A main-group donor–acceptor adduct: 1,3,4,5-tetramethylimidazol-2-yl-idene–tris(pentafluorophenyl)borane

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The solid-state structural analysis of the title compound, $Me_4C_2N_2C{\rightarrow}B(C_6F_5)_3$ or $C_{25}H_{12}BF_{15}N_2$, provides useful metric parameters for the qualitative comparison of the donor strength with other mono- and dicoordinate main-group compounds which feature distinctive lone-pair character.

Comment

The V-shaped dicoordinate ylene species are among the most important low-valent main-group compounds. Among the most studied of this family are the planar five-membered heterocycles where the central element is flanked by two imine groups, (I). The different types of central element include anions (Ga), neutral tetrels (C, Si, Ge and Sn) and cationic pnictogens (P, As and Sb). Imidazol-2-ylidene, (II), is the most developed in terms of synthesis, characterization and reactivity (Arduengo *et al.*, 1992; Bourissou *et al.*, 2000). In parallel work, tris(pentafluorophenyl)borane has been developed into one of the most important Lewis acids for early transition-metal catalysis (Piers & Chivers, 1997) and in the synthesis of unusual low-coordinate main-group complexes (Hino *et al.*, 2004). The strong acceptor properties of $B(C_6F_5)_3$ are useful for probing the donor capabilities of different low-valent main-group compounds with singlet lone-pair character, including terphenyl-stabilized [(IIIa)–(IIIc) (see scheme), $E = $ Ga (Hardman *et al.*, 2003), In (Haubrich & Power, 1998) or Tl (Niemeyer & Power, 1998)] and η^5-C_5Me_5-stabilized [(IV), $E = $ Al (Haaland *et al.*, 1995) or Ga (Loos *et al.*, 1997)] triels and the β-diketiminate-chelated Ga species, (V) (Hardman *et al.*, 2000). In order to construct a qualitative scale to determine the strength of donor–acceptor interactions for the comparison of (II) with (III), (IV) and (V), the synthesis and crystallographic characterization of the title adduct, (VI), consisting of 1,3,4,5-tetramethylimidazol-2-ylidene (imid) and $B(C_6F_5)_3$, was performed.

The structure of (VI) reveals a $B-C_{carbene}$ bond length (Table 1) equal or near to those observed in imidazol-2-ylidene$\rightarrow BF_3$ adducts, including [HCN(Mes)]$_2$C$\rightarrow BF_3$ [Mes = C_6H_2-2,4,6-$(CH_3)_3$; 1.635 (8) Å; Arduengo *et al.*, 2000) and

(II)$\rightarrow BF_3$ [mean 1.646 (8) Å; Kuhn *et al.*, 1997]. Moreover, this distance is equivalent to the B$-$C single bond in the $[H_3C-B(C_6F_5)_3]^-$ anion [1.635 (4) Å; Galsworthy *et al.*, 1998].

The core parameters of the imidazol-2-ylidene unit in (VI) deviate only slightly from those of the uncomplexed form (Arduengo *et al.*, 1992). In particular, the increased N$-$C1$-$N bond angle is consistent with displacement of the lone pair toward B. The three C_6F_5 groups adopt a typical C_3 propeller-type orientation, with one of the *ortho* F atoms pointing directly towards to the central atom C1, generating a short F$\cdots$C distance.

(I) (IIIa) $R_1=R_2={}^iPr$
(IIIb) $R_1={}^iPr$, $R_2=$H
(IIIc) $R_1={}^iPr$, $R_2={}^iBu$
(II) (IV) (V) (VI)
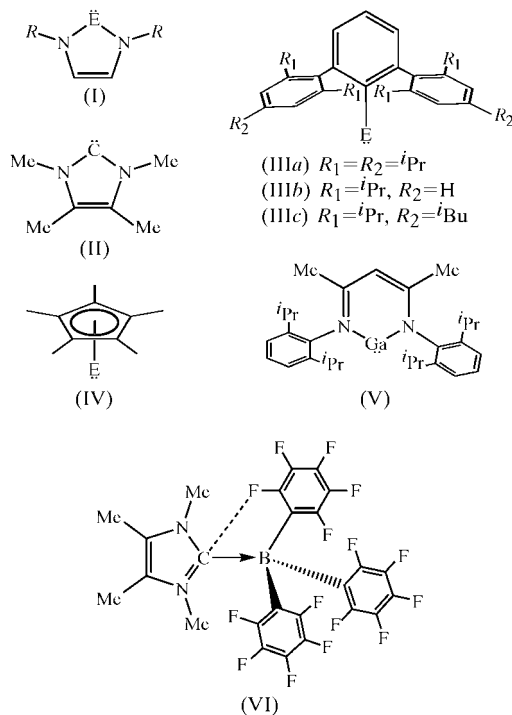
The triel $B(C_6F_5)_5$ adducts feature shorter $E\cdots F$ interactions than that in (VI) (Table 2). The $C_{imid}-B-C_{C_6F_5}$ bond angles in (VI) follow a pattern of increasing $E-B-C_{C_6F_5}$ values, consistent with the triel complexes (Table 2). The largest angle is associated with the C_6F_5 group, which approximately eclipses the imidazol-2-ylidene plane in (VI). The unequal B$-$C$-$N1,2 bond angles in (VI) (Table 1) are the result of steric interactions, which cause a slight tilting of the carbene ring away from the eclipsing C_6F_5 group. The range of $E-B-C_{C_6F_5}$ bond angles in the (III)$\rightarrow B(C_6F_5)_3$ series is narrower, whereas the values resemble those of the $[H_3C-B(C_6F_5)_3]^-$ anion. Interestingly, the $C_{C_6F_5}-B-C_{C_6F_5}$ bond angles for the $B(C_6F_5)_3$ group in (VI) are typified by two large angles and one small angle. The B$-C_{C_6F_5}$ bond lengths correlate to the interaction strength of the coordinating central element with the $B(C_6F_5)_3$ moiety. Comparison of the B$-C_{C_6F_5}$ distances for the series of (IIIa)–(IIIc) and (IV) $B(C_6F_5)_3$ complexes (Table 2) reveals they are identical or very close to the values observed in $B(C_6F_5)_3$ adducts containing weak donors, such as thiophene [1.626 (3) Å; Schaper & Brintzinger, 2002] and Ph_3PO [1.637 (4) Å; Beckett *et al.*, 2001], whereas (VI) has values equivalent to those of the $[H_3C-B(C_6F_5)_3]^-$ anion [1.657 (3) Å; Galsworthy *et al.*, 1998].

organic compounds
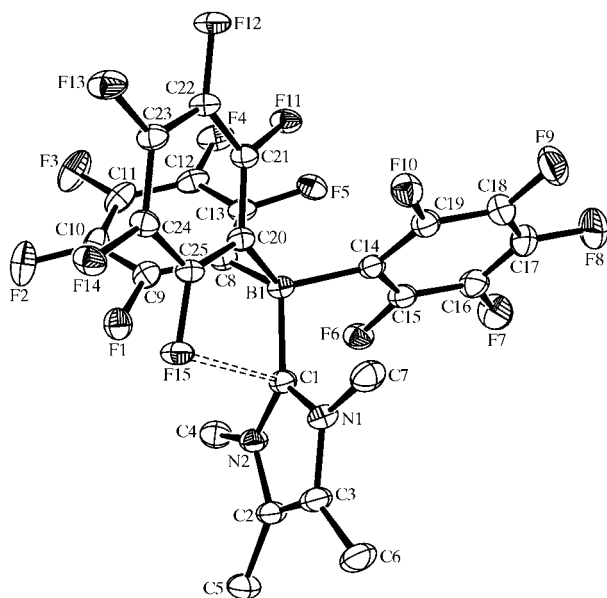
Figure 1
A view of (VI), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms have been omitted for clarity.

In conclusion, considering the geometric parameters given in Table 2, it is evident that (II) is a stronger donor than the triel species (IIIa)–(IIIc), (IV) and (V). However, as expected, it is a weaker donor compared with the methylate anion, as correlated with the measured pK_a values for these compounds [48 *versus* 24 for (II) in dimethyl sulfoxide].

Analysis of the packing structure for (VI) reveals that fluorine groups are engaged in a number of intermolecular hydrogen-bonding interactions, the shortest of which [2.464 (3) Å] is between atoms F11 and H6B.

Experimental

Air- and moisture-sensitive colourless crystals were obtained from the overnight 238 K cooling of a saturated *n*-hexanes solution of (VI), which was prepared by the 1:1 stoichiometric addition of (II) with a 1.0 *M* hydrocarbon solution of $B(C_6F_5)_3$ (B2). Crystal selection and preparation, including mounting, were carried out according to the literature procedure of Hope (1995).

Crystal data

$C_{25}H_{12}BF_{15}N_2$	$D_x = 1.505$ Mg m^{-3}
$M_r = 636.18$	Mo $K\alpha$ radiation
Monoclinic, $C2/c$	Cell parameters from 924
$a = 24.253$ (2) Å	reflections
$b = 13.9530$ (12) Å	$\theta = 2.5$–31.5°
$c = 20.2762$ (19) Å	$\mu = 0.16$ mm^{-1}
$\beta = 125.102$ (2)°	$T = 90$ (2) K
$V = 5613.6$ (9) Å^3	Block, colourless
$Z = 8$	$0.41 \times 0.22 \times 0.20$ mm

Data collection

Bruker SMART 1000 CCD area-detector diffractometer	8716 independent reflections
	6544 reflections with $I > 2\sigma(I)$
ω scans	$R_{int} = 0.026$
Absorption correction: multi-scan (*SADABS*; Blessing, 1995; Sheldrick, 2003)	$\theta_{max} = 31.5°$
	$h = -35 \rightarrow 34$
	$k = -19 \rightarrow 19$
$T_{min} = 0.938$, $T_{max} = 0.968$	$l = -29 \rightarrow 28$
36 849 measured reflections	

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0541P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.037$	$+ 1.1478P]$
$wR(F^2) = 0.103$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.07$	$(\Delta/\sigma)_{max} = 0.001$
8716 reflections	$\Delta\rho_{max} = 0.38$ e Å^{-3}
436 parameters	$\Delta\rho_{min} = -0.22$ e Å^{-3}
H-atom parameters constrained	

Table 1
Selected geometric parameters (Å, °).

N1—C1	1.3572 (14)	C1—B1	1.6407 (16)
N1—C3	1.3870 (15)	C8—B1	1.6555 (16)
N2—C1	1.3529 (14)	C14—B1	1.6500 (17)
N2—C2	1.3968 (15)	C20—B1	1.6552 (15)
C1—N1—C3	111.08 (10)	C1—B1—C20	110.85 (9)
C1—N2—C2	110.49 (10)	C14—B1—C20	115.10 (9)
N2—C1—N1	104.98 (10)	C1—B1—C8	115.91 (9)
N2—C1—B1	132.38 (10)	C14—B1—C8	112.71 (9)
N1—C1—B1	122.59 (9)	C20—B1—C8	99.84 (8)
C1—B1—C14	102.98 (8)		

Table 2
Comparative bond distances (Å) and angles (°) for complexes of the type $L(E) \rightarrow B(C_6F_5)_3$.

L	E	Average B—C	E—B—C	E—B—C	E—B—C	E—F	Reference†
(II)	C	1.652 (5)	103.0 (1)	110.9 (1)	115.9 (1)	2.756 (2)	a
(IV)	Al	1.634 (3)	102.9 (2)	105.6 (2)	107.9 (1)	n/a	QELBAK[b]
(IIIa)	Ga	1.630 (12)	104.6 (3)	106.8 (3)	107.5 (4)	2.394 (2)	WUWPEJ[c]
(IIIb)	Ga‡	1.628 (9)	104.2 (3)	106.5 (3)	107.8 (3)	2.441 (5)	WUWPOT[c]
		1.628 (4)	105.1 (3)	106.0 (3)	107.5 (3)	2.384 (5)	
(IIIc)	Ga	1.633 (5)	104.1 (1)	104.8 (1)	106.2 (1)	2.435 (2)	WUWPIN[b,c]
(IV)	Ga	1.628 (5)	103.0 (1)	105.0 (1)	105.2 (1)	n/a	VOGQUD[d]
(V)	Ga‡	1.645 (6)	104.9 (2)	106.4 (2)	112.6 (2)	2.451 (2)	VOGQOX[d]
		1.637 (9)	104.6 (2)	105.3 (1)	112.5 (2)	2.493 (2)	
(IIIa)	In	1.630 (5)	104.6 (1)	105.9 (1)	108.0 (1)	2.587 (1)	OGAIMOY[e]
(IIIb)	In‡	1.625 (13)	103.1 (1)	105.7 (1)	107.3 (1)	2.604 (1)	OGAMIS[e]
		1.628 (10)	105.2 (1)	105.9 (1)	105.9 (1)	2.535 (1)	
(IIIb)	Tl	1.626 (5)	100.9 (1)	106.8 (1)	107.1 (1)	2.669 (1)	f

† Refcodes are taken from the Cambridge Structural Database (Allen, 2002). ‡ Two crystallographically independent molecules within the unit cell. References: (*a*) this work; (*b*) Gorden *et al.* (2000); (*c*) Hardman *et al.* (2003); (*d*) Hardman *et al.* (2001); (*e*) Wright *et al.* (2002); (*f*) Wright *et al.* (2005).

H atoms were positioned geometrically and refined using a riding model, with $U_{iso} = 1.5U_{eq}(C)$ and C—H distances set at 0.95 Å. A highly disordered region of electron density is present within the unit cell and is presumably a mixture of various hydrocarbon solvates. This could not be satisfactorily modelled and instead its contribution to the overall structure factor was removed using the SQUEEZE procedure contained within *PLATON* (van der Sluis & Spek, 1990). A total of 210 electrons were eliminated, giving a total volume of 1047 Å^3 as a solvent-accessible void.

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 2002); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *XP* in *SHELXTL* (Sheldrick, 1994); software used to prepare material for publication: *SHELXL97*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: DN1084). Services for accessing these data are described at the back of the journal.

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