

# Zirconocene Complexes of [2.2]Paracyclophanes with Formal Triple Bonds in the Bridges

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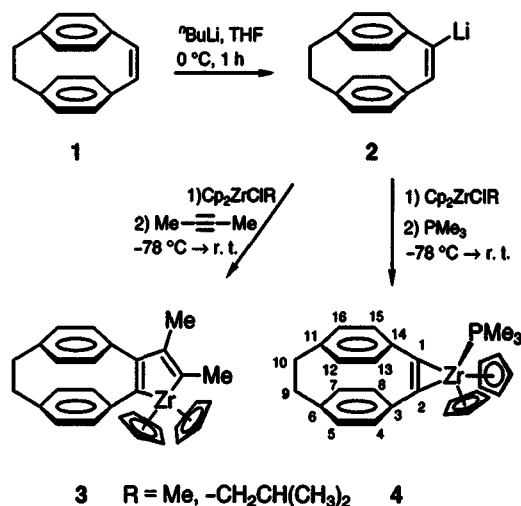
**Abstract:** Zirconocene complexes of [2.2]paracyclophanes with formal triple bonds in the bridges, corresponding to zirconacyclopropenes, were synthesized from [2.2]paracyclophan-1-ene (1) and 1,9(10)-dibromo[2.2]paracyclophan-1,9-diene (5) via their vinyl lithium derivatives and characterized by spectroscopic methods. The zirconocene-alkyne complexes 7, 9 react with bromine or iodine with loss of the bis(cyclopentadienyl)zirconium moiety to yield the expected stable halogenated products 8 and 10, respectively. Insertion of 2-butyne into the initially formed 16e complexes gave zirconacyclopentadiene complexes 3, 9.

Even extremely strained cycloalkynes and dehydroarenes can be stabilized by complexation with 4d and 5d transition metals. The resulting complexes can be fully characterized and frequently also be used as equivalents of the respective cycloalkyne or aryne in synthesis.<sup>1</sup> A highly strained [2.2]paracyclophane-1-yne has been proposed for the first time by Wong<sup>2</sup> as an intermediate in the dehydrobromination of 9,10-benzo-1-bromo[2.2]paracyclophane-1,9-diene and trapped with furan to yield a suitable precursor to 1,2:9,10-dibenzo[2.2]paracyclophane-1,9-diene. The same type of intermediate with a formal triple bond in the C<sub>2</sub> bridge of [2.2]paracyclophane derivatives has subsequently been inferred in the synthesis of various 1,2:9,10-dibenzo[2.2]paracyclophane-1,9-diene derivatives.<sup>3</sup> We here report the first transition metal complexes of a [2.2]paracyclophane with a triple bond in one or both of the C<sub>2</sub> bridges.

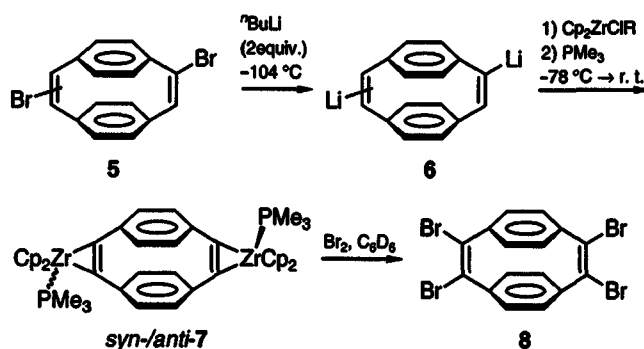
Treatment of [2.2]paracyclophane-1-ene (1)<sup>4</sup> with *n*-BuLi at 0 °C yields the monolithio derivative 2 quantitatively.<sup>5</sup> The reaction of 2 with Cp<sub>2</sub>ZrClMe or Cp<sub>2</sub>ZrClPr according to a procedure of Buchwald *et al.*<sup>6</sup> and stabilisation of the 16e intermediate with PMe<sub>3</sub> gave the alkyne complex 4 (Scheme 1) in 55% yield after workup.<sup>7</sup> Compound 4 is a colourless, air- and moisture-sensitive solid, which is readily soluble in benzene. The <sup>31</sup>P chemical shift (−2.92 ppm) is very close to that of the analogous cyclohexyne complex.<sup>6a</sup> <sup>13</sup>C NMR data indicate a coordination of the zirconium, in which it is symmetrically placed with respect to the two carbon atoms in the C<sub>2</sub> bridge of the [2.2]paracyclophane-1-yne moiety.<sup>8</sup> As reported for other zirconocene-cycloalkyne complexes<sup>6a,9</sup> the new complex 4 can be described as a metallacyclopropene.

The reaction with of the 16e complex initially formed from Cp<sub>2</sub>ZrClMe 2-butyne gave the insertion product 3, a [2.2]paracyclophane-1-ene anellated zirconacyclopentadiene, as an orange solid in 44% yield.

Dilithio[2.2]paracyclophane-1,9-diene 6, as a mixture of 1,9- and 1,10-isomers (ratio 1:1), can be obtained by lithium-bromine exchange on 1,9(10)-dibromo[2.2]paracyclophane-1,9-diene (5)<sup>10</sup> at −104 °C with two equivalents of *n*-butyllithium. Upon treatment of 6 with two equivalents of Cp<sub>2</sub>ZrClMe and excess PMe<sub>3</sub>, a mixture of the diastereomeric binuclear complexes *syn*- and *anti*-7 was obtained as a colourless solid, which is poorly soluble in all common deuterated solvents (Scheme 2). The two <sup>31</sup>P NMR signals at −2.64 and −2.73 ppm<sup>8</sup> indicate a 1:1 ratio of diastereomers. Treatment of the mixture with bromine gave the known 1,2,9,10-tetrabromo[2.2]paracyclophane-1,9-diene (8)<sup>11</sup> in high yield (80%). This confirms the structure of *syn*-/*anti*-7, as the



Scheme 1

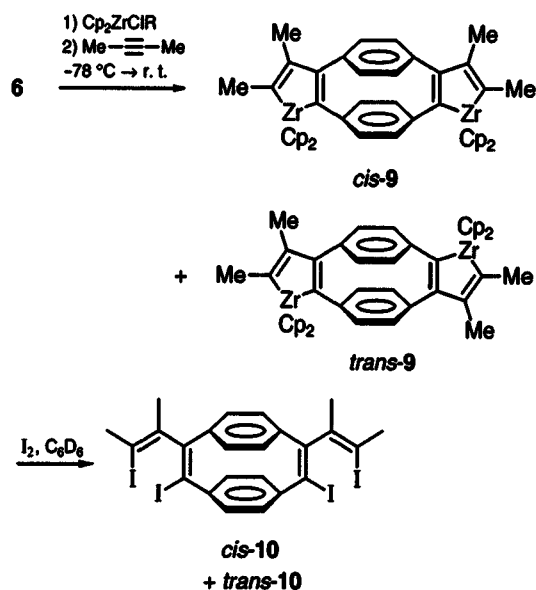


Scheme 2

tetrabromide 8 cannot be formed from any other precursor upon reaction with bromine.

Reaction of the unstabilized intermediate formed from 6 and Cp<sub>2</sub>ZrClMe by insertion into the zirconium alkyne bonds with 2-butyne gave the regioisomeric bis(zirconacyclopentadiene) anellated [2.2]paracyclophanes *cis*- and *trans*-9. Upon treatment of *cis*-/*trans*-9 with iodine,<sup>12</sup> the Cp<sub>2</sub>Zr moieties were removed to give the isomeric tetraiodides *cis*-/*trans*-10 in a 1:1 ratio (Scheme 3).

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Scheme 3

## References and Notes

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(b) A similar yield was obtained employing the improved procedure for *in situ* generation of  $\text{Cp}_2\text{ZrCl}(\text{CH}_2\text{CH}(\text{CH}_3)_2)$ : Barr, K. J.; Watson, B. T.; Buchwald, S. L. *Tetrahedron Lett.* **1991**, *32*, 5465.
- (7) The reaction mixture was evaporated to dryness, the residue dissolved in toluene, the solution filtered, the solvent removed again, the residue washed with diethyl ether and subsequently with pentane, and then dried *in vacuo*.
- (8) Spectroscopic data of relevant compounds (multiplicity of the  $^{13}\text{C}$  signals was determined by the DEPT technique with a last pulse angle of  $135^\circ$ ; (+) =  $\text{CH}_3$  or  $\text{CH}$ , (–) =  $\text{CH}_2$ ; internal standard for  $^{31}\text{P}$  NMR was  $\text{H}_3\text{PO}_4$ ): **4**: IR (KBr)  $\nu$  = 3153, 3107, 3062, 2994, 2914, 1634, 1580, 1500 (s), 1017, 791(s)  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (250 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  = 0.98 (d,  $^2J$  = 6.0 Hz, 9 H,  $\text{P}(\text{CH}_3)_3$ ), 3.07 (s, 4 H, 9(10)-H), 5.51 (d,  $^2J$  = 2.0 Hz, 10 H, cp-H), 5.90 (d,  $^3J$  = 7.9 Hz, 2 H), 6.19 (d,  $^3J$  = 8.0 Hz, 2 H), 6.61 (dd,  $^3J$  = 7.9 Hz,  $^3J$  = 8.0 Hz, 4 H);  $^{13}\text{C}$  NMR (62 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  = 16.83 (d,  $^1J$  = 19.0 Hz, +,  $\text{P}(\text{CH}_3)_3$ ), 30.01 (–, C-9(10)), 104.09 (+, cp-C), 123.52, 124.02 [+ , C-13(15) and C-4(8)], 132.18 [+ , C-5(7,12,16)], 136.23, 136.78, 157.91 and 158.95 ( $\text{C}_{\text{quat}}$ );  $^{31}\text{P}$  NMR (120 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  = –2.92. – 3;  $^1\text{H}$  NMR (250 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  = 1.76 (s, 3 H), 2.00 (s, 3 H), 2.89 (bs, 4 H), 5.72–6.00 (m, 2 H), 6.05 (s, 10 H), 6.40 (m, 6 H);  $^{13}\text{C}$  NMR (62 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  = 16.16 and 21.44 (+), 35.36 and 35.56 (–), 111.14 (+), 128.12, 130.72, 132.21 and 132.46 (+), 136.33, 137.72, 138.06, 143.09, 144.35, 152.33, 165.61 and 198.52 ( $\text{C}_{\text{quat}}$ ). – *syn/anti*-7: IR (KBr)  $\nu$  = 2901, 1634, 1566, 1503, 1441, 1134  $\text{cm}^{-1}$ ;  $^{31}\text{P}$  NMR (120 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  = –2.64 (s), –2.73 (s).
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