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Preliminary communication

A novel slipped tripledecker complex with a 3,4-diborafulvene as bridging ligand *

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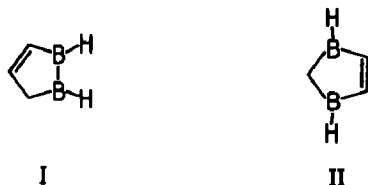
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Abstract

Reaction of the 3,4-diboratafulvene derivative $\text{Li}_2[\text{CH}_2\text{C}\{\text{CHB}(\text{NEt}_2)\}_2]$ with $[\text{RhCl}(\text{COD})]_2$ gives $\mu\text{-}[1\text{-}\eta^5\text{-}1,2,5,6\text{-}\eta^4\text{-}\{\text{CH}_2\text{C}\{\text{CHB}(\text{NEt}_2)\}_2\}][\text{Rh}(\eta\text{-COD})]_2$ (V), the first 3,4-diborafulvene complex. V possesses a doubly-opened triple-decker structure with a bridging 3,4-diborafulvene ligand.

Two unsaturated, five-membered boracarborcycles $\text{C}_3\text{B}_2\text{H}_6$ are conceivable: the 1,2-diborolene (1,2-dibora-3-cyclopentene) I and the 1,3-diborolene (1,3-dibora-4-cyclopentene) II. Derivatives of isomer II have long been known [1] and a rich chemistry of transition metal complexes relating to II has been developed [2]. In contrast, the chemistry of isomer I with adjacent boron atoms has remained unexplored until very recently.



We recently reported the first route to unsaturated, five-membered boracarborcycles with two adjacent boron atoms [3]. Two of the new species are the 3,4-di-

* Dedicated to Professor F.G.A. Stone on the occasion of his 65th birthday.

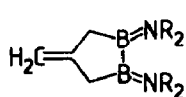
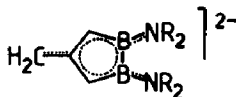
Table 1

Non-hydrogen atom coordinates for V

Atom	x	y	z	U_{eq}^a
Rh(1)	0.6255(1)	0.1894(1)	0.1619(1)	206(2)
Rh(2)	0.7776(1)	0.0074(1)	0.1160(1)	209(2)
N(1)	0.9438(4)	0.1545(2)	0.3134(4)	250(15)
N(2)	0.6547(4)	0.0531(2)	0.3503(3)	221(14)
B(1)	0.8255(6)	0.1285(3)	0.2502(5)	222(19)
B(2)	0.6944(6)	0.0838(3)	0.2684(5)	206(18)
C(1)	0.7859(5)	0.1367(3)	0.1283(4)	226(17)
C(2)	0.6726(5)	0.0962(2)	0.0790(4)	224(17)
C(3)	0.6049(5)	0.0789(3)	0.1561(4)	221(17)
C(4)	0.6536(6)	0.0614(3)	-0.0165(4)	305(19)
C(5)	1.0316(6)	0.1928(3)	0.2701(5)	364(22)
C(6)	1.1343(8)	0.1501(4)	0.2430(8)	634(36)
C(7)	0.9901(6)	0.1468(3)	0.4261(5)	329(20)
C(8)	0.9606(8)	0.2069(4)	0.4852(6)	484(26)
C(9)	0.7148(6)	0.0618(3)	0.4610(4)	301(19)
C(10)	0.8026(7)	0.0036(4)	0.5107(5)	429(24)
C(11)	0.5455(6)	0.0061(3)	0.3284(5)	281(19)
C(12)	0.4145(6)	0.0396(3)	0.3151(5)	384(22)
C(13)	0.7026(7)	0.2892(3)	0.1868(6)	417(26)
C(14)	0.6282(8)	0.2842(3)	0.0868(6)	415(26)
C(15)	0.4935(10)	0.3123(4)	0.0462(8)	676(38)
C(16)	0.3945(9)	0.2820(5)	0.0812(9)	721(37)
C(17)	0.4316(6)	0.2215(3)	0.1523(5)	346(21)
C(18)	0.5078(6)	0.2269(3)	0.2543(5)	332(20)
C(19)	0.5579(11)	0.2929(5)	0.3048(8)	741(41)
C(20)	0.6638(10)	0.3241(4)	0.2746(8)	619(37)
C(21)	0.9455(9)	-0.0245(4)	0.2386(7)	590(30)
C(22)	0.8457(9)	-0.0589(5)	0.2513(5)	590(32)
C(23)	0.8204(11)	-0.1330(5)	0.2209(10)	770(44)
C(24)	0.7421(9)	-0.1422(4)	0.1142(10)	706(43)
C(25)	0.7462(7)	-0.0858(3)	0.0411(6)	537(27)
C(26)	0.8603(9)	-0.0596(3)	0.296(5)	473(28)
C(27)	0.9962(8)	-0.0851(3)	0.0933(8)	597(35)
C(28)	1.0483(8)	-0.0509(4)	0.1954(8)	615(32)

^a Equivalent isotropic displacement factors (pm^2).

borafulvene derivative **III** and the related 3,4-diboratafulvene ion **IV**. Here, we report the results of our first attempt to synthesize transition metal complexes of **IV**.

**III****IV**

When **III** was metalated and the resulting **IV** was treated with $[\text{RhCl}(\text{COD})]_2$, a product $[\text{CH}_2\text{C}(\text{CHB}(\text{NEt}_2))_2][\text{Rh}(\text{COD})]_2$ (**V**) was obtained. An X-ray diffraction study revealed a doubly-opened triple-decker structure (Tables 1 and 2, Fig. 1.) with a bridging 3,4-diborafulvene ligand.

Table 2

Selected bond distances (pm) and bond angles ($^{\circ}$) for V

<i>Bond lengths</i>			
Rh(1)–B(1)	246.9	Rh(2)–C(1)	257.2(5)
Rh(1)–B(2)	252.9(6)	Rh(2)–C(2)	208.1(5)
Rh(1)–C(1)	217.7(6)	Rh(2)–C(3)	252.1(6)
Rh(1)–C(2)	228.9(5)	Rh(2)–C(4)	218.2(5)
Rh(1)–C(3)	220.5(5)		
C(1)–C(2)	145.7(7)	C(2)–C(3)	146.6(9)
C(2)–C(4)	141.8(8)	B(1)–B(2)	174.6(9)
B(1)–C(1)	157.8(8)	B(2)–C(3)	154.7(7)
N(1)–B(1)	141.7(7)	N(2)–B(2)	142.4(8)
<i>Bond angles</i>			
B(2)–B(1)–C(1)	101.7(4)	B(1)–B(2)–C(3)	101.8(5)
N(1)–B(1)–B(2)	137.1(5)	N(2)–B(2)–B(1)	139.3(4)
N(1)–B(1)–C(1)	121.2(5)	N(2)–B(2)–C(3)	118.9(5)
C(1)–C(2)–C(4)	124.6(6)	C(3)–C(2)–C(4)	123.3(5)
C(1)–C(2)–C(3)	109.3(4)	Rh(2)–C(2)–C(4)	74.5(3)
Rh(2)–C(2)–C(1)	91.5(3)	Rh(2)–C(2)–C(3)	88.8(3)

One of the (COD)Rh fragments is pentahapto-bonded to the C_3B_2 ring of the 3,4-diborafulvene. Important structural features are: (i) a pronounced folding of the C_3B_2 ring along the line C(1), C(3) by 19.2° ; (ii) a large slip distortion of 22.6 pm; and (iii) long Rh–B bonds of 246.9(6) and 252.9(6) pm [4]. It should be noted that the exocyclic amino groups engage in a π -interaction with the boron atoms that

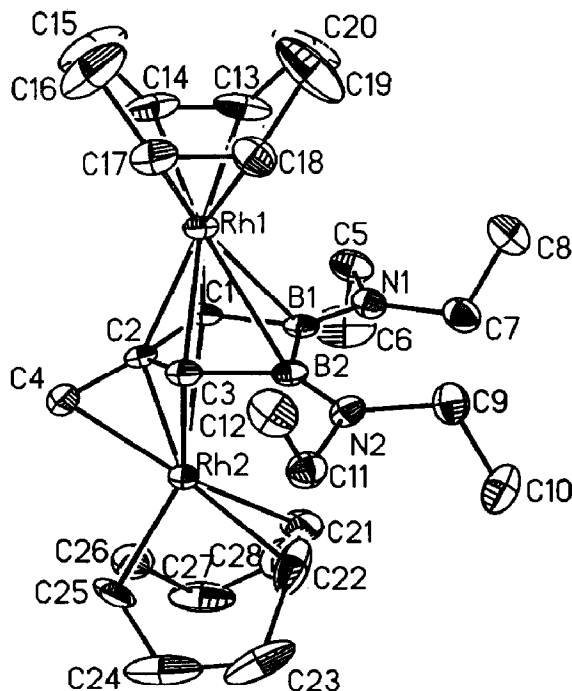


Fig. 1. Doubly-opened triple-decker structure of V.

weakens the rhodium-to-boron bonding [5]. It is also responsible for the hindered rotation around the B–N bonds which is seen in the NMR spectra.

With respect to the second (COD)Rh fragment the structure resembles that of a distorted trimethylenemethane complex [6]. C(4) is bent towards the rhodium whereas C(1) and C(3) are not. This bending suggests that the rhodium atom is also coordinated to C(1) and C(3). The distances Rh(2)–C(1) (257.2(5) pm) and Rh(2)–C(3) (252.1(6) pm) are long, even compared with Rh–C bond lengths (typically 219–239 pm) for other bifacially bonded carbon atoms [7].

The molecule of **V** is fluxional. According to the NMR spectra the two (COD)Rh fragments are equivalent at room temperature, that is they undergo a fast interchange of their bonding mode to the 3,4-diborafulvene bridge. At -60°C the ^{13}C NMR data spectra show the same mirror symmetry which is approximately present in the crystal, or, in other words, the presence of two different (COD)Rh fragments.

Finally, we note the similarity of the bonding in **V** and in true triple-decker complexes [8]. In both situations, the bridging ligands possess three π -orbitals suitable for bifacial bonding, and both situations give rise to the same 30-electron count.

Experimental

Experiments were carried out under nitrogen by Schlenk techniques. THF was distilled from sodium and hexane from Na/K alloy. Oxygen was removed by repeated distillation under nitrogen.

μ -[1-5- η^5 : 1,2,5,6- η^4 -{3,4-Bis(diethylamino)-3,4-dihydro-3,4-diborafulvene}]bis[(η -cyclooctadiene)rhodium] (**V**). LiTMP (0.78 g, 5.3 mmol) [9] was added to a solution of 0.58 g (2.6 mmol) 1,2-bis(diethylamino)-1,2-dibora-4-methylenecyclopentane [3] in 5 ml THF at -78°C . The mixture was stirred for 1 h at ambient temperature and 2.6 g (5.3 mmol) $[\text{RhCl}(\text{COD})]_2$ were added at -78°C . After 3 h stirring at room temperature, volatiles were removed in vacuo. Hexane was added and the red solution filtered through Kieselgur. Crystallization at -30°C gave pure **V** (1.5 g, 1.64 mmol; 62%) as red crystals, m.p. 125°C . Anal. Found: C, 52.32; H, 7.56. $\text{C}_{28}\text{H}_{48}\text{B}_2\text{N}_2\text{Rh}_2$ calc.: C, 52.54; H, 7.56%.

MS (70 eV): m/e (I_{rel}) 640 (70; M^+), 532 (100, $M^+ - \text{COD}$). ^1H NMR ($\delta(^1\text{H})$ (ppm), 270 MHz, int. TMS, CD_2Cl_2): 2.05, 1.75 s ($\text{H}_2\text{C}=\text{BCH}$); 3.20 and 2.99 q (3J 7 Hz, 2×2 NCH₂), 1.10 t (3J 7 Hz, 4 Me); COD: 4.5 s (br, 4 CH), 2.1–2.2 and 1.9–2.0 m (2×2 CH₂). ^{13}C NMR ($\delta(^{13}\text{C})$ (ppm) (J (Hz)), 67.88 MHz, int. TMS, CD_2Cl_2 , 213 K): 123.3 t ($^1J(^{103}\text{Rh}-^{13}\text{C})$ 6 Hz) (C(1)), 59.2 d (1J 149 Hz) (C(2)/C(5)), 41.5 t (1J 157 Hz) (C(6)); NEt₂: 46.9 t (1J 131 Hz) and 45.1 t (1J 129 Hz) (2×2 NCH₂), 17.5 q and 14.8 q (1J 125 Hz) (4 Me); COD: 92.3 dd (1J 158 Hz, $^1J(^{103}\text{Rh}-^{13}\text{C})$ 8.6 Hz) (CH), 79.2 dd (1J 149 Hz, $^1J(^{103}\text{Rh}-^{13}\text{C})$ 11.4 Hz) (CH), 77.3 dd (1J 148 Hz, $^1J(^{103}\text{Rh}-^{13}\text{C})$ 11.7 Hz) (CH), 68.3 dd (1J 153 Hz, $^1J(^{103}\text{Rh}-^{13}\text{C})$ 16 Hz) (CH), 32–29 m (4 CH₂); ($[D_8]$ toluene, 301 K): 137.5 s (C(1)), 60.7 d (br, 1J 150 Hz) (C(2)/C(5)), 43.2 t (1J 156 Hz) (C(6)); NEt₂: 47.6 and 45.9 t (1J 133 Hz) (2×2 NCH₂), 18.1 and 15.7 q (1J 125 Hz) (2×2 Me); COD: 80 d (br, 1J 160 Hz) (CH), 31.8 t (br, 1J 126 Hz) (CH₂). ^{11}B NMR ($\delta(^{11}\text{B})$, 32 MHz, CD_2Cl_2): 30 ppm, vs. ext. $\text{BF}_3 \cdot \text{OEt}_2$.

Determination of the structure of V. $\text{C}_{28}\text{H}_{48}\text{B}_2\text{N}_2\text{Rh}_2$ (**V**); M 640.1 g mol⁻¹, monoclinic, space group: $P2_1/c$ (no. 14), a 1080.0(1), b 1986.2(2), c 1340.7(1) pm, β 106.31(1) $^\circ$, V 2.7603(5) nm³, Z = 4, d_c 1.540 g/cm³, $\mu(\text{Mo-K}_\alpha)$ 1.2 mm⁻¹.

Single crystals were grown from a concentrated hexane solution of V; crystal size $0.42 \times 0.35 \times 0.27 \text{ mm}^3$. The intensity data were collected on a R3m/V automatic four-circle diffractometer (Nicolet) using Mo- K_α radiation with a graphite crystal monochromator. Intensity data for 4222 unique reflections with $3 \leq 2\theta \leq 45^\circ$ were collected at 115 K using the ω scan mode.

The structure was solved by standard heavy atom methods using the SHELXTL-PLUS program system. Extinction correction and an empirical absorption correction on the basis of Ψ -scans were applied. The least-squares full-matrix refinement (378 parameters) was carried out using 4033 reflections with $F_o > 4\sigma(F)$. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed at calculated positions ($d(\text{C-H})$ 96 pm); their thermal parameters were allowed to refine isotropically. Convergence resulted in an R value of 0.049 (R_w 0.051, with $w^{-1} = \sigma^2(F_o) + 0.00004 F_o^2$). Further details of the crystal structure investigation are available on request from the Fachinformationszentrum Energie, Physik, Mathematik GmbH, D-7514 Eggenstein-Leopoldshafen 2, by quoting the depository number CSD-320123, the names of the authors, and the journal reference.

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