

Facile hydroboration with the dimethylsulfide adducts of mono- and bis-(pentafluorophenyl)borane[☆]

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ABSTRACT

The dimethylsulfide adduct of bis(pentafluorophenyl)borane $\text{HB}(\text{C}_6\text{F}_5)_2 \cdot \text{SMe}_2$ reacts on mixing with alkenes such as 1-hexene and styrene, with selectivities closely following those of the Me_2S -free reagent. The mono(pentafluorophenyl)borane $\text{H}_2\text{B}(\text{C}_6\text{F}_5) \cdot \text{SMe}_2$ also undergoes rapid hydroboration reactions to give the dialkylboranes $\text{R}_2\text{B}(\text{C}_6\text{F}_5)$. Treatment of the boranes with trimethylsilylacetylene results in rapid hydroboration to give the trans-vinylborane. The reaction of $\text{H}_2\text{B}(\text{C}_6\text{F}_5) \cdot \text{SMe}_2$ 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_2 adduct, which has been characterized by X-ray crystallography.

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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 $\text{B}(\text{C}_6\text{F}_5)_3$ 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 $[\text{HB}(\text{C}_6\text{F}_5)_2]_2$ (**1**, “Piers’ borane”), neither of which is entirely convenient, since they either require the synthesis of $\text{BCl}(\text{C}_6\text{F}_5)_2$ from BCl_3 and $(\text{C}_6\text{F}_5)_2\text{SnMe}_2$ followed by treatment with Me_2SiHCl [6], or a somewhat inefficient exchange between $\text{B}(\text{C}_6\text{F}_5)_3$ and Et_3SiH [7].

Parks et al. reported that $[\text{HB}(\text{C}_6\text{F}_5)_2]_2$ (**1**) rapidly hydroborates alkenes and alkynes under mild conditions in near quantitative yield, with good chemo- and regio-selectivity [8,9]. Mixtures of $\text{B}(\text{C}_6\text{F}_5)_3$ and $\text{H}_3\text{B} \cdot \text{SMe}_2$ in hexane, thought to give **1**· SMe_2 , have been used to catalyze the hydroboration of alkynes with pinacolborane [10]. While in some instances catalytic amounts of

pentafluorophenylboranes may suffice, $[\text{HB}(\text{C}_6\text{F}_5)_2]_2$ 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 $\text{HB}(\text{C}_6\text{F}_5)_2 \cdot \text{SMe}_2$ (**1**· SMe_2) and $\text{H}_2\text{B}(\text{C}_6\text{F}_5) \cdot \text{SMe}_2$ (**2**· SMe_2) as crystalline solids [12]. These SMe_2 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_2 and of **2**· SMe_2 , for which there is no base-free alternative. The double intramolecular hydroboration reaction of 1,5-cyclooctadiene with **2**· SMe_2 is described, along with the crystal structure of the resulting bicyclic alkyl borane.

2. Results and discussion

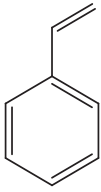
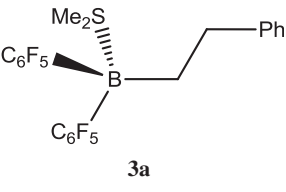

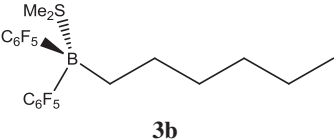
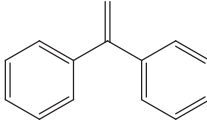
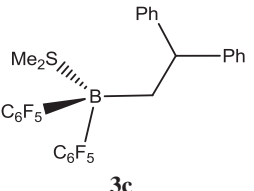

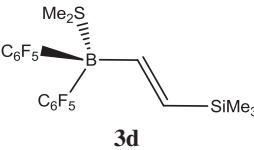
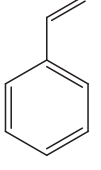
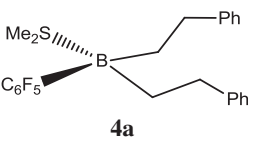

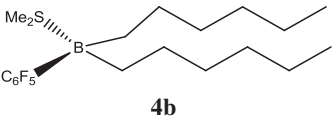
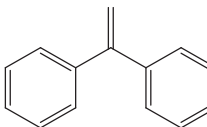
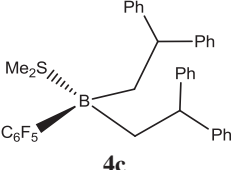

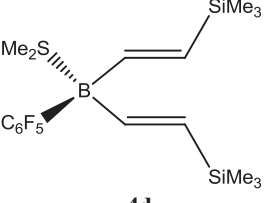
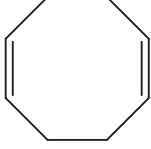
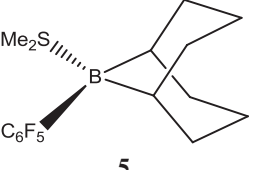
The hydroboration activity of both **1**· SMe_2 and **2**· SMe_2 with styrene, 1-hexene, 1,1-diphenylethylene and trimethylsilylacetylene have been investigated (Table 1). Initial screening reactions were performed in an NMR tube in deuterated benzene without heating. In the case of styrene, 1-hexene 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_2 -free reagent [7]. Hydroboration reactions of the more hindered substrate 1,1-diphenylethylene with **1**· SMe_2 and **2**· SMe_2 proceeded at a much

[☆] In fond memory of F. Gordon A. Stone.

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Table 1
Hydroboration of selected alkene substrates with reagents **1**·SMe₂ and **2**·SMe₂.

Borane	Substrate	Hydroboration product	¹¹ B NMR chemical shift (ppm)	Reaction time ^a
1 ·SMe ₂		 3a	-1.2	<1 min
1 ·SMe ₂		 3b	-0.5	<1 min
1 ·SMe ₂		 3c	-0.9	<12 h
1 ·SMe ₂		 3d	-3.2	<1 min
2 ·SMe ₂		 4a	7.1	<1 min
2 ·SMe ₂		 4b	16	<1 min
2 ·SMe ₂		 4c	-6.9	<12 h
2 ·SMe ₂		 4d	6.8	<1 min
2 ·SMe ₂		 5	3.8	1 h, refluxing toluene

^a Reactions were conducted in C₆D₆ 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 ¹¹B NMR chemical shifts.

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