Synthesis of Tetraborylethenes and 1,1,1′,1′-Tetra- and Hexaborylethanes; Electronic Interactions in Tetraborylethenes and 1,1,1′,1′-Tetraborylethanes, and HF-SCF Calculations

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Dedicated to Prof. Wolf-Peter Fehlhammer on the occasion of his 60th birthday

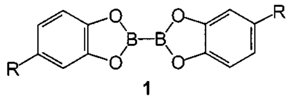
Keywords: Boranes / Homogeneous catalysis / Ab initio calculations / Donor-acceptor systems / X-ray analysis

The catechol-substituted diboranes(4) **1** react with the catechol-substituted diborylacetylenes **2**, in the presence of $[Pt(PPh_3)_2(C_2H_4)]$ or $[Pt(PPh_3)_4]$, to give tetra- and hexaborylethane derivatives. When $[Pt(cod)_2]$ is used as catalyst, the tetraborylethene **5a** is formed exclusively. Catalytic hydrogenation of **5a** affords the 1,1,1′,1′-tetraborylethane **4a**, which has been studied by an X-ray structure analysis. Natural Bond Orbital (NBO) analyses for the RHF/3–21G optimized geometries of **4a** and **5a** reveal intramolecular stabilization of the boron p_z orbital. This covers B–O, B–B, and agostic interactions. The photoelectron spectrum of **5a** is reported

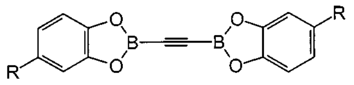
Introduction

The platinum-catalyzed diboration reaction of acetylenes was reported by Suzuki and Miyaura in 1993.[1] Mechanistic studies[2–4] revealed that, in the first step, an oxidative addition of diborane(4) to the platinum occurs followed by the insertion of a π-bonded acetylene into the Pt−B σ bond. Subsequent reductive elimination leads to the 1,2-diborylethene derivatives. Catechol-substituted diboranes(4), which are air-stable and easy to handle, have also been used. The highly reactive tetrachlorodiborane(4) (B_2Cl_4) readily adds, without a catalyst, to acetylene or acetylene derivatives to give (*Z*)-1,2-bis(dichloroboryl)ethenes.[5] Further reaction of $(CH)_2(BCl_2)_2$ with B_2Cl_4 affords tetrakis(dichloroboryl)ethane in excellent yield.[6] Recently a tetraborylethane was proposed as an intermediate in the hydroboration of bis(diethylboryl)acetylene, which rearranges to give carborane clusters.[7] Diboration of ethenes to 1,2-diborylethanes can be achieved by using bis(1,5-cyclooctadiene)platinum[8] $[Pt(cod)_2]$, tris(norbornene)platinum[8] $[Pt(nbe)_3]$ or bis(dibenzylideneacetone)platinum[9] $[Pt(dba)_2]$.

Tetraborylethenes are useful building blocks for the synthesis of new heterocycles, carboranes and for functionalized ethenes. The first example was synthesized in low yields by gas-phase reaction of carbon with B_2F_4.[10] Here we wish to report a detailed investigation into the platinum-catalyzed reactions of catechol-substituted diboranes **1** with the corresponding diborylacetylenes **2**, whereby access to air-stable tetraborylethenes, and tetraboryl- and hexaborylethanes is achieved.

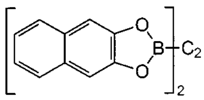


1

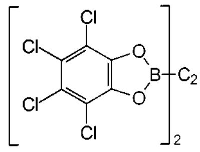


2

1, 2	R
a	H
b	Me
c	*t*Bu



2d



2e

Results and Discussion

Hexaborylethanes 3

In refluxing toluene, an excess of the diborylacetylene **2a** reacts with the diborane(4) **1a** in the presence of (ethene)-bis(triphenylphosphane)platinum catalyst, and **3a** is isolated in 71% yield.[11] This compound is insoluble in nonprotic solvents but slightly soluble in methanol with slow decomposition. The molecule ion of **3a** can be detected by mass spectrometry (EI, CI and FD). In the ^{11}B NMR spectrum (CD_3OD) a broad signal at $\delta = 34$ for **3a** and a sharp one at $\delta = 19$ for the methanolysis product $C_6H_4O_2BOCD_3$ appear. The boron-bound carbon atom is found as a broad signal at $\delta = 23$ in the ^{13}C NMR spectrum ($T = 203$ K).

Other hexaborylethane derivatives are obtained from the substituted diborylacetylene **2d**[12] and the diborane(4) **1a**. Due to steric hindrance in the starting compounds, the

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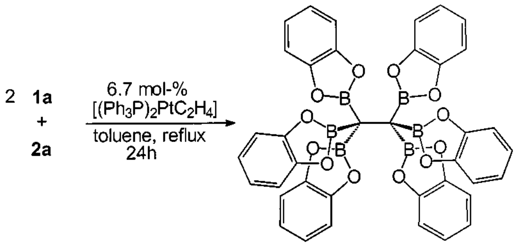
yields of the hexaborylethane derivatives $\mathbf{3a_nd_{6-n}}$ (n = 2−5) are low. During the formation of these compounds an unexpected exchange of the boryl substituents takes place, as indicated by mass spectrometric studies of the products. As shown in Scheme 2, the reaction of **2d** with **1a** in the presence of $[Pt(PPh_3)_2(C_2H_4)]$ leads to a mixture of the derivatives $\mathbf{3a_nd_{6-n}}$ (n = 2−5), in which between five and two boryl substituents of **1a** and between one and four substituents of **2d** are incorporated. It is unknown whether the exchange occurs before or after the formation of the hexaborylethanes.



3a

Scheme 1

These results clearly demonstrate that in refluxing toluene the platinum compounds $[Pt(PPh_3)_2(C_2H_4)]$ or $[Pt(PPh_3)_4]$ catalyze the double diboronation of the diborylacetylene **2a** with the diborane(4) **1a** to give the hexaborylethane **3a**.[11][13] Under these conditions the reaction does not stop at the expected tetraborylethene **5a**,[14] but leads to **3a**. Such a double diboronation of an alkyne in the presence of platinum phosphane catalysts has not previously been described and its formation had been disclaimed on the basis of theoretical calculations.[15] Our findings of a high reactivity of the diborylacetylene **2a** may be due to its flat shape[16] and to the easy formation of catecholboryl platinum compounds[3] relative to that of other derivatives.

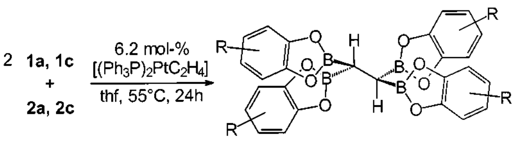
$$2\ \mathbf{1a} + \mathbf{2d} \xrightarrow[\text{toluene, reflux, 24h}]{\text{6.2 mol-\%}\ [(Ph_3P)_2PtC_2H_4]} \mathbf{3a_nd_{6-n}}\ (n = 2\text{-}5)$$

Scheme 2

Tetraborylethanes 4

Surprisingly, the formation of tetraborylethanes[17][18] occurs by catalysis with $[Pt(PPh_3)_2(C_2H_4)]$ or $[Pt(PPh_3)_4]$ under mild conditions (55°C). A 1:1 mixture of **1a** and **2a** reacts in the presence of these platinum complexes to give 1,1,1′,1′-tetra(benzo-1,3-dioxa-2-borol-2-yl)ethane (**4a**) in low yield. The reaction proceeds in tetrahydrofuran and in toluene. Purification of **4a** is achieved by sublimation under high vacuum. Under the same reaction conditions **1c** and **2c** form the tetraborylethane **4c** in very low yield.

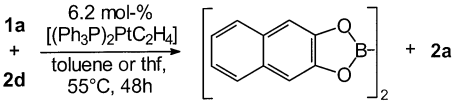
The molecular formula of **4a,c** follows from the molecular ions of **4a** and **4c** found in the EI mass spectrum and from the NMR spectroscopic data. The ^{11}B NMR spectrum (CD_3OD) shows a broad signal at δ = 32.5 for **4a,c** and a sharp one at δ = 19 for the methanolysis product. The signal in the ^{13}C NMR spectrum for the boron-bound carbon atoms of **4a** is observed at δ = 10. In the ^{1}H NMR spectrum, the two hydrogen atoms of the ethane unit appear as a broad singlet at δ = −0.1, which is in the same range for similar compounds.[19]



4a,c

Scheme 3

Attempts have been made to elucidate the origin of the hydrogen atoms in the ethane derivatives **4**. There is no incorporation of deuterium when the reaction is carried out in dry $[D_8]$thf. As the formation of a tetraborylethane also takes place in dry CCl_4 the hydrogen atoms must originate from other sources. Compound **1a** also reacts with the octachloro derivative **2e** to give the tetraborylethane derivative $\mathbf{4a_2e_2}$, which indicates that the hydrogen atoms cannot come from the diborylacetylene **2e**. We assume that a transfer of hydrogen atoms from the aryl substituents of the platinum phosphane catalysts occurs by an *ortho*-metalation reaction. The formation of tetraborylethanes most likely occurs by the intermediate formation[14,18,20,21] of 1,3-benzodioxa-2-borole followed by double hydroboration of the diborylacetylene.



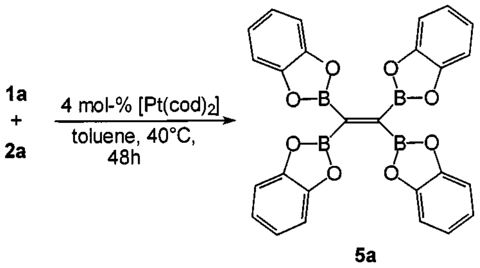
1d

Scheme 4

A different reaction takes place when **1a** and **2d** react in the presence or absence of $[Pt(PPh_3)_2(C_2H_4)]$ at 55°C in tetrahydrofuran, in toluene or in a mixture of both solvents. The expected bis(naphthalene-1,3-dioxa-2-borol-2-yl)-bis(benzo-1,3-dioxa-2-borol-2-yl)ethane does not form but, instead, the new compound 1,1:2,2-bis(2,3-naphthalenedioxy)diborane(4) (**1d**) is formed by an exchange of the boryl groups. The colorless air-stable solid **1d** is obtained in 74% yield. Its mass and NMR spectra prove the formation of the new diborane(4) derivative **1d**, which could not be obtained from the reaction between $B_2(NMe_2)_4$ and naphthalene-1,2-diol.[22] In the ^{1}H NMR spectrum **1d** shows a multiplet for the naphthol substituents and in the ^{13}C NMR spectrum, five signals for the naphthol carbon atoms. The ^{11}B NMR spectrum of **1d** in CD_3OD exhibits a signal at δ = 31.6 and a sharp one at δ = 19 for the methanolysis product of **1d**.

Tetraborylethene 5a

As outlined above, the attempt to synthesize tetraborylethene derivatives leads to the formation of tetraborylethane compounds **4** when triphenylphosphane-platinum catalysts are used. The previously elusive tetraborylethene **5a** is obtained, however, from **1a** and **2a** with the base-free platinum catalyst [Pt(cod)$_2$] under mild conditions in toluene. Compound **5a** is formed in 70% yield as a colorless solid which sublimes at 160°C under high vacuum.



Scheme 5

The molecule ion of **5a** is detected in the EI and CI mass spectra whereas the M$^+$ ion for **4a** is not observed. The boron-bound carbon atoms of the double bond are found as a broad singlet at $\delta = 165$ in the low-temperature ^{13}C NMR spectrum (T = 203 K). The ^{11}B NMR spectrum (CD$_3$OD) shows a broad signal at $\delta = 30$ for **5a** and a sharp one at $\delta = 19$ for the methanolysis product of **5a**. The Raman spectrum of **5a** exhibits a band at 1549 cm^{-1} for the stretching vibration of the double bond. The IR spectrum of **5a** and Raman spectrum of the reference substance **1a** do not contain this band.

At temperatures above 40°C the hexaboryl derivative **3a** forms in toluene, because **1a** adds across the double bond of **5a**. By catalytic hydrogenation of **5a** (palladium/active carbon, 5 bar pressure) **4a** is formed in 35% yield.

Crystal Structure and Geometrical Parameters for 4a

To elucidate the structure of **4a**, an X-ray diffraction study was carried out (crystal data and structure refinement for **4a** are listed in Table 6). A single crystal of **4a**(thf)$_2$ was grown from a tetrahydrofuran solution at 4°C. Table 1 shows some of the structural parameters of **4a** as obtained from the X-ray diffraction structure analysis and the HF/3−21G geometry optimization. The crystal structure determination (Figure 1) shows a staggered conformation for the substituents at the central C−C single bond. The large substituents and the hydrogen atoms adopt the *anti* position. This result is in agreement with ab initio calculations (see Table 1). In the crystal structure, two tetrahydrofuran molecules are coordinated to the boron atoms. The C1−C1′ distance is elongated (1.585 Å, calcd. 1.575 Å), and comparable with that of other characterized tetraborylethane derivatives.[6]

The angles around the carbon atoms of the ethane unit are nearly tetrahedral, the B1−C1−B2 angle being larger (113.30°, calcd. 113.80°) than the H1−C1−B1 angle (107.78°, calcd. 107.15°) and the H1−C1−B2 angle (109.65°, calcd. 107.27°) due to steric reasons. The distances O5−B1 (2.728 Å) and O5−B2 (2.673 Å) confirm a bonding interaction between the tetrahydrofuran molecules and the boron atoms.

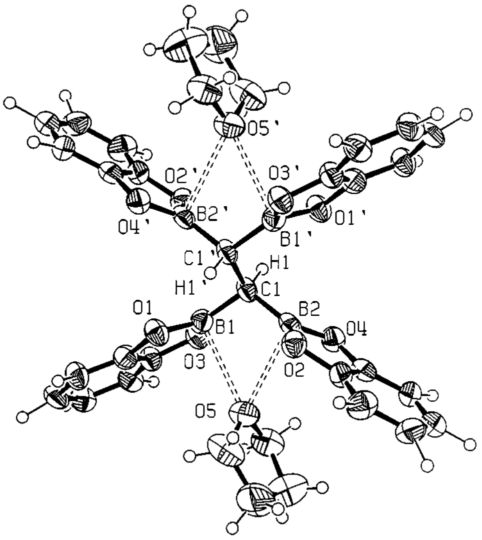


Figure 1. Molecule structure of **4a** in the crystal; selected bond lengths [Å] and angles [°]: C1−C1′ 1.5853(56), C1−B1 1.5511(47), B1−O1 1.3954(38), B2−O5 2.6738(41), B1−O5 2.7283(43), C1−H1 0.9903(287); B1−O5−B2 57.5(15), B1−C1−B2 113.3(16), H1−C1−B1 107.78(1.65), H1−C1−B2 109.65(1.61)

Table 1. Structural parameters for **4a**(thf)$_2$

4a(thf)$_2$	C1−C1′	O5−B1	O5−B2	B1C1B2	H1C1B1	H1C1B2
(exptl.)	1.585	2.728	2.673	113.30	107.78	109.65
(calcd.)	1.575	2.728[a]	2.673[a]	113.80	107.15	107.27

[a] These values remain fixed during the optimization, calcd. = RHF/3−21G//RHF/3−21G-calculations, bond lengths are in Angstrom, angles are in degrees. For the atomic numbering see Figure 1.

Computational Details for 4a and 5a

The geometries of **4a** and **5a** were fully optimized with GAUSSIAN94[23] at the Hartree−Fock level of theory using the split-valence 3−21G basis set. Compound **4a** was optimized in the point group symmetries C$_i$ and C$_{2h}$, and **5a** in C$_{2v}$, C$_{2h}$, D$_2$ and D$_{2h}$ symmetries. HF/3−21G frequency calculations were performed to verify that the structures are minima on the potential energy hypersurface, i.e. the eigenvectors of the Hessian matrix were all positive. The electronic structures of **4a** and **5a** were analyzed by means of a Natural Bond Orbital (NBO) analysis.[24]

Calculated Geometrical Parameters for 5a

Since there are no structural data available for **5a**, geometry optimizations were computed in several point groups. The global minimum on the HF/3−21G potential energy surface of **5a** belongs to the point group C$_{2h}$ (see Figure 2, conformer **A**). In this structure two diametrically opposed catechol rings are twisted by 90° out of the molecular plane while the remaining two are located in the molecular plane containing the four boron atoms. Conformation **A** favors an additional interaction between the lone pairs of the oxygen atoms and the boron centers lying opposite them, as shown in Figure 3.

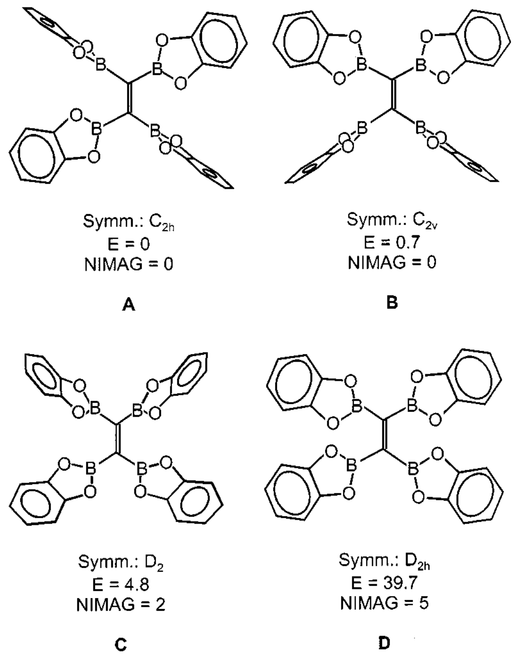


Figure 2. Calculated conformers of **5a**. E: relative energies [kcal/mol] corrected with zero-point energies and thermal enthalpies. NIMAG: number of imaginary frequencies

A conformation which is closely related to that just described belongs to point group C_{2v} (see Figure 2, conformer **B**). It is a local minimum, which is 0.7 kcal/mol less favored than **A**. In **B**, two geminal catechol rings are twisted by 90° to provide a donor-acceptor interaction between two vicinal catechol rings. The other two conformations shown in Figure 2 belong to point groups D_2 (**C**) and D_{2h} (**D**). Both represent higher order saddle points. In conformation **C** all rings are twisted propeller-like 42° out of the molecular plane. This conformation no longer allows donor-acceptor interactions as in the previously discussed conformations. In the case of conformation **D** all four catechol rings are coplanar to the ethylene fragment. This arrangement causes severe steric repulsion between the lone pairs at the oxygen atoms of vicinal catechol rings.

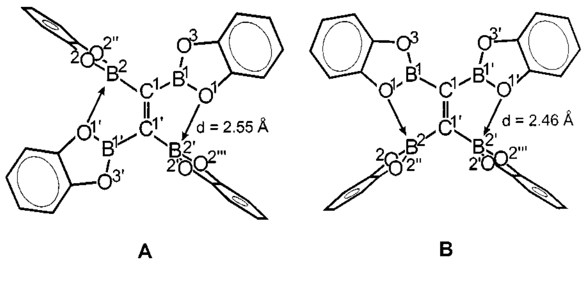


Figure 3. Intramolecular B−O interactions for conformers **A** and **B** (**5a**)

Table 2 summarizes some of the structural parameters of **5a** as obtained from the HF/3-21G geometry optimization in C_{2h}, C_{2v}, D_2 and D_{2h} symmetry. Structure **A** shows two types of boron atoms which are coordinated differently: B1 and B1′ are part of an extensive π system which is delocalized over two catechol moieties connected by the ethylene unit. However, the catechol groups of B2 and B2′ (see Figure 3) are oriented perpendicular to the plane containing the ethylene group and therefore experience a smaller stabilization by π-electron density delocalization from only one catechol group. This is compensated by intramolecular donation of electron density from the oxygen lone pairs of O1 and O1′ to the p_z orbitals of B2 and B2′, which is shown by short B2−O1′ and B2′−O1 interactions for conformers **A** (2.55 Å) and **B** (2.46 Å). The variations in B−O bond lengths in **A** and **B** (1.398−1.415 Å) are in line with electron density being donated from the lone pairs of O1 and O1′thus causing a lengthening of the B1−O1 bond and a shortening of the B1−O3 bond. The length of the B2−O2 bond (of the acceptor boron atom) is slightly longer than the averaged B1−O1 and B1−O3 bond lengths, due to electron donation from O1′ to B2.

Table 2. Calculated structural parameters for **5a**

	C1−C1′[a]	B2−O1′[a]	B2−O3[a]	B1−O1[a]	B1−O3[a]	B2−O2[a]	D1[b]	D2[b]
A	1.347	2.552	3.202	1.409	1.398	1.406	90.0	0.0
B	1.352	2.464	3.353	1.415	1.398	1.405	90.0	0.0
C	1.346	3.000	3.250	1.402	1.406	1.40	139.3	139.3
D	1.366	3.151	2.937	1.402	1.412	1.40	0.0	0.0

[a] Bond lengths in Å. − [b] Dihedral angles D are in degrees; D1 = O2B2C1C1′, D2 = O1B1C1C1′. For the atomic numbering see Figure 3.

To quantify these stabilizing B−O-interactions, a second-order perturbation theory treatment according to the Weinhold Natural Bond Orbital (NBO) localization procedure[23] was performed. As shown in Table 3, there is a stabilization of the empty boron p_z orbital by delocalized π electrons, especially from the neighboring oxygen atoms. The intramolecular donor-acceptor interaction O1−B2′ and O1′−B2 can be clearly seen. Each interaction stabilizes **A** by 15.5 kcal/mol. Although the stabilization is even higher in **B** (21.0 kcal/mol for each interaction) due to shorter O1−B2′ and O1′−B2 distances, this configuration does not represent the global minimum energy structure of **5a** because of repulsive interactions of these geminal catechol rings, which are coplanar with the ethylene fragment. No intramolecular O3−B2 or O3′−B2′ donor-acceptor interactions can be seen, because the distance is too long (3.2 Å in **A**, 3.4 Å in **B**) for an interaction, although the orientation is the same for O3−B2 and O1′−B2. Stabilization by π-electron density from the ethylene fragment can only exist for the boryl groups which are located in this plane (B1 and B1′). Although in close proximity, the amount of stabilization is not much larger than the amount of intramolecular stabilization. The largest stabilization is due to π-electron density donation from the lone pairs of the neighboring oxygen atoms (Table 3).

Table 3. Second-order perturbation theory energies according to the Weinhold natural bond orbital (NBO) localization procedure[29] for **5a**

	Lp (O1′)[a] $\downarrow$ p_Z (B2)	Lp (O3)[a] $\downarrow$ p_Z (B2)	Lp (O2)[a] $\downarrow$ p_Z (B2)	Lp (C1)[a] $\downarrow$ p_Z (B2)	Lp (C1)[a] $\downarrow$ p_Z (B1)
A	15.54	0.00	75.06	0.00	29.01
B	21.00	0.00	75.45	0.00	35.09

[a] Lp = lone pair; energy in kcal/mol. For the atomic numbering see Figure 3.

PE Spectrum of 5a

The He^{I} PE spectrum of **5a** is shown in Figure 4. RHF/3−21G calculations were carried out in order to assign the bands to individual ionization processes. In the range 8.3−9.7 eV there is a broad band of overlapping ionization events (bands 1−3), followed by band 4 at 11.2 eV. The recorded vertical ionization energies agree very well with calculated negative orbital energies, according to Koopmans′ theorem.[25] The bands 1−3 (exp. 8.3−9.7 eV; calcd. 8.8−9.7 eV) are assigned to ionization processes from the eight highest occupied molecular orbitals, which are shown in Figure 5. These orbitals can be described as linear combinations between the π system of the catechol rings and the ethylene π system. The recorded energy differences Δ between band 3 and 4 compare well with the results of the calculations [Δ (exp.) 1.7 eV; Δ (calcd.) 1.5 eV]. Band 4 is assigned to ionization processes from the ethylene π-orbital.

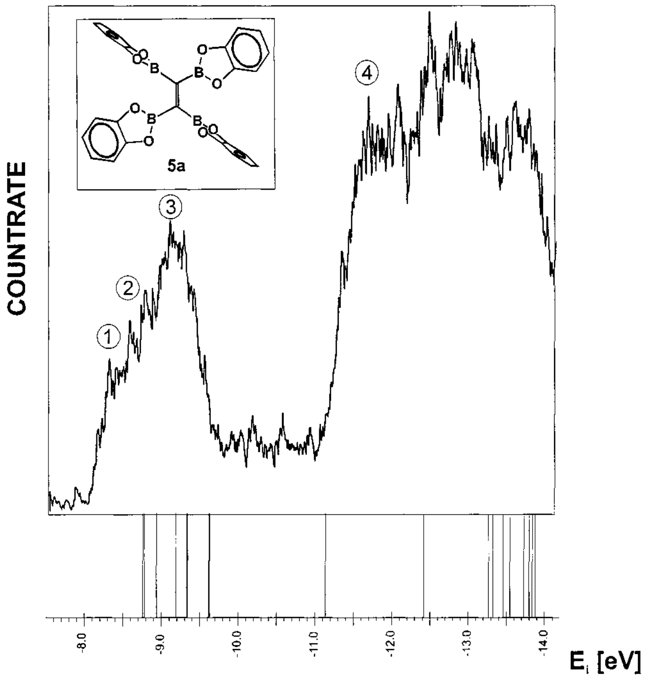


Figure 4. Photoelectron spectrum of **5a**

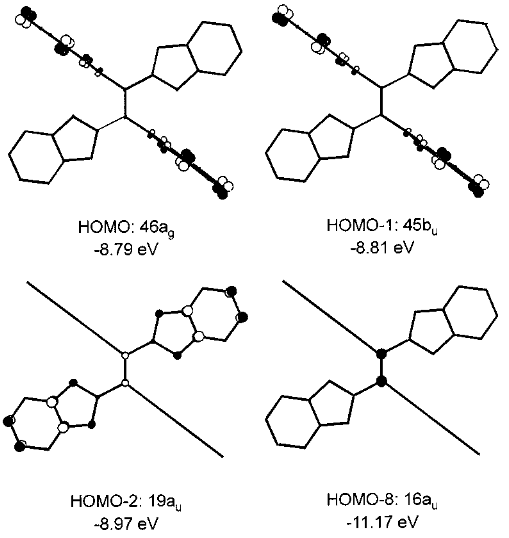


Figure 5. Selected occupied RHF/3−21G orbitals of **A** (**5a**)

Calculated Geometrical Parameters for 4a

Figure 6 shows the most favorable conformations of **4a**, calculated without the coordinated tetrahydrofuran molecules. The global minimum on the HF/3−21G potential energy surface belongs to point group C_i (conformer **E**). In this structure the geminal catechol rings are twisted by 53° to provide a B−O donor-acceptor interaction between two vicinal catechol rings (Table 4). Additionally, there is a B−B interaction between the boron atoms of two geminal catechol rings and an agostic interaction between one boron p_z orbital and the C−H bond of the ethane fragment. In point group C_{2h} (conformer **F**, Figure 6) there is a mirror plane, spanned by the two C−H bonds of the ethane moiety, which disables donor-acceptor interactions. As a consequence, this structure represents a second-order saddle point, which is disfavored by 4.2 kcal/mol (corrected with zero-point energies and thermal energies) relative to **E**.

Table 4. Calculated structural parameters for **4a** (without coordinated thf)

4a	C1−C1′[a]	B1C1B2[a]	H1C1B1[a]	H1C1B2[a]	C1O1C1′O1′[a]	NIMAG[b]
E	1.582	112.97	107.31	108.02	51.3	0
F	1.573	115.00	106.50	106.50	0.0	2

[a] RHF/3−21G-optimizations, bond lengths are in Å, angles are in degrees. − [b] NIMAG: number of imaginary frequencies. For the atomic numbering see Figure 7.

To quantify these stabilizing B−O, B−B and agostic interactions, a second-order perturbation theory treatment according to the Weinhold Natural Bond Orbital (NBO) localization procedure[24] was performed. The relative orientation of the "empty" boron p_z orbital to the C−H bond of the ethane fragment is nearly coplanar and thus enables a stabilization by an agostic interaction. The acceptor boron p_z orbital has an occupation number of 0.318 and stabilizes the geminal boron p_z orbital, which shows an occupation number of 0.323. The larger occupation number

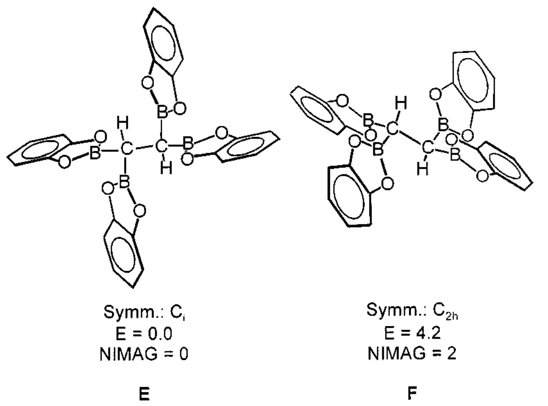


Figure 6. Calculated conformers of **4a**. E: relative energies corrected with zero-point energies and thermal enthalpies. NIMAG: number of imaginary frequencies

is due to an additional intramolecular donor-acceptor interaction from the σ-type oxygen lone pair of the *cis* vicinal catechol group. As for **5a**, the large stabilization by π-electron density donation from the lone pairs of the neighboring oxygen atoms can also be seen (Table 5).

Table 5. Second-order perturbation theory energies according to the Weinhold Natural Bond Orbital (NBO) localization procedure[23] for **4a**.

	Lp (B1)[a] ↓ p_Z (B2)	Lp (O1′)[a] ↓ p_Z (B2)	σ (C1−H1)[a] ↓ p_Z (B1)	σ (C1−H1)[a] ↓ p_Z (B2)	Lp (O2)[a] ↓ p_Z (B2)
E	12.13	12.11	8.96	1.47	71.81

[a] Lp = lone pair; energy in kcal/mol. For the atomic numbering see Figure 7.

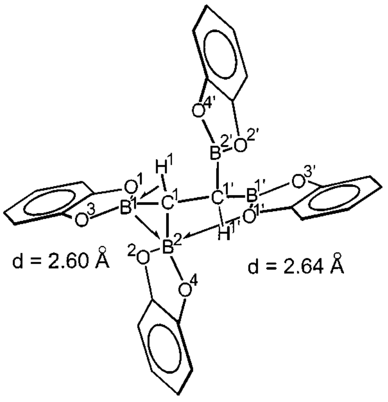


Figure 7. Intramolecular B−O, B−B, and agostic interactions for conformer **E** (**4a**)

Experimental Section

General: Reactions were carried out under dry nitrogen, with standard Schlenk techniques. Solvents were dried, distilled and saturated with nitrogen. Glassware was dried with a heat-gun under high vacuum. ^{1}H, ^{13}C, ^{11}B NMR: Bruker AC 200 and 500 spectrometers; NMR references are $(CH_3)_4Si$ and BF3·Et2O. Mass spectra were obtained on a Finnigan MAT 8200 plus (EI technique) and ZAB-2F VG-Micromass CTD spectrometer (EI and HR-EI techniques) and on a Jeol MS station JMS 700 (EI, HR-EI and CI techniques). − Bis(benzo-1,3-dioxa-2-borol-2-yl)acetylene **2a,**[16] bis(naphthalene-1,3-dioxa-2-borol-2-yl)acetylene **2d,**[12] diborane(4)-compounds **1a−c,**[26] $[Pt(PPh_3)_2(C_2H_4)]$,[27] and $[Pt(cod)_2]$[28] were prepared according to literature procedures.

Bis[(4-*tert*-butylbenzo)-1,3-dioxa-2-borol-2-yl]acetylene (2c): (4-*tert*-Butylbenzo)-2-chloro-1,3-dioxa-2-borole (10 g, 47.6 mmol) in toluene (40 mL) and bis(trimethylstannyl)acetylene (7.6 g, 21.6 mmol) in toluene (40 mL) were simultaneously added dropwise to 200 mL of toluene at −78 °C. The mixture was allowed to warm to room temp. and stirred for 24 h. The solvent was removed, the residue was stirred in pentane, filtered and dried in vacuum. Yield: 5.5 g (68%), sbp. 145 °C/10^{-3} Torr. − ^{1}H NMR (200.1 MHz, $CDCl_3$): δ = 1.32 (s, 18 H, CH_3), 7.18−7.31 (m, 6 H, H_{ar}). − ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 31.7 (CH_3), 34.9 [$C(CH_3)_3$], 110.1, 111.9, 120.4, 145.2, 147.4, 147.5 (C_6H_3). − ^{11}B NMR (64.2 MHz, $CDCl_3$): δ = 24.1 (s). − EI-MS: *m/z* (%) 374 (54) [M$^+$], 359 (100) [M$^+$ − CH_3], 200 (17) [M − $(C_4H_9)C_6H_3O_2B$ + H]$^+$. − HR-MS: *m/z* 374.18655 (M$^+$), calcd. $^{12}C_{22}{}^1H_{24}{}^{11}B_2{}^{16}O_4$: 374.18607 (Δ = 0.48 mmu).

Bis[(tetrachlorobenzo)-1,3-dioxa-2-borol-2-yl]acetylene (2e): (Tetrachlorobenzo)-2-chloro-1,3-dioxa-2-borole (18.3 g, 63 mmol) in toluene (60 mL) and bis(trimethylstannyl)acetylene (10 g, 29 mmol) in toluene (60 mL) were simultaneously added dropwise to 250 mL of toluene at −78 °C. The mixture was allowed to warm to room temp. and stirred for 24 h. The precipitate was filtered and dried in vacuum. Yield: 11.6 g (74%), sbp. 190 °C. − ^{13}C NMR (50.3 MHz, [d$_4$]MeOH): δ = 102 (B*CC*B, br.), 120.4, 123.3, 144.2 (C_6Cl_4). − ^{11}B NMR (64.2 MHz, [d$_4$]MeOH): δ = 22.1 (s), 19.1 (s, $Cl_4C_6O_2BOCD_3$). − EI-MS: *m/z* (%) 538 (18.9) [M$^+$], 282 (70.0) [M$^+$ − $Cl_4C_6O_2B$]. − HR-MS: *m/z* 537.74298 (M$^+$), calcd. $^{12}C_{14}{}^{11}B_2{}^{16}O_4{}^{35}Cl_6{}^{37}Cl_2$: 537.74316 (Δ = 0.18 mmu).

Hexa(benzo-1,3-dioxa-2-borol-2-yl)ethane (3a): Compound **2a** (472 mg, 1.8 mmol), **1a** (431 mg, 1.8 mmol) and (ethene)bis(triphenylphosphane)platinum (83 mg, 0.12 mmol, 6.7 mol-%) were refluxed in 15 mL of toluene for 24 h. The precipitate was then filtered and purified by washing several times with THF and CH_2Cl_2. The colorless solid was dried in vacuum. Yield: 522 mg (71%), sbp. 457 °C. Under the same conditions the catalyst tetrakis(triphenylphosphane)platinum gives **3a** in 57% yield. − ^{1}H NMR (200.1 MHz, [d$_4$]MeOH): δ = 6.61−6.77 (m, H_{ar}). − ^{13}C NMR (50.3 MHz, [d$_4$]MeOH): δ = 146.3, 120.9, 116.4 (C_6H_4). − ^{13}C NMR (125.8 MHz, [d$_4$]MeOH, 203 K): δ = 23 (B_3C, br.). − ^{11}B NMR (64.2 MHz, [d$_4$]MeOH): δ = 34 (s), 19 (s, $C_6H_4O_2BOCD_3$). − HR-MS: *m/z* 738.1860 (M$^+$), calcd. $^{12}C_{38}{}^1H_{24}{}^{16}O_{12}{}^{11}B_6$: 738.1826 (Δ = 3.4 mmu). − $C_{38}H_{24}O_{12}B_6$ (737.47): calcd. C 61.88, H 3.28; found C 61.93, H 3.57.

Mixture of Naphthalene- and Benzo-1,3-dioxa-2-borol-2-ylethanes $\mathbf{3a_nd_{6-n}}$ (n = 2−5): A solution of **2d** (1.00 g, 2.76 mmol), **1a** (660 mg, 2.76 mmol) and (ethene)bis(triphenylphosphane)platinum (128 mg, 0.17 mmol) in 20 mL of toluene was refluxed for 48 h. The precipitate was filtered and purified by washing several times with THF and CH_2Cl_2. The colorless solid was dried in vacuum. Yield: 428 mg. − ^{1}H NMR (200.1 MHz, [d$_4$]MeOH): δ = 6.62−6.85 (m, C_6H_4), 7.10−7.63 (m, $C_{10}H_6$). − ^{13}C NMR (50.3 MHz, [d$_4$]MeOH): δ = 110.5, 116.7, 121.2, 124.4, 127.0, 131.0, 146.5, 147.8. − ^{11}B NMR (64.2 MHz, [d$_4$]MeOH): δ = 31 (s), 19 (s, $C_6H_4O_2BOCD_3$ and $C_{10}H_6O_2BOCD_3$). − EI-MS *m/z* (%) 937 (5.7) [M($\mathbf{3a_2d_4}$) − H]$^+$, 887 (23.6) [M($\mathbf{3a_3d_3}$) − H]$^+$, 838 (63.4) [M($\mathbf{3a_4d_2}$)]$^+$, 787 (68.3) [M($\mathbf{3a_5d_1}$) − H]$^+$, 720 (28.5) [M($\mathbf{3a_4d_2}$) −

$C_6H_4O_2B$ + H]$^+$, 670 (27.6) [M(**3a$_4$d$_2$**) − $C_{10}H_6O_2B$ + H]$^+$ and [M(**3a$_5$d$_1$**) − $C_6H_4O_2B$ + H]$^+$.

Tetra(benzo-1,3-dioxa-2-borol-2-yl)ethane (4a). − Method A: Compound **2a** (1.54 g, 5.9 mmol), **1a** (1.29 g, 5.4 mmol) and tetrakis(triphenylphosphane)platinum (330 mg, 0.27 mmol, 5 mol-%) were heated in 35 mL of THF at 55 °C for 24 h. The solvent was evaporated in vacuum and the precipitate was stirred in diethyl ether and filtered. Washing with diethyl ether gave a yellowish solid that was dried in vacuum. Further purification was performed by sublimation under high vacuum. Yield: 220 mg (11.5%) colorless solid, sbp. 170 °C/10^{-5} Torr. − **Method B:** In a pressure apparatus 300 mg (0.6 mmol) of **5a** was suspended with 70 mg of a palladium/active carbon catalyst in 100 mL of toluene. The apparatus was filled with hydrogen gas (5 bar). After stirring the mixture for 24 h the catalyst was filtered and the solvent was evaporated in vacuum. The remaining solid was dried in vacuum. Yield: 130 mg (43.2%) colorless solid. − ^{1}H NMR (200.1 MHz, [d$_6$]DMSO): δ = 6.36−6.91 (m, 16 H, H$_{ar}$), −0.11 (s, 2 H, B_2CH). − ^{13}C NMR (50.3 MHz, [d$_4$]MeOH): δ = 116.4, 121.0, 146.3. − ^{13}C NMR (125.8 MHz, [d$_4$]MeOH, T = 203 K): δ = 10 (B_2*C*, br.). − ^{11}B NMR (64.2 MHz, [d$_4$]MeOH): δ = 32.5 (s), 19 (s, $C_6H_4O_2BOCD_3$). − HR-MS: *m/z* 502.1390 (M$^+$), calcd. $^{12}C_{26}{}^{1}H_{18}{}^{16}O_8{}^{11}B_4$: 502.1374 (Δ = 1.6 mmu).

Tetra[(4-*tert*-butylbenzo)-1,3-dioxa-2-borol-2-yl]ethane (4c): 672 mg (1.8 mmol) of **2c**, 630 mg (1.8 mmol) of **1c**, and 82 mg (0.1 mmol, 6.2 mol-%) of (ethene)bis(triphenylphosphane)platinum were heated in 20 mL of thf at 55 °C for 40 h. The precipitate was filtered and dried in vacuum. Yield: 33 mg (2.5%). − ^{1}H NMR (200.1 MHz, [d$_4$]MeOH): δ = 6.67−6.82 (m, 12 H$_{ar}$), 1.24 (s, 36 H, CH$_3$), 0.10 (s, 2 H, B_2CH). − ^{13}C NMR (50.3 MHz, [d$_4$]MeOH): δ = 32.3 (CH$_3$), 35.1 (*C*(CH$_3$)$_3$), 114.1, 116.1, 117.7, 144.0, 144.5, 145.9 (C_6H_3). − ^{11}B NMR (64.2 MHz, [d$_4$]MeOH): δ = 32.5 (s), 19 (s, $C_6H_4O_2BOCD_3$). − CI-MS: *m/z* (%) 726 (64.7) [M$^+$], 727 (62.7) [M + H]$^+$, 552 (21.4) [M − $(C_4H_9)C_6H_3O_2B$ + H]$^+$, 377 (38.0) [M − 2 $(C_4H_9)C_6H_3O_2B$ + H]$^+$. − HR-MS: *m/z* 726.3903 (M$^+$), calcd. $^{12}C_{42}{}^{1}H_{50}{}^{16}O_8{}^{11}B_4$: 726.3878 (Δ = 2.5 mmu).

Bis(benzo-1,3-dioxa-2-borol-2-yl)-bis[(tetrachlorobenzo)-1,3-dioxa-2-borol-2-yl)ethane (4a$_2$e$_2$): Compound **2e** (1.00 g, 1.86 mmol), **1a** (42 mg, 1.86 mmol) and bis(triphenylphosphane)(ethene)platinum (97 mg (0.12 mmol, 7 mol-%) were refluxed in 20 mL of toluene for 48 h. The precipitate was filtered and dried in vacuum. Yield: 289 mg (20%). − ^{1}H NMR (200.1 MHz, [d$_4$]MeOH): δ = 6.60−6.77 (m, 8 H, H$_{ar}$), 0.1 (s, 2 H, B_2CH). − ^{13}C NMR (50.3 MHz, [d$_4$]MeOH): δ = 146.3, 121.0, 116.4 (C_6H_4), 144.2, 123.4, 120.5 (C_6Cl_4). − ^{11}B NMR (64.2 MHz, [d$_4$]MeOH): δ = 32.4 (s), 19 (s, $C_6H_4O_2BOCD_3$ and $Cl_4C_6O_2BOCD_3$). − EI-MS: *m/z* (%) 778 (18) [M$^+$], 254 (100) [$C_{12}H_8O_5B_2{}^+$], 392 (48) [$C_{12}H_4O_5B_2Cl_4{}^+$].

1,1:2,2-bis(2,3-naphthalenedioxy)diborane(4) (1d): Compound **2d** (600 mg, 1.66 mmol), **1a** (394 mg, 1.66 mmol) and bis(triphenylphosphane)(ethene)platinum (77 mg, 0.1 mmol, 6.2 mol-%) were heated in 20 mL of toluene at 50 °C for 72 h. The colorless precipitate was filtered, washed with toluene and dried in vacuum. Yield: 416 mg (74%), sbp. 150 °C/10^{-3} Torr. − ^{1}H NMR (200.1 MHz, [d$_4$]MeOH): δ = 7.14−7.55 (m, H$_{ar}$). − ^{13}C NMR (50.3 MHz, [d$_4$]MeOH): δ = 110.8, 124.5, 127.0, 131.1, 147.9 ($C_{10}H_6$). − ^{11}B NMR (64.2 MHz, [d$_4$]MeOH): δ = 31.6 (s), 19 (s, $C_{10}H_6O_2$-$BOCD_3$). − EI-MS: *m/z* (%) 338 (100) [M$^+$], 169 (12) [M$^+$ − $C_{10}H_6O_2B$], 355 (6) [$(C_{10}H_6O_2B)_2O^+$]. − HR-MS: *m/z* 338.09237 (M$^+$), calcd. $^{12}C_{20}{}^{1}H_{12}{}^{16}O_4{}^{11}B_2$: 338.09216 (Δ = 0.21 mmu). − $C_{20}H_{12}O_4B_2$ (338.09): calcd. C 71.08, H 3.57; found C 69.34, H 3.62.

Tetra(benzo-1,3-dioxa-2-borol-2-yl)ethene (5a): Compound **2a** (3.00 g, 11.5 mmol), 1a (2.725 g, 11.5 mmol) and of bis(1,5-cyclooctadiene)platinum (188 mg, 0.46 mmol, 4 mol-%) were heated in 55 mL of toluene at 40 °C for 24 hours. The precipitate was then filtered and washed with CH_2Cl_2 and dried in vacuum. Yield: 4.025 g (70%), sbp. 160 °C/10^{-5} Torr. − ^{1}H NMR (200.1 MHz, [d$_4$]MeOH): δ = 6.60−6.79 (m, H$_{ar}$). − ^{13}C NMR (50.3 MHz, [d$_4$]MeOH): δ = 146.3, 120.9, 116.4 (C_6H_4), 165 (B_2*C*, br., weak). − ^{13}C NMR (125.8 MHz, [d$_4$]MeOH, T = 203 K): δ = 165 (B_2*C*, br.). − ^{11}B NMR (64.2 MHz, [d$_4$]MeOH): δ = 29.9 (s), 19 (s, $C_6H_4O_2BOCD_3$). − CI-MS: *m/z* (%) 500 (100) [M$^+$], 501 (78.4) [M + H]$^+$, 557 (1.8) [M + C_4H_9]$^+$ − HR-MS: *m/z* 500.12158 (M$^+$), calcd. $^{12}C_{26}{}^{1}H_{16}{}^{11}B_4{}^{16}O_8$: 500.12173 (Δ = 0.15 mmu). − Raman: $\tilde{\nu}$ = 1549 cm^{-1} (C=C), 1620 cm^{-1} (ar.), 1471, 1330, 1230, 1150, 1002, 818, 611 cm^{-1}, 3066 cm^{-1} (C−H). − $C_{26}H_{16}O_8B_4$ (499.65): calcd. C 62.50, H 3.23; found C 62.33, H 3.65.

X-ray Crystal Structure Determinations of 4a: Crystal data and details of the structure determination 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). Empirical absorption corrections (ψ-scans) were applied. The structure was solved by direct methods [SHELXS86][29] and refined by least-squares methods based on F^2 with all measured reflections [SHELXL97].[30] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in calculated positions.

Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-116696. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (internat.) + 44-1223/336-001; E-mail: deposit@ccdc.cam.ac.uk

Table 6. Crystal data and structure refinement for **4a**

	4a
Empirical formula	$C_{26}H_{18}O_8B_4\cdot 2C_4H_8O$
Formula weight	645.9
Crystal system	monoclinic
Space group	$P2_1/c$
Unit cell	
A [Å]	8.600(5)
B [Å]	16.139(8)
C [Å]	12.204(6)
β [deg]	104.18(4)
Volume [Å^3]	1642(2)
Z	2
Calcd. density [g/cm^3]	1.306
Adsorp. coeff. [mm^{-1}]	0.09
F(000)	676
Crystal size [mm]	0.40 × 0.45 × 0.55
Θ-range [deg]	25.0
Index-ranges	−10/+9 0/+19 0/+14
No. of reflections	2894
unique	2894
observed [$I > 2\sigma(I)$]	1548
Parameters	285
Final *R* indices	
*R*1 [$I > 2\sigma(I)$]	0.052
*wR*2	0.146
Largest diff.peak/hole[e/Å]	0.18/−0.22

PE spectrum of 5a: The He^{I} PE spectrum was recorded on a Perkin−Elmer PS18 spectrometer. The recording temperature was 230 °C. The calibration was performed with Ar (13.76 and 15.94 eV) and Xe (12.13 and 13.44 eV). A resolution of 20 meV on the $^{2}P_{3/2}$ Ar line was obtained.

Acknowledgments

We thank A. Flatow for recording the PE spectrum and Dr. S. Lebedkin, Forschungszentrum, Karlsruhe, for the Raman spectrum of **5a**. We are grateful to the Graduiertenkolleg der Universität Heidelberg, the Deutsche Forschungsgemeinschaft (SFB 247) and the Fonds der Chemischen Industrie.

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Received April 9, 1999
[I99127]