-3, C-5 and C-9, C-11), 26.4, 26.3 (C-4 and C-10). The NMR assignments were secured by additional 2D NMR measurements. –  $\text{C}_{24}\text{H}_{36}\text{N}_2\text{Zr}$  (443.8): calcd. C 64.96, H 8.18, N 6.31; found C 64.70, H 7.93, N 6.28.

Single crystals of complex **7a** were obtained by slow evaporation of solvent from toluene solution. X-ray crystal structure analysis for **7a**: formula  $\text{C}_{24}\text{H}_{36}\text{N}_2\text{Zr}$ ,  $M = 443.77$ , light yellow crystal  $0.50 \times 0.45 \times 0.30\text{ mm}$ ,  $a = 11.186(1)$ ,  $b = 14.446(1)$ ,  $c = 15.313(1)\text{ \AA}$ ,  $\alpha = 89.24(1)$ ,  $\beta = 72.30(1)$ ,  $\gamma = 73.58(1)^{\circ}$ ,  $V = 2254.0(3)\text{ \AA}^3$ ,  $\rho_{\text{calc}} = 1.308\text{ g cm}^{-3}$ ,  $\mu = 4.98\text{ cm}^{-1}$ , empirical absorption correction ( $0.789 \leq T \leq 0.865$ ),  $Z = 4$ , triclinic, space group  $P1$  bar (No. 2),  $\lambda = 0.71073\text{ \AA}$ ,  $T = 198\text{ K}$ ,  $\omega$  and  $\phi$  scans, 18090 reflections collected ( $\pm h, \pm k, \pm l$ ),  $[(\sin \theta)/\lambda] = 0.68\text{ \AA}^{-1}$ , 11162 independent ( $R_{\text{int}} = 0.015$ ) and 9805 observed reflections [ $I \geq 2\sigma(I)$ ], 489 refined parameters,  $R = 0.027$ ,  $wR^2 = 0.063$ , max. residual electron density  $0.36(-0.50)\text{ e \AA}^{-3}$ , hydrogens calculated and refined as riding atoms, contains two almost identically molecules in the asymmetric unit.

#### Preparation of bis( $\eta^5$ -cyclopentadienyl)( $N,N'$ -diphenylformamidinato)zirconium (7b)

This complex was prepared analogously as it was described in the literature [11]. A solution of 2.00 g (7.97 mmol) of dimethylzirconocene and 1.56 g (7.97 mmol) of  $N,N'$ -diphenylformamidine in 80 ml of toluene was kept at reflux temperature for 4 d. The solvent was removed *in vacuo* and the precipitate stirred up in pentane. The solid product was collected by filtration, washed three times with pentane and dried *in vacuo* to give 2.90 g (84%) of **7b**.  $^1\text{H}$  NMR (200.13 MHz,  $[\text{D}_8]$ -toluene):  $\delta = 7.90$  (s, 1 H, CH), 7.12 (m, 4 H,  $\text{C}_6\text{H}_5$ ), 6.92 (m, 2 H,  $\text{C}_6\text{H}_5$ ), 6.68 (m, 4 H,  $\text{C}_6\text{H}_5$ ), 5.61 (s, 10 H,  $\text{C}_5\text{H}_5$ ),  $-0.05$  (s, 3 H,  $\text{CH}_3$ ). –  $^{13}\text{C}\{^1\text{H}\}$  NMR (50.32 MHz,  $[\text{D}_8]$ -toluene):  $\delta = 160.0$  (CH), 129.5, 128.6, 124.6, 123.8, 122.1, 118.5 ( $\text{C}_6\text{H}_5$ ),

109.5 ( $\text{C}_5\text{H}_5$ ), 31.3 ( $\text{CH}_3$ ); the ipso- $^{13}\text{C}_{\text{Ph}}$  resonances were not observed.

#### Preparation of bis( $\eta^5$ -cyclopentadienyl)( $N,N'$ -diphenylformamidinato)zirconium methyl tris(pentafluorophenyl)borate (9A)

At  $0\text{ }^{\circ}\text{C}$  precooled tetrahydrofuran was added to a mixture of 1.51 g (3.5 mmol) of **7b** and 1.79 g (3.5 mmol) of tris(pentafluorophenyl)borane. The mixture was stirred for 2 h at room temperature and then the solvent removed *in vacuo*. The solvent was stirred up in pentane and the product collected by filtration, washed twice with pentane and dried *in vacuo* to yield 3.21 g (97%) of **9A**. M.p.  $169\text{ }^{\circ}\text{C}$ . –  $^1\text{H}$  NMR (200.13 MHz,  $[\text{D}_8]$ -THF):  $\delta = 8.56$  (s, 1 H, CH), 7.40 (m, 4 H,  $\text{C}_6\text{H}_5$ ), 7.18 (m, 6 H,  $\text{C}_6\text{H}_5$ ), 6.60 (s, 10 H,  $\text{C}_5\text{H}_5$ ), 0.53 (broad, 3 H,  $\text{CH}_3$ ). –  $^{13}\text{C}\{^1\text{H}\}$  NMR (50.32 MHz,  $[\text{D}_8]$ -THF):  $\delta = 159.8$  (CH), 148.1, 130.3, 125.1, 121.3 ( $\text{C}_6\text{H}_5$ ), 115.3 ( $\text{C}_5\text{H}_5$ ); the ipso- $^{13}\text{C}_{\text{Ph}}$  resonances and the  $^{13}\text{C}$  resonances of the  $\text{CH}_3\text{B}(\text{C}_6\text{F}_5)_3$  unit were not observed. –  $^{11}\text{B}\{^1\text{H}\}$  NMR (64.21 MHz,  $[\text{D}_8]$ -THF):  $\delta = -14.9$  ( $\nu_{1/2} = 46\text{ Hz}$ ). –  $\text{C}_{42}\text{H}_{24}\text{N}_2\text{BF}_{15}\text{Zr} \times \text{C}_4\text{H}_8\text{O}$  (1015.8): calcd. C 54.39, H 3.18, N 2.76; found C 54.20, H 3.29, N 2.76.

#### Synthesis of bis( $\eta^5$ -cyclopentadienyl)( $N,N'$ -diphenylformamidinato)zirconium tetraphenylborate (9B)

Tetrahydrofuran (40 ml) was added to a mixture of 1.29 g (2.56 mmol) of tributylammonium tetraphenylborate and 1.10 g (2.56 mmol) of **7b** at room temperature. Gas evolution occurred. The mixture was stirred over night, and then the solvent was removed *in vacuo*. The residue was stirred up in ether and the product collected by filtration. It was washed three times with ether and dried *in vacuo* to yield 1.79 g (95%) of **9B**. M.p.  $147\text{ }^{\circ}\text{C}$ . –  $^1\text{H}$  NMR (599.11 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta = 8.33$  (s, 1 H, CH), 7.45 (m, 4 H,  $\text{N}(m\text{-C}_6\text{H}_5)$ ), 7.36 (m, 8 H,  $\text{B}(m\text{-C}_6\text{H}_5)_4$ ), 7.23 (m, 2 H,  $\text{N}(p\text{-C}_6\text{H}_5)$ ), 7.05 (m, 8 H,  $\text{B}(o\text{-C}_6\text{H}_5)_4$ ), 7.01 (m, 4 H,  $\text{N}(o\text{-C}_6\text{H}_5)$ ), 6.91 (m, 4 H,  $\text{B}(p\text{-C}_6\text{H}_5)_4$ ), 6.29 (s, 10 H,  $\text{C}_5\text{H}_5$ ), 3.60 (m, 4 H, THF), 1.69 (m, 4 H, THF). –  $^{13}\text{C}\{^1\text{H}\}$  NMR (105.67 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta = 164.4$  (q,  $^1J_{\text{CB}} = 49.3\text{ Hz}$ ,  $\text{B}(i\text{-C}_6\text{H}_5)_4$ ), 158.3 (CH), 147.2 ( $\text{N}(i\text{-C}_6\text{H}_5)$ ), 136.3 ( $\text{B}(m\text{-C}_6\text{H}_5)_4$ ), 130.2 ( $\text{N}(m\text{-C}_6\text{H}_5)$ ), 126.0 ( $\text{B}(o\text{-C}_6\text{H}_5)_4$ ), 125.2 ( $\text{N}(p\text{-C}_6\text{H}_5)$ ), 122.1 ( $\text{B}(p\text{-C}_6\text{H}_5)_4$ ), 121.0 ( $\text{N}(o\text{-C}_6\text{H}_5)$ ), 114.4 ( $\text{C}_5\text{H}_5$ ), 73.1 (THF), 25.4 (THF). –  $^{11}\text{B}\{^1\text{H}\}$  NMR (64.21 MHz,  $[\text{D}_8]$ -THF):  $\delta = -6.7$  ( $\nu_{1/2} = 21\text{ Hz}$ ). The NMR assignments were secured by additional 2D NMR measurements. –  $\text{C}_{47}\text{H}_{41}\text{N}_2\text{BZr} \times \text{C}_4\text{H}_8\text{O}$  (808.0): calcd. C 75.81, H 6.11, N 3.47; found C 74.97, H 6.02, N 3.67.

Single crystals were obtained from the filtrate of the reaction mixture at  $-30\text{ }^{\circ}\text{C}$ . X-ray crystal structure analysis for **9B**: formula  $\text{C}_{23}\text{H}_{21}\text{N}_2\text{Zr} \times \text{C}_4\text{H}_8\text{O} \times (\text{C}_6\text{H}_5)_4\text{B}$ ,  $M = 807.95$ , colourless crystal  $0.10 \times 0.10 \times 0.05\text{ mm}$ ,  $a =$

30.827(1),  $b = 10.319(1)$ ,  $c = 27.084(1)$  Å,  $\beta = 111.53(1)^\circ$ ,  $V = 8014.4(9)$  Å<sup>3</sup>,  $\rho_{\text{calc}} = 1.339$  g cm<sup>-3</sup>,  $\mu = 3.16$  cm<sup>-1</sup>, no absorption correction ( $0.969 \leq T \leq 0.984$ ),  $Z = 8$ , monoclinic, space group  $C2/c$  (No. 15),  $\lambda = 0.71073$  Å,  $T = 198$  K,  $\omega$  and  $\phi$  scans, 15033 reflections collected ( $\pm h, \pm k, \pm l$ ),  $[(\sin \theta)/\lambda] = 0.62$  Å<sup>-1</sup>, 8117 independent ( $R_{\text{int}} = 0.065$ ) and 5379 observed reflections [ $I \geq 2\sigma(I)$ ], 505 refined parameters,  $R = 0.051$ ,  $wR^2 = 0.095$ , max. residual

electron density  $0.39(-0.56)$  e Å<sup>-3</sup>, hydrogens calculated and refined as riding atoms.

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