SUPPLEMENTARY INFORMATION

Synthesis and Characterisation of the Persistent Radical [BCl₂(bipy)]⁺

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Experimental

Syntheses of 1
a) From B₂Cl₂(NMe₂)₂: To a stirred solution of B₂(NMe₂)₄ (0.35 cm³, 1.50 mmol) in n-hexane (15 cm³), HCl (6 cm³ of a 1M solution in Et₂O, 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 B₂Cl₂(NMe₂)₂ 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(NMe₂)₂’ portion was not determined. Concentrating an n-hexane solution of 1 yielded purple/black crystals suitable for X-ray crystallography. IR (nujol mull): ν(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 [BCl₂(bipy)]Cl (2): Magnesium turnings (in excess) were added to a THF solution (10 cm³) 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 [BCl₂(bipy)]⁺ (1), although with broad signals due to the presence of THF as the solvent.
c) From reaction of Li[bipy] with BCl₃: 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. BCl₃ (1.8 cm³ 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)] (I). 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 °C, 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$_3$CN, 300 MHz) δ
9.12 (bm, 2H, bipy), 8.79 (m, 4H, bipy), 8.25 (m, 2H, bipy). $^{13}$C-$^1$H NMR (CD$_3$CN,
75.6 MHz) δ 149.7, 145.5, 132.0, 125.3 (bipy). $^{11}$B NMR (CD$_3$CN, 96.13 MHz) δ 6.9
ppm. Mass spectrometry (+ ion E.S.I.) 237.02 (C$_{10}$H$_8$BCl$_2$N$_2$$^+$), 202.05 (C$_{10}$H$_8$BClN$_2$$^+$).

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