Carbon Monoxide and Isonitrile Insertion into the B−B Bond of Five-Membered Cyclic Organo-1,2-diboranes[☆]

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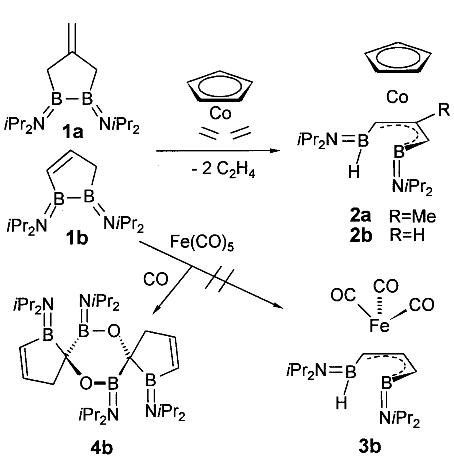
The insertion of CO into the B−B bond of 1,2-bis(diisopropylamino)-2,5-dihydro-1*H*-1,2-diborole (**1b**) and 1,2-bis(diisopropylamino)-3-methylidene-1,2-diborolane (**1c**) leads to the dimeric spiro products 1,7,9,14-tetrakis(diisopropylamino)-6,13-dioxa-1,7,9,14-tetraboradispiro[4.2.4.2]tetradeca-2,10-diene (**4b**) and 1,7,9,14-tetrakis(diisopropylamino)bismethylidene-6,13-dioxa-1,7,9,14-tetraboradispiro[4.2.4.2]tetradecane (**4c**). Insertions of CO into the B−B bonds of the cyclic organo-1,2-diborane compounds **5**, **6**, and **7** are not observed. The reaction of **1b** with *tert*-butyl isocyanide and 2,6-dimethylphenyl isocyanide in THF leads to the formation of the monomeric insertion products 1,3-bis(diisopropylamino)-2-*tert*-butylimino-1,3-diboracyclohex-4-ene (**10b**) and 1,3-bis(diisopropylamino)-2-(2′,6′-dimethylphenylimino)-1,3-diboracyclohex-4-ene (**11b**). The treatment of **1c** with the isonitriles yields 2-*tert*-butylimino-1,3-bis(diisopropylamino)-4-methylidene-1,3-diboracyclohexane (**10c**) and 1,3-bis(diisopropylamino)-2-(2′,6′-dimethylphenylimino)-4-methylidene-1,3-diboracyclohexane (**11c**). The steric requirements of the isonitrile insertion products **10b**, **c** and **11b**, **c** prevent their dimerisation and rearrangement. **11b** rearranges to 1-(diisopropylamino)-2-(diisopropylaminohydroxyboryl)-2-(2′,6′-dimethylphenylamino)-1-boracyclopent-3-ene (**12b**) upon reaction with water from sodium sulfate decahydrate. The compositions of the compounds are derived from the ^{1}H-, ^{11}B-, ^{13}C-NMR data as well as from mass-spectral and C, H, N analyses. In the cases of of **4b** and **12b** they have been proven by X-ray structure analyses.

The synthesis and structural characterization of the η^4-(4-boryl-1-borabutadiene)-η^5-cyclopentadienylcobalt complexes **2a**[1] from the 4-methylene-1,2-diborolane **1a**,[2] as well as **2b**[3] from the 1*H*-1,2-diborole **1b**[3] and bis(ethene)-cyclopentadienylcobalt, led to the expectation that related compounds should be formed with other 14 VE complex fragments. However, **1b** and either $Fe(CO)_5$ or $Fe_2(CO)_9$ did not yield the corresponding η^4-(4-boryl-1-borabutadiene)-tricarbonyliron complex **3b**. A few colorless crystals could be separated from the reaction mixture and mass-spectrometric data indicated the presence of a dimer of a reaction product of carbon monoxide and **1b**. Its constitution was elucidated by an X-ray structure analysis (see below) which showed the presence of the dimeric spiro compound **4b**.[4]

Scheme 1



Reactions of CO with organoboranes are long since known and are well documented.[5] The insertion of CO into the B−B bond of three-membered heterocycles was first observed by Paetzold et al.[6] Tri-*tert*-butylazadiboriridine [$NB_2(CMe_3)_3$] and CO yield the tricyclic compound 1,3,4,5,7,8-hexa-*tert*-butyl-4,9-dioxa-1,7-diaza-2,5,8,10-tetraboradispiro[2.2.2.2]decane. The proposed mechanism describes, in the first step, the insertion of CO into the B−B bond to give a four-membered $NB_2C{=}O$ ring, which then undergoes a [3+3] cyclodimerisation of the BC=O chain to yield the corresponding six-membered ring. Sigmatropic migrations of the amino groups from the boron to the carbon atoms result in the final product.

Analogously, isonitriles (RNC) insert into the B−B bond of $NB_2(CMe_3)_3$ to form the corresponding four-membered rings $NB_2C{=}NR$. With R = Me, Et the primary products undergo a [3+3] cyclodimerisation of the BC=N chain to result in the tricyclic compounds.[7]

In the following we report on our findings concerning CO and C=NR insertion into the B−B bond of five-membered cyclic organodiboranes.

Results and Discussion

Reactions of Cyclic Organo-1,2-diboranes with Carbon Monoxide

The compound **4b**[4] is formed in a good yield when dried CO is bubbled into a THF solution of **1b**.[3] Due to its weak

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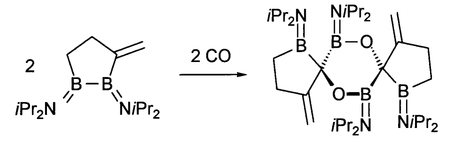
solubility **4b** precipitates as a solid which is less sensitive to air and moisture. The reaction between the 3-methylidene-1,2-diborolane **1c**[1] and CO leads to the analogous dimeric spiro product 1,7,9,14-tetrakis(diisopropylamino)bismethylidene-6,13-dioxa-1,7,9,14-tetraboradispiro[4.2.4.2]tetradecane (**4c**).[4] We assume that, besides **4c**, two other isomers have been formed due to various positions of the exocyclic double bonds. Mass-spectral data and C, H, N analyses were obtained, but no NMR data could be obtained due to its very low solubility in organic solvents. The mass spectra of the reaction product of **1c** and $Fe(CO)_5$ indicate that the η^4-(1-boryl-2-methyl-1-borabutadiene)-tricarbonyliron complex (analogous to **3b**) was present[4], however, it could not be isolated. The reaction of **1a** with $Fe(CO)_5$ also led to traces of the analogous complex.

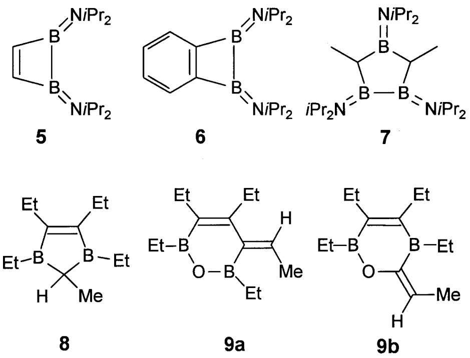
Scheme 2



1c **4c**

In addition to **1a–c**, the cyclic organo-1,2-diborane compounds 1,2-bis(diisopropylamino)-1,2-diboret (**5**)[8], 1,2-bis(diisopropylamino)-1,2-benzodiboret (**6**)[9], and 1,2,4-tris(diisopropylamino)-3,5-dimethyl-1,2,4-triboracyclopentan (**7**)[10] were treated with dried CO. None of the expected insertion products were formed and the starting materials were recovered.

Scheme 3



5 **6** **7**

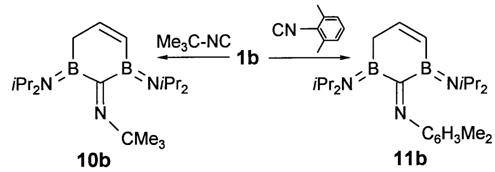
8 **9a** **9b**

It is of interest to note that we did not observe any insertion into the B–C bonds of the compounds **1a–c**. This is in contrast to the reaction of CO with the 1,3,4,5-tetraethyl-2-methyl-2,3-dihydro-1,3-diborole (**8**), which leads to product **9a** and **9b**.[11] The formation of **9b** can be explained by insertion of CO into the B–CHMe bond of **8**, and exchange of the CHMe group for the oxygen of the inserted CO. The product **9a** is formed analogously by insertion of CO into the B–CEt bond and exchange of the CHMe group for the oxygen of the inserted CO, which yields the B–O–B bridge. When **8** is treated with $Ni(CO)_4$,[11] presumably **9a** is the precursor for the formation of a nickel complex with two cyclic allyl ligands.

Reactions of Organo-1,2-diboranes with Isonitriles

The failure of CO to insert into the B–B bond of the compounds **5–7** is also observed with the isonitriles. The reaction of the 1,2-diborole **1b** with *tert*-butyl isocyanide and with 2,6-dimethylphenyl isocyanide at −30°C in THF leads to colorless, slightly soluble monomeric products, 2-*tert*-butylimino-1,3-diboracyclohex-4-ene (**10b**) and 2-(2′,6′-dimethylphenylimino)-1,3-diboracyclohex-4-ene (**11b**). As a sideproduct in the reaction with **1b** its rearrangement to the known 1,3-bis(diisopropylamino)-2,3-dihydro-1,3-diborole[12][13] was observed. MS and ^{1}H-, ^{11}B-, and ^{13}C-NMR data confirmed the composition of the products formed.

Scheme 4



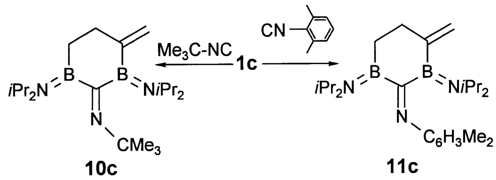
10b **11b**

In the ^{1}H-NMR spectra all four septuplets of the methine protons of the isopropyl groups of **10b** have different chemical shifts, whereas the compound **11b** shows only one multiplet and one septuplet for the four groups. This result indicates a rigid structure at room temperature.[10] There is a high double-bond character between the boron and nitrogen atoms.

Because of the quadrupole effect of the boron atoms the signals of the protons at the vicinal carbon atoms have very low intensities. The methylene protons can be detected near δ = 2.2 as a doublet, and the methine protons of the double bond in the ring are not detected. The signal for the proton in 4-position is observed at δ = 6.30, and that for the 5-position at δ = 6.85. In **11b** the signal of the proton in the 5-position cannot be observed, because the signals of the aromatic substituent appear between δ = 6.8 and 7.1.

The reaction between the 3-methylidene-1,2-diborolane **1c** and the two isonitriles leads to the 2-*tert*-butylimino-4-methylidene-1,3-diboracyclohexane **10c** and the 2-(2′,6′-dimethylphenylimino)-4-methylidene-1,3-diboracyclohexane **11c**.[10]

Scheme 5

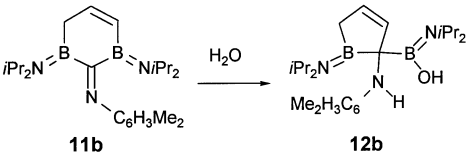


10c **11c**

The ^{11}B-NMR shifts of **10c** and **11c** are δ = 38 and 39, which are within the expected region.[14] The ^{1}H-NMR data of **11c** are comparable to those of **11b**. The products are soluble only in THF.

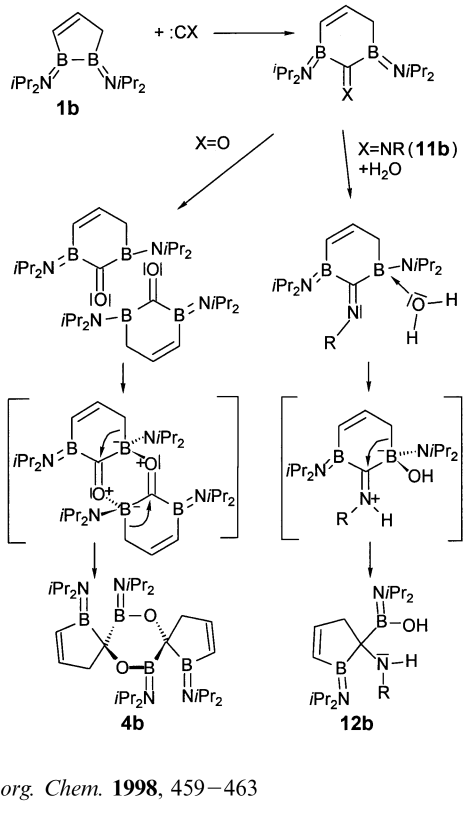
The steric demand of the five-membered rings **1b** and **1c**, and that of the alkyl substituents of the isonitriles both prevent dimerization and rearrangement of the corresponding insertion products **10b**, **c** and **11b**, **c**. To induce a rearrangement a small dipolar reagent such as water is needed. Therefore, **10b** and sodium sulfate decahydrate were heated in THF to yield the hydrolysis product **12**, which was characterized by an X-ray structure analysis. **12** can be described as one half of a spiro dimer, formed by ring contraction. The five-membered ring in **12** contains the terminal carbon atom of the isonitrile and only one boron atom.

Scheme 6



The formation of the dimeric insertion and rearrangement products **4a**, **b**, the insertion compounds **10b**, **c** and **11b**, **c** and the product of hydrolysis **12**, give evidence for the reaction path of insertion and rearrangement to the dimeric molecules. As proposed, the first step is an insertion of carbon monoxide or isonitrile into the B−B bond of the boron heterocycles.[6] The formed products are stable, if the steric requirements of the isonitriles or the heterocycles are suitable as in the isonitrile insertion products **10b**, **c** and **11b**, **c**. Rearrangement under ring contraction is the following step. This is supported by using water as a dipolar reagent to induce rearrangement with formation of **12**. In the case of CO insertion the dimeric spiro compounds **4b**, **c** are formed. The proposed reaction paths are in agreement with the mechanistic conclusions of Paetzold et al.[6][7]

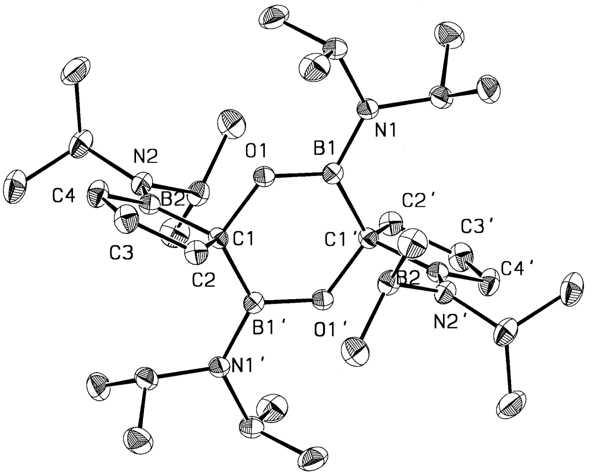
Scheme 7



Crystal Structures of 4b and 12b

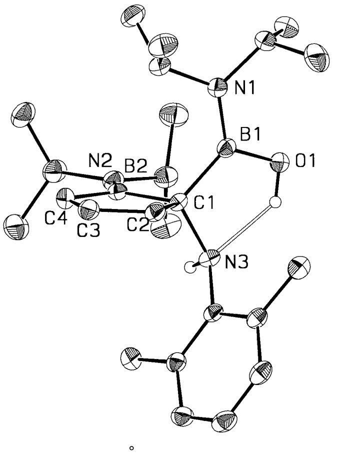
The centrosymmetric molecule in **4b** is built up by the central planar 6-membered ring (max. deviation ±0.01 Å) and, almost perpendicular (88.5°) to it, by the outer BC$_4$ rings, which are slightly puckered (±0.05 Å). The B−N units are planar indicating π interaction. The lengths of the B−C and B−N distances differ, which can be rationalized in terms of the other atoms connected to the boron atoms. The B−N distance at B2, bonded to C1 and C4, is slightly shorter than that at B1, which is bonded to O1 and C1′. The B−C distance involving an sp^2 carbon atom (B2−C4) is significantly shorter than those with sp^3 carbon atoms. In **12b** the same 5-membered ring is present, but instead of the 6-membered ring two independent groups are attached to C1, one of which [B(NiPr$_2$)O] is similar to that part of

Figure 1. Molecular structure of **4b**[a]



[a] Selected bond lengths [Å] and angles [°]: C1−B1′ 1.592(2), C1−O1 1.481(2), C1−C2 1.557(2), C1−B2 1.624(2),O1−B1 1.368(2), B1−N1 1.422(2), B2−N2 1.397(2), B2−C2 1.569(2); C2−C1−B2 103.1(1), B1′−C1−O1 112.5(1), C1−B2−C4 105.1(2), C1−B1′−O1′ 121.2(1), C1−O1−B1 126.3(1).

Figure 2. Molecular structure of **12b**[a]



[a] Selected bond lengths [Å] and angles [°]: C1−B1 1.617(2) C1−N3 1.548(2), C1−C2 1.556(2), C1−B2 1.6 29(2), O1−B1 1.376(2), B1−N1 1.416(2), B2−N2 1.402(2), B2−C2 1.562(2); C2−B1−B2 102.4(1), B1−C1−N3 106.0(1), C1−B2−C4 105.7(1), C1−B1−O1 115.9(1).

the ring in **4b**, while the other $[HN(C_6H_3Me_2)]$ substitutes for the oxygen in **4b**. The distances exhibit the same range of values as found in **4b** and the angles are almost identical, apart from those around C1. The 5-membered ring is planar, in contrast to **4b** where the steric repulsion of the diisopropylamino group at B1 pushes the 5-membered ring towards O1 and causes the distortion of the ring which adopts a slight envelope form. In **12b** this is not possible, as the dimethylphenyl group at N3 does not allow a tipping of the ring, which remains planar and lies symmetrically between the two groups. The angles at C1 in **4b** also show the effect of the distortion. A rotation around the bond C1−N3 would suspend the steric repulsion of the dimethylphenyl group, but the hydrogen atom at O1 forms an intramolecular hydrogen bond with N3, hindering the rotation around C1−N3.

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Experimental Section

All reactions and manipulations were performed in dry glassware under nitrogen by using standard Schlenk techniques. Solvents were distilled from appropriate drying agents under nitrogen before use. The commercial carbon monoxide was bubbled through KOH for drying. − $Et_2O \cdot BF_3$ was used as the external standard for ^{11}B NMR. Internal standards for ^1H and ^{13}C were the signals of the deuterium-labeled solvents. NMR: $CDCl_3$ and C_6D_6 solutions, Jeol-FX-90 and Bruker AC 200. − MS: Varian MAT CH7 and Finnigan Mat 8230. − The following starting materials were prepared by previously described methods: 1,2-bis(diisopropylamino)-2,5-dihydro-1*H*-1,2-diborole (**1b**)[3], 1,2-bis(diisopropylamino)-3-methylidene-1,2-diborolane (**1c**)[3], 1,2-bis(diisopropylamino)-1,2-benzodiboret (**6**)[9], 1,2,4-tris(diisopropylamino)-3,5-dimethyl-1,2,4-triboracyclopentane (**7**).[10]

1,7,9,14-Tetrakis(diisopropylamino)-6,13-dioxa-1,7,9,14-tetraboradispiro[4.2.4.2]tetradeca-2,10-diene (**4b**): CO was bubbled through a solution of 950 mg (3.6 mmol) of **1b** in 40 ml of THF at room temp. for 1 h. After 15 min, a colorless solid was formed. Filtration of the mixture and washing of the residue with THF and hexane yielded 520 mg (0.9 mmol, 50%) of **4b**, m.p. 282°C. The remaining **1b** in the filtrate can be used for further reactions. − ^1H NMR ($CDCl_3$, 200 MHz): δ = 0.86, 0.88, 0.89, 1.12, 1.15, 1.27 (m, 48 H), 2.75, 2.94, 3.25, 3.75 (sept, 8 H), 7.05 (d, 2 H, $^3J_{H,H}$ = 7.95 Hz), 6.19 (d, 2 H, $^3J_{H,H}$ = 7.95 Hz), 2.33 (d, 2 H, $^3J_{H,H}$ = 19.0 Hz), 2.70 (d, 2 H, $^3J_{H,H}$ = 19.5 Hz). − ^{11}B NMR ($CDCl_3$, 29 MHz): δ = 44 (C_2BN), 32 (CB(N)O). − ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 23.0, 23.3, 23.6, 24.9, 25.5, 26.0, 26.4 ($CHCH_3$), 44.6, 45.3, 47.6, 49.3 (NCH), 32.5 (CCH_2C), 159.3 (CCHC), (CB not detected). − MS (EI), *m*/*z* (%): 580 (100) $[M^+]$, 453 (85) $[M^+ - BON(CH(CH_3)_2)_2]$, 289 (45) $[M^+/2 - H]$, 43 (74) $[CH(CH_3)_2]$. − $C_{32}H_{64}O_2B_4N_4$ (580.1) calcd. C 66.25, H 11.12, N 9.66; found C 65.70, H 11.12, N 9.65.

1,7,9,14-Tetrakis(diisopropylamino)bismethylidene-6,13-dioxa-1,7,9,14-tetraboradispiro [4.2.4.2]tetradecane (**4c**): 700 mg (2.54 mmol) of **1c** were treated with CO as in the previous experiment. The workup furnished 440 mg (0.72 mmol, 44%) of the colorless solid **4c**, m.p. 289°C (decomp.). The product was almost insoluble in all organic solvents. − MS (EI), *m*/*z* (%): 608 (45) $[M^+]$, 303 (27) $[M^+/2 - H]$, 481 (36) $[M+ - BON(CH(CH_3)_2)_2]$, 43 (73) $[CH(CH_3)_2]$, 28 (100) [CO; C_2H_4]. − $C_{34}H_{68}O_2B_4N_4$ (608.2) calcd. C 67.15, H 11.27, N 9.21; found C 66.80, H 11.23, N 9.18.

2-tert-Butylimino-1,3-bis(diisopropylamino)-1,3-diboracyclohex-4-ene (**10b**): 415 mg (5 mmol) of *tert*-butyl isocyanide, dissolved in 20 ml of THF, was added to a solution of 1.30 g (5 mmol) of **1b** in 30 ml of THF at −30°C. After 15 h at room temp., the solvent was removed under vacuum. Distillation yielded 600 mg (2.3 mmol, 46%) of colorless **10b**, b.p. 63°C/5 · 10^{-2} Torr. − ^1H NMR (C_6D_6, 200 MHz): δ = 0.9−1.4 [br., 24 H, $CH(CH_3)_2$], 1.43 [s, 9 H, $C(CH_3)_3$], 2.21 (d, 2 H, BCH_2), 2.95 (m, 1 H, NCH), 3.18 (m, 1 H, NCH), 3.53 (m, 1 H, NCH), 4.81 (m, 1 H, NCH), 6.25 (d, br., 1 H, BCH), 6.85 (m, br., 1 H, CH_2CHCH). − ^{11}B NMR (C_6D_6, 64 MHz): δ = 40 (sh), 45.

1,3-Bis(diisopropylamino)-2-(2′,6′-dimethylphenylimino)-1,3-diboracyclohex-4-ene (**11b**): A preparation analogous to **10b,** using 660 mg (5 mmol) of 2,6-dimethylphenyl isocyanide and 1.3 g (5 mmol) of **1b,** resulted in 900 mg (3.5 mmol, 69%) of colorless **11b**, b.p. 80°C/5 · 10^{-2} Torr. − ^1H NMR (C_6D_6, 200 MHz): δ = 0.8−1.4 [m, 24 H, $CH(CH_3)_2$], 2.11 (s, 6 H, H_3CAr), 2.21 (d, 2 H, $CHCHCH_2$), 3.15 [m, 3 H, $CH(CH_3)_2$], 4.5 [sept, 1 H, $CH(CH_3)_2$], 6.25 (d, 1 H, BCHCH), 6.9 (m, 1 H, $CHCHCH_2$), 6.95 (m, 3 H, C_6H_3). − ^{11}B NMR (C_6D_6, 64 MHz): δ = 40. − MS (EI), *m*/*z* (%): 394 (36) $[M^+ + 1]$, 378 $[M^+ - CH_3]$, 43 (100) $[CH(CH_3)_2]$.

2-tert-Butylimino-1,3-bis(diisopropylamino)-4-methylidene-1,3-diboracyclohexane (**10c**): 1.4 g (5 mmol) of **1c** was treated with 415 mg (5 mmol) of *tert*-butyl isocyanide under the same reaction conditions as in the previous experiments to yield 300 mg (0.8 mmol, 16%) of **10c**, b.p. 75°C/5 · 10^{-2} Torr. − ^{11}B NMR (C_6D_6, 64 MHz)): δ = 39. − MS (EI), *m*/*z* (%): 360 (87) $[M^+ + 1]$, 57 (100) $[C_4H_9]$, 43 (89) $[C_3H_7]$.

1,3-Bis(diisopropylamino)-2-(2′,6′-dimethylphenylimino)-4-methylidene-1,3-diboracyclohexane (**11c**): The preparation analogous to **10b** using 1.4 g (5 mmol) of **1c** and 660 mg (5 mmol) of 2,6-dimethylphenyl isocyanide yielded 800 mg (1.8 mmol, 36%) of **11c**, b.p. 105°C/5 · 10^{-2} Torr. − ^1H NMR (C_6D_6, 200 MHz): δ = 0.93 [m, 6 H, $CH(CH_3)_2$], 1.2 (m, 2 H, CH_2CH_2C), 1.45 [m, 18 H, $CH(CH_3)_2$], 2.16 (s, 6 H, H_3CAr), 2.75(m, 2 H, BCH_2CH_2), 3.3 [m, 3 H, $CH(CH_3)_2$], 3.95 [m, 1 H, $CH(CH_3)_2$], 5.2 (m, 1 H, $C{=}CH_2$), 7.00 (m, 1 H, $C{=}CH_2$), 7.06 (m, 3 H, C_6H_3). − ^{11}B NMR (C_6D_6, 64 MHz): δ = 38.

1-(Diisopropylamino)-2-(diisopropylaminohydroxyboryl)-2-(2′,6′-dimethylphenylamino)-1-boracyclopent-3-ene (**12**): 390 mg (1 mmol) of **11c** and 33 mg (0.1 mmol) of $Na_2SO_4 \cdot\cdot 10\ H_2O$, dissolved in 50 ml of THF, were refluxed for 2 h. The hot solution was filtered through a G3 sintered-glass funnel. Crystallisation from a THF solution at 5°C gave 220 mg (0.5 mmol, 50%) of **12**, m.p. 60°C. − ^{11}B NMR (C_6D_6, 64 MHz): δ = 38.

Crystal-Structure Determinations of **4b** *and* **12b**: Crystal data and details of the structure determinations are listed in Table 1. Unique sets of intensity data were collected at −70°C with a four-circle diffractometer (Mo-K_α radiation λ = 0.7107 Å, graphite monochromator, ω scan). An empirical absorption correction (ψ scans) was applied. The structures were solved by direct methods [SHELXS86][15] and refined by least-squares methods based on F^2 with all measured reflections [SHELXL97].[16] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in calculated positions (CH in **4b**), or as part of the rigid group (CH_3 in **4b** and **12b**). All other hydrogen atoms were located in difference Fourier maps and refined.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cam-

Table 1. Crystal data and structure refinement for **4b** and **12b**

	4b	**12b**
Empirical formula	$C_{32}H_{64}B_4NO_2$	$C_{24}H_{43}B_2N_3O$
Formula weight	580.11	411.23
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$
Unit-cell dimensions		
a [Å]	11.027(6)	8.147(5)
b [Å]	10.288(5)	18.337(13)
c [Å]	16.804(8)	17.479(11)
β [°]	108.27(2)	100.80(5)
Volume [Å^3]	1810.2(16)	2565(3)
Z	2	4
Calcd. density [g/cm^3]	1.064	1.065
Absorp. coeff. [mm^{-1}]	0.064	0.064
F(000)	640	904
Crystal size [mm]	0.5 × 0.5 × 0.3	0.7 × 0.6 × 0.6
θ range	1.9−25.0	1.6 - 27.0
Index ranges	−13/12, 0/12, 0/19	−10/10, 0/23, 0/22
No. of reflections		
unique	3180	5600
observed [$I > 2\sigma(I)$]	2355	4232
Transmission	0.94−0.99	0.95−0.99
Parameters	217	337
Goodness-of-fit on F^2	1.006	1.006
Final *R* indices		
*R*1 [$I > 2\sigma(I)$]	0.041	0.042
*wR*2 (all data)	0.103	0.108
Largest diff. peak/hole [e Å^{-3}]	0.23/−0.14	0.27/−0.14

bridge Crystallographic Data Centre as supplementary publication no. CCDC-100715. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: (internat.) + 44(1223)336-003; e-mail: deposit@ccdc.cam.ac.uk].

☆ Dedicated to Professor *Hartmut Bärnighausen* on the occasion of his 65th birthday.

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