

Synthesis and study of new binuclear compounds containing bridging $(\mu\text{-CN})\text{B}(\text{C}_6\text{F}_5)_3$ and $(\mu\text{-NC})\text{B}(\text{C}_6\text{F}_5)_3$ systems

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The new compounds $[\text{K}(18\text{-crown-6})][\text{SCNB}(\text{C}_6\text{F}_5)_3]$ (**1**), $[\text{K}(18\text{-crown-6})][(\text{C}_6\text{F}_5)_3\text{B}(\mu\text{-NC})\text{B}(\text{C}_6\text{F}_5)_3]$ (**2**), $[\text{K}(18\text{-crown-6})][\text{NCB}(\text{C}_6\text{F}_5)_3]$ (**3**), $[\text{Me}_3\text{Si}(\mu\text{-NC})\text{B}(\text{C}_6\text{F}_5)_3]$ (**4**) and $[\text{Hg}\{(\mu\text{-CN})\text{B}(\text{C}_6\text{F}_5)_3\}_2]$ (**5**) have been synthesised. Reaction between $[\text{IrCl}(\text{PPh}_3)_2(\text{CO})]$ and one equivalent of **4** gives $[\text{Ir}\{(\mu\text{-NC})\text{B}(\text{C}_6\text{F}_5)_3\}(\text{PPh}_3)_2(\text{CO})]$ (**6**). Similarly, the reaction between $[\text{Fe}(\eta\text{-C}_5\text{H}_5)(\text{CO})_2\text{Cl}]$ and **4** gives $[\text{Fe}\{(\mu\text{-NC})\text{B}(\text{C}_6\text{F}_5)_3\}(\eta\text{-C}_5\text{H}_5)(\text{CO})_2]$ (**7a**). The NMR-scale reaction between $[\text{Fe}(\eta\text{-C}_5\text{H}_5)(\text{CO})_2\text{CN}]$ and $\text{B}(\text{C}_6\text{F}_5)_3$ gives the isomer $[\text{Fe}\{(\mu\text{-CN})\text{B}(\text{C}_6\text{F}_5)_3\}(\eta\text{-C}_5\text{H}_5)(\text{CO})_2]$ (**7b**). In the compounds **3**, **4**, **6** and **7a** the anion $[\text{NCB}(\text{C}_6\text{F}_5)_3]^-$ is coordinated to the metal through the nitrogen. Complexes **1**, **2** and **7b** incorporate a $(\mu\text{-CN})\text{B}$ unit. The compounds containing the isomeric bridging $(\mu\text{-CN})\text{B}$ or $(\mu\text{-NC})\text{B}$ systems have been investigated by $^{11}\text{B}\{^1\text{H}\}$ NMR spectroscopy and by DFT calculations. The $^{11}\text{B}\{^1\text{H}\}$ NMR spectra enable distinction between the isomers. The single-crystal X-ray structures of **1**, **3** and **7a** have been determined.

Introduction

Compounds incorporating the weakly coordinating anion $[(\text{C}_6\text{F}_5)_3\text{B}(\mu\text{-CN})\text{B}(\text{C}_6\text{F}_5)_3]^-$ together with cationic metallocenes have recently been reported by Bochmann and co-workers to give active homogenous catalysts for olefin polymerisation.^{1,2} The compound $[\text{Zr}\{(\mu\text{-NC})\text{B}(\text{C}_6\text{F}_5)_3\}\text{Me}(\text{Cp}^*)_2]$, where $\text{Cp}^* = 1,3\text{-C}_5\text{H}_3(\text{SiMe}_3)_2$, containing the anionic isonitrile ligand $[\text{NCB}(\text{C}_6\text{F}_5)_3]^-$ has also been reported.² The complexes $[\text{NHMe}_2\text{Ph}]_2[\text{Ni}\{(\mu\text{-CN})\text{B}(\text{C}_6\text{F}_5)_3\}_4]$ and $[\text{Ph}_3\text{C}]_2[\text{Ni}\{(\mu\text{-CN})\text{B}(\text{C}_6\text{F}_5)_3\}_4]$ are active as co-catalysts towards olefin polymerisation.²

Earlier we have described some coordination chemistry of $\text{B}(\text{C}_6\text{F}_5)_3$ and of the anionic ligand $[\text{HOB}(\text{C}_6\text{F}_5)_3]^-$.³⁻⁸ Here we describe the potassium salts of the new anions $[\text{SCNB}(\text{C}_6\text{F}_5)_3]^-$ and $[\text{NCB}(\text{C}_6\text{F}_5)_3]^-$, the adducts of $\text{B}(\text{C}_6\text{F}_5)_3$ with Me_3SiCN and $\text{Hg}(\text{CN})_2$, and the organometallic compounds $[\text{Ir}\{(\mu\text{-NC})\text{B}(\text{C}_6\text{F}_5)_3\}(\text{PPh}_3)_2(\text{CO})]$, $[\text{Fe}\{(\mu\text{-NC})\text{B}(\text{C}_6\text{F}_5)_3\}(\eta\text{-C}_5\text{H}_5)(\text{CO})_2]$ and $[\text{Fe}\{(\mu\text{-CN})\text{B}(\text{C}_6\text{F}_5)_3\}(\eta\text{-C}_5\text{H}_5)(\text{CO})_2]$.

The neutral isonitrile adducts $[\text{RNCB}(\text{C}_6\text{F}_5)_3]$ ⁹ and nitrile adducts $[\text{RCNB}(\text{C}_6\text{F}_5)_3]$ ⁹⁻¹¹ ($\text{R} = \text{alkyl, aryl}$) have been reported previously. They contain the units E_1NCB or E_1CNB , respectively, where $\text{E}_1 = \text{alkyl, aryl, hydrocarbyl}$. The organic compounds E_1NC and E_1CN are commonly described as isonitriles (isocyano) or nitriles (cyano), respectively. However when we consider the bridging systems $\text{E}_1(\mu\text{-CN})\text{E}_2$ or $\text{E}_1(\mu\text{-NC})\text{E}_2$ where E_1 and E_2 are not carbon bonding groups the use of the terms "nitrile" or "isonitrile" can lead to confusion. Of course, for $\text{E}_1(\mu\text{-CN})\text{E}_2$, if E_1 is a hydrocarbyl group and E_2 is, for example, a metal, then description as "an organo nitrile ligand to the metal" would be appropriate. There are in fact only a few two-atom bridging $(\mu\text{-AB})$ ligands which can adopt both $\text{E}_1(\mu\text{-AB})\text{E}_2$ and $\text{E}_1(\mu\text{-BA})\text{E}_2$ structures with a similar facility, and we are not aware of a systematic notation for isomers in the class $\text{E}_1(\mu\text{-CN})\text{E}_2$ and $\text{E}_1(\mu\text{-NC})\text{E}_2$. Therefore, we will describe the compounds containing the units $\text{E}_1(\mu\text{-CN})\text{E}_2$ or $\text{E}_1(\mu\text{-NC})\text{E}_2$ simply by defining the elements E_1 and E_2 in each case. In this work the E_2 atom is boron.

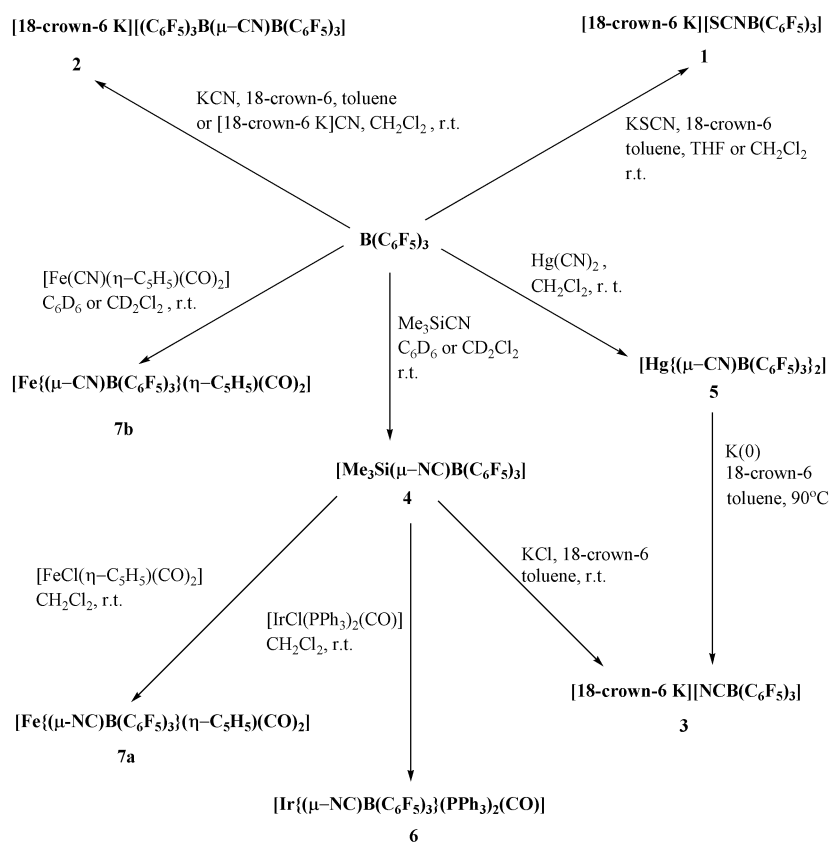
Results and discussion

Syntheses

The reaction between KSCN and $\text{B}(\text{C}_6\text{F}_5)_3$ in the presence of 18-crown-6 ether, in toluene, gave $[\text{K}(18\text{-crown-6})][\text{SCNB}(\text{C}_6\text{F}_5)_3]$ (**1**), and the reaction between 18-crown-6 ether, KCN and $\text{B}(\text{C}_6\text{F}_5)_3$ (in a 1 : 1 : 1 ratio or a 1 : 1 : 2 ratio) in toluene gave $[\text{K}(18\text{-crown-6})][(\text{C}_6\text{F}_5)_3\text{B}(\mu\text{-NC})\text{B}(\text{C}_6\text{F}_5)_3]$ (**2**) instead of the expected $[\text{K}(18\text{-crown-6})][\text{NCB}(\text{C}_6\text{F}_5)_3]$ (**3**). The anion $[(\text{C}_6\text{F}_5)_3\text{B}(\mu\text{-CN})\text{B}(\text{C}_6\text{F}_5)_3]^-$ has been reported earlier as the $[\text{Ph}_3\text{C}]^+$ salt.^{1,2} Alternative routes for the synthesis of **3** via treatment of $[\text{K}(18\text{-crown-6})][\text{CN}]$ with $\text{B}(\text{C}_6\text{F}_5)_3$ were explored. The reaction was performed in toluene, CH_2Cl_2 , THF and CH_3CN , but gave only $[\text{K}(18\text{-crown-6})][(\text{C}_6\text{F}_5)_3\text{B}(\mu\text{-NC})\text{B}(\text{C}_6\text{F}_5)_3]$ (**2**) and not **3**. An NMR scale reaction between Me_3SiCN and $\text{B}(\text{C}_6\text{F}_5)_3$ in C_6D_6 or CD_2Cl_2 gave a clean spectrum consistent with the formation of $[(\text{Me}_3\text{Si})(\mu\text{-NC})\text{B}(\text{C}_6\text{F}_5)_3]$ (**4**). This was surprising, since the product expected was $[(\text{Me}_3\text{Si})(\mu\text{-CN})\text{B}(\text{C}_6\text{F}_5)_3]$. However, we note that rapid equilibrium between R_3SiCN and R_3SiNC is well established.¹²⁻¹⁵ A larger scale synthesis in CD_2Cl_2 led to the formation of **4** in 77% yield. Since a facile cleavage of the anion $[\text{NCB}(\text{C}_6\text{F}_5)_3]^-$ from the adduct **4** was expected, the reaction of this adduct with KCl (in presence of 18-crown-6 ether) was carried out in toluene and the desired compound $[\text{K}(18\text{-crown-6})][\text{NCB}(\text{C}_6\text{F}_5)_3]$ (**3**) was isolated in 73% yield.

Another attempt to synthesise the isonitrile anion $[\text{CNB}(\text{C}_6\text{F}_5)_3]^-$ was made by cleavage, using potassium metal, of the adduct $[\text{Hg}\{(\mu\text{-CN})\text{B}(\text{C}_6\text{F}_5)_3\}_2]$ (**5**). The new compound **5** was synthesised by addition of $[\text{Hg}(\text{CN})_2]$ to $\text{B}(\text{C}_6\text{F}_5)_3$ in CH_2Cl_2 . The adduct **5** is decomposed by water to give, *inter alia*, the known adduct $[\text{H}_2\text{OB}(\text{C}_6\text{F}_5)_3]$.³ Attempts to form either $\text{H}[\text{CNB}(\text{C}_6\text{F}_5)_3]$ or $\text{H}[\text{NCB}(\text{C}_6\text{F}_5)_3]$ by treatment of **5** with H_2S were unsuccessful. The reduction of the $\text{Hg}(\text{II})$ adduct **5** with potassium metal in the presence of 18-crown-6 ether was carried out in toluene at 90 °C. The nitrile compound $[\text{K}(18\text{-crown-6})][\text{NCB}(\text{C}_6\text{F}_5)_3]$ (**3**) was isolated in moderate yield, as white crystals. There was no evidence for the isomer $[\text{K}(18\text{-crown-6})][\text{CNB}(\text{C}_6\text{F}_5)_3]$.

Reaction between $[\text{IrCl}(\text{PPh}_3)_2(\text{CO})]$ and $[\text{Me}_3\text{Si}(\mu\text{-NC})\text{B}(\text{C}_6\text{F}_5)_3]$ (**4**) in CH_2Cl_2 gave an initial pale-yellow mixture which changed to a bright yellow after 2 h. Bright-yellow crystals of the complex $[\text{Ir}\{(\mu\text{-NC})\text{B}(\text{C}_6\text{F}_5)_3\}(\text{PPh}_3)_2(\text{CO})]$ (**6**) were obtained by crystallisation from CH_2Cl_2 . Treatment of $[\text{Fe}(\eta\text{-C}_5\text{H}_5)(\text{CO})_2\text{Cl}]$ with one equivalent of **4** in pentane at room temperature formed red crystals of $[\text{Fe}\{(\mu\text{-NC})\text{B}(\text{C}_6\text{F}_5)_3\}(\eta\text{-C}_5\text{H}_5)(\text{CO})_2]$ (**7a**). The isomer $[\text{Fe}\{(\mu\text{-CN})\text{B}(\text{C}_6\text{F}_5)_3\}(\eta\text{-C}_5\text{H}_5)(\text{CO})_2]$ (**7b**) could be prepared in solution by the treatment of $[\text{Fe}(\eta\text{-C}_5\text{H}_5)(\text{CO})_2(\text{CN})]$ with $\text{B}(\text{C}_6\text{F}_5)_3$ in C_6D_6 and has been characterised only by NMR data in solution.



Scheme 1 Formation of compounds 1–6, 7a and 7b.

Scheme 1 shows the syntheses of compounds 1–6, 7a and 7b, which are highly air- and moisture-sensitive. The new compounds 1–7a, 7b have been characterised by microanalysis and by infrared and NMR spectroscopy and the data are given in the experimental sections or Tables 1 and 2 and are discussed below. The crystal structures of 1, 3 and 7a have been determined.

Spectroscopic studies

The ^{11}B NMR spectra are particularly diagnostic. The ^{11}B resonances differ markedly between three-coordinate borane $\text{B}(\text{C}_6\text{F}_5)_3$ and the four-coordinate boron found in the Lewis acid–base adducts $[(\text{Donor})\text{B}(\text{C}_6\text{F}_5)_3]$ for which the ^{11}B resonance is shifted to lower frequency with respect to $\text{B}(\text{C}_6\text{F}_5)_3$ by more than 50 ppm.^{3–7, 16}

The ^{11}B data for a number of known compounds and for compounds described in this work are listed in Table 2. The data show that when boron is directly bonded to nitrogen, as in $\text{E}_1(\mu\text{-CN})\text{B}$, the $^{11}\text{B}\{^1\text{H}\}$ resonance is *broad* and occurs in the range $\delta -9.0$ to -13.0 ppm. When boron is directly attached to carbon, as in $\text{E}_1(\mu\text{-NC})\text{B}$, the $^{11}\text{B}\{^1\text{H}\}$ resonance is *sharp* and occurs in the range $\delta -20.0$ to -23.0 ppm. On this basis the structures of the isomeric compounds 7a and 7b can be assigned as shown in Table 2.

The ^{19}F NMR spectra of all the new compounds show resonances broadly similar to those of $\text{B}(\text{C}_6\text{F}_5)_3$ but shifted to lower frequency. The *para*-fluorine resonances were found to be the most sensitive of the aromatic fluorine shifts. The ^{19}F NMR data for derivatives of nitrile- or isonitrile-borates, (containing the RCNB and RNCB units) have been found to be distinct from the free borane, however they do not permit a reliable distinction between two isomers such as 7a and 7b.

The IR spectra of compounds 1–6 and 7a in Table 1 show sharp bands in the region $2146\text{--}2284\text{ cm}^{-1}$ which can be assigned to the ν_{CN} or ν_{NC} stretching frequencies. As previously shown,⁹ the coordination of $\text{B}(\text{C}_6\text{F}_5)_3$ to a E_1CN^- group causes a significant band shift to higher wavenumbers. Thus the IR

spectrum of the complex $[\text{Me}_3\text{Si}(\mu\text{-NC})\text{B}(\text{C}_6\text{F}_5)_3]$ (4) shows a band at 2255 cm^{-1} compared to 2190 cm^{-1} for Me_3SiCN . The corresponding wavenumber for $[\text{Fe}(\eta\text{-C}_5\text{H}_5)(\text{CO})_2\text{CN}]$ is 2114 cm^{-1} and for $[\text{Fe}\{(\mu\text{-NCB}(\text{C}_6\text{F}_5)_3)\}(\eta\text{-C}_5\text{H}_5)(\text{CO})_2]$ (7a) it is 2252 cm^{-1} .

X-Ray crystallography

The crystal structures of compounds 1, 3 and 7a have been determined. Selected molecular parameters are given in Table 3 and Table 4 presents the X-ray crystallographic data. Single crystals of 1 suitable for the X-ray structure analysis were grown by diffusion of pentane into a dichloromethane solution. An ORTEP of 1 is presented in Fig. 1. The X-ray crystal structure analysis of 1 confirms that only one equivalent of 18-crown-6 ether is present in the asymmetric unit and

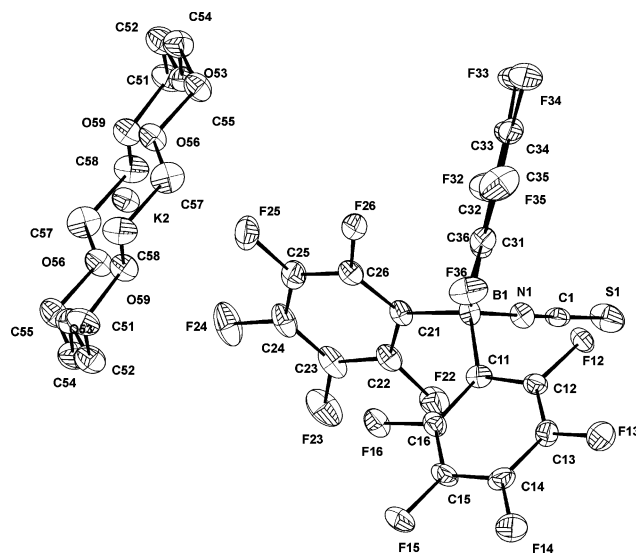


Fig. 1 ORTEP of $[\text{K}(18\text{-crown-6})][\text{SCNB}(\text{C}_6\text{F}_5)_3]$ (1).

Table 1 IR (KBr disks, ν in cm^{-1}) and NMR data (C_6D_6 , δ in ppm) at room temperature

Compound	IR	^1H	$^{11}\text{B}\{^1\text{H}\}$	^{19}F -ortho (d, 2F, $^2J_{\text{F-F}} \approx 20$ Hz)	^{19}F -para (br, 1F)	^{19}F -meta (br, 2F)
$\text{B}(\text{C}_6\text{F}_5)_3$			58	-128.8	-144.6	-161.5
$[\text{K}(18\text{-crown-6})\text{K}][\text{SCNB}(\text{C}_6\text{F}_5)_3] \mathbf{1}$	2146 (ν_{CN})	3.70 (s)	-12.4	-134.7	-160.5	-165.7
$[\text{K}(18\text{-crown-6})][(\text{C}_6\text{F}_5)_3\text{B}(\mu\text{-NC})\text{B}(\text{C}_6\text{F}_5)_3] \mathbf{2}$	2294.8; 2295.3 (ν_{CN})	3.63 (s)	-12.1; -21.9	-134.6; -135.7	-161.3, -161.4	-168.0, -168.4
$[\text{K}(18\text{-crown-6})][\text{NCB}(\text{C}_6\text{F}_5)_3] \mathbf{3}$	2212 (ν_{CN})	3.54 (s)	-22.5	-132.6	-160.5	-165.8
$[\text{Me}_3\text{Si}(\mu\text{-NC})\text{B}(\text{C}_6\text{F}_5)_3] \mathbf{4}$	2256 (ν_{CN})	-0.30 (s)	-21.7	-133.7	-155.2	-163.2
$[\text{Hg}\{(\mu\text{-CN})\text{B}(\text{C}_6\text{F}_5)_3\}_2] \mathbf{5}$	2284 (ν_{CN})		-10.7	-134.4	-156.7	-164.3
$[\text{Ir}\{(\mu\text{-NC})\text{B}(\text{C}_6\text{F}_5)_3\}(\text{PPh}_3)_2(\text{CO})] \mathbf{6}^a$	2232 (ν_{CN})	7.38 (m, 6H)	-22.8	-132.16	-159.8	-164.8
	2012 ($\nu_{\text{CO-sym}}$)	7.56 (m, 4H)				
	1962 ($\nu_{\text{CO-asym}}$)					
$[\text{Fe}\{(\mu\text{-NC})\text{B}(\text{C}_6\text{F}_5)_3\}(\eta\text{-C}_5\text{H}_5)(\text{CO})_2] \mathbf{7a}$	2252 (ν_{CN}) 2076 ($\nu_{\text{CO-sym}}$) 2032 ($\nu_{\text{CO-asym}}$)	5.15 (s)	-22.4	-134.0	-158.6	-164.7
$[\text{Fe}\{(\mu\text{-CN})\text{B}(\text{C}_6\text{F}_5)_3\}(\eta\text{-C}_5\text{H}_5)(\text{CO})_2] \mathbf{7b}$	-	5.28 (s)	-12.0	-135.6	-159.3	-169.5

a $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6) at 25 °C: δ 22.9 (s).

Table 2 Comparative $^{11}\text{B}\{^1\text{H}\}$ NMR data. $^{11}\text{B}\{^1\text{H}\}$ NMR line shape is described here as *sharp* if $\nu_{1/2}$ is $<15 \pm 1$ Hz, and as *broad* if $\nu_{1/2}$ is $>300 \pm 10$ Hz

Compound	δ $^{11}\text{B}\{^1\text{H}\}$	Line shape	Assignment	Ref.
$^a[\text{Ph}_3\text{C}][\text{Pd}\{(\mu\text{-CN})\text{B}(\text{C}_6\text{F}_5)_3\}_4]$	-12.8	-	N-B	1
$^b(\text{MeCN})\text{B}(\text{C}_6\text{F}_5)_3$	-10.3	Broad	N-B	3
$^b[(p\text{-NO}_2\text{C}_6\text{H}_4\text{CN})\text{B}(\text{C}_6\text{F}_5)_3]$	-9.6	Broad	N-B	3
$^b[(p\text{-MeC}_6\text{H}_4\text{CN})\text{B}(\text{C}_6\text{F}_5)_3]$	-10.2	Broad	N-B	3
$^b[\text{Hg}\{(\mu\text{-CN})\text{B}(\text{C}_6\text{F}_5)_3\}_2] \mathbf{5}$	-10.7	Broad	N-B	This work
$^b[\text{Fe}\{(\mu\text{-CN})\text{B}(\text{C}_6\text{F}_5)_3\}(\eta\text{-C}_5\text{H}_5)(\text{CO})_2] \mathbf{7b}$	-12.0	Broad	N-C	This work
$^b[\text{K}(18\text{-crown-6})][(\text{C}_6\text{F}_5)_3\text{B}(\mu\text{-NC})\text{B}(\text{C}_6\text{F}_5)_3] \mathbf{2}$	-12.1	Broad	N-B	This work
	-21.9	Sharp	C-B	
$^c[\text{Ph}_3\text{C}][(\text{C}_6\text{F}_5)_3\text{B}(\mu\text{-NC})\text{B}(\text{C}_6\text{F}_5)_3]$	-11.9	-	N-B	2
	-21.6	-	C-B	
$^b[(^t\text{BuNC})\text{B}(\text{C}_6\text{F}_5)_3]$	-21.8	Sharp	C-B	3
$^b[(\text{Me}_3\text{C-CH}_2\text{-CMe}_2\text{-NC})\text{B}(\text{C}_6\text{F}_5)_3]$	-21.7	Sharp	C-B	3
$^b[(2,6\text{-Me}_2\text{C}_6\text{H}_3)\text{NCB}(\text{C}_6\text{F}_5)_3]$	-21.0	Sharp		
$^a[\text{Zr}\{(\mu\text{-NC})\text{B}(\text{C}_6\text{F}_5)_3\}\text{Me}(\text{Cp}^*)] \mathbf{d}$	-19.6	-	C-B	2
$^b[\text{K}(18\text{-crown-6})][\text{NCB}(\text{C}_6\text{F}_5)_3] \mathbf{3}$	-22.5	Sharp	C-B	This work
$^b[\text{Me}_3\text{SiB}(\mu\text{-NC})\text{B}(\text{C}_6\text{F}_5)_3] \mathbf{4}$	-21.7	Sharp	C-B	This work
$^b[\text{Ir}\{(\mu\text{-NC})\text{B}(\text{C}_6\text{F}_5)_3\}(\text{PPh}_3)_2(\text{CO})] \mathbf{6}$	-22.8	Sharp	C-B	This work
$^b[\text{Fe}\{(\mu\text{-NC})\text{B}(\text{C}_6\text{F}_5)_3\}(\eta\text{-C}_5\text{H}_5)(\text{CO})_2] \mathbf{7a}$	-22.4	Sharp	C-B	This work

NMR data in a CD_2Cl_2 , b C_6D_6 , c CDCl_3 , d $\text{Cp}^* = 1,3\text{-C}_5\text{H}_3(\text{SiMe}_3)_2$.

the thiocyanate group is connected by a B(1)–N(1) bond (1.531(3) Å). Noteworthy, this bond is significantly shorter than the corresponding boron–nitrogen distances found in $[\text{Ph}_3\text{C}][(\text{C}_6\text{F}_5)_3\text{B}(\mu\text{-CN})\text{B}(\text{C}_6\text{F}_5)_3]^-$ (1.593(2) Å), $[\text{Ph}_3\text{C}]_2[\text{Ni}\{(\mu\text{-CN})\text{B}(\text{C}_6\text{F}_5)_3\}_4]$ (1.574(2) Å), $[\text{HNMe}_2\text{Ph}]_2[\text{Ni}\{(\mu\text{-CN})\text{B}(\text{C}_6\text{F}_5)_3\}_4]$ (1.582(3) and 1.578(3) Å) and $[\text{Ph}_3\text{C}]_2[\text{Pd}\{(\mu\text{-CN})\text{B}(\text{C}_6\text{F}_5)_3\}_4]$ (1.577(3) and 1.571(3) Å).^{1,2} In **1**, the C(1)–N(1) bond is 1.180(3) Å, somewhat longer than those found for several neutral $\text{RCNB}(\text{C}_6\text{F}_5)_3$ adducts (1.124(3) for R = Me and 1.135(3) for R = *p*-NO₂C₆H₄),⁹ or for the anion $[(\text{C}_6\text{F}_5)_3\text{B}(\mu\text{-CN})\text{B}(\text{C}_6\text{F}_5)_3]^-$ (1.144(2) Å).^{1,2} The C(1)–S(1) distance is 1.598(2) Å and the N(1)–C(1)–S(2) angle is close to linear (178.3(2)°). The coordination geometry about the boron centre is distorted tetrahedral, with N–B–C angles 108.03(18), 106.35(16)° and 106.89(17)° and the C–B–C angles measuring 112.02(16)° (C(11)–B(1)–C(31)), 112.12(16)° (C(11)–B(1)–C(21)) and 112.86(19)° (C(21)–B(1)–C(31)), and the mean B–C(aromatic) distance is *ca.* 1.650 Å. No solvent molecules are present and the closest intermolecular contact is 2.892(13) Å between K(2) and F(25) in an adjacent molecule in which the C(25)–F(25)–K(2) angle is 136.35(16)°. The cation is bound to $\text{B}(\text{C}_6\text{F}_5)_3$ via fluorine bridges, to form a chain-like supramolecular structure, as shown in Fig. 2. This structure accounts for the exceptional stability of **1** towards the attack of nucleophiles such as H₂O or PMe₃.

X-Ray diffraction methods alone cannot reliably distinguish between carbon and nitrogen in the systems $\text{E}_1(\mu\text{-CN})\text{E}_2$ and $\text{E}_1(\mu\text{-NC})\text{E}_2$. However, the refinement of crystal structures of **3** and **7a** considering a *NCB* system produced better solution to the data set (with smaller *R* and *wR* values) than for the *CNB* isomer. Furthermore, on inspection of the parameters for the thermal ellipsoids, it has been observed that the sizes of the ellipsoids are consistent for the *NCB* systems, without any large discrepancies, unlike the case of the *CNB* systems. The X-ray diffraction data, correlated with the observations from $^{11}\text{B}\{^1\text{H}\}$ NMR spectroscopy, strongly indicate that **3** and **7a** contain BCN units.

The asymmetric unit of **3** consists of one 18-crown-6 macrocycle containing potassium, one $[\text{NCB}(\text{C}_6\text{F}_5)_3]^-$ anion unit and one molecule of toluene in a general position. Also present in the asymmetric unit is half a molecule of toluene disordered about an inversion centre. The asymmetric unit of **7a** contains only $[\text{Fe}\{(\mu\text{-NC})\text{B}(\text{C}_6\text{F}_5)_3\}(\eta\text{-C}_5\text{H}_5)(\text{CO})_2]$. Figs. 3 and 4 show the ORTEP diagrams of the compounds $[\text{K}(18\text{-crown-6})][\text{NCB}(\text{C}_6\text{F}_5)_3]^-$ (**2**) and $[\text{Fe}\{(\mu\text{-NC})\text{B}(\text{C}_6\text{F}_5)_3\}(\eta\text{-C}_5\text{H}_5)(\text{CO})_2]$ (**7a**), respectively. The geometry around the boron centre is distorted tetrahedral in **3** and **7a**. For **3**, the C(1)–N(1) distance is 1.113(4) Å, whereas in **7a**, upon coordination to the Fe(II) centre, the corresponding distance increases to 1.135(3) Å. Both distances are slightly shorter than that found for $[\text{Zr}\{(\mu\text{-NC})\text{B}(\text{C}_6\text{F}_5)_3\}(\eta\text{-C}_5\text{H}_5)(\text{CO})_2]$.

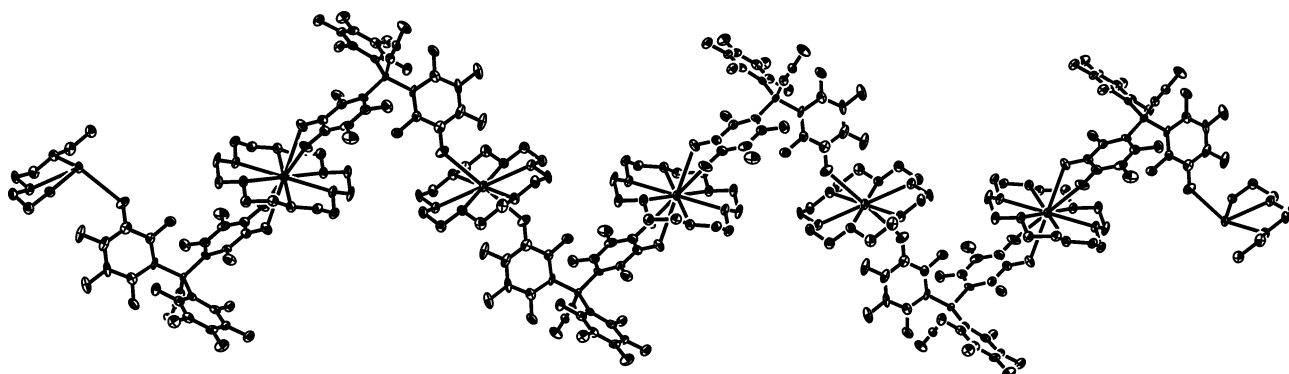


Fig. 2 Extended chain-like structure of $[K(18\text{-crown-6})][\text{SCNB}(\text{C}_6\text{F}_5)_3]$ (**1**).

Table 3 Selected bond lengths (Å) and angles (°) for compounds **1**, **3** and **7a**

1	C(1)–N(1)	1.180(3)	N(1)–C(1)–S(1)	178.3(2)
	C(1)–S(1)	1.598(2)	C(1)–N(1)–B(1)	173.1(2)
	C(11)–B(1)	1.650(3)	C(11)–B(1)–C(21)	112.12(16)
	C(21)–B(1)	1.654(3)	C(11)–B(1)–C(31)	112.02(16)
	C(31)–B(1)	1.647(3)	C(21)–B(1)–C(31)	112.86(19)
	N(1)–B(1)	1.531(3)	C(11)–B(1)–N(1)	106.03(18)
	K(2)–F(25)	2.8902(13)	C(21)–B(1)–N(1)	106.35(16)
	K(2)–O(56)	2.8024(13)	C(31)–B(1)–N(1)	106.89(17)
	K(2)–O(59)	2.8039(13)		
	K(2)–O(59)	2.7855(13)		
3	N(1)–C(1)	1.113(4)	N(1)–C(1)–B(1)	173.7(3)
	C(1)–B(1)	1.609(4)	C(1)–B(1)–C(11)	111.3(2)
	C(11)–B(1)	1.637(4)	C(1)–B(1)–C(21)	104.2(2)
	C(21)–B(1)	1.655(4)	C(11)–B(1)–C(21)	108.3(2)
	C(31)–B(1)	1.649(4)	C(1)–B(1)–C(31)	105.0(2)
	K(1)–N(1)	2.9189(14)	C(11)–B(1)–C(31)	113.0(2)
	K(1)–O(53)	2.9064(14)	C(21)–B(1)–C(31)	114.7(2)
	K(1)–O(56)	2.8387(14)	K(1)–N(1)–C(1)	121.60(11)
	K(1)–O(41)	2.8094(14)		
	K(1)–O(44)	2.8709(14)		
	K(1)–O(47)	2.7734(14)		
	K(1)–O(50)	2.8431(14)		
	7a	Fe(1)–N(2)	1.9198(18)	Fe(1)–N(2)–C(3)
Fe(1)–C(38)		1.809(2)	N(2)–C(3)–B(4)	174.9(2)
Fe(1)–C(40)		1.793(2)	C(3)–B(4)–C(5)	111.55(16)
Fe(1)–C(42)		2.097(2)	C(3)–B(4)–C(16)	105.08(15)
Fe(1)–C(43)		2.078(2)	C(5)–B(4)–C(16)	107.28(15)
Fe(1)–C(44)		2.064(2)	C(3)–B(4)–C(27)	103.97(15)
Fe(1)–C(45)		2.103(2)	C(5)–B(4)–C(27)	113.94(15)
Fe(1)–C(46)		2.117(2)	C(16)–B(4)–C(27)	114.71(15)
N(2)–C(3)		1.135(3)	Fe(1)–C(38)–O(39)	179.7(2)
B(4)–C(3)		1.614(3)	Fe(1)–C(40)–O(41)	177.2(3)
B(4)–C(5)		1.636(3)		
B(4)–C(16)		1.653(3)		
B(4)–C(27)		1.646(3)		
C(38)–O(39)		1.127(3)		
C(40)–O(41)		1.122(3)		

$\text{B}(\text{C}_6\text{F}_5)_3\text{Me}(\text{Cp}'')_2$, where $\text{Cp}'' = \eta\text{-}1,3\text{-C}_5\text{H}_3(\text{SiMe}_3)_2$ (1.149(3) Å).² The C–B distances for **3** and **7a** were found to be 1.609(4) and 1.614(3) Å, respectively, close to the distance found for C–B in $[\text{Zr}\{\mu\text{-NC}(\text{C}_6\text{F}_5)_3\}\text{Me}(\text{Cp}'')_2]$ (1.614(4) Å).² For both compounds, the B–C–N angles are approaching linearity (174.9(2)° in **7a** and 173.7(3)° in **3**). The C(1)–N(1)–K(1) angle found for **3** was 121.60(11)°, whereas the C–N–Fe unit of **7a** is almost linear (178.11(17)°). The latter is close to the angle C–N–Zr in $[\text{Zr}\{\mu\text{-NC}(\text{C}_6\text{F}_5)_3\}\text{Me}(\text{Cp}'')_2]$, $\text{Cp}'' = \eta\text{-}1,3\text{-C}_5\text{H}_3(\text{SiMe}_3)_2$, which is 175.1(2)°.²

DFT calculations

Density functional calculations have been carried out to investigate the relative stability of the system $\text{E}_1(\mu\text{-NC})\text{B}$ vs. $\text{E}_1(\mu\text{-CN})\text{B}$ for several of the new compounds. The C_6F_5 groups were substituted by fluorine atoms to reduce computational

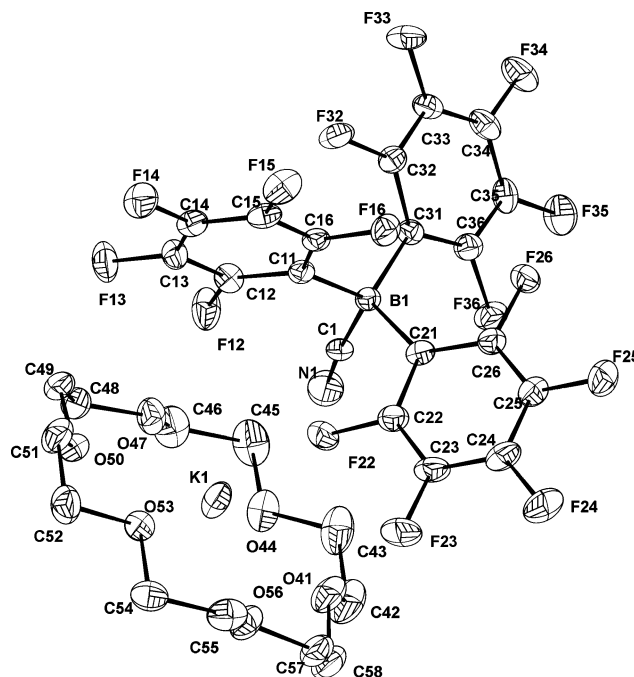


Fig. 3 ORTEP of $[K(18\text{-crown-6})][\text{NCB}(\text{C}_6\text{F}_5)_3]$ (**3**).

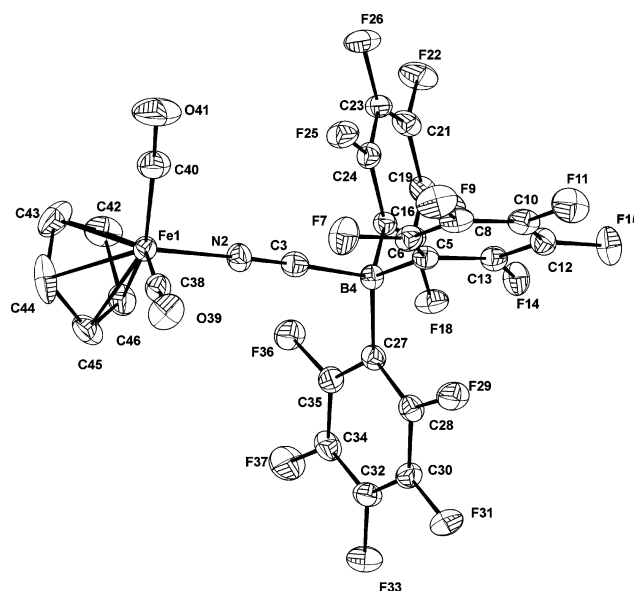


Fig. 4 ORTEP of $[\text{Fe}\{\mu\text{-NC}(\text{C}_6\text{F}_5)_3\}\{\eta\text{-C}_5\text{H}_5\}(\text{CO})_2]$ (**7a**).

time. Geometry optimisations were carried out for the neutral species: $[\text{Me}_3\text{Si}(\mu\text{-NC})\text{BF}_3]$ (**I**), $[\text{Me}_3\text{Si}(\mu\text{-CN})\text{BF}_3]$ (**I'**), $[\text{Hg}\{\mu\text{-NC}(\text{C}_6\text{F}_5)_3\}_2]$ (**II**), $[\text{Hg}\{\mu\text{-CN}(\text{C}_6\text{F}_5)_3\}_2]$ (**II'**), $[\text{Fe}\{\mu\text{-NC}(\text{C}_6\text{F}_5)_3\}\{\eta\text{-C}_5\text{H}_5\}(\text{CO})_2]$ (**III**), $[\text{Fe}\{\mu\text{-CN}(\text{C}_6\text{F}_5)_3\}\{\eta\text{-C}_5\text{H}_5\}(\text{CO})_2]$ (**III'**) and for the anionic species $[\text{NCBF}_3]^-$ (**IV**), $[\text{CNBF}_3]^-$

Table 4 Crystallographic data for compounds **1**, **3** and **7a**

	1	3	7a
Chemical formula	C ₃₁ H ₂₄ NBF ₁₅ KO ₆ S	C ₃₁ H ₂₄ NBF ₁₅ KO ₆ ·C _{10.5} H ₁₂	C ₂₆ H ₅ NBF ₁₅ FeO ₂
Formula weight	873.47	979.62	714.97
Crystal system	Monoclinic	Triclinic	Triclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 1	<i>P</i> 1
Unit cell dimensions:			
<i>a</i> /Å	8.9130(5)	12.8240(5)	9.9080(4)
<i>b</i> /Å	21.0570(15)	12.9440(6)	10.4020(4)
<i>c</i> /Å	18.7380(14)	13.6630(6)	12.6890(6)
<i>α</i> /°	90	108.484(2)	97.594(2)
<i>β</i> /°	97.339(5)	98.684(2)	92.383(2)
<i>γ</i> /°	90	90.807(2)	99.853(2)
<i>V</i> /Å ³	3488.0	2121.7	1274.4
<i>Z</i>	4	2	2
<i>D</i> _c /g cm ⁻³	1.66	1.533	1.86
<i>T</i> /K	150	150	150
<i>μ</i> /mm ⁻¹	0.34	0.240	0.73
Reflections collected	35534	17785	7026
Independent reflections	6629	8022	4866
<i>R</i> _{int}	0.04	0.018	0.03
Final <i>R</i> indices:			
<i>R</i>	0.0884	0.0828	0.0443
<i>wR</i>	0.0152	0.0712	0.0409

Note: criterion for observation, $I > 3\sigma(I)$.

(IV') and [F₃BNCBF₃]⁻ (V). Optimisations have also been performed on the model precursors Me₃SiCN, Me₃SiNC, Hg(NC)₂, Hg(CN)₂, [Fe(NC)(η⁵-C₅H₅)(CO)₂] and [Fe(CN)(η¹-C₅H₅)(CO)₂]. The results of all geometry optimisations are given in Table 5 together with the experimental values for compounds [(C₆F₅)₃B(μ-NC)B(C₆F₅)₃]_{1,2} **7a** and **3**. All E₁-N-C-B and E₁-C-N-B systems are very close to linear. Reasonable agreement between calculated and experimental distances confirms that, in general, the model works well despite the replacement of the C₆F₅ groups with fluorine atoms. In general the N-C(B) distances are shorter than the C-N(B) ones. In both systems the C-N distances decrease very slightly on coordination by BF₃. The N-B distances for the E₁(μ-CN)B unit and the C-B distances for the E₁(μ-NC)B unit show significant variation in the order E₁ = Hg > Me₃Si > Fp > BF₃ > anion for both series. The B-F distances correlate inversely with the B-N and B-C distances.

Energies for the model compounds were calculated using both the local density approximation (LDA) and using gradient corrections (GGA). Table 6 gives the calculated isomerisation energy for both the parent nitriles and isonitriles and the E₁(μ-CN)B vs. E₁(μ-NC)B systems. Both methods give a similar pattern. The almost universal preference is for the isomer (E₁(μ-CN)B).

Isomerisation between simple nitriles and isonitriles has been investigated both experimentally and computationally.^{15,17,18} The general conclusions are that σ-accepting substituents favour nitriles (E₁CN) over isonitriles (E₁NC) and that π-accepting substituents favour isonitriles (E₁NC) over nitriles (E₁CN).¹⁷ Our results are in agreement with this. In particular they agree with the low energy preference found for silylnitriles Si-CN where both σ- and π-accepting effects are important. For example values ranging between 18 and 31 kJ mol⁻¹ have been calculated for the isomerisation energy of H₃Si-CN to H₃Si-NC using DFT.^{18b}

The orbital responsible for the basic properties of the cyanide ion is the HOMO, 5σ (Fig. 5). This has electron density on both

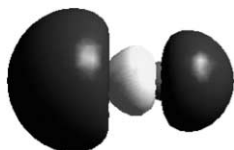


Fig. 5 The 5σ orbital of CN⁻.

the C and the N but is more localised on C. Thus the C is generally the preferred basic atom in coordination to a Lewis acid. As it is primarily non-bonding in character, little change in CN distance results from coordination to a Lewis acid. Table 5 lists the Mulliken charges of C in the E₁NC systems and of N in the E₁CN systems. In the parent E₁-NC and E₁-CN molecules they are reduced compared with free cyanide, and further reduced on coordination to BF₃. Within a series the charge varies Hg < SiMe₃ < Fp < anion (the anion having the most negative charge). This correlates well with the C-B and N-B distances noted above, the least charged atoms forming the longer bonds to BF₃. Thus the better E₁ as a σ acceptor, the weaker the further bond for E₂-BF₃. From Table 6 it can be seen that the isomerisation energies are less favourable after BF₃ coordination. Just as nitriles E₁CN are generally found to be more stable than isonitriles E₁NC because C is the more basic site, the E₁(μ-NC)B systems are relatively more stabilised on BF₃ coordination as in this case it is the C atom that binds to the BF₃ group. The isomerisation energy difference for E₁=SiMe₃ is just sufficient to reverse the preference so that [Me₃Si(μ-NC)BF₃] is found to be marginally more stable than [Me₃Si(μ-CN)BF₃]. Since Me₃SiNC and Me₃SiCN are known to be in equilibrium at room temperature, it is not surprising that treatment of Me₃SiCN with B(C₆F₅)₃ leads to formation of [Me₃Si(μ-NC)B(C₆F₅)₃] (**4**). In all other cases the calculations indicate the complexes E₁(μ-CN)B to be the thermodynamically favoured isomer.

Conclusions

New main group and transition element derivatives of the anions [SCNB(C₆F₅)₃]⁻, [CNB(C₆F₅)₃]⁻ and [NCB(C₆F₅)₃]⁻ have been prepared and characterised. New routes towards formation of complexes containing the bulky anionic ligand [NCB(C₆F₅)₃]⁻ are described. We have observed formation of the E₁(μ-NC)B(C₆F₅)₃ linkages in the complexes **6** and **7a**. Calculations indicate that in general energetic preference is for the E₁(μ-CN)B.

Experimental

All reactions were carried out under dinitrogen, either in a glove-box or using conventional Schlenk-line techniques. The compounds [FeCl(η¹-C₅H₅)(CO)₂],¹⁹ [Fe(CN)(η¹-C₅H₅)(CO)₂],¹⁹

Table 5 Selected DFT calculated distances (Å) and angles (°) for I–V, I'–IV', Me₃SiCN, Me₃SiNC, FpCN, FpNC, Hg(NC)₂ and Hg(CN)₂. Where available experimental distances of the related B(C₆F₅)₃ derivatives are given for comparison (Fp = Fe(η-C₅H₅)(CO)₂)

Type <i>E_INC</i>	E _I –N	N–C	C–B	B–F	Charge on C
I [Me ₃ Si(μ–NC)BF ₃] ^a	1.793	1.160	1.683	1.365	0.08
Me ₃ SiNC	1.760	1.178	–	–	–0.11
II [Hg{(μ–NC)BF ₃ }] ₂	1.935	1.162	1.712	1.361	0.03
Hg(NC) ₂	1.94	1.177	–	–	–0.09
III [Fp(μ–NC)BF ₃]	1.860	1.158	1.655	1.372	–0.07
7a ^b	1.9198(18)	1.135(3)	1.614(3)	–	–
FpNC	1.882	1.175	–	–	–0.19
IV [NCBF ₃] [–]	–	1.161	1.621	1.391	–0.07
3 ^c	–	1.113(4)	1.609(4)	–	–
[CN] [–]	–	1.174	–	–	–0.5
V [BF ₃ (μ–NC)BF ₃] [–]	1.578	1.152	1.644	1.379	0.07
[(μ–NC){B(C ₆ F ₅) ₃ }] ^{–d}	–	1.144(2)	1.583(2)	–	–

Type <i>E_ICN</i>	E _I –C	C–N	N–B	B–F	Charge on N
I' [Me ₃ Si(μ–CN)BF ₃] ^a	1.885	1.152	1.643	1.353	–0.08
Me ₃ SiCN	1.885	1.161	–	–	–0.22
II' [Hg{(μ–CN)BF ₃ }] ₂	1.986	1.150	1.752	1.350	0.03
Hg(CN) ₂	1.989	1.160	–	–	–0.19
III' [Fp(μ–CN)BF ₃]	1.828	1.158	1.596	1.367	–0.13
FpCN	1.872	1.165	–	–	–0.30
IV' [CNBF ₃] [–]	–	1.168	1.537	1.386	–0.20
[CN] [–]	–	1.174	–	–	–0.5
V [BF ₃ (μ–CN)BF ₃] [–]	1.644	1.152	1.578	1.379	–0.2
[(μ–CN){B(C ₆ F ₅) ₃ }] ^{–d}	–	1.144(2)	1.593(2)	–	–

Note: ^a Average distances (Å) for Si–C(Me): 1.845 (**I**) and 1.850 (**I'**). ^b Average distances (Å): Fe–C(Cp) 2.070 (**II'**), 2.074 (**II**); Fe–C(O): 1.743 (**II**), 1.739 (**II'**), C–O 1.148 (**II**) and 1.147 (**II'**). ^c X-Ray values, this work. ^d X-Ray values, literature data.^{1,2}

Table 6 Calculated energies Δ*E*_{isom} (kJ mol^{–1}) for the isonitrile (E_I–NC and E_I(μ–NC)B) → nitrile (E_I–CN and E_I(μ–CN)B) isomerisation energies at both the LDA and the GGA level

Isomerisation		Δ <i>E</i> _{isom} /kJ mol ^{–1} (GGA)	Δ <i>E</i> _{isom} /kJ mol ^{–1} (LDA)
[Me ₃ Si(μ–NC)BF ₃] → [Me ₃ Si(μ–CN)BF ₃]	I → I'	+3	+2
Me ₃ SiNC → Me ₃ SiCN		–20	–18
[Hg{(μ–NC)BF ₃ }] ₂ → [Hg{(μ–CN)BF ₃ }] ₂	II → II'	–96	–102
[Hg(NC) ₂] → [Hg(CN) ₂]		–149	–153
[Fp(μ–NC)BF ₃] → [Fp(μ–CN)BF ₃]	III → III'	–60	–73
[FpNC] → [FpCN]		–79	–87
[NCBF ₃] [–] → [CNBF ₃] [–]	IV → IV'	+24	+20

and B(C₆F₅)₃,²⁰ were prepared according to the literature methods. [IrCl(PPh₃)₂(CO)] was used as supplied by Aldrich. The compound B(C₆F₅)₃ was freshly sublimed before use. NMR spectra were recorded on either a 300 MHz Varian Mercury or a 500 MHz Varian Unity spectrometer, referenced internally using the residual protio-solvent, and chemical shifts were reported with respect to SiMe₄ (¹H and ¹³C, δ = 0), BF₃·Et₂O (¹¹B, δ = 0), H₃PO₄ (³¹P, δ = 0) and CFCl₃ (¹⁹F, δ = 0). All chemical shifts are quoted in δ (ppm) and coupling constants in Hz. Infrared spectra were recorded on either a Perkin-Elmer 1710 IR FT spectrometer or a Perkin-Elmer 1600 FTIR. Elemental analyses and mass spectra were provided by the Micro-analytical Services of the Inorganic Chemistry Laboratory, Oxford.

Preparations

[K(18-crown-6)][SCNB(C₆F₅)₃] (1). In a glove-box, a Schlenk vessel was charged with KSCN (38 mg, 0.39 mmol), B(C₆F₅)₃ (200 mg, 0.39 mmol). A separate Schlenk vessel was charged with 18-crown-6 ether (103 mg, 0.39 mmol) and 50 mL of toluene was added. This solution was added slowly under stirring to the Schlenk vessel containing a mixture of KSCN and B(C₆F₅)₃. The mixture was stirred at room temperature for 5 days. Volatiles were removed under reduced pressure to yield an off-white oily material, which was washed with 20 mL cold pentane. The resulting powder (crude yield: 254 mg,

74.5%) was recrystallised from a mixture of CH₂Cl₂ and pentane to give white crystals of **1**. The reaction was subsequently repeated in benzene, THF or CH₂Cl₂ and similar results were obtained.

Elemental analysis (%). Calc. (found) for C₃₁H₂₄NBF₁₅KO₆S: C 42.6 (42.3), H 2.8 (2.9), N 1.6 (1.5). FAB⁺ *m/z* (intensity (%)): 873.2 (100) [SCNB(C₆F₅)₃][–].

[K(18-crown-6)][(C₆F₅)₃B(μ–CN)B(C₆F₅)₃] (2). *Method 1.* In a glove-box, a Schlenk vessel was charged with KCN (25 mg, 0.38 mmol), B(C₆F₅)₃ (200 mg, 0.39 mmol). A separate Schlenk vessel was charged with 103 mg (0.391 mmol) 18-crown-6 ether and toluene (50 mL) was added and the resulting solution was added slowly to the initial mixture. This was then stirred at room temperature for 24 h and the solution turned orange. The white solid formed was isolated by filtration and dried under reduced pressure. ¹H- and ¹¹B{¹H}-NMR spectra showed that this solid contains mainly starting materials. From the filtrate, volatiles were removed under reduced pressure to yield a brown oil. Recrystallisation from CH₂Cl₂ gave a small amount of light-yellow crystals (yield <10%) characterised by ¹¹B{¹H} NMR as [K(18-crown-6)][(C₆F₅)₃B(μ–CN)B(C₆F₅)₃] (**2**). The reaction was subsequently repeated in a number of different solvents (THF, toluene, CH₂Cl₂ or CH₃CN) using 2 : 2 : 1 or 1 : 1 : 2 ratios of 18-crown-6 ether, KCN and B(C₆F₅)₃. In each case, only the compound [K(18-crown-6)][(C₆F₅)₃B(μ–CN)B(C₆F₅)₃] (**2**) was obtained in low yield.

Method 2. In a glove-box, a Schlenk vessel was charged with 18-crown-6 ether (1 g, 3.8 mmol) and KCN (247 mg, 3.8 mmol). Dry methanol was then added, and the mixture was stirred at 40 °C overnight. The solution was then cooled to room temperature and the MeOH removed under reduced pressure. The residual white solid, was soluble in CH₂Cl₂ and insoluble in toluene and was washed with pentane and dried under reduced pressure to yield 1.16 g (93% yield) of [K(18-crown-6)CN]. Then B(C₆F₅)₃ in CH₂Cl₂ (50 mL) was added slowly to a solution of [K(18-crown-6)CN] (300 mg, 0.91 mmol) in 20 mL CH₂Cl₂. The mixture was stirred at room temperature under N₂ for 30 min. The volatiles were removed from the light-yellow solution under reduced pressure to give a creamy-white solid. This was extracted with toluene (10 mL). The toluene was removed under reduced pressure and the resulting brown, oily solid was recrystallised from a mixture of CH₂Cl₂ and pentane to give light-yellow crystals of [K(18-crown-6)][(C₆F₅)₃B(μ-CN)-B(C₆F₅)₃] (**2**). Yield: 540 mg, 36%.

Elemental analysis (%). Calc. (found) for C₁₃H₂₄NKO₆: C 47.4 (47.7), H 7.3 (7.2), N 4.25 (4.3). Calc. (found) for C₄₀H₂₄NB₂F₃₀KO₆: C 43.5 (43.27), H 1.8 (1.9), N 1.0 (1.0). ES⁻ *m/z* (intensity (%)): 1046.28 (30) [(C₆F₅)₃B(μ-CN)B(C₆F₅)₃]⁻.

[K(18-crown-6)][NCB(C₆F₅)₃] (3**).** *Method 1.* In a glove-box, a two-neck, round bottom flask was charged with potassium metal (230 mg, 5.88 mmol), [Hg{(μ-CN)B(C₆F₅)₃}₂] (**5**) (1 g, 0.783 mmol) (prepared as described below) and 18-crown-6 ether (415 mg, 1.57 mmol). Toluene (200 mL) was added and the mixture was stirred at the room temperature for 1 h. The mixture became cloudy, and was then heated at 90 °C for 7 h. The resulting black solid was removed by filtration. From the light-yellow filtrate, volatiles were removed under reduced pressure to yield an off-white solid. Recrystallisation from toluene at -80 °C gave the compound [K(18-crown-6)][NC{B(C₆F₅)₃}₂] (**3**) (450 mg, 29% yield) as colourless needle-like crystals.

Method 2. A solution of 18-crown-6 ether (140 mg, 0.53 mmol) in toluene (50 mL) was added to KCl (140 mg, 1.88 mmol) and the resulting mixture was stirred for 2 h, at room temperature. A solution of [Me₃Si(μ-NC)B(C₆F₅)₃] (**4**) (0.31 g, 0.53 mmol) (prepared as described below) in toluene (50 mL) was subsequently added and the mixture stirred for 2 h. The solids were removed by filtration and, from the filtrate, volatiles were removed under reduced pressure to give a white solid. After recrystallisation from toluene at -80 °C, 323 mg (73% yield) of compound **3** were obtained as fine colourless crystals, suitable for study by X-ray diffraction.

Elemental analysis (%). Calc. (found) for C₃₁H₂₄NBF₁₅KO₆: C 44.25 (44.0), H 2.8 (2.85), N 1.7 (1.7). ES⁻ *m/z* (intensity (%)): 536.09 (100) [CN{B(C₆F₅)₃}₂]⁻.

[Me₃Si(μ-NC)B(C₆F₅)₃] (4**).** *NMR-scale reaction.* The compounds Me₃SiCN (0.013 mL, 0.1 mmol) and B(C₆F₅)₃ (0.05 g, 0.1 mmol) were mixed at room temperature in a glove-box in a Young's tap NMR tube and C₆D₆ was added. The NMR spectra, recorded within 15 min, showed quantitative formation of [Me₃Si(μ-NC)B(C₆F₅)₃] (**4**). *Synthesis.* Me₃SiCN (0.15 mL, 1.12 mmol) in 40 mL CH₂Cl₂ was added to B(C₆F₅)₃ (0.6 g, 1.17 mmol) in 20 mL CH₂Cl₂ and the resulting mixture was subsequently stirred for 1 h. The solvents were removed under reduced pressure, the crude yellow-white powder was washed with pentane (2 × 15 mL), and the product was recrystallised from a saturated CH₂Cl₂ solution layered with pentane. Compound **4** (530 mg, 77% yield) was isolated as a white, micro-crystalline material.

Elemental analysis (%). Calc. (found) for C₂₂H₉NBF₁₅Si: C 43.2 (42.9), H 1.5 (1.1), N 2.3 (2.0). FAB⁺ *m/z* (intensity (%)): 610.2 (40) [Me₃SiNCB(C₆F₅)₃]⁺.

[Hg{(μ-CN)B(C₆F₅)₃}₂] (5**).** In a glove-box, the compounds [Hg(CN)₂] (0.25 g, 0.97 mmol) and B(C₆F₅)₃ (1 g, 1.95 mmol)

were mixed in a Schlenk vessel and 50 mL CH₂Cl₂ added. The mixture was stirred at room temperature under N₂ for 15 h. From the clear solution, the volatiles were removed under reduced pressure to give a white solid, which was washed with pentane (2 × 10 mL) and dried under reduced pressure to give 1.1 g (87% yield) **5** as a white solid.

Elemental analysis (%). Calc. (found) for C₃₈N₂F₃₀B₂Hg: C 35.75 (36.0), N 2.2 (2.3). FAB⁺ *m/z* (intensity (%)): 1277.6 (85) [Hg{(μ-CN)B(C₆F₅)₃}₂]⁺.

[Ir{(μ-NC)B(C₆F₅)₃}(PPh₃)₂(CO)] (6**).** [Me₃Si(μ-NC)-B(C₆F₅)₃] (**4**) was prepared *in situ* by addition of Me₃SiCN (0.033 mL, 0.25 mmol) to a solution of B(C₆F₅)₃ (128 mg, 0.25 mmol) in CH₂Cl₂ (50 mL). The mixture was then stirred for 5–10 min before being added to a solution of [IrCl(PPh₃)₂(CO)] (195 mg, 0.25 mmol) in CH₂Cl₂ (50 mL). The solution was left stirring for 2 h, and the initially pale yellow colour changed to a bright-yellow. The solution was subsequently filtered, volatiles removed under reduced pressure and the resulting residue was washed with pentane (2 × 20 mL) to yield a yellow powder. The solid was then recrystallised from CH₂Cl₂ at -80 °C to give compound **5** (120 mg, 37% yield) as a microcrystalline yellow powder.

Elemental analysis (%). Calc. (found) for C₅₆H₃₀NOBF₁₅IrP: C 52.4 (52.2), H 1.1 (1.2), N 2.4 (2.65). FAB⁺ *m/z* (intensity (%)): 1282.5 (8.5) [Ir{(μ-NC)B(C₆F₅)₃}(PPh₃)₂(CO)]⁺.

[Fe{(μ-NC)B(C₆F₅)₃}(η-C₅H₅)(CO)] (7a**).** [Me₃Si(μ-NC)-B(C₆F₅)₃] (**4**) was prepared *in situ* by addition of Me₃SiCN (0.13 mL, 1.00 mmol) to a solution of B(C₆F₅)₃ (512 mg, 1.00 mmol) in CH₂Cl₂ (50 mL). The mixture was then stirred for 30 min before being added to a solution of [Fe(η-C₅H₅)(CO)₂Cl] (213 mg, 1.00 mmol) in CH₂Cl₂ (50 mL). The solution was then left stirring overnight, after which time the red colour had darkened to red-brown. The volatiles were subsequently removed under reduced pressure to a red solid. This was washed with light petroleum (bp 40–60 °C) (2 × 15 mL) and recrystallised from a 1 : 1 mixture of pentane and CH₂Cl₂ to give 486 mg (68% yield) of **7a** as a red, microcrystalline solid. Crystals of **7a**, suitable or for X-ray analysis were obtained by diffusion of pentane into a concentrated CH₂Cl₂ solution.

Elemental analysis (%). Calc. (found) for C₂₆H₅NBF₁₅FeNO₂: C 43.7 (43.2), H 0.7 (0.3), N 2.00 (1.8), Fe 7.8 (7.1). FAB⁺ *m/z* (intensity (%)): 715.0(5) [Fe{(μ-NC)B(C₆F₅)₃}(η-C₅H₅)(CO)]⁺, 658.9(13.5) [Fe{(μ-NC)B(C₆F₅)₃}(η-C₅H₅)]⁺.

[Fe(μ-CN)B(C₆F₅)₃(η-C₅H₅)(CO)] (7b**).** The solids B(C₆F₅)₃ (20 mg, 0.039 mmol) and [Fe(CN)(η⁵-C₅H₅)(CO)]₂ (5 mg, 0.025 mmol) were placed in a Young's tap NMR tube and C₆D₆ (or CD₂Cl₂) added. ¹H-, ¹⁹F- and ¹¹B{¹H}-NMR spectra recorded within 15 min showed the quantitative formation of [Fe{(μ-CN)B(C₆F₅)₃}(η-C₅H₅)(CO)] (**7b**).

X-Ray crystallography

In each case, a single crystal was selected under an inert atmosphere, encased in perfluoro-polyether oil, and mounted on the end of a glass fibre. The fibre, secured in a goniometer head was then placed under a stream of cold nitrogen maintained at 150 K and data collected on an Enraf-Nonius DIP2000 image plate diffractometer with graphite monochromated Mo-K α radiation ($\lambda = 0.71069$ Å) The images were processed with the DENZO and SCALEPACK programs²¹ and corrections for Lorentz and polarisation effects were performed. All solution, refinement, and graphical calculations were performed using the CRYSTALS²² and CAMERON²³ software packages. The structures were solved by direct methods using the SIR92²⁴ program and refined by full-matrix least squares procedure on *F*. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were generated and

allowed to ride on their corresponding carbon atoms with fixed thermal parameters. An empirical absorption correction was applied.²⁵ The crystallographic data are summarised in Table 3. In addition, refinement using full-matrix least squares on all F^2 data²⁶ was also performed for **3** and **7a**. Both refinements methods (either on F or on F^2) gave better results (lower R and wR) for the model with the CN group N-bound to the metal (K in case of **3**, or Fe in case of **7a**) than for the model where this group is C-bound to the metal. The inspection of the parameters for the thermal ellipsoids also indicated that the model containing *NCB* units are better solutions to the data sets than those incorporating the *CNB* units. These results are consistent with the observations from $^{11}\text{B}\{^1\text{H}\}$ NMR spectroscopy and the previously reported data.²

CCDC reference numbers 204648–204650.

See <http://www.rsc.org/suppdata/dt/b3/b302163g/> for crystallographic data in CIF or other electronic format.

Computational details

All calculations were performed using density functional methods of the Amsterdam Density Functional Package (version 2000.2).^{27–30} The electronic configurations of the molecular systems were described using type IV basis sets with triple ζ accuracy sets of Slater type orbitals, with a single polarisation function added to the main group atoms. The cores of the atoms were frozen up to 2p for Fe, 4d for Hg, 1s for C, O and N, 2p for Si. First-order relativistic corrections were made to the cores of all atoms using the ZORA formalism. The generalised gradient approximation (GGA non-local) method was used, using Vosko, Wilk and Nusair's local exchange correlation³¹ with non-local exchange corrections by Becke³² and non-local correlation corrections by Perdew.³³ The non-local correction terms were not utilised in calculating gradients during geometry optimisations as better agreement with experimental structure is normally achieved with a local density approximation.

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