

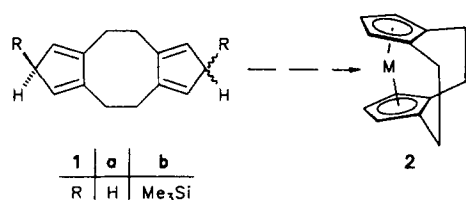
## Synthesis and Structure of the First [2]<sub>2</sub>Metallocenophanes\*\*

Klaus Hafner,\* Carsten Mink, and Hans Jörg Lindner

Dedicated to Professor Virgil Boekelheide  
on the occasion of his 75th birthday

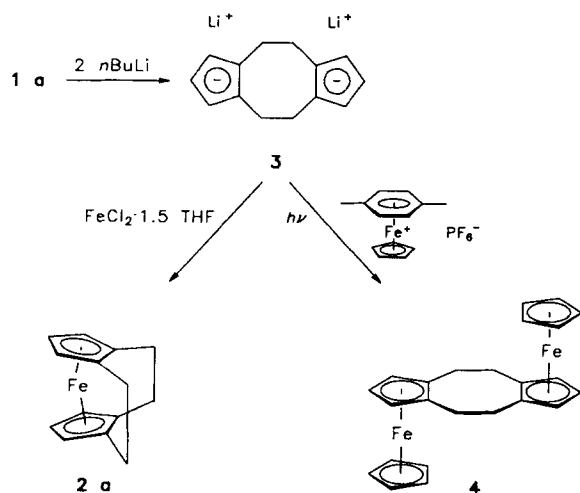
Bent metallocenes with a nonplanar arrangement of the ring ligands proved to be components of efficient catalysts for the stereoselective polymerization of alkenes.<sup>[1]</sup> Rigid metallocene derivatives of the fourth subgroup having a short bridge and consequently exposed metal center were found to be particularly well suited.<sup>[2]</sup> Numerous metallocenophanes have been prepared with one or more bridges of various lengths, but surprisingly [2](1,1')[2](2,2')-metallocenophanes **2** are not known,<sup>[3]</sup> even though the considerable conformational rigidity of the ligand system and the large dihedral angle between the planes of the rings indicates that they could serve as components of homogeneous catalysts.

In the course of investigations on dicyclopenta[*a,e*]cyclooctene, a 14π electron system with cyclic delocalization,<sup>[4]</sup> we discovered a simple route to tricyclo[9.3.0.0<sup>4,8</sup>]tetradeca-4,7,11,14-tetraene (**1**),<sup>[5]</sup> which proved to be a suitable starting material for metallocenophanes of type **2**. We report here on the



synthesis and structure of ferrocenophane **2a** and zirconocenophane dichloride **2b**, the first [2]<sub>2</sub>metallocenophanes.

The dilithium compound **3** was prepared by double deprotonation of **1a** with *n*BuLi in THF at 25 °C. The <sup>1</sup>H, <sup>13</sup>C, and <sup>6</sup>Li



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NMR spectra of **3** indicate that it exists as a contact ion pair at –60 °C.<sup>[5]</sup> The reaction of **3** with ( $\eta^6$ -*p*-xylene)( $\eta^5$ -cyclopentadienyl)iron hexafluorophosphate<sup>[6]</sup> at 25 °C by irradiation with a halogen lamp (300 W, Osram Concentra) provided the *trans*-[2]<sub>2</sub>(1,2)-ferrocenophane (**4**)<sup>[7]</sup> (18 % yield, yellow crystals, decomp > 230 °C), which was previously synthesized by Schlögl et al.<sup>[8]</sup> from substituted ferrocenes in multistep procedures. Compound **3** reacted with FeCl<sub>2</sub>·1.5 THF in THF at 25 °C to afford [2](1,1')[2](2,2')-ferrocenophane **2a** as deep red plates (decomp > 210 °C)<sup>[9]</sup> in 41 % yield.<sup>[10]</sup> The complex is stable at –50 °C under inert gas but rapidly decomposes at room temperature, particularly in solution.

The X-ray structure analysis of **2a**<sup>[11]</sup> (Fig. 1) indicates considerable torsion of the two decks. The dihedral angle between

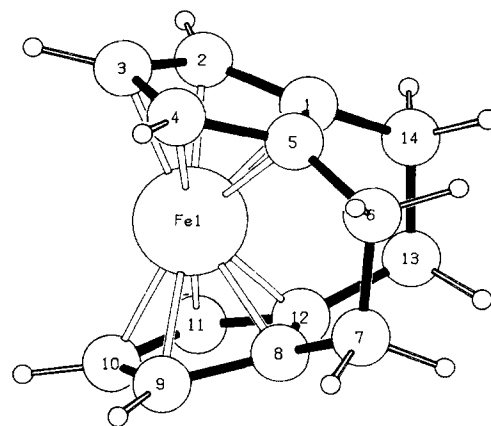


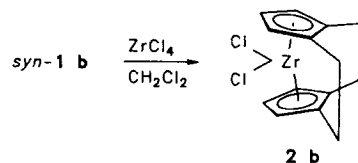
Fig. 1. Crystal structure of **2a** [11]. Selected distances [Å] and angles [°]: C1–C2 143.1(12), C5–C6 149.5(9), C6–C7 150.1(10); C5–C6–C7 113.7(5), C4–C5–C6 128.3(7).

the planes of the two rings is 28.8°, considerably larger than in the known ferrocenophanes.<sup>[3]</sup> The two small dihedral angles in the bridges (8.2(10) and 6.9(10)°) indicate that the five-membered rings are almost perfectly eclipsed. The average C–C bond length in the cyclopentadienyl ligands (141 pm) corresponds to that of other ferrocenophanes, whereas the average Fe–C distance in **2a** (201 pm) is much shorter.

In contrast to [2]ferrocenophane, which is more Lewis basic than ferrocene,<sup>[12]</sup> treatment of **2a** with trifluoroacetic acid in dichloromethane at –60 °C did not provide a well-defined protonation product but rather brown-black products insoluble in standard solvents.

In analogy to the synthesis of zirconocene dichloride<sup>[13]</sup> the reaction of *syn*-6,13-bis-(trimethylsilyl)tricyclo[9.3.0.0<sup>4,8</sup>]-tetradeca-4,7,11,14-tetraene (**1b**) with zirconium tetrachloride in dichloromethane at 25 °C furnished [2](1,1')[2](2,2')-zirconocenophane dichloride (**2b**) in 61 % yield as colorless needles (decomp > 270 °C). Compound **2b** can be obtained in analytically pure form by sublimation at 230 °C/10<sup>–2</sup> mbar.<sup>[14]</sup>

An X-ray structure analysis of **2b**<sup>[11]</sup> (Fig. 2) shows that the average Zr–C distance (249 pm) is considerably longer than that in the known [2]zirconocenophane dichlorides.<sup>[15]</sup> The dihedral angle between the planes of the rings (62.9°) in **2b** is the



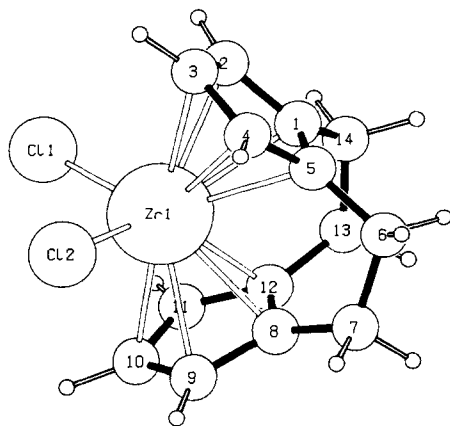


Fig. 2. Crystal structure of **2b** [11]. Selected distances [Å] and angles [°]: C1-C2 140.0(7), C5-C6 150.6(7), C6-C7 149.0(8), Zr-Cl1 244.2(1); C5-C6-C7 114.1(4), C4-C5-C6 127.7(5), Cl-Zr-Cl1 97.9(5).

largest observed in these compounds. As in **2a** the dihedral angles in the bridges of **2b** (18.6(7) and 20.7(8)°) indicate an approximately eclipsed configuration of the five-membered rings.

Owing to the molecular structure of the new rigid zirconocenophane **2b**, catalytic activity for the stereoselective polymerization of alkenes can be anticipated for this compound or substituted chiral derivatives. Moreover, application of complexes of type **2b** appears promising for C-C bond-forming reactions with metallocene derivatives from the fourth subgroup, which are currently of interest,<sup>[16]</sup> as well as for the synthesis of novel metallocycles.<sup>[16, 17]</sup>

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- [9] MS (70 eV): *m/z* (%): 238 (100) ( $M^+$ ), 93 (23) ( $C_5H_5^+$ ), 56 (14) ( $Fe^+$ ); UV (*n*-hexane)  $\lambda_{max}$  (lg  $\epsilon$ ): 223 (4.36), 250 (3.85) (sh), 330 (2.31) (sh), 455 (2.61) (sh), 496 nm (2.70);  $^1H$ NMR (300 MHz,  $C_6D_6$ ):  $\delta$  = 2.98 (s, 4H, 2CH<sub>2</sub> (outer)), 3.20 (s, 4H, 2CH<sub>2</sub> (inner)), 3.65 (s, 2H, 4,4'-H), 4.51 (s, 4H, 3,3'-H, 5,5'-H);  $^{13}C$  NMR (75.47 MHz, CDCl<sub>3</sub>):  $\delta$  = 33.17 (CH<sub>2</sub>), 64.39 (C-4, C-4'), 72.14 (C-3, C-3'), C-5, C-5'), 96.85 (C-1, C-1', C-2, C-2'). The NMR signals of **2a** and **2b** were assigned based on  $^1H$ ,  $^1H$  and  $^1H$ ,  $^{13}C$  COSY spectra and NOE experiments.
- [10] Correct elemental analyses were obtained from all compounds described.
- [11] **2a** (C<sub>14</sub>H<sub>14</sub>Fe, *M<sub>r</sub>* = 238.11) crystallizes from *n*-pentane at -40 °C in the monoclinic space group  $P2_1/n$  with *a* = 1207.9(4), *b* = 758.9(1), *c* = 1228.1(4) pm,  $\beta$  = 112.19(2)°, *Z* = 4, *V* = 1042.4 × 10<sup>6</sup> pm<sup>3</sup>,  $\rho_{calcd}$  = 1.52 g cm<sup>-3</sup>, MoK $\alpha$  radiation, 25 °C, CAD-4 Enraf-Nonius diffractometer.  $\omega/2\theta$  scans, 2293 measured reflections, of which 1449 with  $|F| \geq 4\sigma$  were used for refinement. Structure solution by direct methods, no intensity or absorption correction. *R* = 0.0830; *R<sub>w</sub>* = 0.1656, residual electron density at Fe + 0.042 e Å<sup>-3</sup>. - **2b** (C<sub>14</sub>H<sub>14</sub>Cl<sub>2</sub>Zr, *M<sub>r</sub>* = 344.39) crystallizes from *n*-hexane/dichloromethane

(3:2) at 25 °C in the monoclinic space group  $P2_1/n$  with *a* = 820.0(4), *b* = 1182.8(3), *c* = 1342.9(5) pm;  $\beta$  = 91.39(4)°, *Z* = 4, *V* = 1302.1 × 10<sup>6</sup> pm<sup>3</sup>,  $\rho_{calcd}$  = 1.76 g cm<sup>-3</sup>; MoK $\alpha$  radiation, 25 °C, CAD-4 Enraf-Nonius diffractometer.  $\omega/2\theta$  scans, 1941 measured reflections, of which 1797 with  $|F| \leq 4\sigma$  were used for refinement. Structure solution by direct methods, no intensity or absorption correction. *R* = 0.0399; *R<sub>w</sub>* = 0.0955. Programs: SHELXS-86 and SHELXL-93. Further details of the crystal structure investigations may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (FRG) on quoting the depository number CSD-58249.

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- [14] MS (70 eV): *m/z* (%): 344(72) ( $M^+$ ), 309(40) ( $M^+ - Cl$ ), 270(24) ( $M^+ - 2 Cl$ ), 227(33), 91 (100) ( $Zr^+$ ), 65(92) ( $C_5H_5^+$ ), 39(70); UV (*n*-hexane):  $\lambda_{max}$  (lg  $\epsilon$ ) = 256 (3.53) (sh), 306 (3.36), 339 nm (2.98) (sh);  $^1H$  NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 3.28, 3.36 (AA'BB', *J*<sub>1</sub> = 2.5, *J*<sub>2</sub> = 11.7 Hz, 8H, 4CH<sub>2</sub>), 6.01 (t, *J* = 3.3 Hz, 2H, 4,4'-H), 6.48 (d, *J* = 3.3 Hz, 4H, 3,3'-H, 5,5'-H);  $^{13}C$  NMR (75.47 MHz, CDCl<sub>3</sub>):  $\delta$  = 29.98 (CH<sub>2</sub>), 110.42 (C-4, C-4'), 121.63 (C-3, C-3'), C-5, C-5'), 132.06 (C-1, C-1', C-2, C-2').
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## Heterodimetal-Betaine Chemistry: Catalytic and Stoichiometric Coupling of Alkynyl Ligands under the Joint Influence of Zirconium and Boron Centers\*\*

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We have recently shown that the joint influence of zirconium and boron centers can be used for C-H activation in ( $\mu$ -hydrocarbon)Zr-B complexes.<sup>[1]</sup> Beyond this there is evidence that [Cp<sub>2</sub>ZrR]<sup>+</sup>/BR<sub>4</sub><sup>-</sup> ion pairs and betaines are of significance in homogeneous Ziegler-Natta polymerization.<sup>[2, 3]</sup> We therefore wanted to investigate the previously poorly developed chemistry of Zr-B-containing heterodimetallic betaine complexes.<sup>[2]</sup> It was found that such [(Cp<sub>2</sub>ZrR)<sup>+</sup>{(μ-R)BR<sub>3</sub><sup>-</sup>}] betaine complexes (to date hardly known) form very easily and that they readily rearrange under carbon-carbon coupling in a way that is typical for this class of compounds, to form an interesting heterodimetal-substituted organic skeleton. In this communication we describe a typical example.

Bis(propynyl)zirconocene (**1**) was obtained by the reaction of [Cp<sub>2</sub>ZrCl<sub>2</sub>] with two molar equivalents of propynyllithium.<sup>[4]</sup> The reaction of **1** with tris(pentafluorophenyl)borane in a 1:1 molar ratio in toluene at room temperature rapidly gave the (μ-R)Zr-B betaine complex **3** in 83% yield. The  $^1H$  and  $^{13}C$  NMR spectra of complex **3** show resonance signals at  $\delta$  = 5.32 and 116.3, respectively, for the Cp rings, as well as two singlets at  $\delta$  = 2.26, 1.04 and 29.7, 10.7, respectively, for the methyl groups. The  $^{13}C$  NMR resonances of the  $\mu$ -2,4-hexadiyne ligand, which is unsymmetrically coordinated to the participating metal centers, appear at  $\delta$  = 255.0, 108.5, and 105.0 (the B-C signal was not observed).

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