

## Electronic Supplementary Information for

# A slipped multi-decker zirconium complex with an $\eta^7:\eta^2$ bridging cycloheptatrienyl ligand

*Andreas Glöckner, Constantin G. Daniliuc, Matthias Freytag, Peter G. Jones, and Matthias  
Tamm\**

Institut für Anorganische und Analytische Chemie, Technische Universität Braunschweig,  
Hagenring 30, 38106 Braunschweig, Germany

## Contents

- 1.) Experimental Details
- 2.) X-ray diffraction studies

## 1. Experimental procedures

### General procedures

All synthetic and spectroscopic manipulations were carried out under an atmosphere of purified nitrogen, either in a Schlenk apparatus or in a glovebox. Solvents were dried and deoxygenated either by distillation under a nitrogen atmosphere from sodium benzophenone ketyl (THF) or by an MBraun GmbH solvent purification system (all other solvents).

NMR spectra were obtained on a Bruker DRX 400, a Bruker Avance III 400 or a Bruker Avance II 300 spectrometer. Its residual solvent signal was used as a chemical shift reference ( $\delta_{\text{H}} = 7.16$ ) for the  $^1\text{H}$  spectra and the solvent signal ( $\delta_{\text{C}} = 128.06$  ppm) for the  $^{13}\text{C}$  spectra.  $^{31}\text{P}$  spectra were referenced to virtual external 85 % phosphoric acid ( $\delta_{\text{P}} = 0$ ). Elemental analyses were performed by combustion and gas chromatographical analysis with an Elementar varioMICRO instrument.  $[(\eta^7\text{-C}_7\text{H}_7)\text{ZrCl}(\text{tmeda})]$  (**1**) was prepared according to the literature.<sup>1</sup> All other reagents were obtained commercially and used as received.

### $[(\eta^7\text{-C}_7\text{H}_7)\text{Zr}\{\text{N}(\text{SiMe}_3)_2\}(\text{thf})]$ (**2**)

To a blue solution of  $[(\eta^7\text{-C}_7\text{H}_7)\text{ZrCl}(\text{tmeda})]$  (0.500 g, 1.497 mmol) in THF (25 mL) was slowly added  $\text{Na}\{\text{N}(\text{SiMe}_3)_2\}$  (0.288 g, 1.527 mmol) in THF (11 mL). After stirring for 1 h, the solvent was removed and the product was extracted with pentane. Concentration of the resulting orange solution and crystallization at  $-20$  °C afforded orange crystals (0.344 g, 55 %).

$^1\text{H}$  NMR (300 MHz,  $\text{C}_6\text{D}_6$ , ambient):  $\delta = 4.55$  (s, 7 H,  $\text{C}_7\text{H}_7$ ), 3.26 (m, 4 H, thf), 1.07 (m, 4 H, thf), 0.18 (s, 18 H,  $\text{SiMe}_3$ ).

$^{13}\text{C}$  NMR (75 MHz,  $\text{C}_6\text{D}_6$ , ambient):  $\delta = 84.6$  ( $\text{C}_7\text{H}_7$ ), 72.0 (thf), 25.1 (thf), 3.6 ( $\text{SiMe}_3$ ).

Elemental analysis (%): calculated for  $\text{C}_{17}\text{H}_{33}\text{NOSi}_2\text{Zr}$  (414.8): C = 49.22, H = 8.02; found: C = 48.96, H = 7.95.

### $[(\eta^7\text{-C}_7\text{H}_7)\text{Zr}\{\text{N}(\text{SiMe}_3)_2\}]_n$ (**3**)

Method 1:  $[(\eta^7\text{-C}_7\text{H}_7)\text{Zr}\{\text{N}(\text{SiMe}_3)_2\}(\text{thf})]$  (0.700 g, 1.687 mmol) was sublimed at  $130$  °C under dynamic vacuum (0.1 mbar), which afforded an orange-red solid (0.337 g, 58%).

<sup>1</sup> A. Glöckner, T. Bannenberg, M. Tamm, A. M. Arif and R. D. Ernst, *Organometallics*, 2009, **28**, 5866

Method 2:  $[(\eta^7\text{-C}_7\text{H}_7)\text{ZrCl}(\text{tmeda})]$  (1.0 g, 2.994 mmol) was reacted with  $\text{Na}\{\text{N}(\text{SiMe}_3)_2\}$  (0.575 g, 3.054 mmol) in THF as described above, followed by solvent removal, drying at 70 °C and sublimation at 130 °C under dynamic vacuum. Yield: 0.825 g (80%). Single crystals were obtained by slow sublimation in a sealed glass tube.

Elemental analysis (%): calculated for  $\text{C}_{13}\text{H}_{25}\text{NSi}_2\text{Zr}$  (342.7): C = 45.56, H = 7.35; found: C = 45.26, H = 7.25.

### Generation of $[(\eta^7\text{-C}_7\text{H}_7)\text{Zr}\{\text{N}(\text{SiMe}_3)_2\}(\text{PMe}_3)]$ (4) in an NMR tube experiment

Trimethylphosphine (0.006 g, 8  $\mu\text{L}$ ) was added to a suspension of  $[(\eta^7\text{-C}_7\text{H}_7)\text{Zr}\{\text{N}(\text{SiMe}_3)_2\}]_n$  (0.025 g, 0.073 mmol) in  $\text{C}_6\text{D}_6$ . After a few minutes a clear, red-orange solution was obtained.

$^1\text{H}$  NMR (300 MHz,  $\text{C}_6\text{D}_6$ , ambient):  $\delta = 5.26$  (s, 7 H,  $\text{C}_7\text{H}_7$ ), 0.65 (d,  $^2J_{\text{PH}} = 4.5$  Hz, 9 H,  $\text{PMe}_3$ ), 0.17 (s, 9 H,  $\text{SiMe}_3$ ).

$^{13}\text{C}$  NMR (75 MHz,  $\text{C}_6\text{D}_6$ , ambient):  $\delta = 84.6$  ( $\text{C}_7\text{H}_7$ ), 16.3 (d,  $^1J_{\text{PC}} = 3.5$  Hz,  $\text{PMe}_3$ ), 4.4 ( $\text{SiMe}_3$ ).

$^{31}\text{P}$  NMR (121 MHz,  $\text{C}_6\text{D}_6$ , ambient):  $\delta = -51.7$ .

### $[(\eta^7\text{-C}_7\text{H}_7)\text{Zr}(\text{OSiPh}_3)]_2$ (5)

Solid  $\text{Ph}_3\text{SiOH}$  (0.081 g, 0.292 mmol) was added to  $[(\eta^7\text{-C}_7\text{H}_7)\text{Zr}\{\text{N}(\text{SiMe}_3)_2\}]_n$  (0.100 g, 0.292 mmol) in toluene/THF (8mL/2mL) and the mixture was stirred for 42 h at 60 °C. A white precipitate was formed, which was filtered off from the pale red solution. All volatiles were removed under vacuum, the residue was redissolved in toluene and layered with pentane. After one night, brown micro-crystals were isolated (0.057 g, 43%). Single crystals were obtained from the slow diffusion of pentane into a toluene solution.

$^1\text{H}$  NMR (300 MHz,  $\text{C}_6\text{D}_6$ , ambient):  $\delta = 7.61 - 7.56$  (m, 6 H, phenyl), 7.24 - 7.17 (m, 3 H, phenyl), 7.14 - 7.07 (6 H, phenyl), 5.04 (s, 7 H,  $\text{C}_7\text{H}_7$ ).

$^{13}\text{C}$  NMR (75 MHz,  $\text{C}_6\text{D}_6$ , ambient):  $\delta = 135.6$  (*ipso*-phenyl), 135.1 (phenyl), 130.9 (phenyl), 128.9 (phenyl), 87.0 ( $\text{C}_7\text{H}_7$ ).

Elemental analysis (%): calculated for  $\text{C}_{50}\text{H}_{44}\text{O}_2\text{Si}_2\text{Zr}_2$  (915.5): C = 65.60, H = 4.84; found: C = 65.88, H = 5.03.

## 2. X-ray diffraction studies

Single crystals of each compound were examined under inert oil. Data collection was performed on various Oxford Diffraction diffractometers using monochromated Mo  $K\alpha$  or mirror-focussed Cu  $K\alpha$  radiation. Absorption corrections were performed on the basis of multi-scans. The data were analyzed using the SHELXL97 program.<sup>2</sup> In all cases, the non-hydrogen atoms were refined anisotropically. Hydrogen atoms were either located and refined isotropically (for all hydrogen atoms directly attached to the 7-membered ring), incorporated as idealised methyl groups allowed to rotate but not tip, or were allowed to ride on their attached carbon atoms. *Special features:* For compound **2** an extinction correction was applied. Structure **3** showed one significant residual peak of ca. 2.4 e  $\text{\AA}^{-3}$  at a chemically impossible position; this might reasonably be assigned to a minor unidentified twinning component, because its  $x$  and  $z$  coordinates were related to those of the Zr site, and because sublimation often leads to twinned crystals.

### Crystallographic data

|                                      | <b>2</b>   | <b>3</b>  | <b>5</b>   |
|--------------------------------------|--|---|--|
| Empirical Formula                    | C <sub>17</sub> H <sub>33</sub> NOSi <sub>2</sub> Zr | C <sub>13</sub> H <sub>25</sub> NSi <sub>2</sub> Zr | C <sub>50</sub> H <sub>44</sub> O <sub>2</sub> Si <sub>2</sub> Zr <sub>2</sub> |
| Formula Weight                       | 414.84   | 342.74  | 915.47   |
| $T/K$                                | 100(2)   | 100(2)  | 100(2)   |
| Wavelength $\lambda/\text{\AA}$      | 1.54184  | 0.71073   | 1.54184  |
| Crystal System                       | monoclinic   | monoclinic  | monoclinic   |
| Space Group                          | $P2_1/c$   | $C2/c$  | $P2_1/n$   |
| $a/\text{\AA}$                       | 10.2102(2)   | 15.8898(6)  | 11.24964(15)   |
| $b/\text{\AA}$                       | 10.7387(2)   | 7.1098(6)   | 20.2119(2)   |
| $c/\text{\AA}$                       | 19.2391(4)   | 28.0195(12)   | 18.3958(3)   |
| $\alpha$ (°)                         | 90   | 90  | 90   |
| $\beta$ (°)                          | 99.648(2)  | 99.564(4)   | 100.504(2)   |
| $\gamma$ (°)                         | 90   | 90  | 90   |
| Volume [ $\text{\AA}^3$ ]            | 2079.62(7)   | 3121.5(2)   | 4112.67(9)   |
| $Z$                                  | 4  | 8 (monomeric units)                                 | 4  |
| Reflections Collected                | 22020  | 47045   | 117623   |
| Independent reflections              | 4301 [ $R_{\text{int}} = 0.0178$ ]                   | 2962 [ $R_{\text{int}} = 0.0511$ ]                  | 8152 [ $R_{\text{int}} = 0.0256$ ]   |
| $\rho_c/\text{g cm}^{-3}$            | 1.325  | 1.459   | 1.479  |
| $\mu/\text{mm}^{-1}$                 | 5.437  | 0.839   | 5.026  |
| $R(F_o)$ , [ $I > 2\sigma(I)$ ]      | 0.0203   | 0.0425  | 0.0183   |
| $R_w(F_o^2)$                         | 0.0518   | 0.0942  | 0.0477   |
| Goodness of fit on ( $F^2$ )         | 1.051  | 1.291   | 1.067  |
| $\Delta\rho/\text{e}\text{\AA}^{-3}$ | 0.407/−0.514   | 2.375/−1.112  | 0.304/−0.442   |

<sup>2</sup> (a) G. M. Sheldrick, *SHELXL-97, Program for the Refinement of Crystal Structure from Diffraction Data*, University of Göttingen, Göttingen, Germany, 1997; (b) G. M. Sheldrick, *Acta Cryst.*, 2008, **A64**, 112-122.

