

## Reaction of dimethylzirconocene with imidazole in the presence of tris(pentafluorophenyl) borane

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### Abstract

Dimethylzirconocene (**1**) reacts with the imidazole · B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> adduct (**2**) to give methane and the methylzirconocene/imidazole/tris(pentafluorophenyl)borane–betaine complex **3**. Subsequent stoichiometric hydrolysis yields the corresponding dinuclear  $\mu$ -hydroxy-bridged betaine complex **4**, that was characterized by an X-ray crystal structure analysis.

**Keywords:** Dimethylzirconocene; Tris(pentafluorophenyl)borane; Zirconium; Metallocene cation; Lewis acid; Betaine; Metallocenes

### 1. Introduction

We have shown that the reaction of the five-membered hetarenes pyrrol and pyrazole respectively with Cp<sub>2</sub>Zr(CH<sub>3</sub>)<sub>2</sub>/B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> or the Cp<sub>2</sub>Zr–CH<sub>3</sub><sup>+</sup> cation system leads to some interesting electrophilic Group 4 metallocene chemistry around the Zr–N bond [1,2]. In the reactions involving the pyrazole moiety this is dominated by the special features of the additional nitrogen atom adjacent to the Zr–N linkage, that invariably leads to  $\eta^2$ -N1,N2-coordinated products [3]. We thought it would be interesting to know in which way this typical reaction course is altered when the two nitrogen atoms are 1,3-positioned (instead of 1,2-oriented) in the substrate and, therefore, have tried to react imidazole with Cp<sub>2</sub>Zr(CH<sub>3</sub>)<sub>2</sub>.

### 2. Results and discussion

As it turns out, imidazole does not react with dimethylzirconocene in benzene at ambient temperature to eliminate methane. It appears that this aromatic five-membered heterocycle is not acidic enough to cleave the zirconium to carbon bond. Addition of one molar equivalent of the strong Lewis acid tris(pentafluorophenyl)borane results in the rapid evolution of methane

(probably one equivalent) from the reaction mixture. We assume that the imidazole · B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> adduct possesses a sufficient Brønsted acidity to allow for the typical protolytic cleavage of the Zr–CH<sub>3</sub> bond with formation of methane and the [(Cp<sub>2</sub>ZrCH<sub>3</sub>)imidazole · B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>]betaine complex **3**.

Complex **3** was characterized by NMR spectroscopy. It exhibits the <sup>11</sup>B NMR borate resonance at  $\delta$  –8 ppm (in benzene-*d*<sub>6</sub>). The <sup>1</sup>H/<sup>13</sup>C NMR signals of the imidazole moiety of **3** are at  $\delta$  7.26, 6.83 and 5.91/126.4, 125.1 and 114.0 ppm. The Cp resonance is at  $\delta$  5.47/113.6 and the <sup>1</sup>H/<sup>13</sup>C NMR signal of the Zr bound CH<sub>3</sub> group appears at  $\delta$  0.27/41.6 ppm. The –C<sub>6</sub>F<sub>5</sub> <sup>13</sup>C resonances are at  $\delta$  148.5, 139.7, 137.5 (*ipso* carbon signal not observed).

When a benzene-*d*<sub>6</sub> solution of **3** was exposed to the atmosphere, the complex slowly hydrolyzed with evolution of methane. The product crystallized from the solution and was characterized by X-ray diffraction. Reaction of **3** with H<sub>2</sub>O probably produces a hydroxyzirconocene complex [Cp<sub>2</sub>Zr(OH)imidazole · B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>] that rapidly dimerizes under the reaction conditions. A dinuclear complex (**4**) is obtained that contains two hydroxy bridges to form a central four-membered ring containing an alternating array of two oxygen atoms and two zirconium centers. The characteristic bonding features of **4** (Zr–O 2.142(2) Å, Zr–O' 2.153(2) Å, Zr–O–Zr' 114.9(1)°, O–Zr–O' 65.1(1)°) are similar to those found in the related doubly hydroxy-bridged

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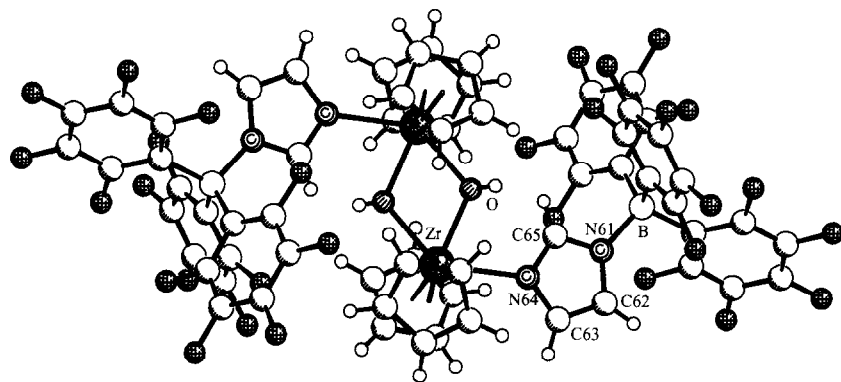
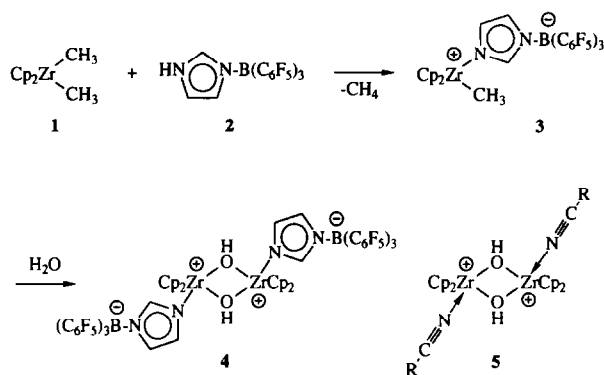


Fig. 1. A view of the molecular structure of complex **4**. Selected bond lengths (Å) and angles (°): Zr–O 2.142(2), Zr–O' 2.153(2), Zr–N64 2.408(3), Zr–Zr' 3.620(1), Zr–C<sub>Cp</sub> 2.532(4), N64–C65 1.316(4), C65–N61 1.324(4), N61–B 1.584(4), N61–C62 1.351(4), C62–C63 1.361(5), C63–N64 1.357(4), B–C<sub>ar</sub> 1.643(5); O–Zr–O' 65.1(1), Zr–O–Zr' 114.9(1), O–Zr–N64 73.20(9), O'–Zr–N64 138.26(9), Zr–N64–C65 117.6(2), Zr–N64–C63 133.7(2), N64–C65–N61 109.2(2), C65–N61–B 117.2(2), C62–N61–B 133.6(3), C65–N61–C62 109.0(3), N61–C62–C63 106.2(3), C62–C63–N64 107.8(3).



Scheme 1.

bis(zirconocene) dication **5** (Zr–O 2.154(3) Å, Zr–O' 2.174(3) Å) that is formed when zirconocene dichloride is treated with sodium tetraphenyl borate in H<sub>2</sub>O followed by addition of the stabilizing organonitrile ligand [4].

In contrast to **5**, complex **4** is a neutral compound. In a formal sense each cationic hydroxymetalocene moiety in **4** bears its borate anion with it, connected by means of the Zr···B bridging imidazole group. Both the symmetry equivalent imidazoles are oriented in the major metallocene plane (i.e. the  $\sigma$ -ligand plane). The resulting Zr–N64 distance is 2.408(3) Å, the B–N61 bond is 1.584(4) Å. Three bond lengths inside the imidazole moiety are similar to those found in the free ligand [5] (N61–C62 1.351(4) Å, C62–C63 1.361(5) Å, C63–N64 1.357(4) Å), whereas two are slightly shorter at 1.316(4) Å (N64–C65) and 1.324(4) Å (C65–N61). The O'–Zr–N64 angle at the bent metallocene is 138.26(9)° (139.5(2)° in **5**) [6].

### 3. Conclusions

The straightforward formation of **4** and its structural features show that the imidazole moiety appears to be

well suited to connect zirconocene cation centers with their borate anion counterparts. This might be of value in designing synthetic routes to related Group 4 metallocene betaine (or zwitterion) complexes that still contain a zirconium to carbon or hydrogen  $\sigma$ -bond and thus may potentially exhibit catalytic activities [7].

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### References and notes

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- [6] *Experimental details*: all reactions were carried out in an argon atmosphere using Schlenk-type glassware or in a glovebox. Solvents were dried and distilled under argon prior to use. For additional general information including a list of equipment for

physical characterization of compounds see Ref. [1]. To a solution of tris(pentafluorophenyl)borane (53 mg, 104  $\mu\text{mol}$ ) and imidazole (7 mg, 103  $\mu\text{mol}$ ) in 0.8 ml of benzene- $d_6$  was added dimethylzirconocene **1** (26 mg, 103  $\mu\text{mol}$ ). The evolution of methane was finished after ca. 5 min and a colorless solution of **3** was obtained.  $^1\text{H}$  NMR (200.1 MHz, benzene- $d_6$ ):  $\delta$  7.26 (br s, 1 H), 6.83 (br s, 1 H), 5.91 (pt, 1 H, imidazole), 5.47 (s, 10 H, Cp), 0.27 (s, 3 H,  $\text{CH}_3$ ).  $^{13}\text{C}$  NMR (50.3 MHz, benzene- $d_6$ ):  $\delta$  148.5 ( $^1J_{\text{CF}} = 243$  Hz, o- $\text{C}_6\text{F}_5$ ), 139.7 ( $^1J_{\text{CF}} = 243$  Hz, p- $\text{C}_6\text{F}_5$ ), 137.5 ( $^1J_{\text{CF}} = 249$  Hz, m- $\text{C}_6\text{F}_5$ ), 126.4, 125.1, 114.0 (imidazole), 113.6 (Cp), 41.6 ( $\text{CH}_3$ ), *ipso*- $\text{C}_6\text{F}_5$  not observed.  $^{19}\text{F}$  NMR (282.4 MHz, benzene- $d_6$ ):  $\delta$  -132, -157, -163 (each m,  $\text{C}_6\text{F}_5$ ).  $^{11}\text{B}$  NMR (64.2 MHz, benzene- $d_6$ ):  $\delta$  -8 (b s,  $\text{N}-\text{B}(\text{C}_6\text{F}_5)_3$ ). Exposure of a benzene- $d_6$  solution of **3** to air leads to slow hydrolysis and formation of **4**, which forms colorless crystals characterized by X-ray diffraction. X-ray crystal structure analysis of **4**: formula  $\text{C}_{31}\text{H}_{14}\text{BF}_{15}\text{N}_2\text{OZr}\cdot 2/2\text{C}_6\text{D}_6$ ,  $M = 901.58$ ,  $0.5 \times 0.4 \times 0.1$  mm,  $a = 11.158(2)$ ,  $b = 12.191(1)$ ,  $c = 14.531(2)$

$\text{\AA}$ ,  $\alpha = 69.97(1)$ ,  $\beta = 69.12(1)$ ,  $\gamma = 85.01(1)^\circ$ ,  $V = 1733.7(4) \text{\AA}^3$ ,  $\rho_{\text{calc}} = 1.716 \text{ g cm}^{-3}$ ,  $\mu = 3.67 \text{ cm}^{-1}$ , empirical absorption correction,  $Z = 2$ , triclinic, space group  $P\bar{1}$  (No. 2), Enraf-Nonius CAD4 diffractometer,  $\lambda = 0.71073 \text{ \AA}$ ,  $\omega/2\theta$  scans, 7461 reflections measured ( $-h, \pm k, \pm l$ ),  $[\sin \theta / \lambda]_{\text{max}} = 0.62 \text{ \AA}^{-1}$ , 7082 independent and 6698 observed reflections [ $I \leq 2\sigma(I)$ ], 518 refined parameters,  $R = 0.052$ ,  $wR^2 = 0.146$ , max. residual electron density 1.14 ( $-1.29$ )  $\text{e \AA}^{-3}$ , direct methods, hydrogen atoms calculated and riding. Programs used: SHELXS 86, SHELXL 93, SCHAKAL 92. Further information about the X-ray structure analysis can be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, on quoting the depository number CSD-404331, the names of the authors and the journal citation.

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