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# Journal of Organometallic Chemistry

journal homepage: www.elsevier.com/locate/jorganchem

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#### ARTICLE INFO

Article history: Received 18 June 2012 Received in revised form 6 July 2012 Accepted 9 July 2012

Keywords: Boranes Hydroboration Alkenes Lewis adduct <sup>11</sup>B NMR spectroscopy

# ABSTRACT

The dimethylsulfide adduct of bis(pentafluorophenyl)borane  $HB(C_6F_5)_2 \cdot SMe_2$  reacts on mixing with alkenes such as 1-hexene and styrene, with selectivities closely following those of the Me<sub>2</sub>S-free reagent. The mono(pentafluorophenyl)borane  $H_2B(C_6F_5) \cdot SMe_2$  also undergoes rapid hydroboration reactions to give the dialkylboranes  $R_2B(C_6F_5)$ . Treatment of the boranes with trimethylsilylacetylene results in rapid hydroboration to give the trans-vinylborane. The reaction of  $H_2B(C_6F_5) \cdot SMe_2$  with 1,5-cyclooctadiene at room temperature yields a kinetic mixture of the 1,4- and 1,5-dihydroboration products which quantitatively isomerizes on heating to the 1,5-isomer, pentafluorophenyl-9-borobicyclo[3.3.1]nonane. This bicyclic borane crystallizes as the SMe<sub>2</sub> adduct, which has been characterized by X-ray crystallography. © 2012 Elsevier B.V. All rights reserved.

# 1. Introduction

Since the first report of the synthesis of tris(pentafluorophenyl) borane by Stone et al. in 1963 [1], the chemical stability and resistance to hydrolysis have made perfluoroaryl boranes and borates attractive reagents [2], with a wide range of uses in organic synthesis and as catalyst activators [3,4]. While the synthesis of  $B(C_6F_5)_3$  is facile [5], borane derivatives with only one or two pentafluorophenyl groups present considerable synthetic challenges [2]. In particular, there are two reported routes to  $[HB(C_6F_5)_2]_2$  (1, "Piers' borane"), neither of which is entirely convenient, since they either require the synthesis of  $BCl(C_6F_5)_2$  from BCl<sub>3</sub> and  $(C_6F_5)_2$ SnMe<sub>2</sub> followed by treatment with Me<sub>2</sub>SiHCl [6], or a somewhat inefficient exchange between  $B(C_6F_5)_3$  and Et<sub>3</sub>SiH [7].

Parks et al. reported that  $[HB(C_6F_5)_2]_2$  (1) rapidly hydroborates alkenes and alkynes under mild conditions in near quantitative yield, with good chemo- and regio-selectivity [8,9]. Mixtures of  $B(C_6F_5)_3$  and  $H_3B \cdot SMe_2$  in hexane, thought to give 1  $\cdot SMe_2$ , have been used to catalyze the hydroboration of alkynes with pinacolborane [10]. While in some instances catalytic amounts of

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pentafluorophenylboranes may suffice,  $[HB(C_6F_5)_2]_2$  has recently been used to modify ligands, and for these and other synthetic applications there is a requirement for a convenient synthetic alternative to **1** [11]. We have recently reported facile syntheses of HB(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>·SMe<sub>2</sub> (**1**·SMe<sub>2</sub>) and H<sub>2</sub>B(C<sub>6</sub>F<sub>5</sub>)·SMe<sub>2</sub> (**2**·SMe<sub>2</sub>) as crystalline solids [12]. These SMe<sub>2</sub> adducts are more soluble in hydrocarbons than base-free **1** and are easier to prepare and handle. Herein we report the hydroboration activity of **1**·SMe<sub>2</sub> and of **2**·SMe<sub>2</sub>, for which there is no base-free alternative. The double intramolecular hydroboration reaction of 1,5-cyclooctadiene with **2**·SMe<sub>2</sub> is described, along with the crystal structure of the resulting bicyclic alkyl borane.

## 2. Results and discussion

The hydroboration activity of both  $1 \cdot SMe_2$  and  $2 \cdot SMe_2$  with styrene, 1-hexene, 1,1-diphenylethylene and trimethylsilylacetylene have been investigated (Table 1). Initial screening reactions were performed in an NMR tube in deuterated benzene without heating. In the case of styrene, 1-hexene and trimethylsilylacetylene, hydroboration reactions proceeded quantitatively, with the reaction being complete by the time the NMR tube was inserted into the spectrometer. This hydroboration activity therefore closely follows that observed by Piers et al. for the SMe<sub>2</sub>-free reagent [7]. Hydroboration reactions of the more hindered substrate 1,1diphenylethylene with  $1 \cdot SMe_2$  and  $2 \cdot SMe_2$  proceeded at a much





<sup>☆</sup> In fond memory of F. Gordon A. Stone.

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Borane	Substrate	Hydroboration product	<sup>11</sup> B NMR chemical shift (ppm)	Reaction time <sup>a</sup>
1∙SMe <sub>2</sub>		$C_6F_5$ Ph $C_6F_5$ B $C_6F_5$ 3a	-1.2	<1 min
1 SMe₂	~	$\begin{array}{c} Me_{2}S\\ C_{6}F_{5}\\ C_{6}F_{5}\end{array}$	-0.5	<1 min
1.SMe₂		$\begin{array}{c} Ph \\ Me_2S_{HII}, B \\ C_6F_5 \\ C_6F_5 \\ C_6F_5 \end{array}$	-0.9	<12 h
<b>1</b> ∙SMe <sub>2</sub>	HSiMe <sub>3</sub>	$C_6F_5$ $C_6F_5$ $C_6F_5$ $C_6F_5$ $C_6F_5$ $C_6$ B $SiMe_3$	-3.2	<1 min
<b>2</b> ∙SMe <sub>2</sub>		$     Me_2S_{IIIIIIIIIIIIIIIIIIIIIIIIIIIIIIIIIII$	7.1	<1 min
$2$ ·SMe $_2$		Me <sub>2</sub> S <sub>///,,B</sub> C <sub>6</sub> F <sub>5</sub> 4b	16	<1 min
<b>2</b> ∙SMe <sub>2</sub>		Ph Ph Ph Ph Ph Ph Ph Ph Ph Ph Ph Ph Ph Ph Ph Ph Ph Ph Sim	-6.9	<12 h
<b>2</b> ∙SMe <sub>2</sub>	HSiMe <sub>3</sub>	Me <sub>2</sub> S <sub>11,11,1</sub> C <sub>6</sub> F <sub>5</sub> SiMe <sub>3</sub>	6.8	<1 min
<b>2</b> ∙SMe <sub>2</sub>		4d Me <sub>2</sub> S <sub>1111,1,1</sub> C <sub>6</sub> F <sub>5</sub> 5	3.8	1 h, refluxing toluene

<sup>a</sup> Reactions were conducted in C<sub>6</sub>D<sub>6</sub> at room temperature unless otherwise stated. A large excess of dimethylsulfide was added before recording the NMR spectra to drive the dissociation equilibrium to the adducted form and facilitate a meaningful comparison of the <sup>11</sup>B NMR chemical shifts.

slower rate, with complete conversion requiring 12 h at room temperature.

Minor signals were observed in the <sup>11</sup>B NMR spectra of hydroboration reactions with both  $1 \cdot SMe_2$  and  $2 \cdot SMe_2$ , which we attribute to the products of slow ligand redistribution in solution. Monitoring the <sup>19</sup>F and <sup>11</sup>B NMR spectra of the dihydroboration reaction between  $2 \cdot SMe_2$  and 1,1-diphenylethylene at hourly intervals suggests that the second hydroboration step proceeds at a similar rate to the first. An intermediate is observed in the <sup>19</sup>F NMR spectrum (-129.8 (m, 2F, o-F), -157.8 (t,  ${}^{3}J_{FF} = 21$  Hz, 1F, p-F), -163.7 (m, 2F, m-F)), which is consistent with monohydroboration to give (C<sub>6</sub>F<sub>5</sub>)B(H)(CHPh<sub>2</sub>), alongside resonances for  $2 \cdot SMe_2$  and the final product. The expected doublet for the intermediate was not seen in the <sup>11</sup>B NMR spectrum, presumably because it is obscured by resonances of the starting material and final product.

# 2.1. Hydroboration reaction of 2 · SMe<sub>2</sub> with 1,5-cyclooctadiene

1,5-cyclooctadiene (1,5-COD) reacts with  $2 \cdot \text{SMe}_2$  in a 1:1 M ratio at room temperature in toluene through double hydroboration (Scheme 1). The <sup>11</sup>B NMR spectrum of the product shows two signals in an approximately 2:1 ratio, consistent with the formation of a mixture of 1,4- and 1,5- addition products,  $6 \cdot \text{SMe}_2$  and  $5 \cdot \text{SMe}_2$ , respectively (Scheme 1). The monohydroboration intermediate **A**, was not sufficiently long-lived to be observed spectroscopically. A similar product mixture has been reported in the hydroboration of 1,5-COD with H<sub>3</sub>B·L (L = THF [13], SMe<sub>2</sub> [14]).

The 1,5-isomer **5** is thermodynamically favored and was formed quantitatively after heating the reaction mixture in refluxing toluene for 1 h. The adduct  $5 \cdot \text{SMe}_2$  was isolated through recrystallization of the crude product in the presence of excess

dimethylsulfide. The solid state structure of  $\mathbf{5} \cdot \text{SMe}_2$  was determined by single crystal X-ray diffraction methods and is depicted in Fig. 1.

The geometry at the boron center is essentially tetrahedral, with a C(11)-B(1)-C(7) bond angle of  $105.6(3)^{\circ}$ . This is significantly smaller than the C–B–C bond angle of  $111.6(2)^{\circ}$  for dimeric 9-BBN [15] and is slightly larger than the BBN-cycloalkane borate anions reported by Braunschweig et al. [16].

#### 3. Conclusion

The toluene soluble and thermally stable crystalline solids  $HB(C_6F_5)_2 \cdot SMe_2$  and  $H_2B(C_6F_5) \cdot SMe_2$  are readily prepared through the ligand exchange reaction between  $B(C_6F_5)_3$  and  $H_3B \cdot SMe_2$ . These borane dimethylsulfide adducts react rapidly with unhindered alkenes to give the hydroboration products under mild conditions and in high yield. The reaction proceeds more slowly with 1,1-disubstituted alkenes. Hydroboration of alkynes is also possible and the stoichiometric reaction with trimethylsilylacetylene proceeds cleanly to give trans-alkenylboranes. The synthetic potential of  $H_2B(C_6F_5) \cdot SMe_2$  is illustrated by the synthesis of pentafluorophenyl-9-borabicyclo[3.3.1]nonane through the reaction with 1,5-cyclooctadiene. Given their ease of handling, we anticipate that these boranes will prove to be a useful addition to the arsenal of hydroboration reagents.

#### 4. Experimental

All synthetic procedures were carried out under dry nitrogen using standard Schlenk-line techniques. Toluene was dried over sodium metal and distilled prior to use. Each substrate, where applicable, was dried over alumina prior to use. NMR samples were prepared with deuterated benzene which had been dried over 4 Å



Scheme 1. Mono- and di-hydroboration of 1,5-cyclooctadiene.



**Fig. 1.** ORTEP representation of **5** · SMe<sub>2</sub>. Displacement ellipsoids are shown at 50% probability. Hydrogen atoms have been removed for clarity. Selected bond lengths (Å) and angles (deg): B1–C1 1.648(5), B1–S1 2.026(4), B1–C7 1.612(5), B1–C11 1.635(5), C11–B1–C7 105.6(3), C11–B1–C1 116.3(3), C7–B1–C1 115.6(3), C7–B1–S1, 107.6(2), C11–B1–S1 105.6(2), C1–B1–S1 105.4(2).

molecular sieves and degassed. <sup>1</sup>H, <sup>13</sup>C, <sup>19</sup>F and <sup>11</sup>B NMR spectra were recorded using a Bruker Avance DPX300 spectrometer at 23 °C. All chemical shifts are reported in parts per million and referenced to residual solvent resonances; <sup>19</sup>F and <sup>11</sup>B resonances are quoted relative to CFCl<sub>3</sub> and BF<sub>3</sub>·OEt<sub>2</sub>, respectively. Elemental analyses were performed at the Department of Health and Human Sciences, London Metropolitan University. The syntheses of **1** ·SMe<sub>2</sub> and **2** ·SMe<sub>2</sub> were carried out according to literature procedures [12].

# 4.1. Spectroscopic investigation of hydroborations with $1 \cdot \text{SMe}_2$ and $2 \cdot \text{SMe}_2$

The data in Table 1 summarize hydroboration reactions performed in deuterated benzene at room temperature (unless otherwise stated). In a typical experiment, the substrate was dissolved in deuterated benzene and added to an NMR tube containing a solution of the borane. The tubes were shaken to mix prior to insertion into the spectrometer. The time taken to affect quantitative hydroboration was determined by <sup>1</sup>H, <sup>11</sup>B and <sup>19</sup>F NMR spectroscopy. In solution, there is an equilibrium between the dimethyl sulfide adducted and dimethyl sulfide free boranes such that the <sup>11</sup>B NMR chemical shift is highly dependent on the amount of dimethylsulfide present. In order to favor the adduct and facilitate comparison of the <sup>11</sup>B NMR spectroscopic data an excess of dimethylsulfide was added to the NMR samples.

The bis(pentafluorophenyl)boranes 3a-3d were isolated as the SMe<sub>2</sub> adducts following the general procedure presented below for  $3a \cdot SMe_2$ , while the pentafluorophenylboranes 4a-4d were

isolated base-free following essentially the same procedure. All but **3d** · SMe<sub>2</sub> and **5** were obtained as air-sensitive oils, which precluded purification and elemental analysis.

# 4.1.1. $(C_6F_5)_2BCH_2CH_2(C_6H_5) \cdot SMe_2$ (**3a** · SMe\_2)

Styrene (0.14 ml, 1.2 mmol) was added dropwise with stirring to a solution of  $1 \cdot \text{SMe}_2$  (0.5 g, 1.2 mmol) in toluene (5 ml). The volatiles were removed under reduced pressure giving the product as a pale yellow oil in quantitative yield.

# 4.1.2. $(C_6F_5)B(CH_2CH_2(C_6H_5))_2$ (4a)

$$\begin{split} &\delta_{H} \left(300.1 \text{ MHz}, C_{6}D_{6}\right): 6.9-7.3 \ (m, 10H, C_{6}H_{5}), 2.6 \ (t, \, {}^{3}\!J_{H,H} = 8 \text{ Hz}, \\ &4H, CH_{2} \right), 1.5 \ (t, \, {}^{3}\!J_{H,H} = 8 \text{ Hz}, 4H, CH_{2} ). \, \delta_{C} \left(75.5 \text{ MHz}, \{ {}^{1}\text{H} \}, C_{6}D_{6} \right): 144.2 \\ &(C_{ipso}), 129.3 \ (CH), 129.2 \ (CH), 126.8 \ (CH), 32.5 \ (BCH_{2}), 31.5 \ (CH_{2}). \, \delta_{F} \\ &(282.4 \text{ MHz}, C_{6}D_{6}): -133.1 \ (m, 2F, o-F), -152.8 \ (t, \, {}^{3}\!J_{F,F} = 20 \text{ Hz}, 1F, \\ &p-F), -161.6 \ (m, 2F, m-F). \, \delta_{B} \ (96.3 \text{ MHz}, C_{6}D_{6}): 81.1 \ (br). \end{split}$$

#### 4.1.3. $(C_6F_5)_2B(CH_2)_5CH_3 \cdot SMe_2$ (**3b** $\cdot SMe_2$ )

 $\delta_{H}$  (300.1 MHz, C<sub>6</sub>D<sub>6</sub>): 1.1–1.4 (m, 10H, CH<sub>2</sub>), 1.1 (s, 6H, SMe<sub>2</sub>), 0.9 (t,  ${}^{3}J_{H,H} = 7$  Hz, 3H, CH<sub>3</sub>).  $\delta_{C}$  (75.5 MHz, { $}^{1}H$ }, C<sub>6</sub>D<sub>6</sub>): 33.9 (CH<sub>2</sub>), 32.7 (CH<sub>2</sub>), 27.4 (CH<sub>2</sub>), 23.8 (CH<sub>2</sub>), 23.1 (BCH<sub>2</sub>), 19.6 (SMe<sub>2</sub>), 14.9 (CH<sub>3</sub>).  $\delta_{F}$  (282.4 MHz, C<sub>6</sub>D<sub>6</sub>): -130.7 (m, 4F, o-F), -155.7 (t,  ${}^{3}J_{F,F} = 21$  Hz, 2F, p-F), -162.7 (m, 4F, m-F).  $\delta_{B}$  (96.3 MHz, C<sub>6</sub>D<sub>6</sub>): 6.2 (br).

#### 4.1.4. $(C_6F_5)B((CH_2)_5CH_3)_2$ (**4b**)

 $\delta_{H}$  (300.1 MHz, C<sub>6</sub>D<sub>6</sub>): 1.1–1.7 (m, 20H, CH<sub>2</sub>), 0.9 (t,  ${}^{3}J_{H,H} = 6$  Hz, 6H, CH<sub>3</sub>).  $\delta_{C}$  (75.5 MHz, {<sup>1</sup>H}, C<sub>6</sub>D<sub>6</sub>): 33.3 (CH<sub>2</sub>), 32.6 (CH<sub>2</sub>), 31.8 (BCH<sub>2</sub>), 25.4 (CH<sub>2</sub>), 23.6 (CH<sub>2</sub>), 14.8 (CH<sub>3</sub>).  $\delta_{F}$  (282.4 MHz, C<sub>6</sub>D<sub>6</sub>): –134.0 (m, 2F, o-F), –153.5 (t,  ${}^{3}J_{F,F} = 20$  Hz, 1F, p-F), –161.7 (m, 2F, m-F).  $\delta_{B}$  (96.3 MHz, C<sub>6</sub>D<sub>6</sub>): 84.9 (br).

# 4.1.5. $(C_6F_5)_2B(CH_2CH(C_6H_5)_2) \cdot SMe_2 (3c \cdot SMe_2)$

 $δ_{\rm H}$  (300.1 MHz, C<sub>6</sub>D<sub>6</sub>): 6.8–7.3 (m, 10H, C<sub>6</sub>H<sub>5</sub>), 3.9 (t,  ${}^{3}J_{\rm H,H}$  = 7 Hz, 1H, CH), 2.2 (d,  ${}^{3}J_{\rm H,H}$  = 7 Hz, 2H, CH<sub>2</sub>), 0.9 (s, 6H, SMe<sub>2</sub>).  $δ_{\rm C}$ (75.5 MHz, { ${}^{1}$ H}, C<sub>6</sub>D<sub>6</sub>): 147.4 (C<sub>ipso</sub>), 128.3 (CH), 127.3 (CH), 125.8 (CH), 49.9 (CH), 27.4 (BCH<sub>2</sub>), 18.8 (SMe<sub>2</sub>).  $\delta_{\rm F}$  (282.4 MHz, C<sub>6</sub>D<sub>6</sub>): -130.0 (d,  ${}^{3}J_{\rm F,F}$  = 20 Hz, 4F, o-F), -156.1 (t,  ${}^{3}J_{\rm F,F}$  = 21 Hz, 2F, p-F), -162.8 (m, 4F, m-F).  $\delta_{\rm B}$  (96.3 MHz, C<sub>6</sub>D<sub>6</sub>): 1.6 (br).

#### 4.1.6. $(C_6F_5)B(CH_2CH(C_6H_5)_2)_2$ (**4c**)

 $\delta_{\rm H}$  (300.1 MHz, C<sub>6</sub>D<sub>6</sub>): 6.8–7.2 (m, 20H, C<sub>6</sub>H<sub>5</sub>), 4.2 (t,  $^{3}J_{\rm H,H}$  = 8 Hz, 2H, CH), 2.3 (d,  $^{3}J_{\rm H,H}$  = 8 Hz, 4H, CH<sub>2</sub>).  $\delta_{\rm C}$  (75.5 MHz, {<sup>1</sup>H}, C<sub>6</sub>D<sub>6</sub>): 145.9 (C<sub>ipso</sub>), 128.5 (CH), 127.5 (CH), 126.2 (CH), 47.7 (CH), 38.5 (BCH<sub>2</sub>).  $\delta_{\rm F}$  (282.4 MHz, C<sub>6</sub>D<sub>6</sub>): –132.7 (m, 2F, o-F), –153.0 (t,  $^{3}J_{\rm F,F}$  = 21 Hz, 1F, p-F), –162.0 (m, 2F, m-F).  $\delta_{\rm B}$  (96.3 MHz, C<sub>6</sub>D<sub>6</sub>): 83.4 (br).

### 4.1.7. $(C_6F_5)_2B(CHCH(SiMe_3)) \cdot SMe_2 (\mathbf{3d} \cdot SMe_2)$

Formed a microcrystalline solid following removal of solvents. Elemental analysis found (%): C, 44.98; H, 3.30. Calculated for  $C_{19}H_{17}BF_{10}SSi:$  C, 45.07; H, 3.38.  $\delta_H$  (300.1 MHz,  $C_6D_6$ ): 7.0 (dm,  ${}^3J_{H,H} = 21$  Hz, 1H, CH), 5.9 (d,  ${}^3J_{H,H} = 21$  Hz, 1H, CH), 2.1 (s, 6H, SMe<sub>2</sub>), 0.07 (s, 9H, SiMe<sub>3</sub>).  $\delta_C$  (75.5 MHz, { ${}^{1}H$ },  $C_6D_6$ ): 145.8 (CH), 117.4 (BCH), 20.6 (SMe<sub>2</sub>), -1.2 (SiMe<sub>3</sub>).  $\delta_F$  (282.4 MHz,  $C_6D_6$ ): -130.9 (m, 4F, o-F), -157.2 (t,  ${}^3J_{F,F} = 20$  Hz, 2F, p-F), -163.8 (m, 4F, m-F).  $\delta_B$  (96.3 MHz,  $C_6D_6$ ): -0.5 (br).

#### 4.1.8. $(C_6F_5)B(CHCH(SiMe_3))_2$ (4d)

 $\delta_{H}$  (300.1 MHz, C<sub>6</sub>D<sub>6</sub>): 7.3 (m, 2H, CH), 6.2 (m, 2H, CH), 0.08 (s, 9H, SiMe<sub>3</sub>), 0.05 (s, 9H, SiMe<sub>3</sub>).  $\delta_{C}$  (75.5 MHz, {<sup>1</sup>H}, C<sub>6</sub>D<sub>6</sub>): 168.6 (CH), 141.7 (BCH), 0.13 (SiMe<sub>3</sub>), -1.4 (SiMe<sub>3</sub>).  $\delta_{F}$  (282.4 MHz, C<sub>6</sub>D<sub>6</sub>): -129.9 (m, 2F, o-F), -152.2 (t,  ${^3J_{EF}}=$  20 Hz, 1F, p-F), -161.9 (m, 2F, m-F).  $\delta_{B}$  (96.3 MHz, C<sub>6</sub>D<sub>6</sub>): 63.5 (br).

# 4.2. Preparation of pentafluorophenyl-9-borobicyclo[3.3.1] nonane · SMe<sub>2</sub> (**5** · SMe<sub>2</sub>)

A sample of **2** · SMe<sub>2</sub> (1.04 g, 4.3 mmol) was dissolved in toluene (75 ml). To this was added dropwise 1,5-cyclooctadiene (0.53 ml, 4.3 mmol) at room temperature. The mixture was heated to reflux for 1 h. Once cooled, the toluene was removed to give a colorless oil. X-ray quality crystals were obtained by dissolution in 1 ml of neat dimethylsulfide and cooling. The conversion was quantitative by <sup>11</sup>B NMR spectroscopic analysis and the product was isolated as a colorless solid (1.18 g, 79%). Elemental analysis found (%): C, 54.81; H, 5.67. Calculated for C<sub>16</sub>H<sub>20</sub>BF<sub>5</sub>S: C, 54.88; H, 5.76. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  1.5–2.2 (14H, mm), 1.1 (6H, s). <sup>19</sup>F NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  –130.4 (2F, m, o-F), –155.2 (1F, m, *p*-F), –162.9 (2F, m, *m*-F). <sup>11</sup>B NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  19. <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>, partial):  $\delta$  33.3 (CH<sub>2</sub>), 25.1 (CH<sub>2</sub>), 24.3 (CH), 17.3 (SMe<sub>2</sub>).

Crystals of **5**·SMe<sub>2</sub> were examined at 140 K on an Oxford Diffraction Xcalibur-3/Sapphire3-CCD diffractometer, equipped with Mo-K $\alpha$  radiation and graphite monochromator. Intensity data were measured by thin-slice  $\omega$ - and  $\varphi$ -scans. Data were processed using the CrysAlisPro-CCD and -RED programs [17]. The structure

was solved using XS [18] (incorporated in SHELXTL). Non-hydrogen atoms were refined with anisotropic thermal parameters and hydrogen atoms were placed in idealized positions and refined using the riding model. No missed symmetry was reported by PLATON [19]. The structure was refined (weighted least-squares refinement on  $F^2$ ) and the final least-squares refinement converged to  $R_1 = 0.0425$  ( $I > 2\sigma(I)$ , 3145 data) and w $R_2 = 0.1331$  ( $F^2$ , 3273 data, 210 parameters, 2 restraints).

# Acknowledgement

We thank the University of East Anglia for financial support. EJ is the recipient of an A. R. Katritzky scholarship. The authors would like to thank Dr. Anna-Marie Fuller for helpful discussions.

#### Appendix A. Supplementary material

CCDC 885114 ( $\mathbf{5} \cdot \text{SMe}_2$ ) contains the crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/ data\_request/cif.

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