SUPPLEMENTARY INFORMATION

Protonolysis and Thermolysis Reactions of Functionalised NHC-carbene Boranes and Borates

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Attempted deprotonation of 3d $(^tBu)CH(OBEt_3)CH_2\{CH[NC(CH_3)C(CH_3)N(Mes)]\}$

$K[N(SiMe_3)_2]$

3d (0.05 g, 0.1036 mmol) and $K[N(SiMe_3)_2]$ (0.0207 g, 0.1036 mmol) were combined in dry THF (0.5 mL) in a J-Young's tap NMR tube. ^1H NMR spectroscopy indicated that no reaction had taken place at room temperature or upon heating at 70°C for 2h.

KH

3d (0.05 g, 0.1036 mmol) and KH (0.0042 g, 0.1036 mmol) were combined in dry THF (0.5 mL) in a J-Young's tap NMR tube to yield a pale yellow suspension. The yellow solution was filtered off and the volatiles removed *in vacuo* to yield a yellow solid which was assigned as **3d** by ^1H NMR spectroscopy.

KBn

3d (0.05 g, 0.1036 mmol) and KH (0.0042 g, 0.1036 mmol) were combined in dry THF (0.5 mL) in a J-Young's tap NMR tube to yield a red-brown suspension. The yellow solution was filtered off and the volatiles removed *in vacuo* to yield a yellow solid which was assigned as **3d** by ^1H NMR spectroscopy.

$Li[N(SiMe_3)_2]$

3d (0.05 g, 0.1036 mmol) and $K[N(SiMe_3)_2]$ (0.0207 g, 0.1036 mmol) were combined in dry THF (0.5 mL) in a J-Young's tap NMR tube to yield a colourless solution. ^1H NMR spectroscopy showed broad overlapping resonances which could not be assigned.

$Sc(OTf)_3$

3d (0.05 g, 0.1036 mmol) and KH (0.0042 g, 0.1036 mmol) were combined in d_5-pyridine in a J-Young's tap NMR tube to yield a colourless solution. NMR spectroscopy indicated the formation of the scandium-borate adduct shown in Fig. SI1. ^1H NMR (400 MHz, d_5-pyridine): 9.58 (s, 1H, $\underline{H}_{imidazole-2}$), 8.21-7.54 (m, 7H, naphthyl-C$\underline{H}$), 6.89 (s, 1H, Ph$\underline{H}$), 6.87 (s, 1H, Ph$\underline{H}$), 5.79-5.76 (dd, 1H, naphthyl-C$\underline{H}$O), 5.06-5.01 (dd, 1H, naphthyl-CHO-C$\underline{H}_2$), 4.95-4.90 (dd, 1H, naphthyl-CHO-C$\underline{H}_2$), 2.30 (s, 3H, imidazole-C$\underline{H}_3$), 2.23 (s, 3H, imidazole-C$\underline{H}_3$), 1.91 (s, 3H, para-PhC$\underline{H}_3$), 1.86 (s, 3H, ortho-PhC$\underline{H}_3$), 1.83 (s, 3H, ortho-PhC$\underline{H}_3$), 0.91-0.88 (t, 9H, $CH_2C\underline{H}_3$), 0.81-0.75 (m, 6H, B-C$\underline{H}_2$) ppm.

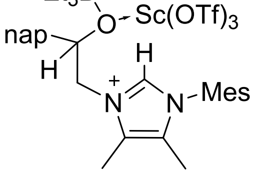

Figure SI1: identity of the scandium borate adduct of 3d suggested by NMR spectroscopy

Treatment of 1c (^{t}Bu)C(O)CH$_2${CH[NCHCHN(tBu)]} with 2 eq. KHBEt$_3$

1c (20 mg, 0.08 mmol) was suspended in C_6D_6 and KHBEt$_3$ (160 µL, 0.16 mmol, 1M solution in THF) added. ^{1}H NMR spectroscopy showed a complex mixture of products however neither **3c** nor **6** were present.

X-ray Crystal Structure of 4f

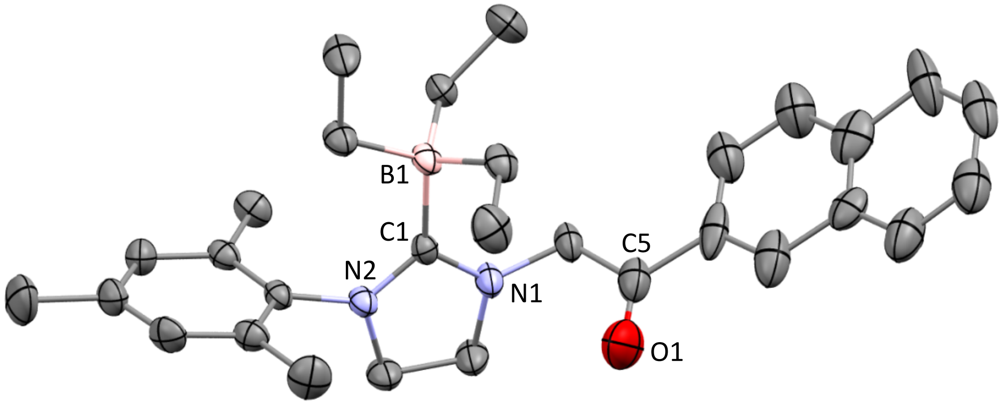

Figure 2: Solid-state structure of **4f**. For clarity, all hydrogen atoms, and all solvent molecules are omitted (displacement ellipsoids are drawn at 50% probability). Selected distances (Å) and angles (°):B1-C1 1.663(4), O1-C5 1.208(6), C1-N1 1.331(3), C1-N2 1.3246(4), O1-C5-C4 120.9(4), N1-C1-N2 107.3(3)

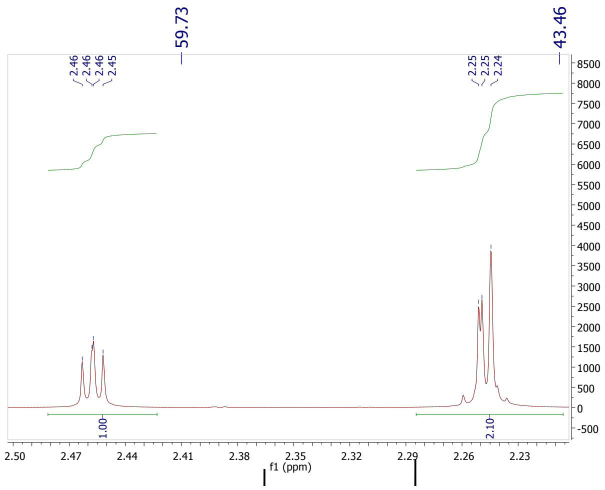

Figure 4a: ^{1}H NMR spectrum between 2.5-2.2 ppm of 2-*tert*-butyloxirane in C_6D_6.

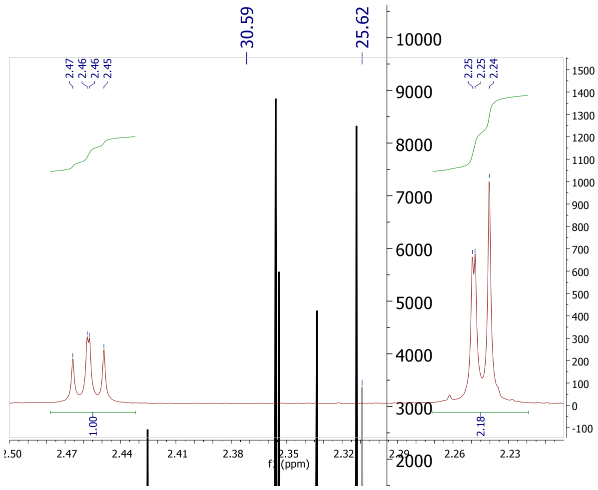

Figure 4b: ^{1}H NMR spectrum between 2.5-2.2 ppm of **3c** after heating to 80°C in C_6D_6 for 24h showing extruded 2-*tert*-butyloxirane.

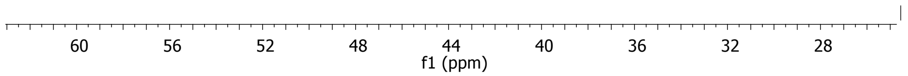

Figure 5: Overlayed ^{13}C NMR spectra between 65-20ppm in C_6D_6 of 2-tert-butyloxirane (grey) and the reaction mixture (black) after heating **3c** to 60°C for 2h.

NMR evidence for extrusion of 2-*tert*-butyloxirane

Experimental X-ray Crystallographic Details

General Details

All experiments were carried out with Mo *K*α radiation using a Xcalibur, Eos diffractometer. For all the structures but **1d** absorption corrections were carried out using the multi–scan procedure CrysAlisPro.[49] For **1d** the Analytical procedure for CrysAlisPro was used. All datasets were collected at 100 K. All structures were solved by SIR-92 and refined by full–matrix least squares against F^2 using SHELXL.[50] All non–hydrogen atoms were refined anisotropically, while hydrogen atoms were placed in calculated positions, constrained to ride on their parent atom with group U_{iso} values assigned [$U_{iso}(H) = 1.2U_{iso}$ for aromatic carbons and $1.5U_{iso}$ for methyl atoms]. The structures of **3d** and **4e** were obtained from weak data cut at 0.8 Å. **3d** contains three disordered toluene molecules per unit cell and was crystallised as a merohedral twin. **5d** also contains a toluene molecule disordered over two sites.

Table 1. Experimental details

	1d	**3c**	**3d**
Crystal data			
Chemical formula	$C_{26}H_{27}BrN_2O$	$C_{19}H_{39}BN_2O$	$C_{42.50}H_{55}BN_2O$
M_r	463.41	322.33	620.69
Crystal system, space group	Monoclinic, $P2_1/n$	Monoclinic, $P2_1/n$	Triclinic, $P\bar{1}$
Temperature (K)	170	170	170
a, b, c (Å)	9.7624 (4), 13.2901 (4), 18.1845 (4)	10.0790 (7), 13.6684 (7), 15.3802 (6)	11.7096 (6), 15.6144 (9), 22.0422 (18)
α, β, γ (°)	90, 104.391 (3), 90	90, 92.472 (5), 90	85.313 (6), 86.194 (6), 68.487 (5)
V (Å^3)	2285.29 (13)	2116.9 (2)	3734.0 (4)
Z	4	4	4
μ (mm^{-1})	1.82	0.06	0.06
Crystal size (mm)	0.37 × 0.27 × 0.11	0.51 × 0.34 × 0.24	0.31 × 0.18 × 0.08
Data collection			
T_{min}, T_{max}	0.576, 0.828	0.772, 1.000	0.616, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	11387, 5235, 3595	18885, 4851, 2774	13011, 13011, 7373
R_{int}	0.033	0.123	0.142
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.649	0.650	0.590
Refinement			
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.046, 0.105, 1.02	0.087, 0.312, 1.03	0.077, 0.201, 0.94
No. of reflections	5235	4851	13011
No. of parameters	276	217	886
No. of restraints	0	0	126
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.83, -0.66	0.35, -0.34	0.31, -0.30

	4e	**4f**	**5d**	**6**	**7**
Crystal data					

Chemical formula	$C_{24}H_{41}BN_2O$	$C_{30}H_{39}BN_2O$	$C_{35}H_{41}BN_2O$	$C_{17}H_{33}BN_2O$	$C_{13}H_{27}BN_2$
M_r	384.40	454.44	516.51	292.26	222.18
Crystal system, space group	Triclinic, $P\bar{1}$	Triclinic, $P\bar{1}$	Monoclinic, $P2_1/c$	Monoclinic, $P2_1/c$	Monoclinic, $P2_1/n$
Temperature (K)	170	153	170	170	170
a, b, c (Å)	9.2340 (19), 11.811 (3), 12.577 (3)	8.1720 (4), 8.6088 (3), 20.0510 (8)	9.9318 (3), 27.3125 (10), 10.7984 (3)	12.9028 (5), 11.8814 (4), 12.6969 (3)	10.7950 (4), 10.2921 (4), 13.4612 (4)
α, β, γ (°)	69.63 (2), 70.562 (19), 76.389 (19)	81.502 (3), 84.547 (4), 68.047 (4)	90, 100.301 (3), 90	90, 104.000 (3), 90	90, 97.670 (3), 90
V (Å^3)	1201.5 (5)	1292.75 (9)	2881.99 (16)	1888.66 (11)	1482.20 (9)
Z	2	2	4	4	4
μ (mm^{-1})	0.06	0.07	0.07	0.06	0.06
Crystal size (mm)	0.66 × 0.25 × 0.09	0.72 × 0.48 × 0.14	0.55 × 0.13 × 0.10	0.53 × 0.23 × 0.13	0.98 × 0.23 × 0.05
Data collection					
T_{min}, T_{max}	0.404, 1.000	0.878, 1	0.838, 1.000	0.792, 1.000	0.786, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	4846, 3474, 1921	20429, 4734, 3576	33866, 6592, 4614	18205, 4488, 3150	18430, 3390, 2501
R_{int}	0.065	0.033	0.047	0.041	0.041
(sin θ/λ)$_{max}$ (Å^{-1})	0.698	0.602	0.649	0.658	0.649
Refinement					
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.102, 0.335, 1.05	0.089, 0.274, 0.99	0.078, 0.232, 1.05	0.058, 0.143, 1.02	0.056, 0.133, 1.02
No. of reflections	3474	4734	6592	4488	3390
No. of parameters	262	313	359	198	145
No. of restraints	36	2	52	0	0
Δρ$_{max}$, Δρ$_{min}$ (e Å^{-3})	0.68, -0.42	1.28, -0.42	0.34, -1.05	0.22, -0.16	0.22, -0.16

Computer programs: *CrysAlis PRO*, Agilent Technologies, Version 1.171.35.19 (release 27-10-2011 CrysAlis171 .NET) (compiled Oct 27 2011,15:02:11), *CrysAlis PRO*, Agilent Technologies, Version 1.171.36.24 (release 03-12-2012 CrysAlis171 .NET) (compiled Dec 3 2012,18:21:49), *SIR92*, sir-92, *SIR* 92, *SHELXL97* (Sheldrick, 2008), *SHELXL2014* (Sheldrick, 2014), *ORTEP*, mecury, *POV-RAY*, *Mercury* 2012.

Table 2. Selected distances (Å) and angles (°)

1d		**3c**		**3d**		**4e**		**4f**	
C1—N2	1.328 (3)	C1—N2	1.328 (3)	C1—N2	1.325 (7)	C1—N1	1.331 (4)	C1—N1	1.331 (4)
C1—N1	1.334 (3)	C1—N1	1.329 (3)	C1—N1	1.327 (7)	C1—N2	1.345 (4)	C1—N2	1.345 (4)
C16—O1	1.216 (3)	C9—O1	1.385 (3)	C16—O1	1.385 (7)	C1—B1	1.663 (4)	C1—B1	1.663 (4)
		B1—O1	1.544 (3)	B1—O1	1.536 (8)	C5—O1	1.208 (5)	C5—O1	1.208 (5)
N2—C1—N1	108.6 (2)	N2—C1—N1	109.0 (2)	N2—C1—N1	108.8 (5)	N1—C1—N2	123.5 (2)	N2—C1—B1	107.3 (3)
O1—C16—C17	121.5 (2)	O1—C9—C8	109.40 (17)	O1—C16—C17	111.2 (5)	N1—C1—B1	120.9 (3)	O1—C5—C4	129.2 (3)
O1—C16—C15	121.2 (2)	C8—C9—C10	114.76 (19)	C17—C16—C15	109.9 (5)	N2—C1—B1	120.9 (3)	O1—C5—C4	123.5 (2)
		C9—O1—B1	123.64 (16)	C16—O1—B1	120.7 (4)	O1—C5—C4	120.9 (3)	O1—C5—C4	120.9 (3)

5d		**6**		**7**	
O1—C16	1.393 (3)	C5—O1	1.4140 (18)	C4—N2	1.3252 (18)
O1—B1	1.513 (3)	C7—N2	1.329 (2)	C4—N1	1.3447 (17)
N2—C1	1.353 (3)	C7—N1	1.3353 (19)	N2—B1	1.6346 (19)
N2—C3	1.400 (3)	C8—C13	1.362 (2)		
		C13—N1	1.3872 (19)		
		C13—B1	1.643 (2)		
		O1—B1	1.519 (2)		
C16-O1-B1	117.32 (18)	N2-C7-N1	107.96 (13)	N2-C4-N1	110.88 (12)
C1-N1-C2	111.8 (2)	C8-C13-N1	103.81 (13)	C4-N2-B1	128.76 (12)
O1-B1-C1	105.62 (19)	O1-B1-C13	106.24 (12)	C6-N2-B1	124.77 (12)