Supplementary Material (ESI) for Chemical Communications

An imidazol-2-ylidene borane complex exhibiting inter-molecular [C-H$^{\delta+}$•••H$^{\delta-}$-B] dihydrogen bonds

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Analytical data for 1·BH_3:

^{1}H NMR (400 MHz, benzene) δ 6.96 (s, 4H, Ar-H), 6.17 (s, 2H, C=CH), 2.34 (s, 6H, *p*-C*H*$_3$), 2.30 (s, 12H, *o*-CH_3). 0.4 (q, 3H, BH_3) IR (Nujol):3170(m), 2971(m), 2919(s), 2348(s), 1484(s), 1413(s), 1262(s), 1233(s), 1016(s), 932(w), 801(s),733(s). Anal. Calcd for $C_{21}H_{27}N_2B_2$: C, 79.25; H, 8.55; N, 8.80. Found: C, 79.30; H, 8.40; N, 8.87.

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Crystallography

EXPERIMENTAL:

Crystals of $C_{21}H_{27}B_1N_2$ were grown from a concentrated methylene chloride solution. A colourless block was cut and then mounted on a glass fibre. Data were collected at low temperature (-123 °C) on a Nonius Kappa-CCD diffractometer with COLLECT (Nonius B.V., 1998). The unit cell parameters were calculated and refined from the full data set. Crystal cell refinement and data reduction were carried out using DENZO (Nonius B.V., 1998). The data were scaled using SCALEPACK (Nonius B.V., 1998). The crystal data and refinement parameters for $C_{21}H_{27}B_1N_2$ are listed in Table I. Interatomic distances and angles are listed in Table III. The reflection data and systematic absences were consistent with an orthorhombic space group: Pbcn.

The SHELXTL-NT V6.1 (Sheldrick, G.M.) suite of programs was used to solve the structure by direct methods. Subsequent difference Fourier syntheses allowed the remaining atoms to be located. Only half of the molecule was found as it was located on a two-fold axis of rotation. The molecule was very well behaved. All of the non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atom positions were calculated geometrically and were included as riding on their respective carbon atoms. The B-H (1.21 Å) distances and the C-H (1.09 Å) distance of C4 were normalized using standard procedures to the values determined by neutron diffraction .

The largest residue electron density peak (0.431 e/Å^3) was associated with the mesitylene ring. Full-matrix least squares refinement on F^2 gave $R_1 = 6.82$ for 2σ data and $wR_2 = 20.56$ for all data (GOOF = 1.029).

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Table 1. Crystal data and structure refinement for 1·BH_3

Identification code	02144b	
Empirical formula	C21 H27 B N2	
Formula weight	318.26	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	Pbcn	
Unit cell dimensions	a = 16.0680(3) Å	α= 90°.
	b = 7.24710(10) Å	β= 90°.
	c = 16.1949(4) Å	γ = 90°.
Volume	1885.84(6) $Å^3$	
Z	4	
Density (calculated)	1.121 Mg/m^3	
Absorption coefficient	0.065 mm^{-1}	
F(000)	688	
Crystal size	0.73 x 0.53 x 0.28 mm^3	
Theta range for data collection	2.82 to 27.48°.	
Index ranges	-20<=h<=20, -9<=k<=9, -20<=l<=21	
Reflections collected	21686	
Independent reflections	2160 [R(int) = 0.052]	
Completeness to theta = 27.48°	99.8 %	
Absorption correction	Integration	
Max. and min. transmission	0.9822 and 0.9544	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2160 / 0 / 110	
Goodness-of-fit on F^2	1.032	
Final R indices [I>2sigma(I)]	R1 = 0.0683, wR2 = 0.1915	
R indices (all data)	R1 = 0.0924, wR2 = 0.2078	
Largest diff. peak and hole	0.431 and -0.261 e.$Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for 02144b. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
B(1)	5000	4430(4)	7500	34(1)
C(2)	5000	2228(3)	7500	26(1)
N(3)	4676(1)	1084(2)	6922(1)	28(1)
C(4)	4796(1)	-746(2)	7138(1)	33(1)
C(11)	4255(1)	1675(2)	6181(1)	26(1)
C(12)	3383(1)	1610(3)	6167(1)	32(1)
C(13)	2990(1)	2135(3)	5442(1)	35(1)
C(14)	3429(1)	2739(2)	4757(1)	31(1)
C(15)	4295(1)	2807(2)	4805(1)	28(1)
C(16)	4723(1)	2255(2)	5505(1)	26(1)
C(17)	2896(1)	1020(4)	6916(1)	47(1)
C(18)	2988(1)	3279(3)	3972(1)	43(1)
C(19)	5659(1)	2273(3)	5528(1)	34(1)

Table 3. Bond lengths [Å] and angles [°] for 02144b.

B(1)-C(2)	1.596(4)
C(2)-N(3)	1.354(2)
C(2)-N(3)#1	1.354(2)
N(3)-C(4)	1.385(2)
N(3)-C(11)	1.444(2)
C(4)-C(4)#1	1.344(4)
C(11)-C(16)	1.393(2)
C(11)-C(12)	1.401(3)
C(12)-C(13)	1.388(3)
C(12)-C(17)	1.505(3)
C(13)-C(14)	1.385(3)
C(14)-C(15)	1.394(3)
C(14)-C(18)	1.507(3)
C(15)-C(16)	1.386(2)
C(16)-C(19)	1.503(3)

N(3)-C(2)-N(3)#1	104.5(2)
N(3)-C(2)-B(1)	127.75(10)
N(3)#1-C(2)-B(1)	127.75(10)
C(2)-N(3)-C(4)	111.03(16)
C(2)-N(3)-C(11)	124.99(15)
C(4)-N(3)-C(11)	123.98(15)
C(4)#1-C(4)-N(3)	106.72(10)
C(16)-C(11)-C(12)	122.58(17)
C(16)-C(11)-N(3)	119.26(15)
C(12)-C(11)-N(3)	118.15(15)
C(13)-C(12)-C(11)	117.32(16)
C(13)-C(12)-C(17)	121.53(17)
C(11)-C(12)-C(17)	121.14(17)
C(14)-C(13)-C(12)	122.16(17)
C(13)-C(14)-C(15)	118.36(17)
C(13)-C(14)-C(18)	121.18(17)
C(15)-C(14)-C(18)	120.45(17)
C(16)-C(15)-C(14)	122.10(16)

C(15)-C(16)-C(11)	117.44(16)
C(15)-C(16)-C(19)	120.96(16)
C(11)-C(16)-C(19)	121.60(16)

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,y,-z+3/2

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for 02144b. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
B(1)	52(2)	21(1)	29(2)	0	-4(1)	0
C(2)	30(1)	25(1)	23(1)	0	1(1)	0
N(3)	37(1)	24(1)	24(1)	-1(1)	-2(1)	-1(1)
C(4)	45(1)	23(1)	32(1)	-2(1)	-1(1)	-2(1)
C(11)	31(1)	26(1)	21(1)	-2(1)	-2(1)	0(1)
C(12)	32(1)	37(1)	27(1)	0(1)	4(1)	-1(1)
C(13)	25(1)	45(1)	36(1)	4(1)	0(1)	-1(1)
C(14)	33(1)	30(1)	28(1)	1(1)	-4(1)	0(1)
C(15)	33(1)	28(1)	22(1)	0(1)	2(1)	-3(1)
C(16)	30(1)	22(1)	24(1)	-2(1)	0(1)	-1(1)
C(17)	40(1)	65(2)	36(1)	9(1)	10(1)	-2(1)
C(18)	41(1)	50(1)	37(1)	8(1)	-11(1)	-3(1)
C(19)	30(1)	35(1)	36(1)	1(1)	1(1)	0(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for 02144b.

	x	y	z	U(eq)
H(1A)	5219	4987	8170	51
H(1B)	4306	4987	7353	51
H(1C)	5476	4987	6977	51
H(4A)	4605	-1909	6801	50
H(13A)	2400	2079	5413	42
H(15A)	4601	3246	4343	33
H(17A)	2299	1064	6791	70
H(17B)	3018	1855	7376	70
H(17C)	3053	-241	7068	70
H(18A)	3399	3659	3558	64
H(18B)	2608	4307	4085	64
H(18C)	2671	2223	3763	64
H(19A)	5848	3083	5975	51
H(19B)	5873	2729	5000	51
H(19C)	5865	1018	5625	51

1·BH3 optimised geometry

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.679034	0.084055	1.969654
2	6	0	-0.678980	0.084070	1.969677
3	7	0	1.086273	0.041932	0.625567
4	7	0	-1.086269	0.041962	0.625604
5	6	0	2.473513	0.015990	0.218229
6	6	0	-0.000011	0.015182	-0.218859
7	6	0	-2.473525	0.016093	0.218312
8	6	0	-3.113777	-1.225847	0.058919
9	6	0	-3.149062	1.234131	0.021608
10	6	0	-4.472992	-1.224604	-0.284226
11	6	0	3.148927	1.234105	0.020795
12	6	0	3.113863	-1.225857	0.059464
13	6	0	-4.507130	1.184577	-0.320529
14	6	0	4.473172	-1.224596	-0.283736
15	6	0	4.506883	1.184569	-0.321357
16	6	0	-5.185310	-0.032767	-0.478419
17	6	0	5.185291	-0.032870	-0.478531
18	5	0	-0.000008	-0.068896	-1.806219
19	6	0	-2.358031	-2.524450	0.220483
20	6	0	-2.426397	2.555966	0.133691
21	6	0	2.425966	2.555839	0.132144
22	6	0	2.358355	-2.524534	0.221573
23	6	0	-6.642875	-0.058988	-0.882907
24	6	0	6.643032	-0.058556	-0.882437
25	1	0	1.390284	0.109257	2.776469
26	1	0	-1.390201	0.109286	2.776518
27	1	0	-4.981327	-2.176604	-0.409048
28	1	0	-5.042113	2.117514	-0.474942
29	1	0	4.981636	-2.176566	-0.408127
30	1	0	5.041699	2.117523	-0.476357
31	1	0	-1.010652	0.448271	-2.238083
32	1	0	0.000262	-1.261761	-2.102783
33	1	0	1.010443	0.448663	-2.238082
34	1	0	-3.032547	-3.379444	0.119792
35	1	0	-1.865031	-2.595792	1.197497
36	1	0	-1.577837	-2.612485	-0.545196
37	1	0	-3.123167	3.390195	0.012782
38	1	0	-1.658115	2.637608	-0.644984
39	1	0	-1.922942	2.671936	1.100789
40	1	0	3.122536	3.390159	0.010710
41	1	0	1.922541	2.672251	1.099206

42	1	0	1.657624	2.636822	-0.646540
43	1	0	3.033081	-3.379441	0.121559
44	1	0	1.578398	-2.613189	-0.544278
45	1	0	1.865089	-2.595431	1.198480
46	1	0	-7.184315	0.807958	-0.489374
47	1	0	-7.142876	-0.964084	-0.522537
48	1	0	-6.748690	-0.040515	-1.976049
49	1	0	7.189736	0.795017	-0.467267
50	1	0	6.750068	-0.013626	-1.974672
51	1	0	7.136754	-0.975345	-0.543868

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[NH_3 BH_3] optimised geometry

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	-0.745020	0.000007	0.000009
2	5	0	0.940773	0.000005	-0.000036
3	1	0	-1.080764	0.540311	0.796678
4	1	0	-1.080701	-0.960097	0.069589
5	1	0	-1.080834	0.419765	-0.866236
6	1	0	1.251110	-0.657542	-0.968805
7	1	0	1.251195	-0.510333	1.053867
8	1	0	1.251267	1.167823	-0.084974

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