Directed functionalization of Ferrocene

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Abstract

New routes for the site selective multiple borylation of ferrocene have been investigated. Direct borylation of di-t-butylferrocene and hexamethylferrocene with excess boron tribromide yielded exclusively the diborylated species. Formation of a 1,2,1',2'-tetraborylated ferrocene was attempted via synthesis of a more reactive precursor, the novel 1,2,1',2'-tetramercurated di-t-butylferrocene.

Introduction

Inorganic polymers have over the past twenty years received much attention as a result of their interesting properties, which include unusual electronic, magnetic and preceramic characteristics.¹ It has recently been discovered that the electronic and photophysical properties of organic conducting polymers can be modulated through the incorporation of Lewis acidic boron centers into the polymer backbones.²

Our research aims at synthesizing ferrocene compounds suitable for selective introduction of multiple boryl groups in the 1,2,1',2'-positions of ferrocenes as shown in Fig. 1. These borylated ferrocenes will serve as precursors for future work, which will aim at exploring their reactivity towards simple bifunctional amines such as paraphenylenediamines to give boron-containing polymers.



The proposed routes for the borylation of the ferrocene compounds involved the direct reaction of boron tribromide with ferrocene derivatives. Other routes involved the reaction of boron tribromide with acetoxymercurioferrocene.

Synthetic concept

As shown in Figure 2, electrophilic borylation of ferrocene with 1 equivalent of boron tribromide leads to a monoborylated ferrocene. The reaction of ferrocene with 2 equivalents of boron tribromide results in the 1,1'-diborylated ferrocene. However, the reaction of ferrocene with excess boron tribromide leads to the 1,1',3,3'-tetrakis-(dibromoboryl)ferrocene.³



Directed synthesis is therefore necessary to obtain the unknown 1,2,1',2'-tetraborylated ferrocene. This directed synthesis may be done through the use of either sterically or electronically directing groups.

Sterically directing groups:



We chose two different ferrocene derivatives to explore the application of sterically directing substituents, di-tbutylferrocene (Figure 3) and hexamethylferrocene (Figure 4). Introduction of t-butyl groups on ferrocene can be expected to

sterically protect the adjacent hydrogen atoms from substitution. This protection should make it possible to selectively replace the β hydrogen atoms leading to a 1,2,1',2'substitution pattern. An alternative method is the introduction of six methyl groups on

ferrocene. Replacement of the remaining hydrogen atoms should again lead to a 1,2,1',2'-substitution pattern.





Electronically directing groups:



To probe the suitability of electronically directing groups, we chose to introduce an ortho-directing substituent, the p-tolylsulfonyl group on ferrocene⁴ (Figure 5). Selective replacement of the hydrogen atoms in the α position to this group leads to a 1,2disubstitution pattern. Similarly, 1,1'bis(tolylsulfonyl)ferrocene may be used in the synthesis of 1,2,1',2'-tetrasubstituted ferrocenes.

Results and discussion

Di-t-butylferrocene and hexamethylferrocene were successfully synthesized. The borylation of both ferrocene compounds resulted in mixtures of two isomeric diborylated species (Figure 6). Even with large excess of boron tribromide and under reflux conditions, the desired tetraborylated ferrocene was not observed.



We therefore decided to investigate an alternative route to the tetraborylated ferrocene via initial formation of a tetramercurated ferrocene derivate (Figure 7). A carbon-mercury bond is weaker than a carbon-hydrogen bond. It will therefore be easier to break the carbon-mercury bond to achieve substitution. The mercuration of di-t-butylferrocene with 4 equivalents of mercuric acetate yielded the desired di-t-

butyl[tetrakis- (acetoxymercurio)]ferrocene as a yellow solid.⁵ We are currently investigating this product as a precursor to the desired tetraborylated ferrocene.



Experimental methods

Synthesis of 1,1'-di-t-butylferrocene⁶

A mass of 20.25 g (0.17 mol) of t-butylcyclopentadiene (t-BuCp) was charged to a 500 ml round bottom flask equipped with a stir bar. Dry tetrahydrofuran (THF) was added to dissolve the t-BuCp. The solution was stirred and allowed to cool to -78°C under a nitrogen atmosphere. 108.5 ml of a 1.6M solution of n-butyl lithium (0.17 mol) was added dropwise. The reaction mixture was stirred for half an hour and allowed to warm to room temperature. The lithium t-butylcyclopentadienide (Li t-BuCp) was slowly added to a separate 500 ml Schlenk flask containing a cool suspension of 10 g of iron (II) chloride in THF. The reaction mixture was stirred overnight (12 h). A dark orange solution was separated and washed three times with ether and water. After drying with sodium sulfate, the solvent was removed. The residue was recrystallized from methanol. The yellow solid was filtered, dried under vacuum and characterized with GCMS, ¹H NMR and ¹³C NMR.

- ¹H NMR (DMSO): 1.17 (s, 18H, t-Bu), 4.03 ppm (m, 8H, Cp-H).
- ¹³C NMR (DMSO): 30.2 (CMe), 31.4 (CMe), 64.9 (Cp-C), 67.1 (Cp-C), 101.0 ppm (ipso Cp-C).
- GCMS: 298 (M⁺), 283 (M⁺ Me).

Borylation of di-t-butylferrocene

A mass of 1.5 g (5.03 mmol) of di-t-butylferrocene was charged to a 250 ml Schlenk flask equipped with a stir bar. While under a nitrogen atmosphere, 4.7 ml (50 mmol) of boron tribromide was added with a syringe. The reaction mixture was allowed to reflux overnight (12 h). The product was isolated by crystallization from hexanes and characterized with ¹H NMR, ¹³C NMR and ¹¹B NMR. Two isomers were observed.

Isomer 1

- ¹H NMR (C₆D₆): 1.03 (s, 18H, t-Bu), 4.25 (d, 4H, Cp-H) 4.47 (2H, Cp-H), 4.56 ppm (2H, Cp-H).
- ¹³C NMR (C₆D₆): 30.9 (CMe), 31.2 (C-Me), 74.6 (Cp-C), 76.1 (Cp-C), 77.7 (Cp-C), 80.0 (Cp-C), 112.0 ppm (ipso Cp-C).

Isomer 2

- ¹H NMR (C₆D₆): 1.02 (s, 18H, t-Bu), 4.37 (d, 4H, Cp-H), 4.50 (2H, Cp-H), 4.58 ppm (2H, Cp-H)
- ¹³C NMR (C₆D₆): 31.1 (CMe), 31.3 (C-Me), 74.8 (Cp-C), 76.2 (Cp-C), 78.0 (Cp-C), 80.0 (Cp-C), 114.0 ppm (ipso Cp-C).
- ¹¹B NMR (C₆D₆): 51.5 ppm

Synthesis of Hexamethylferrocene⁷



The synthesis of hexamethylferrocene is shown in Figure 8. A mass of 3.0 g (27.8 mmol) of trimethylcyclopentadiene was dissolved in THF in a 500 ml Schlenk flask and cooled to -78°C. A volume of 17.4 ml (27.8 mmol) n-butyl lithium was slowly added. The reaction mixture was stirred for 0.5 h and allowed to warm to room temperature. In a separate 500 ml Schlenk flask, 1.76 g (13.9 mmol) of iron (II) chloride was suspended in THF and cooled to 0°C. The lithium trimethylcyclopentadienide was slowly added to the suspension of FeCl2. The reaction mixture was stirred overnight (12 h). The product was extracted with ether and washed three times with water. The ether layer was separated and dried over sodium sulfate. After removal of the solvent, the product was extracted and crystallized from methanol. A yellow solid was obtained and dried under high vacuum.

• GCMS: 270 (M⁺), 255 (M⁺ - Me).

Borylation of hexamethylferrocene



Fig. 9

A mass of 0.53 g (1.9 mmol) of hexamethylferrocene was charged to a 250 ml Schlenk flask equipped with a stir bar. A volume of 1.76 ml (19 mmol) of boron tribromide was added. The reaction mixture was refluxed for 12 hours. The product was isolated and characterized with ¹H NMR, ¹³C NMR and ¹¹B NMR. Two isomers were observed.

Isomer 1

- ¹H NMR (C₆D₆): 1.39 (s, 6H, Me), 1.52 (s, 6H, Me), 1.83 (s, 6H, Me), 4.24 ppm (s, 2H, Cp-H).
- ¹³C NMR (C₆D₆): 9.4 (CMe), 11.4 (CMe), 12.5 (CMe), 80.1 (Cp-C), 90.2 (Cp-C), 91.2 (Cp-C), 92.8 ppm (Cp-C).

Isomer 2

- ¹H NMR (C₆D₆): 1.42 (s, 6H, Me), 1.54 (s, 6H, Me), 1.92 (s, 6H, Me), 4.32 ppm (s, 2H, Cp-H).
- ¹³C NMR (C₆D₆): 9.6 (CMe), 11.8 (CMe), 12.5 (CMe), 81.3 (Cp-C), 90.4 (Cp-C), 91.4 (Cp-C), 93.2 ppm (Cp-C).
- ¹¹B NMR (C₆D₆): 51.7 ppm.

Di-t-butyl [tetrakis (acetoxymercurio)] ferrocene⁵

A 250 ml Schlenk flask equipped with a stir bar and condenser was charged with 1 g (3.4 mmol) of di-t-butylferrocene. A mass of 4.27 g (1.3 mmol) of mercuric acetate was added. A volume of 100 ml of dry 1,2-dichloroethane was also added. The mixture was stirred for 12 hours. A yellow solid formed, which was separated by filtration and washed with 1,2-dichloroethane. The product was characterized with ¹H NMR, ¹³C NMR, IR and elemental analysis (EA).

¹H NMR (DMSO): 1.25 (s, 18H, t-Bu), 1.93 (s, 12H, Me), 4.39 (s, 2H, Cp-H), 4.46 ppm (s, 2H, Cp-H).

¹³C NMR (DMSO): 23.7 (CMe), 30.9 (CMe), 32.0 (C-Me), 70.2 (Cp-C), 76.4 (Cp-C), 82.4 (Cp-C), 88.4 (Cp-C), 104.9 (ipso Cp-C), 174.9 ppm (C=O).

IR: 1576, 1363, 1298, 690 cm-1

EA, Calculated: C 24.43, H 2.57 Found: C 23.11, H 2.39

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