Reversible Formation of Organyl(oxo)boranes (RBO) (R = C_6H_5 or CH_3) from Boroxins ($(RBO)_3$): A Matrix Isolation Study

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Flash vacuum pyrolysis of triphenyl- and trimethylboroxin and subsequent trapping of the gas phase products in a large excess of argon at $T < 20$ K allows matrix isolation and characterization by IR spectroscopy of phenyl(oxo)borane and methyl(oxo)borane. The nature of the matrix isolated species, monomeric CH_3BO, 1:1 dimer complex of CH_3BO, $(CH_3BO)_2$, and $(CH_3BO)_3$, depends strongly on the trapping temperature and matrix host gas (Ar vs Xe) with the boroxin dominating at 30 K (Ar) or 55 K (Xe). An ab initio investigation (second-order Møller−Plesset perturbation theory) of the potential energy surface for trimerization of CH_3BO is in agreement with the experimental observations.

Introduction

Oxoboranes XBO are fundamental yet highly elusive boron compounds.[1] Inorganic derivatives of XBO, X = H, N, O, F, Cl, Br, or I, have been obtained previously by reaction of either the boron halides with B_2O_3 at temperatures exceeding 1000 K or by co-condensation of boron atoms with small molecules (H_2O, O_2, or NO).[2−9] Such techniques are clearly not suitable for the generation of organyl(oxo)boranes (RBO) (**1**; R = organyl), the monomeric anhydrides of the boronic acids **2**. These are invaluable reagents in modern organic synthesis (e.g., in the Suzuki[10] cross-coupling reactions) and are currently receiving increased interest as molecular building blocks in crystal engineering as they combine both hydrogen bonding and Lewis acidic motifs.[11−13] As compared to boronic acids, the dicoordinated boron center in **1** is expected to show increased Lewis acidity, while the oxygen atom should still be able to act as a hydrogen bond acceptor. Such aspects of the chemistry of **1** have never been investigated due to the lack of generally applicable access to these systems. A straightforward route, dehydration of **2**, yields the trimeric boroxins **3** instead of **1**,[14,15] due to the kinetic and thermodynamic instability of **1** toward trimerization (Scheme 1).[16,17]

Organoboroxins have been structurally characterized[18−20] and are rather stable compounds under anhydrous conditions (e.g., they form 1:1 complexes with nitrogen bases without degradation of the six-membered heterocyclic ring),[21,22] and their thermal decomposition is reported to go along with the degradation of the organic ligands.[23] Consequently, other routes to **1** were sought, and the methyl-1,3,2-diborolane-4,5-dione (**4**) proved useful. After the mass spectrometric detection of **1b** (R = Me) in 1977,[16] the first direct spectroscopic characterization of an oxoborane **1b** in the pyrolysis mixture of **4** was achieved by Bock et al.[24] using photoelectron spectroscopy (Scheme 2).

As organic groups larger than a methyl group resulted in insoluble derivatives of **4** which lack the necessary volatility for gas phase experiments, no organyl(oxo)boranes other than **1b** have been studied by direct spectroscopic techniques to date. Lanzisera and Andrews characterized **1b** by IR spectroscopy as one of the products of the reaction of boron atoms with methanol under the conditions of matrix isolation.[25] A number of trapping experiments have furnished additional evidence for the existence of RBO (R = 2,4,6-tri-*t*-butylphenyl,[26,27] 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl,[28] or $C(SiMe_3)_3$[29]) as reactive intermediates since the mid-1980s, while the detection of C_2BO and C_4BO from $(CH_3)_3Si\text{-}(C{\equiv}C)_n\text{-}B(O\text{-}i\text{Pr})_2$ ($n = 1$ or

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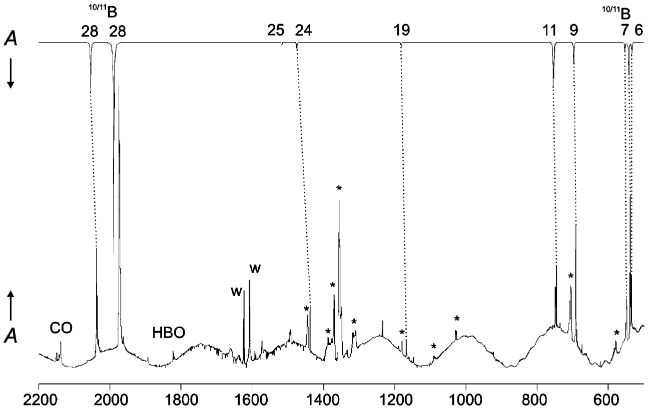


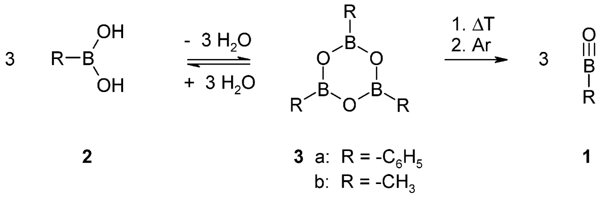
Figure 1. IR spectra of the triphenylboroxin pyrolysis products trapped in Ar at 10 K (bottom trace) and spectrum computed for C_6H_5BO (**1a**) at the MP2/cc-pVTZ level of theory (top trace). Bands due to CO, HBO, and water (w) are labeled. Stars identify signals due to triphenylboroxin **3a**.

Table 1. Vibrational Frequencies (in cm^{-1}) and Infrared Intensities of Phenyl(oxo)borane 1a from Experiment (Ar Matrix, 10 K) and Theory[a]

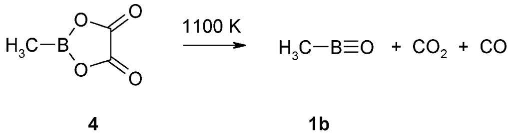
Number	symmetry species	υ_{exp} (cm^{-}1)	rel intensity	ω_{theor} (cm^{-}1) (I (km mol^{-}1))
33	A_1			3240.1 (5.6)
32	B_2	3053	0.02	3232.6 (10.7)
31	A_1			3221.9 (2.7)
30	B_2			3214.9 (0.1)
29	A_1			3208.8 (0.1)
28	A_1	2040, 2038, 2035	0.21	2054.5 (248.6)[b]
28	A_1	1977, 1975,1972, 1971	1.00	1989.2 (232.1)
27	A_1			1645.9 (0.6)
26	B_2			1617.1 (0.7)
25	A_1			1518.7 (4.9)
24	B_2	1438	0.06	1475.2 (8.2)
23	B_2			1439.4 (2.3)
22	B_2			1339.0 (1.0)
21	A_1			1210.3 (0.7)
20	B_2			1185.1 (0.0)
19	A_1	1168	0.02	1182.1 (6.6)
18	B_2			1100.8 (1.2)
17	A_1			1051.6 (2.5)
16	A_1			1010.7 (0.9)
15	B_1			984.7 (0.0)
14	A_2			974.7 (0.0)
13	B_1			930.0 (1.2)
12	A_2			869.9 (0.0)
11	B_1	749, 747	0.13	754.9 (46.7)
10	A_1			733.6 (0.0)
9	B_1	692	0.18	697.3 (20.8)
8	B_2			624.6 (1.0)
7	B_1	551, 550	0.03	554.6 (39.9)[b]
7	B_1	540, 539	0.17	543.9 (36.3)
6	B_2	535	0.05	535.0 (14.0)
5	A_1			426.8 (0.6)
4	A_2			395.3 (0.0)
3	B_1			379.3 (5.5)
2	B_2			127.5 (5.4)
1	B_1			125.2 (1.9)

[a] MP2/cc-pVTZ, unscaled; intensities in km mol^{-1} given in parentheses. [b] ^{10}B isotopomer, natural abundance 19.2%.

Scheme 1. Dehydration of Boronic Acids 2 Generally Yields Trimeric Anhydrides, Boroxins 3



Scheme 2. Synthesis of Methyl(oxo)borane (1b) by Thermolysis of Methyl-1,3,2-diborolane-4,5-dione (4) as Reported by Bock et al.[24]



2) by chemical ionization in a mass spectrometer has been reported more recently.[30] A stabilized oxoborane has also been obtained recently.[31]

We report here that the organyl(oxo)boranes **1a** ($R = C_6H_5$) and **1b** ($R = CH_3$) can be generated thermally form the corresponding boroxins **3** by pyrolysis in the gas phase, isolated in cryogenic noble gas matrices, and studied by FTIR spectroscopy (Scheme 1). This allows, for the first time, for the synthesis of phenyl(oxo)borane **1a** and the observation of the thermally initiated aggregation of **1b** in argon and xenon matrices.

Results and Discussion

Fragmentation of Boroxins and Recyclization. Subjecting the boroxin **3a** to flash vacuum pyrolysis (FVP; $T \approx 650$ °C, quartz tube) and freezing the gaseous products in a large excess of Ar at $T < 20$ K, IR signals (Figure 1) due to the usual contaminants in FVP experiments (CO_2, CO, and H_2O), **3a**, and traces of HBO[4] are observed. The yield of the latter species increases at higher thermolysis temperatures. The remaining IR bands can be assigned to **1a** based on comparison with ab initio data (MP2/cc-pVTZ, see Table 1).

The signal pairs at 2037/1975 and 550/540 cm^{-1} have a 1:4 intensity typical for boron compounds with a natural isotope composition ($^{10}B/^{11}B = 1:4.1$) and are due to the B−O stretching (a_1) and bending (b_1) vibrations, respectively. These bands, along with the CH wagging mode at around 750 cm^{-1}, show a pronounced fine structure, probably due to matrix site effects. In an attempt to investigate the interaction of **1a** with CO, pyrolysis products were trapped with Ar/CO (1000:1) mixtures. Additional signals at 2145.9 and 1967.5 cm^{-1} result, which upon annealing to 38 K increase, while signals due to CO (2139 cm^{-1}) and **1a** decrease. We assign these two signals to the ν(CO) and ν(BO) vibrations of a $C_6H_5{-}BO\cdots CO$ complex, which is bound by only 1 kcal mol^{-1} (CCSD(T)/cc-pVTZ//MP2/cc-pVTZ). The shifts of the CO (7 cm^{-1} blue) and BO (7 cm^{-1} red) stretching vibrations are in reasonable agreement with ab initio (MP2/cc-pVDZ) data (6 and 4 cm^{-1}, respectively).

The thermal fragmentation of boroxins is not limited to the phenyl system **3a**. Carrier gas pyrolysis of **3b** (0.01% in Ar) yields **1b**, whose IR spectral data in solid argon are in excellent agreement with those reported previously by Lanzisera and Andrews (see Table 2).[25] The trapping temperature proved to be extremely important for the detection of **1b**. Increasing the temperature of the spectroscopic window from 18 to 30 K and above does not yield any **1b** under otherwise identical experimental conditions. Rather, **3b** is observed as the only product demonstrating the high kinetic instability of **1b**.

The composition of the trapped thermolysis mixture does not only depend on the temperature of the cold window but also

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Table 2. Vibrational Frequencies (in cm^{-1}) and Infrared Intensities of Methyl(oxo)borane 1b from Experiment (Ar Matrix, 10 K) and Theory[a]

υ_{exp} (cm^{-1})			
present	literature[b]	ω_{theor} (cm^{-1}) (I (km mol^{-1})), symmetry species	assignment
		3186 (0.1), E	[^{11}B]-**1b**, ν(CH)
		3092 (0.2), A_1	[^{11}B]-**1b**, ν(CH)
2038.8	2038.5	2040 (148.1), A_1	[^{10}B]-**1b**, ν(BO)
2030.2	2029.9	combination in Fermi resonance with ν(^{10}BO)[b]	[^{10}B]-**1b**[b]
2021.2		2027 (180.1), A′	[^{10}B,^{11}B]-**6b**, ν(BO)
1972.8	1972.4	1975 (138.9), A_1	[^{11}B]-**1b**, ν(BO)
1962.2		1966 (306.6), B_u	[$^{11}B_2$]-**6b**, ν(BO)
1957.7		1962 (136.3), A′	[^{10}B,^{11}B]-**6b**, ν(BO)
		1479 (10.7), E	[^{11}B]-**1b**, δ(CH)
1305.2	1305.0	1344 (11.0), A_1	[^{11}B]-**1b**
1299.7		1336 (37.9), B_u	[$^{11}B_2$]-**6b**
904.7, 903.5	904.5, 903.3	929 (45.1), E	[^{10}B]-**1b**
897.2, 895.8	896.8, 895.6	922 (42.1), E	[^{11}B]-**1b**
		821 (0.0), A_1	[^{11}B]-**1b**
		356 (23.3), E	[^{11}B]-**1b**

[a] MP2/aug-cc-pVTZ, unscaled; intensities in km mol^{-1} are given in parentheses. [b] Ref 25.

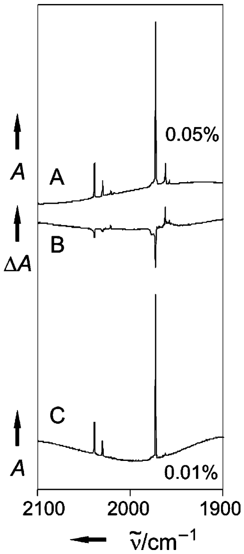

Figure 2. IR spectra of the pyrolysate of trimethylboroxin (**3b**) in the BO stretching region. (A) 0.05% in Ar; (B) difference spectrum: bands pointing downward decrease in intensity upon annealing the matrix in trace A to 38 K; and (C) 0.01% in Ar.

on the flow rate through the pyrolysis tube and on the boroxin concentration in the gas mixture. In addition to the signals due to **1b**, we observe weak signals at 2021.2, 1962.2, 1957.7, and 1299.7 cm^{-1} when using a 0.05% mixture of **3b** in Ar for carrier gas pyrolysis. The intensities of these signals increase upon subsequent annealing of the matrix to 35−38 K, while they are not observed if the concentration of **3b** in the pyrolysis gas mixture is lowered to 0.01% (Figure 2). We hence assign these absorptions to the dimeric complex **6b** of **1b** (Scheme 3). More extended annealing in argon does not give any convincing evidence for the cyclization of **6b** to the 1,3-dioxa-2,4-diboretane **7b**.

There is, however, some indication for the formation of **7b** during freezing of the pyrolysate mixture onto the cold spectroscopic window, in particular if xenon is used as the host gas. As with argon, a strong dependence of the composition of the matrix on the trapping temperature and boroxin concentration is observed. Under various decomposition conditions, a set of three very weak signals (1210, 1271, and a shoulder at 1343 cm^{-1}) is reproducibly observed, and these are tentatively assigned to **7b**. The highest yield of **7b** is obtained (750 °C; 0.2% mixture of **3b** in Xe) at a trapping temperature of 30 K, which gives **6b** as the most prevalent species. Trapping at lower (18 K) or higher temperatures (50 K) gives **1b** or **3b**, respectively, as the dominating compounds. The tentative assignment of the weak bands to **7b** is supported by further experiments and by theory. Two-photon absorption during irradiation with light of a KrF excimer laser (248 nm) allows thermal energy transfer from the solid xenon matrix to the entrapped molecules.[32] This technique, successfully employed by Maier and co-workers for the generation of radicals,[32−34] provides a means for thermal excitation of molecules, which themselves do not absorb at 248 nm, a condition fulfilled by the molecules investigated here. Such treatment (10 Hz pulse repetition) of the xenon matrix described previously results in an increase of the 1210 cm^{-1}, 1271 cm^{-1}, and 1343 cm^{-1} absorptions (see Supporting Information). However, not only the signals of **6b** but also those of **1b** and **3b** reduce in intensity under these conditions, although **6b** decreases slightly more than **1b**. The loss of almost all species, except for that responsible for the three new signals, is most likely due to laser ablation of the xenon matrix, whose low optical quality (it is opaque rather than transparent) is a consequence of the necessary deposition conditions (FVP; CsI window at 30 K). The tentative assignment of the signals to **7b** is also supported by computational data (Table 3).

Finally, as expected, the IR spectra of **1b** and **3b** are only slightly shifted in Xe as compared to the data obtained in Ar. The most pronounced difference is that the splitting of the ν(^{10}BO) signal in **1b**, previously ascribed to a Fermi resonance with a combination band,[25] is not observed in solid Xe. The observed vibrational frequencies, 2038.6 ν(^{10}BO), 1974.8 ν(^{11}BO), 1300.1, 901.9/899.5, and 894.2/891.9 cm^{-1}, show boron isotopic ratios of 1.03231 (exptl) in good agreement with theory (1.03307).

Computational Analysis. A computational investigation of the cyclotrimerization of **1b** at the MP2/aug-cc-pVTZ level of theory is in agreement with the experimental observations (see Figure 3). The formation of **3b** from **1b** is a strongly exothermic process (ΔH_R (0 K) = −99 kcal mol^{-1}) involving the complexes **6b** and **8b** as well as the 1,3-dioxa-2,4-diboretane **7b** as intermediates, which are all lower in energy than three separated molecules of **1b**.

The methyl derivative **1b** has been the subject of a number of computational investigations aimed at understanding its electronic structure as well as at deriving experimentally inaccessible data.[35−39] The similarity of the photoelectron spectrum of **1b** with that of the isoelectronic CH_3CN molecule led Bock et al. to conclude that the BO bond in this oxoborane is a triple bond.[24] This interpretation of the bonding in **1b** is in

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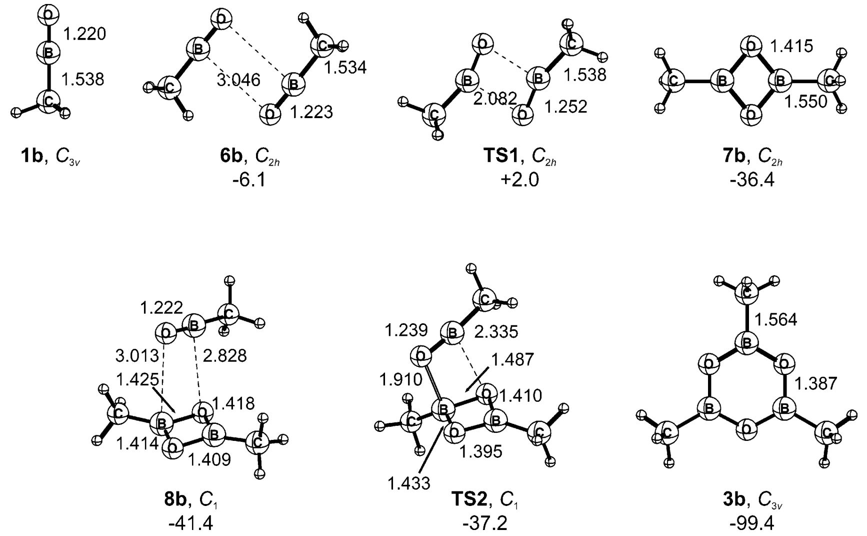
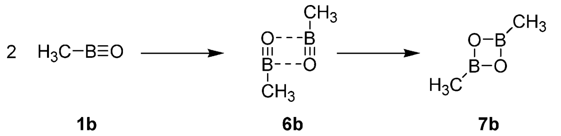


Figure 3. Geometries of species involved in the cyclotrimerization of methyl(oxo)borane **1b** as computed at the MP2/aug-cc-pVTZ level of theory. Energies (in kcal mol^{-1}) given for the dimeric (**6b**, **TS1**, and **7b**) and trimeric (**8b**, **TS2**, and **3b**) species are relative to two and three monomers **1b**, respectively.

Scheme 3. Dimerization of Methyl(oxo)borane 1b, 1:1 Dimer Complex 6b, and 1,3-Dioxa-2,4-diboretane 7b



Scheme 4. Stepwise Trimerization of Methyl(oxo)borane 1b To Give Trimethylboroxin 3b

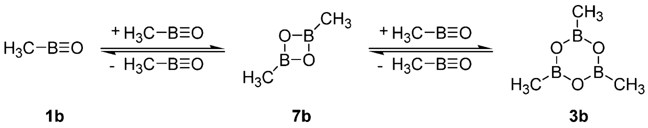


Table 3. Vibrational Frequencies (in cm^{-1}) of 1,3-Dioxa-2,4-dimethylboretane (7b) from Experiment (Xe Matrix, 30 K) and Theory[a]

Number	symmetry species	ν_{exp} (cm^{-1})	ω_{theor} (cm^{-1}) (I (km mol^{-1}))
19	B_u	1343	1382.9 (550.4)
17	A_u	1270	1302.9 (309.6)
16	B_u	1211	1248.8 (344.5)
13	B_u		927.3 (65.5)
9	B_u		737.6 (35.1)

[a] MP2/aug-cc-pVTZ, unscaled; intensities in km mol^{-1} given in parentheses. Only bands with an absolute intensity larger than 10 km mol^{-1} are given. Experimental intensities could not be obtained due to overlap with bands of **1b**.

agreement with a computational analysis of HBO, which was concluded to have “essentially a dative triple character”.[36]

Our MP2 computations using the large aug-cc-pVTZ basis set give a dipole moment of 3.60 D for **1b**. This number is somewhat larger than the 3.4 D reported earlier at the MP2/DZP level of theory.[36] The strong association (−6 kcal mol^{-1}) of the two molecules of **1b** to yield the 1:1 complex **6b** is driven by the annihilation of this large dipole moment. The long intermolecular B···O distances of 3.05 Å in **6b** and a minor change in the BO bond lengths in the individual monomers are clearly incompatible with dative boron···oxygen interactions. Thus, **6b** is best considered a dipole−dipole complex.

The barrier through **TS1** for the exothermic formation ($\Delta H_R(0\ \mathrm{K}) = -30$ kcal mol^{-1}) of the 1,3-dioxa-2,4-diboretane (**7b**) from this complex is 8.1 kcal mol^{-1} (Figure 3). In the transition state **TS1**, the intermolecular BO distances are much shorter, 2.08 Å, while the BO bonds have stretched significantly to 1.25 Å. The relatively high barrier explains why annealing experiments in argon yield **6b**, while **7b** could not be observed. The association of **7b** with another molecule of **1b** to give the adduct **8b** is also exothermic ($\Delta H_R(0\ \mathrm{K}) = -5$ kcal mol^{-1}). The formation of **3b** from **8b** is significantly more exothermic than the formation of **7b** from **6b**, and consequently, the barrier (**TS2**) for reaction is significantly smaller (4 kcal mol^{-1}). In the transition state **TS2**, there is a pronounced asymmetry in the newly forming B−O bonds (1.91 and 2.34 Å), while the BO bond of the attacking monomer is much less stretched than in **TS1**. The fact that the barrier of formation of **7b** is higher than that for its disappearance by reaction with another molecule of **1b** explains why **7b** could only be detected in low concentrations. The rather low barriers and their relative heights are responsible for the facile de novo generation of **3b** at slightly elevated trapping temperatures and/or **1b** concentration.

Comparison with Iminoboranes. The trimerization of oxoboranes RBO (Scheme 4) appears to be analogous to that of iminoboranes RBNR, which is known to involve cyclic dimers $(RBNR)_2$.[40,41]

These $(RBNR)_2$ dimers can be isolated in the presence of bulky substituents R, in analogy to the known 1,3-dioxa-2,4-diboretanes **7** bearing large groups.[26,42,43] The presence of trimers resembling Dewar benzene, established in the RBNR series,[44,45] is not observed here. Indeed, the attempted geometry optimization of a Dewar boroxole resulted in **3b** instead.

Conclusion

In summary, we have shown that the hitherto unknown phenyl(oxo)borane **1a**, the monomeric anhydride of the syn-

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thetically important benzeneboronic acid **2a**, can be synthesized by FVP of its boroxin trimer **3a** and trapped in an argon matrix at cryogenic temperatures. This approach to monomeric anhydrides of organoboronic acids allows for the study of methyl(oxo)borane **1b** and its facile reaction back to trimethylboroxin **3b** under the conditions of matrix isolation. We find that 1,3-dioxa-2,4-diboretane **7b** is formed only in low concentrations at elevated trapping temperatures using xenon as a matrix host gas, indicating that the trimerization of **1b** is stepwise and involves **7b** as an intermediate. As the chemistry of boron oxides RBO has received very limited attention until now, we are currently studying complex formation and possible reactions with Lewis bases.

Experimental and Computational Procedures

Triphenylboroxin (**3a**) was obtained by dehydration of benzeneboronic acid (Aldrich, 97%), which was recrystallized twice from water and washed with petrol ether,[46] by heating[47] in vacuo or by reaction with $SOCl_2$ in diethylether as described by Frohn et al.[48] for pentafluorophenylboronic acid. Trimethylboroxin was purchased from Aldrich (99%) and was used without further purification. Matrix experiments were carried out according to standard techniques[49] with APD CSW-20 displex closed-cycle helium cryostats. Pyrolyses were performed with a quartz tube (10 mm i.d., 200 mm length), which was resistively heated by Ta wire coiled around it. Temperatures were measured with Ni−Cr/Ni thermocouples (Thermocoax). The boroxin **3a** was sublimed out of a glass flask by heating it between 90 and 120 °C (Büchi GKR-51), and all gaseous materials leaving the pyrolysis tube were condensed onto a cold CsI window with a large excess of argon (Messer Griesheim, 99.9999%), which was dosed to 2.0 sccm by a mass flow controller (MKS Mass Flow Type 247 four-channel read out). The more volatile **3b** was premixed with argon (1:10 000 to 2:1000) by standard manometric techniques, and these mixtures were bled into the vacuum system at 2.0 sccm by a mass flow controller. The experiments with **3b** also employed xenon gas (Air Liquide, 4.0). The CsI window was either kept at the lowest possible temperature (18−20 K, rather than the usual 10 K, due to radiative heating from the pyrolysis oven) or was warmed to a defined temperature by resistive heating using an Oxford ITC 503 temperature controller. IR spectra were measured between 4000−400 cm^{-1} on Bruker IFS 66 and IFS 66/S spectrometers using a resolution of 0.5 cm^{-1}.

The computational investigations used second-order Møller−Plesset perturbation theory (MP2) in conjunction with the cc-pVTZ and aug-cc-pVTZ correlation consistent basis sets.[50] Geometries of stationary points were optimized, and harmonic vibrational frequencies were computed at the MP2/cc-pVTZ level of theory for all compounds. In addition, harmonic vibrational frequencies were also obtained at the MP2/aug-cc-pVTZ level of theory for **1b**. The geometries of species involved in the cyclotrimerization of **1b** (i.e., **3b**, **6b**, **7b**, **TS1**, and **TS2**) were further optimized using the aug-cc-pVTZ basis set, but the corrections for zero-point vibrational energies obtained at MP2/cc-pVTZ were used for deriving the relative energies given in Figure 4. The interaction energy of the binary complex of **1a** with CO was corrected for basis set superposition errors by the counterpoise method a posteriori.[51] All computations employed the frozen-core approximation and were performed with Gaussian 03.[52]

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Supporting Information Available: Cartesian coordinates of all stationary points. This material is available free of charge via the Internet at http://pubs.acs.org.

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