

**DT-ART-04-2011-010709 Supplementary information**

**Tris(pyrazolyl)borate Amidoborane Complexes of the Group 4 Metals**

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Page S2: Discussion of reaction between **1** and  $\text{TpTi}(\text{NMe}_2)_3$

Page S4: Figure S1, Selected regions of the  $^1\text{H}$  NMR of **2**

Page S5: Figure S2,  $^{19}\text{F}$  NMR spectra at reaction times of (a) 1 hour, (b) 4 hours and (c) 10 hours in the generation of **2**.

### Discussion of reaction between **1** and $\text{TpTi}(\text{NMe}_2)_3$

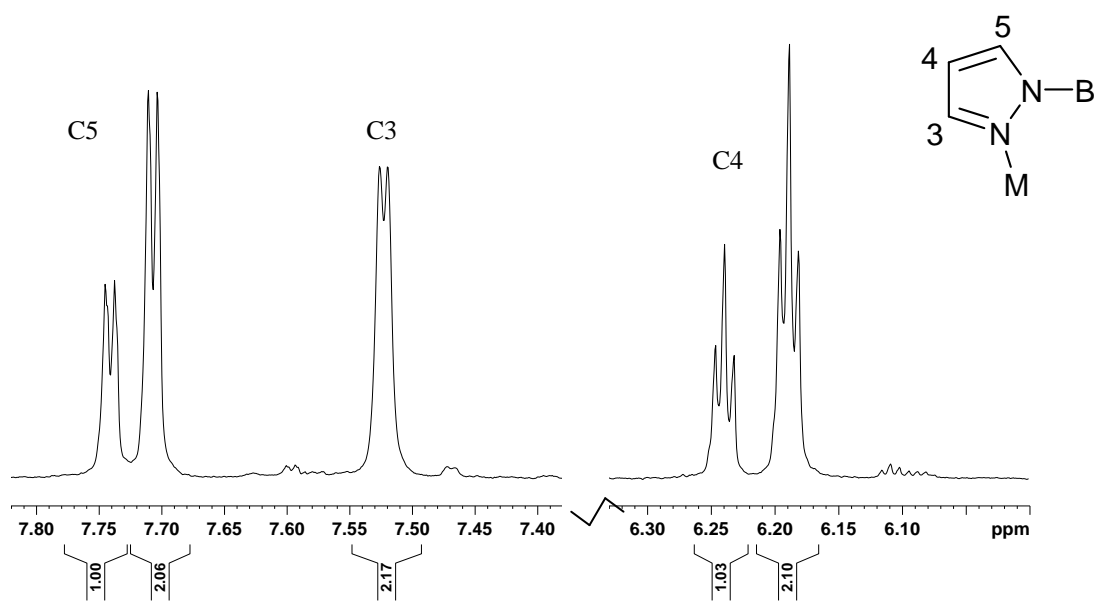
The reaction between **1** and  $\text{TpTi}(\text{NMe}_2)_3$  was relatively slow such that progress could be monitored by  $^{19}\text{F}$  NMR over four hours at room temperature; growth in intensity of the peaks corresponding to the product was observed until the reaction was approximately 90% complete. Further extending the reaction time resulted in no further change in the product : reactant ratio. In an attempt to drive the reaction to completion through removal of  $\text{NMe}_2\text{H}$ , nitrogen was bubbled through the solution. Unfortunately this strategy proved unsuccessful; integration of the subsequent  $^{19}\text{F}$  NMR spectra showed a relative increase in the signals associated with **1** (figure S2). We attribute this observation to the rate of concomitant hydrolysis exceeding the rate of further conversion leading to the regeneration of **1** and an increase in its apparent concentration. Further attempts employing intermittent sparging and application of vacuum did not favour completion over hydrolysis.

Additional evidence for competing hydrolysis was provided by the isolation and subsequent identification of  $\{\text{TpTi}(\text{NMe}_2)_2\}_2\{\mu\text{-O}\}$  (**3**) (Scheme S1). Compound **3** was not observed in the reaction monitoring  $^1\text{H}$  NMR spectra because it precipitates from the toluene reaction medium but is inconspicuous because of the intense brown colour of the solution. Compound **3** did prove to be soluble in chloroform and the proposed structure was established by multinuclear NMR. The  $^{19}\text{F}$  NMR spectrum served to prove that **3** was fluorine free; likewise, the  $^{11}\text{B}$  NMR only displayed a single broad signal corresponding to the boron atom in the Tp ligand at  $\delta -3.9$  ppm, at lower frequency than those observed for **2** and  $\text{TpTi}(\text{NMe}_2)_3$ .<sup>15</sup> The  $^1\text{H}$  NMR again included three sets of pyrazolyl peaks in the 2:1 ratio expected for a tridentate Tp ligand bound to a  $\text{M}(\text{NMe}_2)_2\text{X}$  fragment. The  $\text{NMe}_2$  signal appeared at  $\delta 3.42$  ppm, at

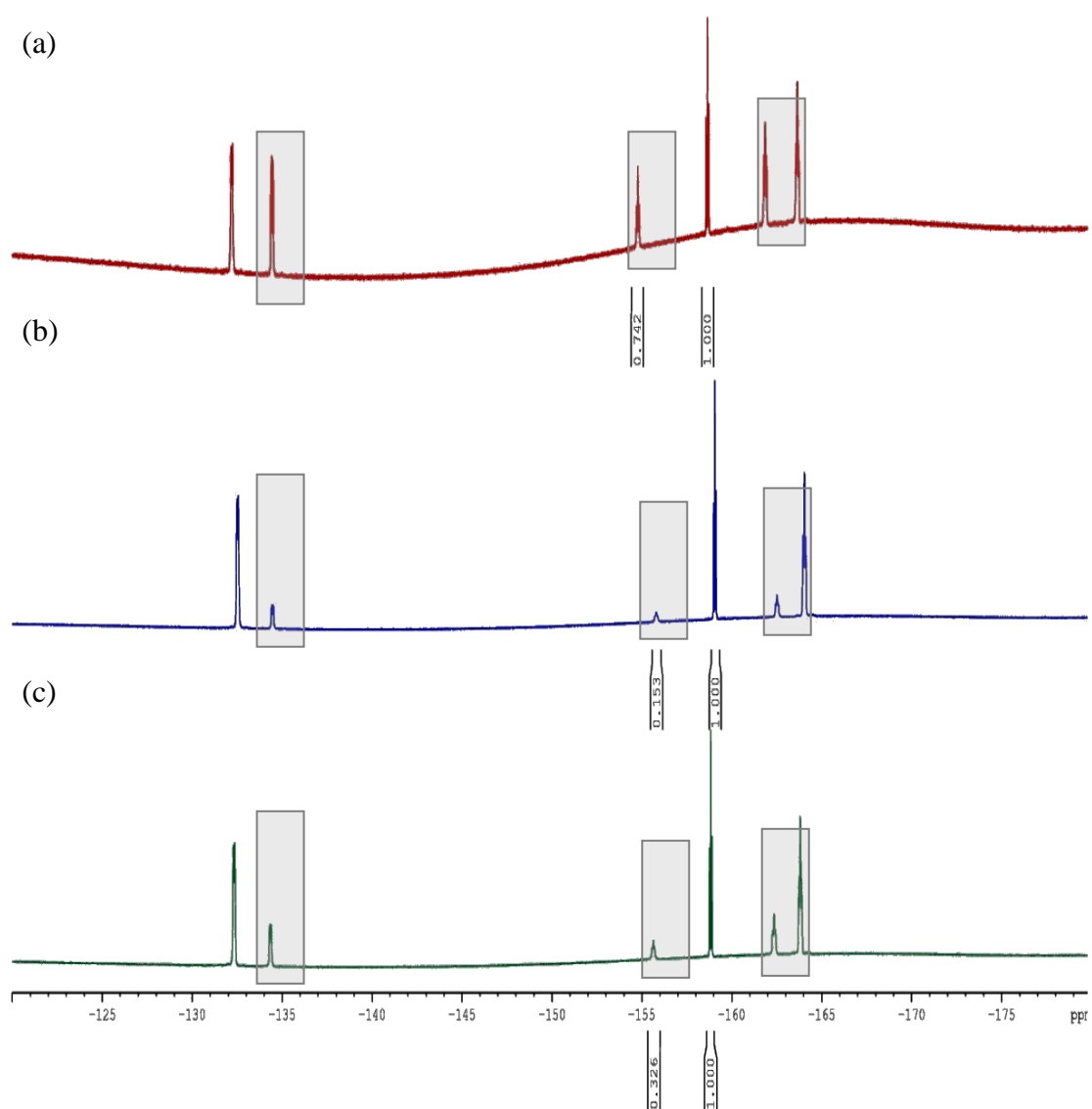
higher frequency shift from those of  $\text{TpTi}(\text{NMe}_2)_3$  and **2** at  $\delta$  3.13 and 3.18 ppm respectively.

**S**

**cheme S1.**



**Figure S1.** Selected regions of the  $^1\text{H}$  NMR of **2** in  $\text{CDCl}_3$  at  $25^\circ\text{C}$  showing the Tp CH signals, the missing signal is coincident with the solvent peak.



**Figure S2.**  $^{19}\text{F}$  NMR spectra at reaction times of (a) 1 hour, (b) 4 hours and (c) 10 hours in the generation of **2**. The major signals correspond to **2** whilst the minor set, shaded, correspond to **1**

**Table S1.** Hydrogen bond distances (Å) and angles (°) with standard deviations in parentheses

	D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
<b>2</b>	N(51)—H(51a)...F(62)	0.83(2)	2.22(2)	2.780(2)	125(2)
	N(51)—H(51a)...F(82)	0.83(2)	2.35(2)	2.830(2)	118(2)
<b>4.CH<sub>2</sub>Cl<sub>2</sub></b>	N(51)—H(51a)...F(62)	0.79(2)	2.37(2)	2.698(2)	107(2)
	N(51)—H(51a)...F(82)	0.79(2)	2.37(2)	2.859(2)	121(2)
	N(51)—H(51b)...F(76)	0.87(3)	2.33(3)	2.877(3)	121(2)
<b>6.pentane</b>	N(51)—H(51a)...F(62)	0.90	2.12	2.773(8)	129
	N(51)—H(51a)...F(82)	0.90	2.24	2.883(8)	128