Electronic Supplementary Information

“Twisted” scorpionates: synthesis of a tris(2-pyridonyl)-borate (Thp) ligand; lessons in the requirements for successful $B(L_2D)_3$ type ligands.

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Experimental Details

All reactions were carried out under an atmosphere of dry, oxygen-free dinitrogen, using standard Schlenk techniques. Solvents were distilled and dried by standard methods or used directly from a Glass Contour solvent purification system and further degassed before use where necessary. NMR spectra were recorded on a Bruker ava400 or a Bruker ava500 spectrometer operating at room temperature. ^{1}H and ^{13}C chemical shifts are reported in ppm relative to SiMe4 (d = 0) and were referenced internally with respect to the protio solvent impurity or the ^{13}C resonances respectively. ^{11}B NMR spectra were externally referenced to neat BF_3-OEt_2 (δ -19.4). Multiplicities and peak types are abbreviated: singlet, s; doublet, d; triplet, t;multiplet, m; broad, br; aromatic, ar. Infra red spectra were recorded from solution using cells with CaF_2 windows on a Jasco FT-IR 410 spectrometer. All chemicals were obtained from Sigma-Aldrich and used as received.

Electrochemical experiments were performed with an Autolab PGSTAT 302. A three compartment cell was used with an Ag/AgCl reference electrode, Pt foil counter electrode, and a glass coated Pt working electrode. Freshly distilled and degassed DMF was used as the solvent with tetra-n-butylammonium tetrafluoroborate as the supporting electrolyte (0.2 M). Solutions contained 1 mmol of analyte in 10 mL of solvent. The measured potentials were corrected for junction potentials relative to ferrocenium/ferrocene (0.543 mV vs Ag/AgCl). All $E_{1/2}$ values were calculated from (Epa + Epc)/2 at a scan rate of 300 mV/s.

[(Me_2HN)B(2-pyridonyl)$_3$] (1)

2-hydroxypyridine (400.6mg, 4.21mmol) was suspended in toluene (20mL). Tris(dimethylamino)borane (245µL, 1.40mmol) was added and the reaction mixture was refluxed for 4 hours. After 15 mins a basic gas was evolved. The reaction mixture was allowed to cool to ambient temperature. Solvent was half removed *in vacuo*. The precipitate which formed was filtered by cannula, washed with toluene (3 x 5mL) and diethyl ether (3 x 10mL) and dried *in vacuo* to give the target material as a white powder (286mg, 60.3%); MS (EI) 339.1m/z $(M+1)^+$; ^{1}H NMR ($CDCl_3$) (360 MHz) (δ): 2.84 (d, 6H, *J*= 4.8 Hz), 6.71 (td, 3H, *J*= 1.51 Hz and 13.0 Hz), 6.86 (d, 3H, *J*= 8.2 Hz), 7.42 (td, 3H, *J*= 2.1, 7.7 Hz), 7.81 (s, 1H), 8.01 (dd, 3H, *J*= 8.3 Hz); ^{13}C-NMR, δ: 36.8 ($N(CH_3)_2$), 113.7 (CH_{Ar}), 116.6 (CH_{Ar}), 138.5 (CH_{Ar}), 147.2 (CH_{Ar}), 163.4 (C_q). ^{11}B NMR ($CDCl_3$, 128 MHz) (δ): 2.2 (s). Anal. Calcd. for C17H19BN4O3: C, 60.38; H, 5.66; N, 16.57; Found, %C = 60.23, %H = 5.50, %N = 16.46

[(DMAP)B(2-pyridonyl)$_3$] (2)

2-Hydroxypyridine (1.0033g, 10.55mmol) was suspended in toluene (15mL). Tris(dimethylamino)borane (616µL, 3.52mmol) was added and the reaction mixture was refluxed for 24 hours. After 15 mins, a basic gas was evolved. After this time DMAP (431.1 mg , 3.53 mmol) was added to the reaction mixture and the reaction was refluxed for a further 6 hours during which time a white precipitate formed. The precipitate was filtered by cannula and washed with toluene (3 x 5mL) and Et_2O (3 x 10mL) to give the target material as a white solid (1.005g, 69%); Analytically pure samples were prepared by recrystallisation of the ligand from chloroform and diethyl ether. Crystals suitable for X-ray structure determination were obtained by slow diffusion of diethyl ether into a concentrated solution of the ligand in DCM. MS (FAB^+) m/z = 414.7 (M^+-1); ^{1}H NMR ($CDCl_3$) (360 MHz) (δ): 3.10 (s, 6H), 6.52 (d, 2H, J=7.6 Hz), 6.65 (td, 3H, J= 1.0 and 5.9 Hz), 6.98 (d, 3H, J= 8.2

Hz), 7.38 (td, 3H, J= 2.2 and 7.4 Hz), 8.04 (dd, 3H, J= 1.6 and 4.9 Hz), 8.78 (d, J= 7.4 Hz); ^{13}C-NMR, δ: 39.6 ($N(CH_3)_2$), 105.5 (CH_{DMAP}), 144.3 (CH_{DMAP}), 156.2 (C_{qDMAP}), 113.0 (CH_{Ar}), 115.8 (CH_{Ar}), 138.3 (CH_{Ar}), 147.8 (CH_{Ar}), 162.9 (C_{qAr}). ^{11}B NMR ($CDCl_3$, 128 MHz) (δ): 2.5 (s); Anal. Calcd. $C_{22}H_{22}BN_5O_3.0.5CHCl_3$ (573.94) %: C, 56.90; H, 4.78; N,14.75; Found, C, 56.53, H, 4.60, N, 14.98.

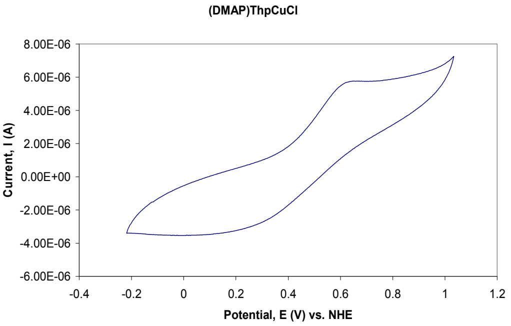
[(DMAP)B(2-pyridonyl)$_3$CuCl] (3)

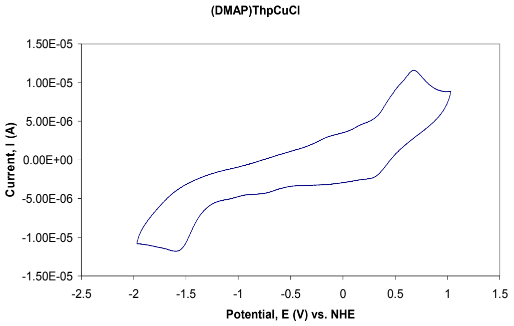
(DMAP)B(2-pyridonyl)$_3$ (250mg, 0.6 mmol) and copper (I) chloride (59.6mg, 0.6 mmol) were suspended in DCM. The suspension immediately turned yellow. The suspension was stirred for 2h before the precipitate was filtered and washed with DCM (3 x 5mL) and Et_2O (3 x 5mL) and dried in vacuo to give the target material as an insoluble yellow solid (100 mg, 33%).^{1}H NMR (500 MHz, DMSO-d^6) δ 3.10 (s, 6 H), 6.76 (br. s., 3 H), 6.81 (d, J = 6.80 Hz, 2 H), 6.86 (d, J = 7.25 Hz, 3 H), 7.50 (t, J = 7.1 Hz, 3 H), 7.77 - 8.21 (br. s., 3 H), 8.51 (d, J = 6.78 Hz, 2 H); ^{13}C-NMR, δ: 39.2 ($N(CH_3)_2$), 106.0 (CH_{DMAP}), 112.8 (CH_{Ar}), 116.0 (CH_{Ar}), 138.4 (CH_{Ar}), 142.9 (CH_{DMAP}), 147.4 (CH_{Ar}), 155.9 (C_{qDMAP}), 162.3 (C_{qAr}); ^{11}B NMR (DMSO-d^6) (128 MHz) (δ): 2.2 (s). Anal. Calcd. $C_{22}H_{22}BClCu N_5O_3$ (514.25), %: C, 51.38; H, 4.31; N, 13.62; Found, C, 51.28, H, 4.42, N, 13.76.

Attempted synthesis of [{(DMAP)Thp}CuPPh$_3$][Cl]

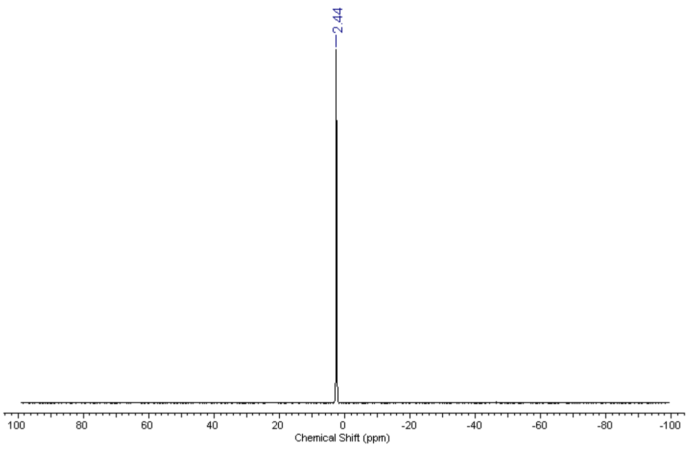
(DMAP)B(2-pyridonyl)$_3$ (50mg, 0.12 mmol) and copper (I) chloride triphenylphosphine (44mg, 0.12 mmol) were suspended in $CDCl_3$. The NMR tube was left at room temperature overnight and a few small crystals formed at the bottom of the NMR tube. X-ray crystallography confirmed these to be crystals of [(DMAP)B(2-pyridonyl)$_3$CuCl] (**3**).

Cyclovoltametry of [{(DMAP)Thp}CuCl (3) (1mM in DMF, 0.2M (Bu^t)$_4$N BF_4)

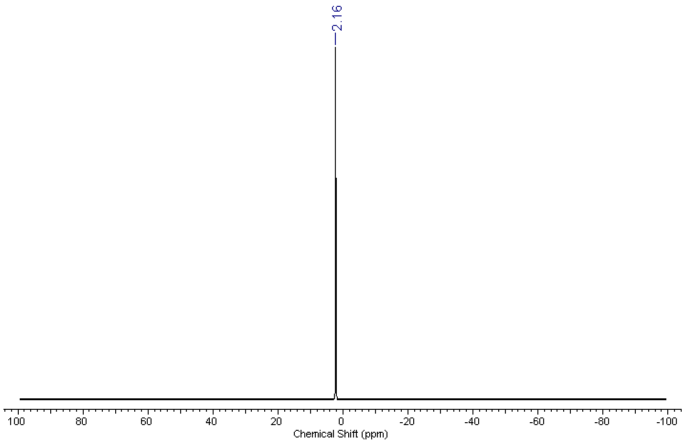




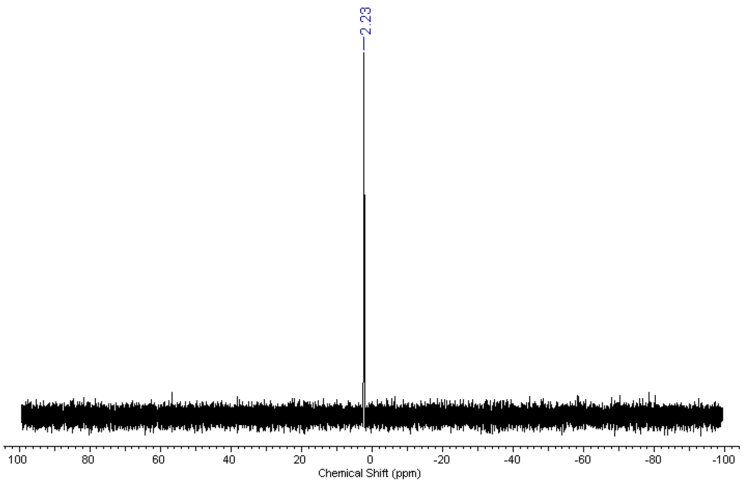
^{11}B nmr spectrum of [(**HNMe$_2$)Thp] (1)**



^{11}B nmr spectrum of [(**DMAP)Thp] (2)**



^{11}B nmr spectrum of [{(**DMAP)Thp}CuCl] (3)**



X-ray crystallography.

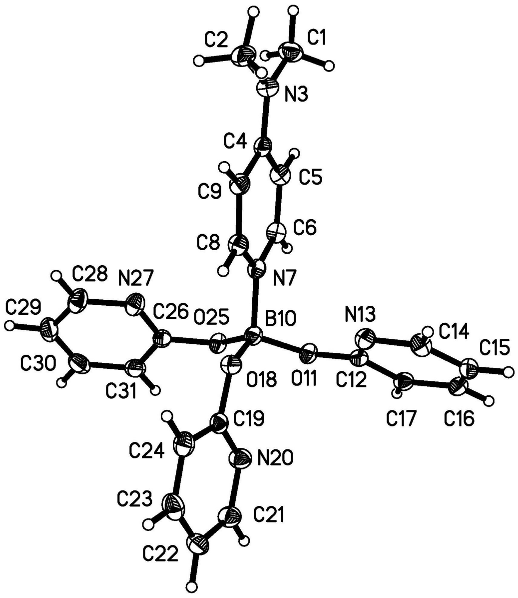
Crystal data for ***2****:* $C_{22}H_{22}BN_5O_3$, *F*w= 415.26, monoclinic, space group P21/n, *a*= 11.5746(2), *b*= 10.6207(2), c= 16.5475(3) Å, $\alpha = 90$, $\beta = 93.5990(10)$, $\gamma = 90°$, *U*= 2030.18(6) Å^3, *Z*= 4, λ= 0.71073 Å, D_{calc}= 1.359 Mgm^{-3}, μ(Mo-Kα)= 0.092 mm^{-1}. Data were collected on a Bruker SMART APEX diffractometer equipped with an Oxford Cryosystems low-temperature device at 100(2) K and using a colourless block oil-coated crystal of dimension 0.59 x 0.33 x 0.16 mm using the θ/ω method ($2.09 \leq 2\theta \leq 30.50°$). Of a total of 38547 reflections collected 5167 were independent. The structure was solved by direct methods and refined by full-matrix least-squares on F^2 to final values of $R1$ = 0.0391 (for 4101 data with $F > 4\sigma F$) and $wR2$ = 0.1004 (all data). Goodness of fit on F^2= 1.067, 282 parameters. Largest difference between peak and hole in the final difference map were 0.288 and -0.238 eÅ^{-3}.

Crystal data for ***3****:* $C_{24}H_{24}BCl_7CuN_5O_3$, *F*w= 753.01, monoclinic, space group P121/c1, *a*= 8.5238(2), *b*= 16.9403(5), c= 21.7245(6) Å, $\alpha = 90$, $\beta = 91.247(3)$, $\gamma = 90°$, *U*= 3136.17(16) Å^3, *Z*= 4, λ= 1.54184 Å, D_{calc}= 1.595 Mgm^{-3}, μ(Mo-Kα)= 6.778 mm^{-1}. Data were collected on a Agilent Technologies SuperNova diffractometer equipped with an Oxford Cryosystems low-temperature device at 100(2) K and using a colourless block oil-coated crystal of dimension 0.176 x 0.151 x 0.102 mm using the θ/ω method ($3.309 \leq 2\theta \leq 72.847°$). Of a total of 29658 reflections collected 6197 were independent. The structure was solved by direct methods and refined by full-matrix least-squares on F^2 to final values of $R1$ = 0.0570 (for

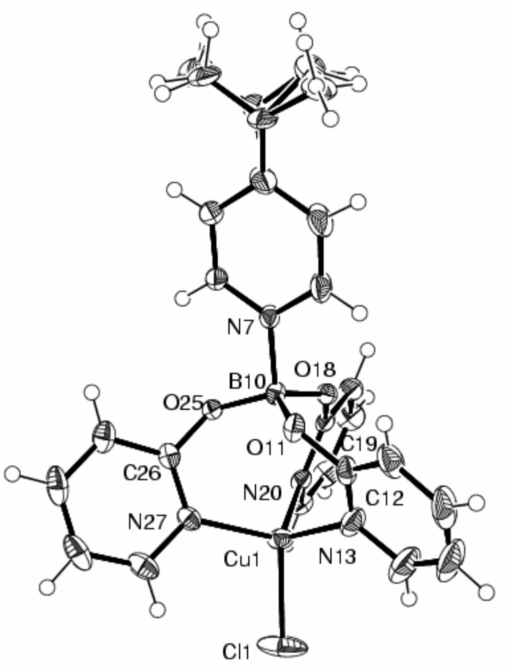
5739 data with $F > 4\sigma F$) and $wR2 = 0.1444$ (all data). There are two disordered chloroform molecules in the structure both of which are modelled over two sites each, to varying extents. Restraints were used to maintain sensible anisotropic displacement parameters. Additionally, the dimethylamino group was disordered over 2 sites. Goodness of fit on $F^2 = 1.0016$, 460 parameters. Largest difference between peak and hole in the final difference map were 1.20 and -1.15 eÅ^{-3}.

Table 1. Selected bond lengths (Å) and angles (°) for **2** and **3**.

	2	**3**
N7—B10	1.5928 (16)	1.609 (4)
B10—O18	1.4518 (15)	1.461 (3)
B10—O11	1.4578 (15)	1.457 (4)
B10—O25	1.4641 (15)	1.443 (4)
O18—B10—O11	118.00 (10)	113.5 (2)
O18—B10—O25	113.93 (10)	113.3 (2)
O11—B10—O25	101.09 (9)	115.6 (2)
O18—B10—N7	104.58 (9)	104.9 (2)
O11—B10—N7	108.93 (9)	103.2 (2)
O25—B10—N7	110.27 (9)	104.7 (2)
C12—O11—B10	126.56 (9)	127.9 (2)
C19—O18—B10	125.13 (9)	128.2 (2)
C26—O25—B10	124.14 (9)	128.4 (2)
Cu1—Cl1		2.3033 (9)
Cu1—N13		2.034 (3)
Cu1—N20		2.036 (2)
Cu1—N27		2.025 (2)
Cl1—Cu1—N13		109.52 (9)
Cl1—Cu1—N20		111.94 (7)
N13—Cu1—N20		105.58 (10)
Cl1—Cu1—N27		107.77 (8)
N13—Cu1—N27		112.36 (11)
N20—Cu1—N27		109.72 (10)



X-ray structure of [(DMAP)Thp] ligand (**2**)



X-ray structure of the complex [{(DMAP)Thp}CuCl] (**3**)