Tris(2,6-dimethoxyphenyl)borane and its adducts

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Abstract

Tris(2,6-dimethoxyphenyl)borane, Φ_3B (Φ = 2,6-$(MeO)_2C_6H_3$), an air-stable crystalline compound, formed isolable 1 : 1 adducts with ammonia and some primary amines but not with tertiary amines, secondary amines, or sec-alkylamines. Some tetraalkylammonium tris(2,6-dimethoxyphenyl)cyanoborates $[R_4N][\Phi_3B-CN]$ are soluble both in water and in benzene, and the stearyltrimethylammonium salt is soluble even in n-hexane. The freezing point depression measurements for some tetraalkylammonium salts suggested that they are associated in benzene by several molecules.

1. Introduction

We have been interested in the chemistry of 2,6-dimethoxyphenyl derivatives [1] since (a) the organolithium reagent ΦLi (Φ=2,6-$(MeO)_2C_6H_3$) is easily prepared from direct lithiation of 1,3-dimethoxybenzene with butyllithium, (b) the combination of steric and electronic effects of the Φ group often resulted in compounds having unusual properties compared with common phenyl derivatives, (c) the 3,5-positions of the Φ group are activated and are easily substituted to alter the steric and electronic effects and (d) the ^{1}H NMR spectra are very simple, sharp and useful for the characterization of the derivatives. During the study of tris(2,6-dimethoxyphenyl)carbenium salts $[\Phi_3C]X$ [1], we have also been interested in the properties of tris(2,6-dimethoxyphenyl)borane (Φ_3B), the isoelectronic compound [2].

2. Results and discussion

2.1. Preparation of tris(2,6-dimethoxyphenyl)borane, Φ_3B

Φ_3B was prepared by the reaction of ΦLi and boron trifluoride diethyl etherate [2]. In contrast to phenyl-

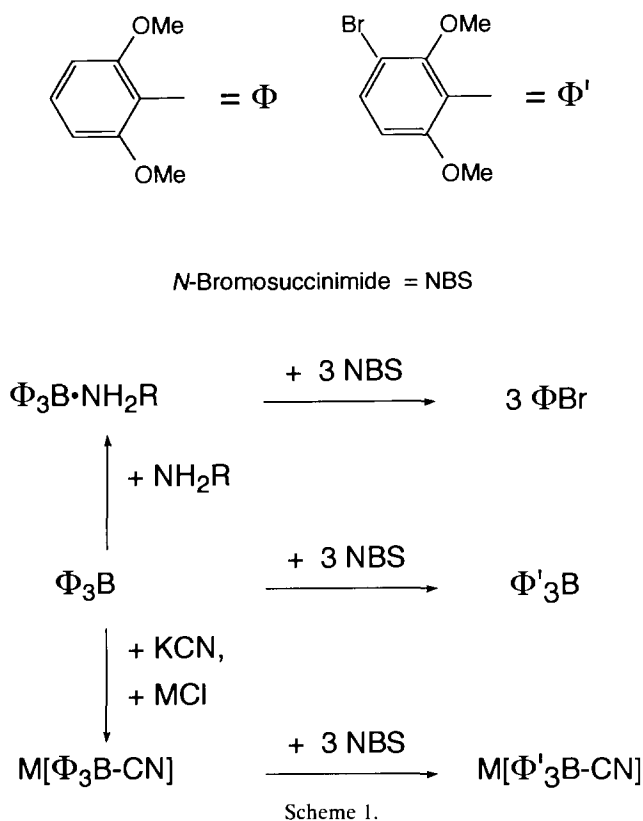lithium, the borate salt $Li[\Phi_4B]$ was not produced even if ΦLi was used in excess. When trimethoxyborane was used in place of boron trifluoride diethyl etherate, white crystals of hydroxytris(2,6-dimethoxyphenyl)-borate $Li[\Phi_3B-OH]$ were obtained. Φ_3B is an air-stable crystalline compound soluble in a variety of organic solvents, although it decomposes in acidic conditions.

Treatment of Φ_3B with *N*-bromosuccinimide (NBS) in acetone resulted in tris(3-bromo-2,6-dimethoxyphenyl)borane (Φ'_3B) (Φ' = 3-Br-2,6-$(MeO)_2C_6H_2$; see Scheme 1).

2.2. Amine adducts of Φ_3B

Owing to the presence of a vacant 2p orbital, triorganoboranes (R_3B), in general, can accept the fourth nucleophile to form an $R_3B \cdot L$ adduct or $[R_3BX]^-$ anion [3,4]. Triphenylborane has been known to form 1 : 1 adduct with tertiary amines [3]. While some primary amines NH_2R (R = Me, Et, n-Bu) and ammonia formed isolable 1 : 1 adducts $\Phi_3B \cdot NH_2R$, tertiary amines, secondary amines and pyridines did not form isolable adducts with Φ_3B. Isobutylamine also formed an analogous adduct, but sec-butylamine did not. This result is consistent with the high kinetic stability of $[\Phi_3C]ClO_4$ in secondary alcohols [1]. In contrast, no evidence was obtained that Φ'_3B formed any amine adduct. It is expected that the presence of a bromine atom in the Φ' group would force the adjacent methoxy

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OMe

OMe

OMe = Φ

Br OMe

OMe

OMe = Φ'

N-Bromosuccinimide = NBS

$\Phi_3B \cdot NH_2R$ $\xrightarrow{+ \ 3\,NBS}$ $3\ \Phi Br$

$\uparrow\ + NH_2R$

Φ_3B $\xrightarrow{+ \ 3\,NBS}$ Φ'_3B

$\downarrow\ + KCN,$
$+ MCl$

$M[\Phi_3B\text{-}CN]$ $\xrightarrow{+ \ 3\,NBS}$ $M[\Phi'_3B\text{-}CN]$

Scheme 1.

group away towards the boron atom by the so-called "buttressing effect" [5], and the boron atom in Φ'_3B must be more confined by three such methoxy groups to protect the coordination of the amine molecule. Nitriles, aldehydes, dimethyl sulphoxide and nitroalkanes did not form isolable adduct with Φ_3B. ^1H and ^{13}C NMR spectral data for $\Phi_3B \cdot NH_2R$ are given in Tables 1 and 2, respectively.

When $\Phi_3B \cdot NH_2^iBu$ was mixed with an equimolar amount of methylamine in benzene-d_6, the ^1H NMR spectrum showed the presence of two adducts, $\Phi_3B \cdot NH_2^iBu$ and $\Phi_3B \cdot NH_2Me$, in a 43 : 57 ratio, in addition to the free amines, which suggested the occurrence of partial dissociation of the amine ligand in

$\Phi_3B \cdot NH_2R$. Whereas treatment of Φ_3B with NBS gave Φ'_3B, treatment of $\Phi_3B \cdot NH_2R$ with NBS resulted in Φ–boron bond cleavage to give 1-bromo-2,6-dimethoxybenzene (ΦBr).

2.3. Cyano-tris(2,6-dimethoxyphenyl)borates

Although Φ_3B is insoluble in water, it is soluble in an aqueous solution of potassium cyanide to form $K[\Phi_3B\text{-}CN]$. The salt was best isolated from methanol solution containing potassium cyanide, and this was used for the preparation of various tetraalkylammonium and alkyltris(2,6-dimethoxyphenyl)phosphonium salts by cation exchange in acetone, methanol, benzene or n-hexane. The phosphonium cations were chosen because of the ease of preparation of the chlorides, $[\Phi_3P\text{-}R]Cl$, which are very soluble in water and alcohols [6]. Treatment of $[\Phi_3P\text{-}R][\Phi_3B\text{-}CN]$ with NBS gave cyanotris(3-bromo-2,6-dimethoxyphenyl)borates such as $[\Phi_3P\text{-}Me][\Phi'_3B\text{-}CN]$. The Φ groups bonded to the phosphorus atom were not brominated even with excess of NBS, probably owing to the cationic character. $K[\Phi_3B\text{-}CN]$ reacted with silver perchlorate in water to precipitate silver cyanide and Φ_3B. All attempts to obtain analogous borates $M[\Phi_3B\text{-}X]$ failed with sodium hydride, sodium chloride, sodium iodide, sodium azide, sodium cyanate and potassium thiocyanate. Lithium hydroxide and methoxide reacted to give $Li[\Phi_3B\text{-}OH]$.

It is well known that potassium and tetraalkylammonium tetraphenylborates are practically insoluble in water, and that sodium tetraphenylborate has been used as a reagent for quantitative analysis of these cations. The solubilities of $[\Phi_3B\text{-}CN]^-$ salts prepared in the present work are shown in Table 3. Most $[\Phi_3B\text{-}CN]^-$ salts are soluble in hot or cold water, and an aqueous solution of $K[\Phi_3B\text{-}CN]$ showed UV spectral absorptions at λ_{max} (log ϵ) 207 (4.91), 235 (4.34, sh) and 273 (3.36) nm. Tetraalkylammonium tetraphenylborates are insoluble in organic solvents except for acetone and haloalkanes, but analogous $[\Phi_3B\text{-}CN]^-$ salts are fairly soluble in alcohols, acetone and

Table 1
^1H NMR spectral data (δ/ppm, in $CDCl_3$) for tris(2,6-dimethoxyphenyl)borane and its amine adducts

Compound	4-H [a]	3,5-H [b]	MeO [c]	Others [d]
Φ_3B	7.18	6.47	3.45	
$\Phi_3B \cdot NH_3$	7.00	6.47	3.32	5.48bs
$\Phi_3B \cdot NH_2Me$	6.97	6.38	3.41	5.74bs, 2.19t [6]
$\Phi_3B \cdot NH_2Et$	6.97	6.38	3.41	5.72bs, 2.53q [7], 1.11t [7]
$\Phi_3B \cdot NH_2^nBu$	6.97	6.37	3.41	5.71bs, 2.48m (2H), 1.47 m (2H), 1.23 m (2H), 0.86t [7]
$\Phi_3B \cdot NH_2^iBu$	6.97	6.37	3.41	5.76bs, 2.50m (2H), 1.71 m (1H), 1.25d [7] (6H)
Φ'_3B	7.44 [b]	6.52	3.47 and 3.41	
$Li[\Phi_3B\text{-}OH]$	6.94	6.46	3.26	4.48s

[a] Triplet with J_H 7–8 Hz. [b] Doublet with J_H 7–8 Hz. [c] Singlet. [d] s = Singlet, bs = broad singlet, d = doublet, t = triplet, q = quartet and m = multiplet; the coupling constants (Hz) are given in square brackets.

Table 2
^{13}C NMR spectral data (δ/ppm, in CDCl$_3$) for tris(2,6-dimethoxyphenyl)borane and its amine adducts

Compound	C-1 [a]	C-2,6	C-3,5	C-4	OMe	Others
Φ_3B	129.8	162.6	105.2	130.2	56.6	
Φ_3B · NH$_3$	–	163.4	106.2	125.2	56.1	
Φ_3B · NH$_2$Me	–	163.6	103.9	125.0	55.3	29.5
Φ_3B · NH$_2$Et	–	163.5	103.8	125.0	55.3	38.3, 16.2
Φ_3B · NH$_2$^{n}Bu	–	163.5	103.8	124.9	55.3	42.5, 33.2, 19.9, 13.8
Φ_3B · NH$_2$^{i}Bu	–	163.5	103.7	124.9	55.2	50.3, 29.4, 20.2
Φ'_3B	–	161.8, 158.7	108.5, 108.0	134.7	61.4, 56.2	
Li[Φ_3B–OH]	–	163.0	107.1	124.6	56.7	

[a] The resonance is very weak, in general.

haloalkanes. Most [Φ_3B–CN]$^-$ salts are poorly soluble in diethyl ether, but they are fairly soluble in benzene. Stearyltrimethylammonium salt is soluble even in n-hexane and in cyclohexane (ca. 6×10^{-4} M, at 23°C). Similar UV spectra to that of K[Φ_3B–CN] were obtained for [Me$_3$(C$_{18}$H$_{37}$)N][Φ_3B–CN] both in ethanol and in n-hexane. Ford and co-workers [4d,e] reported that some tetraalkylammonium tetraalkylborates are liquid at room temperature and that these salts are soluble in benzene but insoluble in water and in alkanes. [Φ_3P–R][Φ'_3B–CN] are much more soluble than [Φ_3P–R][Φ_3B–CN] in benzene. Owing to the "buttressing effect", the free rotation of the MeO group around the O–C^2 must be frozen to be situated close to the centre of the negative charge around the B–CN moiety. The negative centre of the [Φ_3B–CN]$^-$ anion

must then be confined by these methoxy groups to decrease the electrostatic interaction with the cation.

The tetraalkylammonium salts of [Φ_3B–CN]$^-$ and [Φ'_3B–CN]$^-$ anions are thermally stable in aromatic hydrocarbons. Thus, toluene solutions of [Me$_3$(Ph-CH$_2$)N][Φ_3B–CN] and [Φ_3P–Me][Φ'_3B–CN] in sealed glass tubes showed no change in their ^{1}H NMR spectra after heating at 120°C for 15 h. These salts in dimethyl sulphoxide at 160°C, however, decomposed gradually to give black suspensions. Since [Φ_3P–Me][Φ'_3B–CN] are more soluble in organic solvents, we have attempted to isolate the tetraalkylammonium salts of the [Φ'_3B–CN]$^-$ anion. As expected, they seemed to be too soluble in many solvents to crystallize enough for isolation or purification.

The molar conductivity of some salts was measured

Table 3
Solubilities of organoborates [a]

Cation	Anion	Solvent [b]							
		A	B	C	D	E	F	G	H
K$^+$	[Φ_3B–CN]$^-$	O	O	×	×	×	×	×	×
[Me$_3$(PhCH$_2$)N]$^+$	[Φ_3B–CN]$^-$	⊚	⊚	O	O	⊚	×	⊚	×
	[Ph$_4$B]$^-$	×	×	×	×	O	×	×	×
[Me$_3$(HOCH$_2$CH$_2$)N]$^+$	[Φ_3B–CN]$^-$	O	⊚	O	O	O	×	O	×
	[Ph$_4$B]$^-$	×	×	×	×	O	×	×	×
[Me$_3$(C$_{18}$H$_{37}$)N]$^+$	[Φ_3B–CN]$^-$	×	⊚	⊚	O	⊚	O	⊚	O
	[Ph$_4$B]$^-$	×	O	×	×	⊚	×	O	×
[Me$_4$N]$^+$	[Φ_3B–CN]$^-$	O	O	×	×	×	×	×	×
	[Ph$_4$B]$^-$	×	×	×	×	O	×	×	×
[Et$_4$N]$^+$	[Φ_3B–CN]$^-$	⊚	⊚	⊚	O	⊚	×	⊚	×
	[Ph$_4$B]$^-$	×	×	×	×	O	×	×	×
[Φ_3P–Me]$^+$	[Φ_3B–CN]$^-$	×	⊚	O	O	O	×	×	×
	[Φ'_3B–CN]$^-$	×	⊚	O	O	⊚	×	⊚	×
	[Ph$_4$B]$^-$	×	O	×	×	⊚	×	×	×
[Φ_3P–Bu]$^+$	[Φ_3B–CN]$^-$	×	⊚	O	O	⊚	×	O	×
	[Φ'_3B–CN]$^-$	×	⊚	O	O	⊚	×	⊚	×
	[Ph$_4$B]$^-$	×	O	×	×	⊚	×	×	×
[Φ_3P–CH$_2$Ph]$^+$	[Φ_3B–CN]$^-$	×	⊚	O	O	⊚	×	×	×
	[Ph$_4$B]$^-$	×	O	×	×	⊚	×	×	×

[a] ⊚, The salt (0.100 g) is soluble in 1–5 ml at 20°C; O, soluble in 5–10 ml on heating; ×, incompletely soluble under these conditions; Φ = 2,6-(MeO)$_2$C$_6$H$_3$ and Φ' = 3-Br-2,6-(MeO)$_2$C$_6$H$_2$. [b] A = water; B = methanol; C = 2-propanol; D = octanol; E = acetone; F = diethyl ether; G = benzene; and H = n-hexane.

Table 4

Molar conductivities of borates at infinite dilution. Λ^0_m /S cm^2 mol^{-1}, at 25°C

Cation	Anion	Solvent		
		MeCN	H$_2$O	ClCH$_2$CH$_2$Cl
[Me$_3$(PhCH$_2$)N]$^+$	[Φ_3B–CN]$^-$	126	56	42 [a]
	[Ph$_4$B]$^-$	141		
[Me$_3$(HOCH$_2$CH$_2$)N]$^+$	[Φ_3B–CN]$^-$	133		
	[Ph$_4$B]$^-$	144		
[Et$_4$N]$^+$	[Φ_3B–CN]$^-$	130	54	67 [a]
	[Ph$_4$B]$^-$	139		
[Φ_3P–Me]$^+$	[Φ'_3B–CN]$^-$	92		
[Φ_3P–Bu]$^+$	[Φ_3B–CN]$^-$	100		

[a] Values at 10^{-5} M.

in acetonitrile, in water and in 1,2-dichloroethane (Table 4). These salts must be completely dissociated both in acetonitrile and in water, as observed by the linear relationship to the square root of concentration, except in 1,2-dichloroethane. The molar ionic conductivities were obtained for [Φ_3B–CN]$^-$ as 45.1 S cm^2 mol^{-1} (in acetonitrile) and 21.6 S cm^2 mol^{-1} (in water) and for [Φ_3P–Me]$^+$ as 54.9 S cm^2 mol^{-1} (in acetonitrile). The

freezing point depression was measured for benzene solutions of [Me$_3$(PhCH$_2$)N][Φ_3B–CN] and [Et$_4$N][Φ_3B–CN]. Although the values were too small to obtain a reliable mean molecular weight (see Experimental), it is obvious that these salts are associated by several molecules in benzene to form clusters. The benzene solutions did not show any conductivity.

2.4. ^1H NMR spectra

The ^{1}H NMR spectra of Φ_3B and its derivatives show a triplet due to the 4-H of the Φ group, a doublet due to 3,5-H and a sharp singlet due to 2,6-OMe protons (Tables 1 and 5). Those of Φ'_3B and [Φ'_3B–CN]$^-$ salts show two doublets due to 4-H and 5-H and two sharp singlets due to OMe protons. In chloroform-d_1, the proton chemical shifts of [Φ_3B–CN]$^-$ anion are affected by the counter cation, probably owing to their association; 2,6-OMe proton resonance was observed at δ 3.28 ± 1 ppm for [Me$_3$RN]$^+$ salts and at δ 3.35 ± 1 ppm for [Et$_4$N]$^+$ and [Φ_3P–R]$^+$ salts. The proton chemical shifts of [Φ_3P–Me]$^+$ cation are also affected

Table 5

^{1}H NMR spectral data (δ/ppm) for some cyanotris(2,6-dimethoxyphenyl)borates

Compound	Solvent	4-H [a]	3,5-H [b]	MeO [c]	Others
K[Φ_3B–CN]	D$_2$O	7.08	6.57	3.36	
[Me$_4$N][Φ_3B–CN]	D$_2$O	7.06	6.56	3.36	3.16s
[Me$_3$(HOCH$_2$CH$_2$)N][Φ_3B–CN]	CDCl$_3$	6.88	6.36	3.27	5.05br, 3.68br, 3.03br, 2.71s
[Me$_3$(C$_{18}$H$_{37}$)N][Φ_3B–CN]	CDCl$_3$	6.87	6.36	3.29	3.0–2.9br, 2.81s, 1.5–1.4br, 1.26br, 0.88t
[Et$_4$N][Φ_3B–CN]	D$_2$O	7.06	6.57	3.36	3.23, [d] 1.25 [a]
	CDCl$_3$	6.85	6.35	3.35	2.88, [d] 1.04 [a]
	CD$_2$Cl$_2$	6.85	6.35	3.32	2.97, [d] 1.10 [a]
	C$_6$D$_6$	7.09	6.51	3.43	2.63, [d] 0.70 [a]
	Δ [e]	+0.24	+0.16	+0.11	−0.34, −0.40

		4-H [a]	3,5-H [b]	MeO [c]	NMe$_3$ [c]	NCH$_2$ [c]	Ph [f]
[Me$_3$(PhCH$_2$)N][Φ_3B–CN]	D$_2$O	7.06	6.57	3.37	3.08	4.48	7.6–7.5
	CDCl$_3$	6.85	6.33	3.26	2.72	4.14	7.4–7.3
	CD$_2$Cl$_2$	6.85	6.32	3.29	2.79	4.20	7.5–7.4
	C$_6$D$_6$	7.09	6.49	3.36	2.50	4.17	7.2–7.1
	Δ [e]	+0.24	+0.17	+0.07	−0.29	−0.03	−0.3

		4'-H [a]	3',5'-H [b]	Me'O [c]	4-H [a]	3,5-H [b]	MeO [c]	P–R
[Φ_3P–Me][Φ_3B–CN]	CDCl$_3$	6.82	6.37	3.34	7.49	6.58	3.51	2.55 [g]
[Φ_3P–Bu][Φ_3B–CN]	CDCl$_3$	6.83	6.37	3.35	7.48	6.57	3.55	– [h]
[Φ_3P–CH$_2$Ph][Φ_3B–CN]	CDCl$_3$	6.83	6.38	3.34	7.42	6.49	3.55	7.01br, 4.71 [g]
[Φ_3P–Me][Ph$_4$B]	CDCl$_3$	– [i]	– [i]	–	– [i]	6.51	3.44	2.50 [g]

		4'-H [b]	5'-H [b]	Me'O [c]	4-H [a]	3,5-H [b]	MeO [c]	P–Me [g]
[Φ_3P–Me][Φ'_3B–CN]	CDCl$_3$	7.10	6.34	3.36, 3.34	7.51	6.60	3.54	2.57
	CD$_2$Cl$_2$	7.12	6.37	3.37, 3.29	7.54	6.63	3.55	2.59
	C$_6$D$_6$	7.40	6.32	3.78, 3.29	7.27	6.35	3.18	2.39
	Δ [e]	+0.28	−0.05	+0.41, 0.00	−0.27	−0.28	−0.37	−0.20
[Φ_3P–Bu][Φ'_3B–CN]	CDCl$_3$	7.10	6.33	3.37, 3.34	7.49	6.58	3.56	– [j]

[a] Triplet with J_H = 7–8 Hz. [b] Doublet with J_H = 7–8 Hz or double doublets with J_H = 8 Hz and J_P = 5–6 Hz. [c] Singlet. [d] Quartet with J_H = 7–8 Hz. [e] Differences between the δ values measured for CD$_2$Cl$_2$ and C$_6$D$_6$ solutions. [f] Multiplet. [g] Doublet with J_P = 15–17 Hz. [h] The other resonances: 3.15–3.03m, 1.42–1.26m and 0.87t (J_H = 8 Hz). [i] Overlapped. [j] The other resonances: 3.1m, 1.45–1.24m and 0.87t (J_H = 8 Hz).

by the counter anion. They were observed at higher magnetic field in the order of the counter anions $[Ph_4B]^-<[\Phi_3B-CN]^-<[\Phi'_3B-CN]^-$. In D_2O, the chemical shifts seem to be unaffected by the counter cation, and proton resonances of $[\Phi_3B-CN]^-$ anion were observed at δ 7.07 ± 1, 6.57 ± 1 and 3.36 ± 1 ppm for tetraalkylammonium salts. Unfortunately, $[\Phi_3P-R][\Phi_3B-CN]$ were not soluble enough in D_2O for NMR measurement. NMR spectra of numerous quaternary onium salts in a variety of solvents have been discussed, and the magnitude of the solvent shift in benzene was explained by the size and shape of the ion, solvent polarity and the nature of the counter ion [4d,e]. Spectra for some tetraalkylammonium salts were measured both in dichloromethane-d_2 and in benzene-d_6. The chemical shifts of $[\Phi_3B-CN]^-$ protons were observed at considerably lower fields in benzene-d_6 than in dichloromethane-d_2 (Δ values in Table 5). The chemical shifts of tetraalkylammonium protons, on the other hand, were observed at higher magnetic fields in benzene-d_6. These results are consistent with the general concept associated with the ring current anisotropy caused by benzene, which might solvate to the tetraalkylammonium cation in the cluster on its face and to the cyanoborate on its edge [4e]. A particularly large benzene shift was observed for the 2-MeO protons in $[\Phi'_3B-CN]^-$ anion. This can be understood again in terms of the "buttressing effect" caused by the *meta*-bromination. This is consistent with the observation of little benzene shift for 5-H and 6-MeO protons, since these protons must be situated apart from the negative centre. ^{13}C NMR spectra data are given in Table 6.

3. Experimental details

3.1. Physical measurements

^1H and ^{13}C NMR spectra were recorded using a JEOL JNM-GX-270 spectrometer. IR spectra were recorded for Nujol mulls using a Shimadzu FTIR-4200 spectrometer. UV spectra were recorded using a Shimadzu UV-160 spectrophotometer. Conductivities (Table 4) were measured for acetonitrile, 1,2-dichloroethane and aqueous solutions at 10^{-2}, 10^{-3}, 10^{-4} and 10^{-5} M at 25°C when the salt was soluble.

3.2. Preparation of Φ_3B

To a solution of 1,3-dimethoxybenzene (5.7 ml, 45 mmol) and a catalytic amount of N,N,N',N'-tetramethylethylenediamine (TMEDA, 0.2 ml) in diethyl ether (50 ml) was added a 15% n-hexane solution of n-butyllithium (27.9 ml, 45 mmol) at 0°C under argon. The mixture was stirred for 3 h to afford the precipitates of ΦLi. To this suspension was added boron trifluoride diethyl etherate (2.0 ml, 15 mmol) in benzene (50 ml), and the mixture was refluxed for 4 h. Methanol (15 ml) was added at room temperature, and the insoluble materials were recrystallized from tetrahydrofuran or acetone to give white crystals of Φ_3B in 54% yield; m.p. 222°C (m.p. was not reported in Ref. [2]). Anal. Found: C, 68.2; H, 6.48. Calcd. for $C_{24}H_{27}B_1O_6$: C, 68.3; H, 6.44%.

Φ_3B (0.1 g) is soluble at room temperature in dichloromethane (2 ml), chloroform (2 ml), 1,2-dichlo-

Table 6
^{13}C NMR spectral data (δ/ppm, in $CDCl_3$) for some cyanotris(2,6-dimethoxyphenyl)borates

Compound	1-C [a]	2,6-C	3,5-C	4-C	MeO	Others [b]
$K[\Phi_3B-CN]$ (in D_2O)	–	166.2	110.0	127.8	57.0	
$[Me_3(HOCH_2CH_2)N][\Phi_3B-CN]$	–	164.1	106.4	123.9	56.4	67.7, 56.1, 54.1
$[Me_3(C_{18}H_{37})N][\Phi_3B-CN]$	–	164.2	106.5	123.7	56.5	53.0 (NMe) [c]
$[Et_4N][\Phi_3B-CN]$	–	164.2	106.3	123.5	56.5	52.0, 7.5
$[Me_3(PhCH_2)N][\Phi_3B-CN]$	–	164.2	106.3	123.7	56.4	69.1, 52.3 [d]
$[\Phi_3P-Me][\Phi_3B-CN]$	101.5 [e]	162.4	104.8 [f]	135.7	56.2	17.4d [65]
	–	164.5	106.5	122.9	56.6	
$[\Phi_3P-Bu][\Phi_3B-CN]$	100.3 [e]	162.5	104.6 [f]	135.6	56.0	27.4d [56], 26.0d [4],
	–	164.5	106.6	122.9	56.7	24.2d [21], 13.7
$[\Phi_3P-CH_2Ph][\Phi_3B-CN]$	100.4 [e]	162.2	104.3 [f]	135.6	55.9	35.5d [54]
	–	164.5	106.5	122.9	56.7	128.3 (CN) [g]
$[\Phi_3P-Me][\Phi'_3B-CN]$	101.0 [e]	162.3	104.8 [f]	135.7	56.2	17.4d [65],
	–	164.5	108.6	127.9	60.0	
		159.4	108.3		55.7	
$[\Phi_3P-Bu][\Phi'_3B-CN]$	–	162.5	104.6 [f]	135.6	56.0	27.4d [54], 26.0d [3],
		164.5	108.6	127.9	60.1	24.1d [20], 13.7
		159.5	108.3		55.7	

[a] Very weak or not observed. [b] J_P values (Hz) are given in square brackets. [c] The other resonances: 76.4, 66.9, 32.0, 29.72, 29.68, 29.62, 29.55, 29.49, 29.37, 29.26, 26.18, 23.11, 22.70, 22.65 and 14.1. [d] The other resonances: 133.0, 130.4, 129.0 and 127.8. [e] Doublet with $J_P = 97$–100 Hz. [f] Doublet with $J_P = 6$–9 Hz. [g] The other resonances: 132.6d [7], 129.2d [9], 128.0d [2] and 127.2d [3].

roethane (7 ml) and toluene (10 ml), it is soluble on heating in 10–30 ml of methanol, acetone, tetrahydrofuran and benzene and it is poorly soluble in ethanol, 2-propanol and diethyl ether.

3.3. Reaction of B(OMe)₃ with ΦLi

To a suspension of ΦLi, prepared from 1,3-dimethoxybenzene (15 mmol), TMEDA and n-butyllithium (15 mmol) as above, was added trimethoxyborane (0.56 ml, 5 mmol) at 0°C, and the mixture was stirred at 0°C for 15 h. Methanol (10 ml) was added and the resultant precipitates were recrystallized from acetone to give Li[Φ_3B–OH] in 80–90% yield; m.p. 158–160°C, decomposed; IR 3450 cm^{-1} (νOH). Anal. Found: C, 64.5; H, 6.39. Calcd. for $C_{24}H_{28}B_1Li_1O_7$: C, 64.6; H, 6.32%.

This salt could also be obtained by the reaction of Φ_3B with LiOH in aqueous methanol in 98% yield.

3.4. Preparation of amine adducts

To a suspension of Φ_3B (0.422 g, 1 mmol) in methanol (10 ml) was added a solution of ammonia (2 mmol) in methanol (1 ml). The mixture was stirred at room temperature for 2 h, and the resultant precipitates were recrystallized from acetone or hexane to give Φ_3B · NH₃ in 93% yield, m.p. 200–202°C; IR 3330 cm^{-1} (νNH). Anal. Found: C, 65.8; H, 7.01; N, 3.22. Calcd. for $C_{24}H_{29}N_1O_6B_1$: C, 65.5; H, 6.64; N, 3.19%.

To a suspension of Φ_3B (1 mmol) in acetone (10 ml) was added aqueous methylamine (0.2 ml, an excess) to give a clear solution. The solvent was removed under reduced pressure, and the residue was recrystallized from methanol to give Φ_3B · NH₂Me in 72% yield, m.p. 143°C; IR 3300 cm^{-1} (νNH). Anal. Found: C, 66.2; H, 7.18; N, 3.06. Calcd. for $C_{25}H_{31}N_1O_6B_1$: C, 66.2; H, 7.12; N, 3.09%.

An analogous mixture of Φ_3B and aqueous ethylamine in acetone was stirred at room temperature for 3 h, and the resultant precipitates were recrystallized from hexane to give white crystals of Φ_3B · NH₂Et in 82% yield, m.p. 222°C; IR 3290 cm^{-1} (νNH). Anal. Found: C, 66.8; H, 7.38; N, 2.98. Calcd. for $C_{26}H_{34}N_1O_6$: C, 66.8; H, 7.33; N, 3.00%.

An analogous mixture of Φ_3B and n-butylamine in methanol was cooled to −30°C to give white crystals of Φ_3B · NH₂^{n}Bu in 71% yield, m.p. 211°C (from hexane); IR 3320 cm^{-1} (νNH). Anal. Found: C, 67.8; H, 7.37; N, 2.79. Calcd. for $C_{28}H_{38}N_1O_6B_1$: C, 67.9; H, 7.73; N, 2.83%.

An analogous mixture of Φ_3B and isobutylamine in acetone was cooled to −30°C to give slowly white crystals of Φ_3B · NH₂^{i}Bu in 85% yield, m.p. 219°C (from hexane); IR 3300 cm^{-1} (νNH). Anal. Found: C, 68.0; H, 7.75; N, 2.83. Calcd. for $C_{28}H_{38}N_1O_6B_1$: C, 67.9; H, 7.73; N, 2.83%.

3.5. Preparation of K[Φ_3B–CN]

To a suspension of Φ_3B (5 mmol) in methanol (30 ml) was added aqueous solution of potassium cyanide (5.1 mmol/3 ml). The mixture was stirred at room temperature for 18 h to give a precipitate of K[Φ_3B–CN] in 83% yield; m.p. was not observed below 235°C; IR 2160 cm^{-1} (νCN); UV (H₂O)λ_{max} (log ϵ) 207 (4.91), 235 (4.34, sh) and 273 (3.36) nm.

3.6. Preparation of [R₄N][Φ_3B–CN]

A mixture of K[Φ_3B–CN] (5 mmol) and [Me₃(PhCH₂)N]Cl (5.1 mmol) was dissolved in acetone (50 ml). The resultant precipitate of KCl was filtered off, the solvent was removed under reduced pressure and the residual solid was recrystallized from n-hexane (50 ml)–2-propanol (25 ml) to give white crystals of [Me₃(PhCH₂)N][Φ_3B–CN] in 79% yield, m.p. 130–133°C; IR 2160 cm^{-1}.

In an analogous manner to the above, using [Et₄N]Br, white crystals of [Et₄N][Φ_3B–CN] were obtained in 82% yield, m.p. 220–225°C, decomposed (from 2-propanol (5 ml)–n-hexane (50 ml)); IR 2160 cm^{-1}.

In an analogous manner to the above, using [Me₃(HOCH₂CH₂)N]Cl, white crystals of [Me₃(HOCH₂CH₂)N][Φ_3B–CN] were obtained in 64% yield, m.p. 214–215°C, decomposed (from 2-propanol); IR 2160 cm^{-1}.

A mixture of [Me₄N]Br (1.1 mmol) and K[Φ_3B–CN] (1 mmol) was dissolved in methanol (10 ml) on heating. The resultant precipitate of KBr was filtered off, and the filtrate was cooled to −30°C to give white crystals of [Me₄N][Φ_3B–CN] in 72% yield; m.p. was not observed below 235°C; IR 2160 cm^{-1}.

A mixture of [Me₃(C₁₈H₃₇)N]Cl (3 mmol) and K[Φ_3B–CN] (3 mmol) in benzene (30 ml) was heated until dissolved. The precipitate of KCl was removed by filtration, the solvent was removed under reduced pressure and the residual viscous material was treated with n-hexane to give white crystals of [Me₃(C₁₈H₃₇)N][Φ_3B–CN] in 80% yield, m.p. 86–88°C; IR 2160 cm^{-1}; UV λ_{max} (log ϵ) in EtOH, 212 (4.89), 235 (4.30, sh), 272 (3.26) nm, and in n-hexane, 213 (4.91), 240 (4.30, sh), 273 (3.54) nm.

The freezing point depressions measured for benzene solutions, were 0.059°C for [Me₃(PhCH₂)N][Φ_3B–CN] (0.400 g/17.87 g benzene) and 0.032°C for [Et₄N][Φ_3B–CN] (0.500 g/26.67 g benzene).

3.7. Preparation of [Φ_3P–R][Φ_3B–CN]

A solution of [Φ_3P–Bu]Cl · 0.5H₂O (1.088 g, 2 mmol) [6] in water (20 ml) was added to a solution of K[Φ_3B–CN] (0.974 g, 2 mmol) in water (200 ml) to afford a

white precipitate of $[\Phi_3P-Bu][\Phi_3B-CN]$ in 74% yield, m.p. 185°C, decomposed (from 2-propanol); IR 2160 cm^{-1} (νCN).

The following compounds were obtained in analogous manners to the above.

$[\Phi_3P-CH_2Ph][\Phi_3B-CN]$ using $[\Phi_3P-CH_2Ph]Cl$ [6]; 83% yield, m.p. 190°C, decomposed (from 2-propanol); IR 2160 cm^{-1} (νCN).

$[\Phi_3P-Me][\Phi_3B-CN]$ using $[\Phi_3P-Me]Cl$ [6]; 84% yield, m.p. 180–181°C, decomposed (from acetone); IR 2160 cm^{-1} (νCN). Anal. Found: C, 64.4; H, 6.52; N, 1.64. Calcd. for $C_{50}H_{57}B_1N_1O_{12}P_1$: C, 66.3; H, 6.34; N, 1.55%.

3.8. Preparation of $[\Phi_3P-R][Ph_4B]$

A solution of $[\Phi_3P-H]Cl \cdot 2.5H_2O$ (2 mmol) [6] in water (10–60 ml) was added to a solution of $Na[Ph_4B]$ (2 mmol) in water (100 ml) to afford a white precipitate of $[\Phi_3P-H][Ph_4B]$, which was filtered at 0°C and dried in vacuum and then at 60°C, m.p. 170–172°C.

In analogous manners to the above, using $[\Phi_3P-Me]Cl$, $[\Phi_3P-Bu]Cl \cdot 0.5H_2O$ and $[\Phi_3P-CH_2Ph]Cl$, were obtained $[\Phi_3P-Me][Ph_4B]$ (86% yield, m.p. 190°C), $[\Phi_3P-Bu][Ph_4B]$ (86% yield, m.p. 183–185°C) and $[\Phi_3P-CH_2Ph][Ph_4B]$ (85% yield, m.p. 213–214°C).

3.9. Reaction of Φ_3B with N-bromosuccinimide (NBS) to give $\Phi'_3B[\Phi' = 3\text{-}Br\text{-}2,6\text{-}(MeO)_2C_6H_2]$

To a suspension of Φ_3B (1 mmol) in acetone (10 ml) was added an acetone solution (10 ml) of NBS (3 mmol) to give a light-green solution. Volatile materials were removed under reduced pressure, and the residual solid was washed with ethanol and recrystallized from hexane to give Φ'_3B in 68% yield, m.p. 122–124°C. Anal. Found: C, 43.7; H, 3.76. Calcd. for $C_{24}H_{24}Br_3O_{12}B_1$: C, 43.7; H, 3.67%.

3.10. Reaction of $\Phi_3B \cdot NH_3$ with NBS to give ΦBr

A solution of NBS (0.267 g, 1.5 mmol) in acetone (10 ml) was added dropwise with stirring to a suspension of $\Phi_3B \cdot NH_3$ (0.220 g, 0.5 mmol) in acetone (10 ml) at 0°C. At the end of addition a clear yellow solution was obtained which was stirred for 1 h at 0°C. Water (20 ml) was added to afford a white precipitate, the mixture was concentrated under reduced pressure to about half its volume, and the crystals of ΦBr were precipitated in 62% yield. It was characterized as reported [7].

3.11. Reaction of $[\Phi_3P-Me][\Phi_3B-CN]$ with NBS

A solution of $[\Phi_3P-Me][\Phi_3B-CN]$ (2.715 g, 3 mmol) in acetone (40 ml) was added dropwise to a yellow solution of NBS (9 mmol) in acetone (30 ml) with stirring to afford a colourless solution. It was stirred for 1 h, water (50 ml) was added and the mixture was concentrated under reduced pressure to ca. 50 ml to afford a white precipitate of $[\Phi_3P-Me][\Phi'_3B-CN]$ in 92% yield. The analytical sample was obtained by recrystallization from 2-propanol; m.p. 154–155°C. Anal. Found: C, 52.5; H, 4.81; N, 1.18. Calcd. for $C_{50}H_{54}B_1Br_3N_1O_{12}P_1$: C, 52.6; H, 4.76; N, 1.23%.

In an analogous manner to the above, white crystals of $[\Phi_3P-Bu][\Phi'_3B-CN]$ were obtained in 96% yield (70% after recrystallization from 2-propanol), m.p. 95–100°C.

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