Isocyanide and Ylidene Complexes of Boron: Synthesis and Crystal Structures of (2-(Trimethylsiloxy)phenyl isocyanide)−Triphenylborane and (1,2-Dihydrobenzoxazol-2-ylidene)−Triphenylborane

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2-(Trimethylsiloxy)phenyl isocyanide (**1**) reacts at −60 °C with triphenylborane to form the isocyanide adduct (2-(trimethylsiloxy)phenyl isocyanide)−triphenylborane (**2**). Upon desilylation in MeOH with a catalytic amount of KF at −30 °C **2** is converted into the ylidene adduct (1,2-dihydrobenzoxazol-2-ylidene)−triphenylborane (**3**). The X-ray crystal structures of **2** and **3** are reported. When it is heated, **2** dimerizes to give 1,4-bis(2-(trimethylsiloxy)-phenyl)-2,2,3,5,5,6-hexaphenyl-2,5-dibora-2,5-dihydropyrazine (**4**). Si−O bond cleavage leads to 1,4-bis(2-hydroxyphenyl)-2,2,3,5,5,6-hexaphenyl-2,5-dibora-2,5-dihydropyrazine (**5**). Attempts to induce formation of a boron-bridged diylidene complex *via* attack of the hydroxyl oxygens in **5** at the pyrazine carbon atoms failed. Instead, complex **6**, containing one bridging N,O-ylidene ligand, was obtained by partial hydrolysis of **5**. The molecular structure of **6**, which crystallizes with one molecule of methanol and acetone each per formula unit, is reported.

Introduction

We have demonstrated the use of 2-(trimethylsiloxy)-phenyl isocyanide (**1**) for the synthesis of transition-metal carbene complexes. Complexes with the 1,2-dihydrobenzoxazol-2-ylidene ligand are obtained from complexes of **1** after Si−O bond hydrolysis *via* an intramolecular cycloaddition of the hydroxyl oxygen atom to the isocyanide carbon atom.[1] Even complexes of **1** with low-valent transition metals, where the isocyanide is normally deactivated toward nucleophilic attack by strong (d→p)π back-bonding from the metal center, will yield carbene complexes.[1] For example, the complex $[W(CNC_6H_4\text{-}2\text{-}OSiMe_3)(CO)_5]$ gives after Si−O bond cleavage the corresponding carbene complex,[1b] while the complex $[W(CNCH_2CH_2\text{-}2\text{-}OSiMe_3)(CO)_5]$ after Si−O bond cleavage remains the isocyanide complex $[W(CNCH_2CH_2\text{-}2\text{-}OH)(CO)_5]$.[2a] However, late or high-valent transition metals also give complexes with oxazolidin-2-ylidene ligands from coordinated 2-hydroxylalkyl isocyanides.[2] Recently we have shown that the intramolecular ylidene formation can be suppressed by the generation of 2-hydroxyphenyl isocyanide at metal fragments where enhanced (d→p)π back-bonding occurs.[3]

After having studied the cyclization of 2-hydroxyphenyl isocyanide at relatively electron-rich metal fragments, we became interested in examining the carbene formation in a system where the isocyanide **1** is coordinated to a Lewis acid exclusively as a σ-donor with no back-bonding from the metal center. The lack of back-bonding should facilitate the intramolecular carbene formation after Si−O bond cleavage. Recently we described preliminary results of the reaction of **1** with $TiCl_4$.[4]

In this contribution we wish to report on the reaction of **1** with triphenylborane to yield the isocyanide adduct $[(C_6H_5)_3B(\mathbf{1})]$ (**2**) and the conversion of **2** to the ylidene complex $\{(C_6H_5)_3B[CN(H)(C_6H_4\text{-}2\text{-}O)]\}$ (**3**) and on our attempts to prepare diborane heterocycles containing two bridging 1,2-dihydrobenzoxazol-2-ylidene ligands. Although Casanova and Hesse have already studied isocyanide[5] and carbene[6] adducts of alkylboranes in the 1960s, the availability of stable nucleophilic carbenes[7] has recently stimulated some interest in the synthesis of novel carbene adducts of main-group elements.[8]

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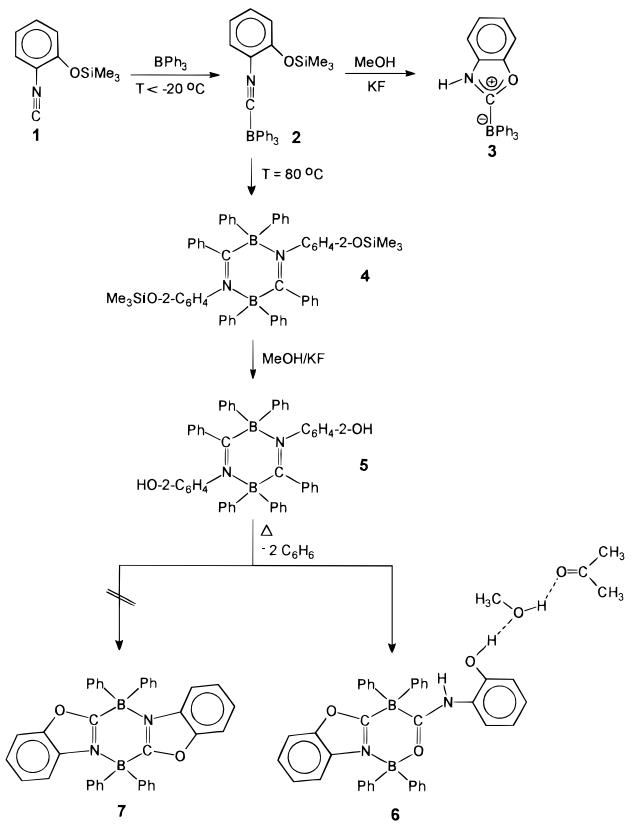
Scheme 1



Results and Discussion

Synthesis of Complexes 2 and 3. 1:1 adducts of isocyanides with triorganoboranes are normally unstable compounds at ambient temperature which tend to dimerize and rearrange to 2,5-dibora-2,5-dihydropyrazines.[5b,c] On the other hand, aliphatic isocyanides form moderately stable 1:1 adducts with Ph_3B.[5d,9] However, triphenylborane adducts with aromatic isocyanides are still unstable and tend to dimerize.[5d] To prevent phenyl migration from boron to the isocyanide carbon and subsequent dimerization, we synthesized the borane complex **2** from **1** and Ph_3B in CH_2Cl_2 at low temperature (below −20 °C, Scheme 1).

If kept below −20 °C, complex **2** is stable in solution and in the solid state for longer periods. It can be crystallized from diethyl ether at −26 °C. In the IR spectrum of **2** the absorption for the CN stretching frequency (2244 cm^{-1}) is shifted to significantly higher wavenumbers compared to the free isocyanide **1** (2120 cm^{-1}),[10] showing the isocyanide to act exclusively as a σ-donor. A substantial increase of ν(CN) upon coordination of isocyanides to Lewis acidic centers is normal and was previously observed in boron[5,9] and lanthanide[11] adducts of various isocyanides.

Warming to room temperature causes the almost colorless crystalline **2** to darken. IR spectra taken from samples left at room temperature for 24 h show the absence of **2** (no ν(CN)) and are almost identical with those reported for 2,5-dibora-2,5-dihydropyrazines (strong absorption around 1550−1560 cm^{-1} for the B(R)C═N-(R)B moiety),[5] indicating complete dimerization of **2** to **4** (Scheme 1). The tendency toward dimerization upon warming is also observed if samples of **2** which have been kept cool right until the measurement are subjected to mass spectroscopy. The spectrum exhibits signals at m/z 433 for monomeric **2** and at m/z 866 for dimeric **4**.

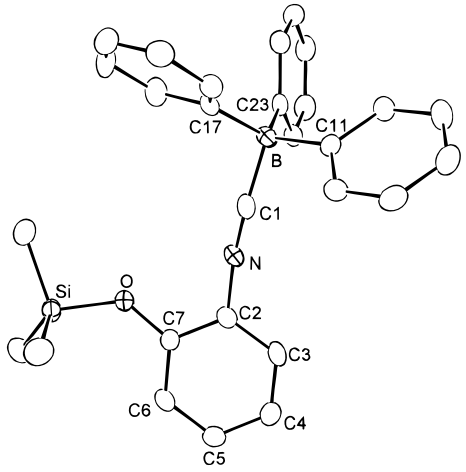


Figure 1. ORTEP plot of the molecular structure of **2**, showing 50% probability thermal ellipsoids.

To establish **2** unequivocally as a monomeric isocyanide adduct of triphenylborane, we carried out an X-ray structure determination. Structure investigations are rare for triorganoborane Lewis base adducts, and only a few molecular structures have been reported for Lewis bases with carbon donor atoms.[8c,12,13] To our knowledge **2** is so far the only crystallographically characterized isocyanide adduct of a triorganoborane Lewis acid.

A plot of the molecular structure of **2** is presented in Figure 1. It confirms that Ph_3B and **1** form a monomeric 1:1 adduct at low temperature. The boron atom in **2** resides in the center of a slightly distorted tetrahedron (smaller C1−B−C(Ph) angles, larger C(Ph)−B−C(Ph) angles; Table 1). Thus, the distortion is determined by the sterically less demanding isocyanide ligand. The distance B−C1 is shorter than the B−C(Ph) distances, which we attribute to the different hybridization (sp for C1, sp^2 for C(Ph)) of the carbon ligands at the boron atom.

Within the 3σ error range, the C1−N bond distance (1.148(2) Å) is comparable to the corresponding C−N distances found in the free 2-alkoxyphenyl isocyanide $CH_2(O-C_6H_4\text{-}2\text{-}NC)_2$[14] (1.153(3) and 1.150(3) Å).[14] The isocyanide in **2** is coordinated exclusively as a σ-donor to the borane fragment. However, the lack of back-bonding in **2** does not cause a shortening of the C−N distance when compared to tungsten(0) complexes of 2-alkoxyaryl isocyanides. In the tungsten complexes the effect of back-bonding is clearly visible by a reduction of ν(CN) up to 100 cm^{-1}.[15]

Coordinated **1** reacts upon cleavage of the Si−O bond under carbene formation,[1,3] if the isocyanide carbon is not deactivated for nucleophilic attack by back-bonding. The force constant for the CN bond of coordinated **1**

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Table 1. Selected Bond Distances (Å) and Angles (deg) for 2 and 3[a]

2		3	
B−C1	1.616(2)		1.633(2)
N−C1	1.148(2)		1.321(2)
N−C2	1.400(2)		1.401(2)
C2−C3	1.387(2)		1.391(2)
C2−C7	1.395(2)		1.375(2)
C3−C4	1.373(3)		1.387(2)
C4−C5	1.385(2)		1.401(2)
C5−C6	1.382(3)		1.393(2)
C6−C7	1.387(2)		1.378(2)
O−C1			1.3431(13)
O−C7	1.353(2)		1.3889(14)
O−Si	1.6796(12)		
B−C11	1.639(2)	B−C8	1.631(2)
B−C17	1.635(3)	B−C14	1.638(2)
B−C23	1.634(2)	B−C20	1.639(2)
O−C1−N			108.11(10)
O−C1−B			121.40(10)
N−C1−B	176.5(2)		130.47(10)
C1−N−C2	172.5(2)		111.01(10)
C1−O−C7			108.27(9)
Si−O−C7	131.25(10)		
N−C2−C3	118.66(14)		134.23(11)
N−C2−C7	119.19(14)		104.21(10)
C3−C2−C7	122.2(2)		121.57(11)
C2−C3−C4	119.3(2)		115.96(12)
C3−C4−C5	119.4(2)		121.80(12)
C4−C5−C6	121.2(2)		121.80(12)
C5−C6−C7	120.4(2)		115.24(12)
O−C7−C2	117.72(14)		108.40(10)
O−C7−C6	124.8(2)		127.97(11)
C2−C7−C6	117.5(2)		123.63(11)
C1−B−C11	103.40(13)	C1−B−C8	107.36(9)
C1−B−C17	106.32(13)	C1−B−C14	106.80(9)
C1−B−C23	107.33(13)	C1−B−C20	107.22(9)
C11−B−C17	113.64(14)	C8−B−C14	111.76(9)
C11−B−C23	112.67(13)	C8−B−C20	114.18(10)
C17−B−C23	112.62(14)	C14−B−C20	109.14(9)

[a] Estimated standard deviations are given in parentheses.

allows us to predict if the intramolecular cyclization can occur, and we have calculated a limiting value of approximately 1730 N m^{-1} for immediate carbene formation.[3b] The force constant for the CN bond in **2** was calculated to be 1918 N m^{-1}, which illustrates that coordination of **1** to Ph_3B actually activates the isocyanide toward cyclization. Consequently, **2** reacts in methanol at −30 °C in the presence of a catalytic amount of KF to give the ylidene complex **3** as colorless crystals in 73% yield (Scheme 1).

In the ^1H NMR spectrum of **3** (in $CDCl_3$) a broad singlet is found at 10.76 ppm for the resonance of the NH proton. No absorption in the isocyanide region is found in the IR spectrum. Once formed, **3** is stable toward dimerization and no indication for the formation of a dimer is obtained from the mass spectrum, which shows a signal at *m*/*z* 361 (M^+) with 98% intensity.

The molecular structure of **3** was determined by X-ray diffraction (Figure 2). The boron atom in **3** is tetrahedrally coordinated. All four B−C distances are identical within statistical limits. The B−C(Ph) distances are identical in **2** and **3**, but the B−C(ylidene) distance in **3** is significantly longer than the B−C(isocyanide) distance in **2** (Table 1). Again the different hybridization states (sp for the isocyanide, sp^2 for the ylidene) are responsible for the observed elongation of the B−C(ylidene) bond. The similarity in the four B−C distances is not surprising, since the B−C(ylidene) bond is not really dative but instead can be considered to be similar

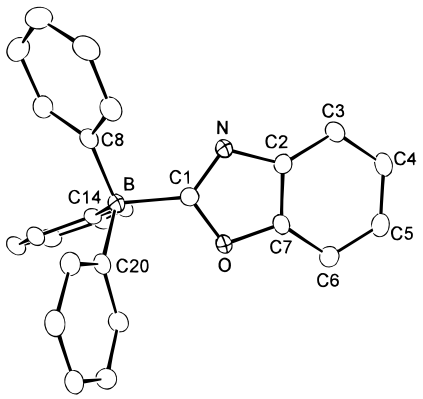
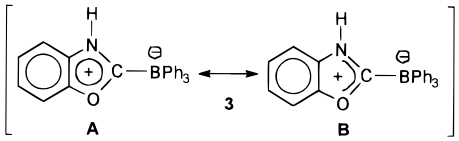


Figure 2. ORTEP plot of the molecular structure of **3**, showing 50% probability thermal ellipsoids.



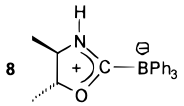


Figure 3. Resonance stabilization of **3** and schematic representation of complex **8**.

to a B−C(aryl) bond. The hybridizations of all four boron-bound carbon atoms are identical (sp^2).

The structural characterization of **3** allows a direct comparison of the molecular parameters for a triphenylborane-bound ylidene resulting from cyclization of an aromatic isocyanide with those of {$Ph_3B[\overline{CN(H)CH_2-CH_2O}]$} (**8**) (Figure 3), formed after cyclization of the aliphatic isocyanide in [$Ph_3B-CNCH_2CH_2-OSi(CH_3)_3$].[13] The boron−C(ylidene) distances in both complexes are almost identical (1.633(2) Å in **3** and 1.623(4) Å in **8**). In **3** one finds longer C(ylidene)−heteroatom distances and shorter distances between the heteroatoms and the other attached carbon atoms than in **8**. This indicates less stabilization of the carbene center by (p→p)π bonding from the heteroatoms (Figure 3, **B**) and a contribution of aromatic stabilization in **3** as shown by **A** in Figure 3. The former stabilization is not possible in **8**, containing, apart from the carbene carbon, only saturated carbon atoms in the five-membered chelate ring. Comparison of the structural parameters of the ylidene ligand in **3** to those found in other low-valent transition-metal complexes with the 1,2-dihydrobenzoxazol-2-ylidene ligand[1,3] reveals little sensitivity toward the attached metal fragment, showing the ylidene to act exclusively as a σ-donor no matter whether backbonding is feasible or not.

In the course of studying the preparation of **3** from **2** at room temperature, we obtained on one occasion, after multiple recrystallizations from methanol/acetone, colorless crystals of a new compound. The X-ray crystal structure analysis (Figure 4) revealed that this compound was the dimeric 2,5-dibora heterocycle **6**, depicted in Scheme 1.

The structure analysis shows a six-membered ring in which two Ph_2B fragments are bridged by a C- and N-diborated benzoxazol-2-yl group and by a C- and

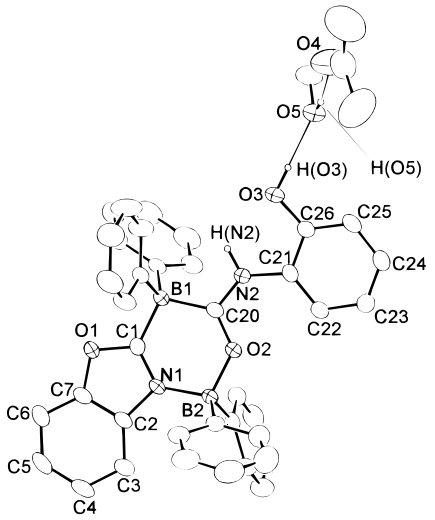


Figure 4. ORTEP plot of the molecular structure of **6**, showing 50% probability thermal ellipsoids.

Table 2. Selected Bond Distances (Å) and Angles (deg) for 6[a]

O1−C1	1.353(2)	C2−C7	1.373(3)
O1−C7	1.384(2)	C3−C4	1.385(3)
O2−C20	1.278(2)	C4−C5	1.386(4)
O2−B2	1.536(3)	C5−C6	1.380(3)
O3−C26	1.355(3)	C6−C7	1.379(3)
N1−C1	1.307(3)	C20−B1	1.622(3)
N1−C2	1.407(3)	C21−C22	1.375(3)
N1−B2	1.590(3)	C21−C26	1.394(3)
N2−C20	1.322(3)	C22−C23	1.381(3)
N2−C21	1.420(3)	C23−C24	1.370(3)
C1−B1	1.597(3)	C24−C25	1.371(3)
C2−C3	1.382(3)	C25−C26	1.383(3)
C1−O1−C7	106.3(2)	O1−C7−C2	108.5(2)
C20−O2−B2	128.7(2)	O1−C7−C6	127.5(2)
C1−N1−C2	108.3(2)	C2−C7−C6	124.0(2)
C1−N1−B2	125.6(2)	O2−C20−N2	116.9(2)
C2−N1−B2	126.1(2)	O2−C20−B1	126.1(2)
C20−N2−C21	132.6(2)	N2−C20−B1	117.0(2)
O1−C1−N1	111.1(2)	N2−C21−C22	125.1(2)
O1−C1−B1	121.5(2)	N2−C21−C26	114.7(2)
N1−C1−B1	127.4(2)	C22−C21−C26	120.2(2)
N1−C2−C3	133.5(2)	C21−C22−C23	119.8(2)
N1−C2−C7	105.7(2)	C22−C23−C24	120.2(2)
C3−C2−C7	120.8(2)	C23−C24−C25	120.4(2)
C2−C3−C4	116.4(2)	C24−C25−C26	120.3(2)
C3−C4−C5	121.7(2)	O3−C26−C21	116.6(2)
C4−C5−C6	122.4(2)	O3−C26−C25	124.2(2)
C5−C6−C7	114.8(2)	C21−C26−C25	119.2(2)

[a] Estimated standard deviations are given in parentheses.

O-diborated (2-hydroxyphenyl)formamide. Complex **6** crystallizes with one molecule each of methanol and acetone per formula unit, which are hydrogen-bonded to the phenolic hydrogen and to each other (the positional parameters for H(N2), H(O3) and H(O5) were identified and refined in the least-squares refinement). Bond distances and angles of the benzoxazol-2-ylidene fragment in **6** (C1−C7, N1, O1; Table 2) are within statistical limits identical with those found for the same fragment in **3**. However, the C1−B1 distance (1.597(3) Å) is now even shorter than in **3**. Formation of the N1−B2 bond is not surprising, since we have shown that coordinated 1,2-dihydrobenzoxazol-2-ylidene ligands are easily alkylated at the carbene nitrogen atom.[1,3]

Because **3** is stable against dimerization once it has formed, we assume that formation of **6** can only have occurred after dimerization of **2**. This is conceivable, since all reactions leading to isolation of **6** were carried out at room temperature. We suspect that the formation of **6** results from the partial hydrolysis of the intermediate bis(benzoxazol-2-yl)-bridged 2,5-diborapyrazine **7**, which could have been formed in the reaction sequence shown in Scheme 1.

In order to gain insight into the formation of **6**, we wanted to evaluate the possibility of synthesizing **7** intentionally. Although we could obtain and characterize the dimeric compounds **4** and **5** unambiguously by thermal dimerization of **2** and consecutive desilylation, we have not yet been able to convert **5** into the cyclic bis(ylidene) complex **7** and to find any indication of benzene evolution at this stage. The attempted dimerization of the ylidene complex **3** under thermal conditions failed as well. Further investigations toward a controlled synthesis of **7** and related compounds are currently going on.

Conclusions

2-(Trimethylsiloxy)phenyl isocyanide (**1**) reacts at low temperature with Ph_3B to give the first monomeric, crystallographically characterized Ph_3B isocyanide (1:1) adduct **2**. Desilylation of **2** leads to the ylidene adduct of Ph_3B **3**, which is thermally stable. The isocyanide complex **2** dimerizes at room temperature to the 2,5-dibora-2,5-dihydropyrazine **4**. Desilylation of **4** is possible. In the course of this reaction an ylidene-bridged, six-membered 2,5-dibora heterocycle was obtained by a presently unknown mechanism.

Experimental Section

All operations were performed under an atmosphere of dry argon by using Schlenk and vacuum techniques. Solvents were dried by standard methods and distilled prior to use. NMR spectra were recorded on Bruker AM 250 (250 MHz) or AM 270 (270 MHz) instruments. Infrared spectra were taken on a Perkin-Elmer 983 instrument in KBr. Elemental analyses (C, H, N) were performed at the Freie Universität Berlin on a Heraeus CHN-Rapid elemental analyzer. Mass spectra (EI, 70 eV) were recorded on a Varian MAT 711 instrument. 2-(Trimethylsiloxy)phenyl isocyanide (**1**) was synthesized according to the method of Jutzi.[10] Triphenylborane was purchased from Aldrich and was used as received.

(2-(Trimethylsiloxy)phenyl isocyanide)−Triphenylborane (2). A solution of triphenylborane (3.44 g, 14 mmol) in 50 mL of dichloromethane was cooled to −60 °C, causing BPh_3 to precipitate. **1** (2.72 g, 14 mmol) was slowly added to the stirred suspension. A clear yellowish solution was formed, and stirring was continued for 1 h at −60 °C. The solvent was removed at −30 °C, and **2** was obtained as a white solid in quantitative yield. Dissolving a 900 mg (2 mmol) sample of **2** in 20 mL of diethyl ether and cooling to −26 °C gave colorless crystals of **2** suitable for X-ray diffraction. The major fraction (5.1 g, 12 mmol) was directly converted to **3**. IR: ν 2244 (s, CN). MS (LR, 70 eV, m/z): 866 (M_2^+, 7.1), 789 (M_2^+ − Ph, 9.5), 624 [M_2^+ − Ph − (C_6H_4-2-$OSiMe_3$), 24.1], 551 [M_2^+ − Ph − (C_6H_4-2-$OSiMe_3$) − $SiMe_3$, 33.0], 433 (M^+, 12.0), 360 (M^+ − $SiMe_3$, 26.1), 165 (BPh_2^+, 82.9), 73 ($SiMe_3$, 100). Elemental analyses were impossible to obtain due to the rapid dimerization of **2** at room temperature, giving **4** with identical values for C, H, and N.

(1,2-Dihydrobenzoxazol-2-ylidene)−Triphenylborane (3). A 50 mL portion of methanol was condensed onto a cooled sample of **2** (5.10 g, 12 mmol) obtained from the reaction described above. A catalytic amount of KF (10 mg, 0.2 mmol) was added, and the suspension was stirred at −30 °C for 2 h. The reaction mixture was warmed to 0 °C, giving a clear

Table 3. Summary of Crystal Structure Data[a]

	2	3	6
cryst size, mm	0.41 × 0.35 × 0.17	0.36 × 0.29 × 0.12	0.55 × 0.35 × 0.15
formula	$C_{28}H_{28}BNOSi$	$C_{25}H_{20}BNO$	$C_{42}H_{40}B_2N_2O_5$
fw	433.44	361.26	674.42
space group	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)
a, Å	11.007(4)	9.535(3)	9.201(5)
b, Å	11.374(3)	9.945(2)	20.108(8)
c, Å	11.346(4)	10.759(5)	10.379(2)
α, deg	108.03(2)	80.53(3)	80.33(2)
β, deg	98.82(3)	79.91(3)	108.01(3)
γ, deg	108.72(2)	73.81(2)	90.71(4)
V, Å^3	1228(2)	957.4(6)	1799(2)
Z	2	2	2
d_c, g/cm^3	1.172	1.253	1.245
d_o, g/cm^3	1.16	1.26	1.23
μ_c, cm^{-1}	1.10	0.70	0.75
radiation (*λ*, Å)		Mo Kα, 0.710 73	
data collecn temp, °C	−120(2)	−100(2)	−120(2)
2*θ* range, deg	$4.5 \le 2\theta \le 46$	$4.5 \le 2\theta \le 50$	$2 \le 2\theta \le 50$
hkl range	$-11 \le h \le 12$, $-11 \le k \le 11$, $-11 \le l \le 0$	$-11 \le h \le 12$, $-12 \le k \le 12$, $0 \le l \le 13$	$0 \le h \le 10$, $-23 \le k \le 23$, $-11 \le l \le 11$
scan speed (*θ*), deg/min	variable: min 1.65, max 16.5	variable: min 2.35, max 16.5	variable: min 1.65, max 5.49
no. of unique data	3544	4109	6331
no. of obsd data, $F_o^2 \ge 3\sigma(F_o^2)$	2979	3598	4283
R, %[b]	3.35	3.89	4.71
R_w, %[b]	5.05	5.99	6.34
p factor[b]	0.08	0.08	0.08
GOF[b]	1.178	1.333	1.351
no. of variables	402	334	478
max shift/error	<0.01	<0.01	0.02
residual electr dens, e/Å^3	−0.10, 0.31	−0.09, 0.37	−0.09, 0.28

[a] Estimated standard deviations are given in parentheses. [b] See ref 19.

solution, from which a colorless solid started to precipitate after 5 min. Stirring was continued at 0 °C for 2 h and at room temperature overnight. The solvent was removed *in vacuo*, and the white solid was recrystallized from acetone/methanol at −26 °C (3.11 g, 73%). Anal. Calcd for $C_{25}H_{20}BNO$ (M_r = 361.25): C, 83.12; H, 5.58; N, 3.88. Found: C, 82.81; H, 5.64; N, 3.61. ^{1}H NMR (250 MHz, acetone-d_6): *δ* 7.05 (tt, 3 H, BPh_3 4-C*H*), 7.15 (td, 6 H, BPh_3 3,5-C*H*), 7.34 (dd, 6 H, BPh_4 2,6-C*H*), 7.46 (m, 2 H, Ar *H*), 7.68 (m, 1 H, Ar *H*), 7.78 (m, 1 H, Ar *H*). The N*H* resonance at *δ* 10.76 was only observed in $CDCl_3$. ^{11}B NMR (28.69 MHz, acetone-d_6): *δ* −9.2 (s). MS (LR, 70 eV, *m*/*z*): 361 (M^+, 98.0), 284 (M^+ − Ph, 21.9), 165 (BPh_2^+, 100).

1,4-Bis(2-(trimethylsiloxy)phenyl)-2,2,3,5,5,6-hexaphenyl-2,5-dibora-2,5-dihydropyrazine (4). A solution of triphenylborane (5.49 g, 23 mmol) in 70 mL of dichloromethane was cooled to −60 °C, causing the BPh_3 to precipitate. **1** (4.34 g, 23 mmol) was slowly added to the stirred suspension. A clear yellowish solution was formed, and stirring was continued for 1 h at −60 °C. The solvent was removed at 0 °C. The residue was kept at 80 °C for 30 min by the use of a water bath, causing the reaction mixture to turn dark green. The residue was treated with hot pentane (80 mL) and filtered. Washing with pentane and drying under vacuum gave **4** as a white powder (4.5 g, 46%). Anal. Calcd for $C_{56}H_{56}B_2N_2O_2Si_2$ (M_r = 866.86): C, 77.59; H, 6.51; N, 3.23. Found: C, 77.07; H, 6.53; N, 3.18. MS (LR, 70 eV, *m*/*z*): 866 (M^+, 24.5), 789 (M^+ − Ph, 27.9), 712 (M^+ − 2Ph, 24.1), 598 [M^+ − Ph − Me_3SiO-2-C_6H_4-NC, 20.4], 551 [M^+ − Ph − (C_6H_4-2-OSiMe_3) − SiMe_3, 19.6], 521 (M^+ − 2Ph − Me_3SiO-2-C_6H_4-NC, 13.6), 433 [M^+ − Me_3SiO-2-C_6H_4-NC-BPh_3, 17.8], 360 (M^+ − Me_3SiO-2-C_6H_4-NC-BPh_3 − SiMe_3, 30.7), 268 ($Ph_3B{-}CN^+$, 28.7), 165 (BPh_2^+, 37.9), 73 (SiMe_3, 100).

1,4-Bis(2-hydroxyphenyl)-2,2,3,5,5,6-hexaphenyl-2,5-dibora-2,5-dihydropyrazine (5). A suspension of **4** (2.0 g, 2.3 mmol) in 60 mL of $CHCl_3$/MeOH (1:1) was treated with a catalytic amount of KF (10 mg, 0.2 mmol) and heated under reflux for 2 days. The solvent was removed *in vacuo*, and the residue was extracted with 100 mL of methanol. After filtration the clear solution was evaporated to dryness, and **5** was obtained as a white powder (1.03 g, 62%). Anal. Calcd for $C_{50}H_{40}B_2N_2O_2$ (M_r = 722.50): C, 83.12; H, 5.58; N, 3.88. Found: C, 82.22; H, 5.64; N, 3.62. MS (LR, 70 eV, *m*/*z*): 722 (M^+, 3.2), 644 (M^+ − H − Ph, 13.7), 566 (M^+ − 2H − 2Ph, 3.0), 527 (M^+ − Ph − O-2-C_6H_4-NC, 11.0), 449 (M^+ − 2Ph − HO-2-C_6H_4-NC, 16.5), 360 (M^+ − H − HO-2-C_6H_4NC−BPh_3, 100), 284 (M^+ − H − Ph − HO-2-C_6H_4NC−BPh_3, 41.9), 165 (BPh_2^+, 55.1).

Preparation of 6. Complex **6** was obtained in approximately 20% yield (relative to **2**) by stirring 2 g of **2** in methanol for 3 days at room temperature followed by multiple recrystallization of the product from wet methanol/acetone.

Crystal Structure Analyses. Crystals of **2** and **6** are temperature-sensitive (dimerization or loss of solvent), while **3** is stable at room temperature. Suitable specimens of **2** and **6** were selected at −120 °C using a device similar to that described by Veith[16] and mounted in the cold stream (−120(2) °C) of an Enraf-Nonius CAD-4 diffractometer. A crystal of **3** was selected in air and mounted at −100(2) °C on an Enraf-Nonius CAD-4 diffractometer. Important crystal and data collection details are listed in Table 3. Data for all three compounds were collected using *ω*−2*θ* scans. Raw data were reduced to structure factors[17] (and their esd's) by correcting for scan speed, Lorentz, and polarization effects. No crystal decay was detected, and no absorption corrections were applied. The space group was found to be $P\bar{1}$ for all three compounds. All three structures were solved by direct meth-

(16) Veith, M.; Bärnighausen, H. *Acta Crystallogr.* **1974**, *B30*, 1806.
(17) Neutral scattering factors were used: *International Tables for X-Ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.2B. Terms of anomalous dispersion from: *International Tables for X-Ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.3.1.
(18) Churchill, M. R. *Inorg. Chem.* **1972**, *12*, 1213.
(19) MolEN: Molecular Structure Solution Procedures, Program Descriptions; Enraf-Nonius, Delft, The Netherlands, 1990. Definition of residuals: $R = \sum||F_o| - |F_c||/\sum|F_o|$, $R_w = [\sum w||F_o| - |F_c||^2/\sum w|F_o|^2]^{1/2}$, and GOF = $[\sum w||F_o| - |F_c||^2/(n_o - n_p)]^{1/2}$ with n_o = number of structure factors, n_p = number of parameters, $w = 1/[\sigma_F]^2$, $\sigma_F = \sigma_{F^2}/2F$, and $\sigma_{F^2} = \{[\sigma_I]^2 + [pF^2]^2\}^{1/2}$.
(20) Johnson, C. K. ORTEP II; Report ORNL-5138; Oak Ridge National Laboratory: Oak Ridge, TN, 1971.

ods. The positional parameters for all non-hydrogen atoms were refined by using first isotropic and later anisotropic thermal parameters. Difference Fourier maps calculated at this stage showed for all three molecules the positional parameters of the hydrogen atoms. All hydrogen positions were refined for **2** and **3**. For **6** the positional parameters for all N- and O-bonded hydrogens as well as those for the methanol molecule were refined; the others were added to the structure model at calculated positions (d(C−H) = 0.95 Å)[18] and are unrefined. The isotropic temperature factors for hydrogens were fixed to be 1.3 times the B_{eq} value of the parent atom. All calculations were carried out with the MolEN package.[19] ORTEP[20] was used for all molecular drawings.

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Supporting Information Available: For **2**, **3**, and **6**, tables of atomic coordinates, all bond distances and angles, and anisotropic thermal parameters and figures giving additional atom labeling (15 pages). Ordering information is given on any current masthead page.

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