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# Zirconocene-Mediated Cyclization of Alkynyl–Diborylmethanes to 1,3-Diborolanes

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*Summary: The carbon–carbon triple bond in bis[(dialkylamino)(phenylethynyl)boryl]methanes* ***2a,b*** *can be easily cyclized using zirconocene to give derivatives* ***3a,b*** *of the new pentalene-like 6,8-dibora-3-zirconabicyclo[3.3.0]octa-1,4-diene, containing a zirconacyclopentadiene ring attached to a 1,3-diboracyclopentane unit. These heterocycles are characterized by NMR methods and by an X-ray structure determination of* ***3b****. Compound* ***3b*** *crystallizes from pentane in the monoclinic space group C2/c with a = 23.11(2) Å, b = 8.123(1) Å, c = 40.08(3) Å, β = 97.63(6)°, V = 7458(8) Å$^3$, and ρ(calc) = 1.175 Mg/m$^3$ for M = 659.7 g/mol and Z = 8.*

Metallacyclopentadienes have long been proposed as intermediates in transition-metal catalyzed cyclization reactions.[1] Since 1986, when Negishi and co-workers published an easy experimental procedure for the *in-situ* generation of zirconocene "$cp_2Zr$" (cp = $\eta^5$-cyclopentadienyl)[2] and the cyclization of acetylenes therewith,[3–5] frequent use has been made of this reaction in organic synthesis[4,6] as well as for the preparation of main-group element heterocycles.[7–9] We now demonstrate that the zirconocene-mediated cyclization can also be carried out with boron-substituted alkynes, and we report the first crystal structure of a heteroatom-substituted zirconacyclopentadiene.

Bis[(dialkylamino)(phenylethynyl)boryl]methanes **2a,b** are obtained in good yields by reacting lithium phenylacetylide with bis[(dimethylamino)chlorboryl]methane (**1a**) and bis[(diisopropylamino)chloroboryl]methane (**1b**), respectively.[10] **2a,b** and zirconocene produce the 3,3-dicyclopentadienyl-6,8-dibora-3-zirconabicyclo[3.3.0]octa-1,4-diene derivatives **3a,b** in 57 and 39% yields after recrystallization.[11]

Whereas the dimethylamino-substituted **3a** was obtained as a microcrystalline orange powder, **3b** crystallized in red plates from pentane at −78 °C, which were suitable for X-ray analysis. These new zirconapentalenes are remarkably stable toward dry air but decompose rapidly in solution when only trace amounts of moisture are present.

The $^{11}B$ NMR spectra of **3a,b** showed a single broad resonance at 45.5 and 44.2 ppm ($C_6D_6$), respectively. As the starting materials had $^{11}B$ NMR signals at 33.6 and 33.0 ppm, the observed downfield shift of about 12 ppm is due to the absence of the cone of anisotropy of the carbon–carbon triple bond.

At ambient temperature, the $^1H$ and $^{13}C$ NMR spectra of **3b** gave two pairs of signals for the dialkylamino groups. The 2D-NOESY spectrum in $C_6D_6$ showed only one cross-peak between the methine proton of one $^iPr$ group and the diborylmethylene group and another cross-peak between

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† Crystal structure determination.

(1) For extensive studies on Co-mediated alkyne cyclization reactions, see: Vollhardt, K. P. C. *Angew. Chem.* **1984**, *96*, 525–541; *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 539–555. Bönnemann, H. *Angew. Chem.* **1985**, *97*, 264–279; *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 248–263. For a comprehensive review see: Schore, N. E. *Chem. Rev.* **1988**, *88*, 1081–1119. For tantalacyclopentadienes as models for alkyne cyclization with early transition metals see: Strickler, J. R.; Wexler, P. A.; Wigley, D. E. *Organometallics* **1988**, *7*, 2067–2069.

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(11) All reactions described in this communication were carried out in an atmosphere of dry dinitrogen in Schlenk glassware that was dried *in vacuo*. Solvents were dried by standard procedures, destilled and stored under dinitrogen. $^{11}B$ NMR: Bruker AC-P 200 (external $BF_3{\cdot}OEt_2$). $^1H$ and $^{13}C$ NMR: JEOL EX 400 (TMS or internal $CDCl_3$ or $C_6D_6$ as secondary standards), a positive sign indicates a downfield shift from the standard. For all new compounds, an unambiguous assignment of all NMR signals was achieved with 2D NMR spectra (H–H COSY, NOESY and $^{13}C$–$^1H$ HETCOR). Synthesis of 6,8-bis(diisopropylamino)-3,3-bis($\eta^5$-cyclopentadienyl)-2,4-diphenyl-6,8-dibora-3-zirconabicyclo[3.3.0]octa-1,4-diene (**3b**): To a solution of 0.31 g (1.06 mmol) $cp_2ZrCl_2$ in 5 mL of THF was added dropwise at −78 °C 1.25 mL (2 mmol) of $^nBuLi$ in hexane. After stirring for 2 h, 0.45 g (1.03 mmol) of **2b**,[10] dissolved in 10 mL of THF, was added. The mixture was then warmed to room temperature and stirred for an additional 4 h. After removal of the solvent, the residue was extracted three times with 10 mL of benzene (0.14 g of solid white residue, 3.3 mmol calculated as LiCl), and the benzene was removed *in vacuo* from the red solution. The crude product (0.72 g) was dissolved in 8 mL of pentane and the clear solution cooled to −78 °C. After 2 days, 0.27 g (0.41 mmol, 39%) of **3b** was isolated as red crystals, one of which was suitable for an X-ray structure determination. Mp: >220 °C dec. IR (cm$^{-1}$, Nujol/Hostaflon): ν 1588.9 (s), 814.2 (m), 789.3 (s). $^{11}B$ NMR ($C_6D_6$): $\delta = 44.2$. $^1H$ NMR ($C_6D_6$): $\delta = 0.6$ (d, $J = 6.8$ Hz, 12 H, H5,6,11,12), 1.30 (d, $J = 6.9$ Hz, 12 H, H2,3,8,9), 1.41 (s, 2 H), 3.41 (sept, $J = 6.9$ Hz, 2 H, H4,10), 3.94 (sept, $J = 6.8$ Hz, 2 H, H1,7) 5.73 (s, 10 H), 7.10 (m, 2 H, $H_p$), 7.19 (dd, 4 H, $H_o$), 7.30 (m, 4 H, $H_m$). $^{13}C$ NMR ($C_6D_6$): $\delta = 22.3$ (C2,3,8,9), 24.8 ($CH_2$), 25.4 (C5,6,11,12), 46.2 (C4,10), 51.3 (C1,7), 108.2 ($C_{cp}$), 125.0 ($C_p$), 127.7 ($C_o$), 128.5 ($C_m$), 131.6 ($C_i$), 150.5 (C–B), 190.3 (C–Zr). Anal. Calcd for $C_{39}H_{50}B_2N_2Zr$ (659.69 g/mol): C, 71.01; H, 7.64; N, 4.25. Found: C, 71.83; H, 8.00; N, 4.42. Synthesis of 6,8-bis(dimethylamino)-3,3-bis($\eta^5$-cyclopentadienyl)-2,4-diphenyl-6,8-dibora-3-zirconabicyclo[3.3.0]octa-1,4-diene (**3a**): The dimethylamino derivative **3a** was prepared by following the same experimental protocol (precipitated from hexane after removal of benzene in 57% yield) from **2a**.[10] Mp: 159 °C dec. IR (cm$^{-1}$, Nujol/Hostaflon): ν 1587.2 (s), 795.2 (s). $^{11}B$ NMR ($C_6D_6$): $\delta = 45.5$. $^1H$ NMR ($C_6D_6$): $\delta = 1.15$ (s, 2 H), 2.03 (s, 6 H), 2.65 (s, 6 H), 5.76 (s, 10 H), 7.09 (m, 2 H, $H_p$), 7.23 (dd, 4 H, $H_o$), 7.32 (m, 4 H, $H_m$). $^{13}C$ NMR ($C_6D_6$): $\delta = 19.0$ ($CH_2$), 40.9, 108.4 ($C_{cp}$), 124.8 ($C_p$), 126.9 ($C_o$), 127.9 ($C_m$), 128.3 ($C_i$), 151.0 (C–B), 192.8 (C–Zr). Anal. Calcd for $C_{31}H_{34}B_2N_2Zr$ (547.47 g/mol): C, 68.01; H, 6.26; N, 5.12. Found: C, 65.02; H, 6.42; N, 4.73.

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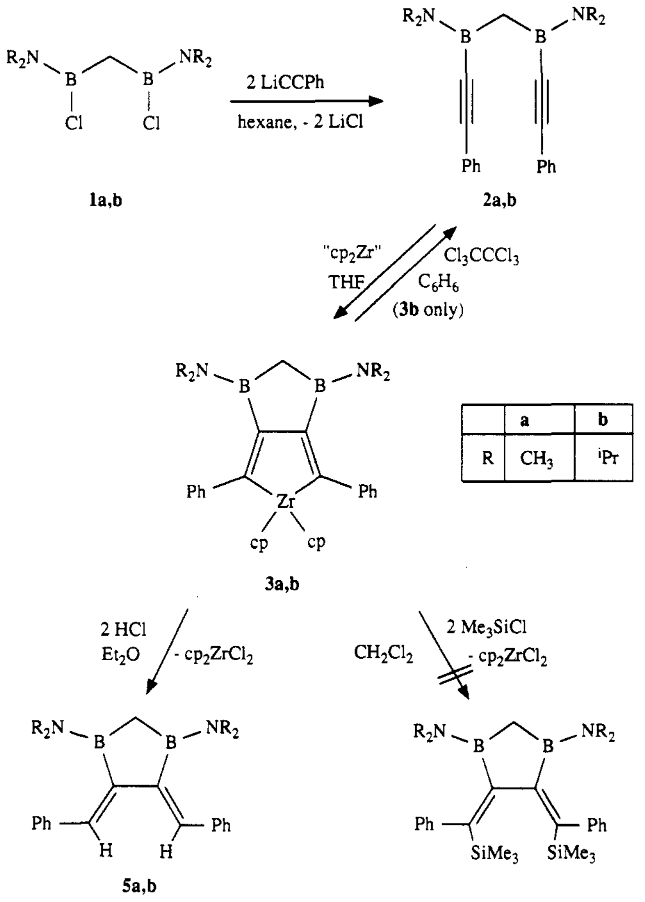
**Scheme I**



the meta protons of the phenyl rings and the methine proton of the other $^i$Pr group. This observation is in agreement with a hindered rotation at the B-N bond, but not with a "gear-mesh" mechanism of hindered rotation for the diisopropylamino group at room temperature, which has been suggested by other authors.[12]

The $^{13}$C NMR signals of the metallacyclopentadiene ring with $\delta(^{13}C)$ = 192.8 (**3a**) / 190.3 (**3b**) (*C*-Zr) and 151.0 (**3a**) / 150.5 (**3b**) (*C*-B) resemble those reported in previous work[4] and suggest a planar zirconacyclopentadiene ring system with $C_{2v}$ symmetry. To prove this assumption, we performed an X-ray structure determination of **3b**.

The X-ray structure analysis of **3b**[13] reveals a slight envelope conformation of the zirconacyclopentadiene ring (interplanar angle between the plane C14-C13-C21-C22 and the C14-Zr-C22 planes is only 10.9°) as well as an attached envelope-type diboracyclopentane ring (the B1-C-B2 plane forms a 46° folding angle with the B1-C13-C21-B2 plane). For steric reasons the two phenyl substituents are twisted by 50 and 66°, respectively, against the carbon skeleton of the zirconacyclopentadiene unit. Compared to the known crystal structure of 1,1-bis($\eta^5$-cyclopentadienyl)-2,3,4,5-tetraphenylzirconacyclopentadiene, **4**,[15] the two independent Zr-C $\sigma$-bonds in **3b** are 6.7(1.2) and 7.8(1.1) pm shorter, and since the zirconium atom is closer to the carbon skeleton, the C14-Zr-C22 angle increases by 14.2(4)° as compared to **4**.

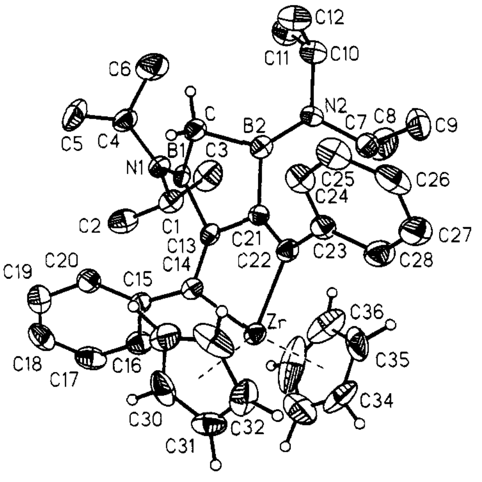


**Figure 1.** ORTEP plot of **3b**, with most H atoms omitted for clarity. Selected bond distances (Å): Zr–C14 2.198(6), Zr–C22 2.172(6), Zr–C13 2.745(6), Zr–C21 2.711(6), Zr–C($\eta^5$, average) 2.493(12), C21–C22 1.344(8), C13–C21 1.559(9), C13–C14 1.369(9), C22–C23 1.482(9), C14–C15 1.453(9), B1–C13 1.620(9), B2–C21 1.586(10), B1–C 1.599(10), B2–C 1.590(10), B1–N1 1.385(9), B2–N2 1.379(10). Selected bond angles (deg): C14–Zr–C22 91.7(2), Zr–C14–C13 97.9(4), Zr–C22–C21 98.1(4), C14–C13–C21 124.6(5), C13–C21–C22 126.3(5), C22–C21–B2 128.3(6), C14–C13–B1 130.1(6), B1–C–B2 96.0(5), C–B2–C21 104.5(6), B2–C21–C13 104.7(5), C21–C13–B1 104.3(5), C13–B1–C 105.6(5), C–B2–N2 130.5(6), C–B1–N1 127.5(6).

The two carbon atoms C13 and C21 are bound to electropositive boron atoms, and hence these bonds have more s character than suggested by their formal sp$^2$ hybridization. Therefore, it appears logical that the C13–C21 bond (with more p character) is by 5.9(1.8) pm longer than the corresponding bond in **4**. On the other hand, the fact that the C14-C13-C21 and the C22-C21-C13 angles are about 6° larger than those in **4** indicates the influence of the attached diborolane ring on the structure of the zirconacyclopentadiene. The Zr-C13 and Zr-C21 distances are about 24 pm (or 10%) longer than the averaged

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[12] (a) Herberich, G. E.; Englert, U.; Ganter, C.; Wesemann, L. *Chem. Ber.* **1992**, *125*, 23–29. (b) Berg, U.; Liljefors, T.; Roussel, C.; Sandstroem, J. *Acc. Chem. Res.* **1985**, *18*, 80.

[13] **3b** crystallizes from pentane at −78 °C in red sticks in the monoclinic space group *C*2/*c* with unit cell dimensions $a$ = 23.11(2) Å, $b$ = 8.123(1) Å, $c$ = 40.08(3) Å, $\beta$ = 97.63(6)°, and $Z$ = 8. The crystal used for X-ray analysis was 0.11 × 0.29 × 0.6 mm$^3$. Data collection was at 20 °C with Mo*K*$\alpha$ radiation on a graphite monochromator. Intensity data were collected with $\omega$-scans in the range $2\theta$ = 3–45°. Out of 5562 observed reflections 4964 were independent ($R_{int}$ = 2.77%), and 3241 were considered as observed ($F > 3\sigma(F)$. No correction for absorption was carried out ($\mu$ = 0.315 mm$^{-1}$). Full-matrix least-squares analyses ($\sum_w(F_o - F_c)^2$) described non-H atoms anisotropically and hydrogen atoms with a riding model ($d_{H-C}$ = 0.96 Å) and fixed isotropic $U$, $w^{-1} = \sigma^2(F) + 0.0002F^2$. The refinement converged with 397 parameters (8.2:1 data:parameters ratio) at a final $R$ = 0.0586 ($R_w$ = 0.0480). The largest difference peak was 0.37 e Å$^{-3}$.

[14] 1,3-Bis(diisopropylamino)-*cis*-bis(4,5-phenylmethylidene)-1,3-diborolane (**5b**): To 1.83 g (2.77 mmol) of **3b**, dissolved in 20 mL of diethyl ether, was added a solution of 5.55 mmol of HCl in 11.2 mL of diethyl ether at −40 °C. After stirring for 14 h the solvent was removed in vacuo and the residue suspended in 40 mL of hexane and filtered under dinitrogen (0.85 g, 2.9 mmol of almost white $Zrcp_2Cl_2$ ($^1$H NMR)). The pale orange filtrate was concentrated and the precipitated product **5b** (0.42 g, 0.9 mmol, 33% yield) removed from the solution. The product was recrystallized from dichloromethane to yield 0.39 g (0.84 mmol, 32%) of pure, white **5b** at −78 °C. Mp: 154–157 °C. IR (cm$^{-1}$, Nujol/Hostaflon): $\nu$ 597.9 (w). $^{11}$B NMR ($CDCl_3$): $\delta$ = 43.1. $^1$H NMR ($CDCl_3$): $\delta$ = 0.70 (d, $J$ = 7.6 Hz, 12 H), 0.94 (s, 2 H), 1.35 (d, $J$ = 6.6 Hz, 12 H), 3.32 (sept, $J$ = 7.6 Hz, 2 H), 3.62 (sept, $J$ = 6.6 Hz, 2 H), 6.57 (s, 2 H), 7.15 (m, 2 H, $H_p$), 7.26 (m, 8 H, $H_{o,m}$). $^{13}$C NMR ($CDCl_3$): $\delta$ = 13.9 ($-CH_2-$, $h_{1/2}$ = 30 Hz), 21.6 ($CH_3$), 24.8 ($CH_3$), 44.6 (N—CH), 52.0 (N—CH), 125.0 ($C_\beta$), 126.1 ($C_p$), 127.9 ($C_o$), 128.0 ($C_m$), 140.8 ($C_i$), 160 (b, B—C═). Anal. Calcd for $C_{29}H_{42}B_2N_2$ (440.14 g/mol): C, 79.11; H, 9.62; N, 6.36. Found: C, 77.20; H, 9.29; N, 6.10. 1,3-Bis(dimethylamino)-*cis*-bis(4,5-phenylmethylidene)-1,3-diborolane (**5a**): **5a** was obtained analogously to **5b** from **3a** and hydrogen chloride in diethyl ether. The recrystallized product gave satisfactory elemental analysis and showed physical data very similar to those for **5b**.

Zr–C($\eta^5$) bond to the carbon atoms of the cp rings, or even more than about 55 pm (25%) longer than the Zr–C14/C22 bonds. These findings suggest a weak $\pi$-interaction, if any, and support the conclusion from NMR data, confirming that the bonding in **3a,b** is more readily described as a metallacyclopentadiene than as a $\pi$-complex.

In order to further elucidate the role of the attached diboracyclopentane ring on the chemical properties of **3a,b**, these were reacted with 2 equiv of hydrogen chloride in diethyl ether.[14] We obtained the *cis*-bis(4,5-phenylmethylidene)-1,3-bis(dialkylamino)-1,3-diborolanes **5a,b** (alkyl = Me in **5a**, $^{i}$Pr in **5b**) in almost quantitative yield.[16]

On the other hand, there was no reaction of **3a,b** with trimethylchlorosilane in boiling dichloromethane within 24 h. Paralleling the observation made by Mohamadi and Spees,[6] iodination[17] of **3a,b** gave none of the anticipated product. Moreover, oxidation of **3b** with hexachloroethane in benzene at room temperature did not yield a cyclobutadiene derivative but, in a clean reaction, led back to the bis(alkynylboryl)methane **2b** instead.[18]

Although further studies seem mandatory until a thorough understanding of the effect of heteroatom substitution on zirconacyclopentadienes is achieved, we hope that the exciting new pentalene analogs described in this paper will prove to be powerful synthons for the preparation of new main-group element heterocycles. Such investigations are already underway in our laboratory.

**Acknowledgment.** The authors are grateful to Miss Andrea Appel for her help in part of the experiments and to Dr. Bernd Ederer for many helpful hints and his constant interest in this project.

**Supplementary Material Available:** Tables listing the details of the crystal structure of **3b** (crystal data, data collection, solution, and refinement parameters, positional and thermal parameters, bond lengths and angles) (9 pages). Ordering information is given on any current masthead page.

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(16) Although this cleavage of the zircon–carbon bond with hydrochloric acid in water has long been known,[4] Regitz et al. suggest the use of hydrogen chloride in anhydrous diethyl ether, when the use of water is undesirable.[17]

(17) Binger, P.; Wettling, T.; Schneider, R.; Zurmühlen, F.; Bergsträsser, U.; Hoffmann, J.; Maas, G.; Regitz, M. *Angew. Chem.* **1991**, *103*, 208–211; *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 207–210.

(18) Reaction of **3b** with hexachloroethane: 0.30 g (1.26 mmol) of hexachloroethane in 5 mL of benzene was added dropwise to a solution of 0.83 g (1.26 mmol) of **3b** in 5 mL of benzene. After stirring for 14 h, the benzene was removed in vacuo, and the residue was suspended in hexane and filtered under inert gas. After the white precipitate was washed twice with 5 mL of hexane (0.28 g, 0.96 mmol calculated as cp$_2$ZrCl$_2$) and the clear, colorless solution was cooled to −30 °C, 0.75 g (1.14 mmol) of **2b** crystallized in two fractions (second fraction at −78 °C). The identity of **2b** was established by $^{1}$H, $^{13}$C, and infrared spectroscopy.