SUPPLEMENTARY INFORMATION

Synthesis and Characterisation of the Persistent Radical $[BCl_2(bipy)]^{\bullet}$

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Experimental

Syntheses of 1

a) From $B_2Cl_2(NMe_2)_2$: To a stirred solution of $B_2(NMe_2)_4$[1] (0.35 cm^3, 1.50 mmol) in *n*-hexane (15 cm^3), HCl (6 cm^3 of a 1M solution in Et_2O, 6.0 mmol) was added at room temperature affording a colourless precipitate. After stirring for 2 h, the reaction mixture was filtered giving a clear, colourless solution of $B_2Cl_2(NMe_2)_2$[1] in *n*-hexane. Addition of 2,2'-bipy (0.234 g, 1.50 mmol) at room temperature with stirring immediately resulted in a clear yellow solution which became darker and cloudy upon stirring overnight. The solution was filtered (porosity 3 sinter) giving a clear dark yellow/orange solution and the solvent was removed *in vacuo* to give a black solid (0.295 g, 1.24 mmol, 83% yield). The fate of the '$B(NMe_2)_2$' portion was not determined. Concentrating an *n*-hexane solution of **1** yielded purple/black crystals suitable for X-ray crystallography. IR (nujol mull): $\nu(cm^{-1})$ 1716, 1619, 974, 755, 722. Mp 140 ºC (decomposed). Despite repeated attempts satisfactory elemental analysis was not obtained, presumably on account of the high air-sensitivity of solid **1**.

b) From reduction of $[BCl_2(bipy)]Cl$ (**2**): Magnesium turnings (in excess) were added to a THF solution (10 cm^3) of **2** (0.547 g, 2.0 mmol) together with 2 drops of 1,2-dibromoethane and the mixture was stirred for 12 h. ESR spectroscopy showed the formation of the stable radical species $[BCl_2(bipy)]$ (**1**), although with broad signals due to the presence of THF as the solvent.

c) From reaction of Li[bipy] with BCl_3: Li[bipy] (0.296 g, 1.8 mmol), formed from the reaction between 2 equivalents of Li and bipy in THF, was suspended in toluene and cooled to -78 ºC. BCl_3 (1.8 cm^3 of a 1 M solution in heptane, 1.9 mmol) was added slowly and the black solution was stirred for 16 h at room temperature. Filtration through

a porosity 3 sinter filled with Celite gave an orange solution and ESR spectroscopy demonstrated the formation of the stable radical species [BCl_2(bipy)] (**1**). Removal of the solvent under reduced pressure gave a black product (70 mg, 0.29 mmol, 16 %).

Synthesis of 2

To a rapidly stirred solution of 2,2'-bipy (0.626 g, 4.0 mmol) in dichloromethane (20 cm^3) at -78 ºC, a solution of BCl_3 (4 cm^3 of a 1 M solution in heptane, 4.0 mmol) was added dropwise. The reaction mixture was allowed to reach room-temperature and was stirred for a further 16 h during which time a large quantity of white precipitate formed. The solid was isolated by filtration and redissolved in acetonitrile (10 cm^3). Concentration under reduced pressure to *ca*. 3 cm^3 and storage at -10 °C afforded colourless crystals of **2** (0.181 g, 0.66 mmol, 17% yield). ^{1}H NMR (CD_3CN, 300 MHz) δ 9.12 (bm, 2H, bipy), 8.79 (m, 4H, bipy), 8.25 (m, 2H, bipy). ^{13}C-{^{1}H} NMR (CD_3CN, 75.6 MHz) δ 149.7, 145.5, 132.0, 125.3 (bipy). ^{11}B NMR (CD_3CN, 96.13 MHz) δ 6.9 ppm. Mass spectrometry (+ ion E.S.I.) 237.02 ($C_{10}H_8BCl_2N_2^+$), 202.05 ($C_{10}H_8BClN_2^+$).

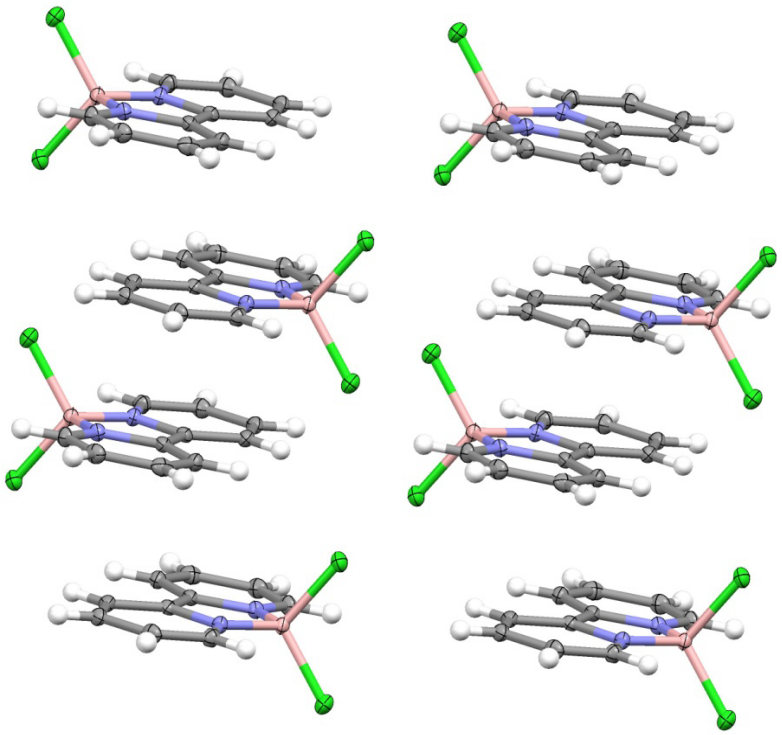

Figure S1. A view of the packing in the crystal structure of **1**.

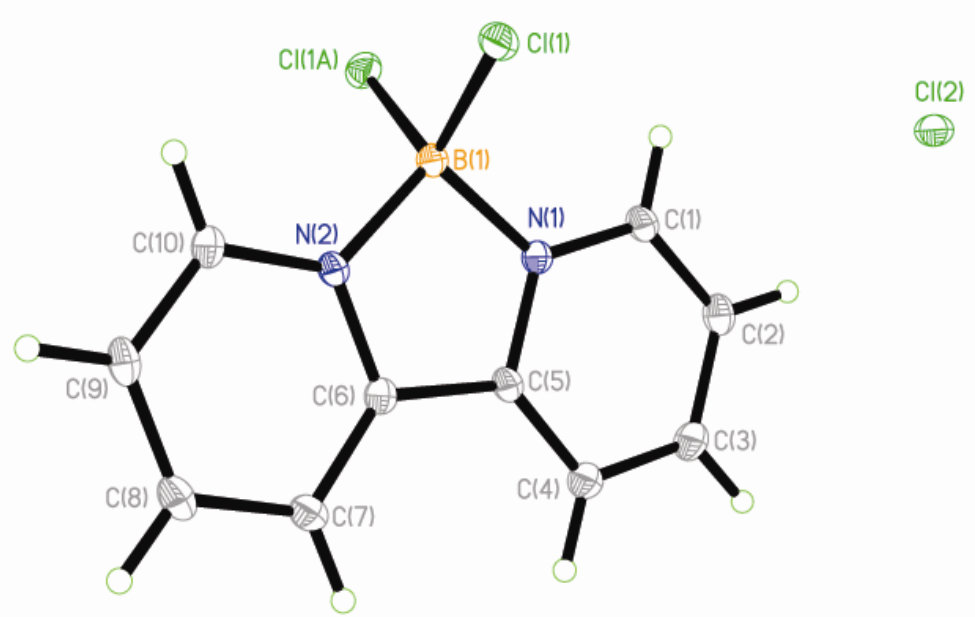

Figure S2. A view of the molecular structure of compound **2** (thermal ellipsoids are set at 50% probability level). Selected bond distances and angles are presented in Table 1 in the main manuscript.

References

1. M. J. G. Lesley, N. C. Norman and C. R. Rice, *Inorg. Synth.*, 2004, **34**, 1.