



Structure and reactivity of a planar chiral naphthylferrocenylcopper heteroaggregate

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ABSTRACT

A chiral 2-naphthylferrocenylcopper heteroaggregate (**2**) was prepared in high yield by reaction of (*S*_p-2-naphthylferrocenyl)trimethyltin with (C₆F₅Cu)₄ and fully characterized by multinuclear NMR, single crystal X-ray diffraction, and elemental analysis. The reactivity of **2** toward boron halides was examined. Rearrangement reactions resulted in formation of 1,2-, 1,3-, and 1,1'-disubstituted naphthylferrocenylboranes.

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1. Introduction

Pentafluorophenyl copper, which was first introduced by Cairncross and Sheppard more than 40 years ago [1], exists as a tetrameric aggregate in the solid state, which is also believed to be the predominant species in solution [2,3]. A variety of structurally intriguing complexes with Lewis bases have been reported also and, in recent years, the electron-deficient character of pentafluorophenyl copper has been exploited in the assembly of luminescent supramolecular structures [4,5]. With respect to synthetic applications, initial exploration has focused on its use in organic synthesis, most notably in Ullmann-type coupling and carbocupration reactions [6]. However, pentafluorophenyl copper also serves as a mild reagent in organometallic synthesis, specifically in (a) metal exchange reactions with formation of other arylcopper species and (b) metathesis reactions that involve transfer of the C₆F₅ groups to other metals and metalloids (Scheme 1) [7,8]. Of particular interest is the aryl group transfer to boron with generation of perfluoroarylboranes [9–13]. This class of compounds has attracted tremendous interest in areas ranging

from Lewis acid catalysis to activators in olefin polymerization, and as components of so-called “frustrated Lewis pairs”, which are able to promote metal-free activation of small molecules, most notably H₂ [14].

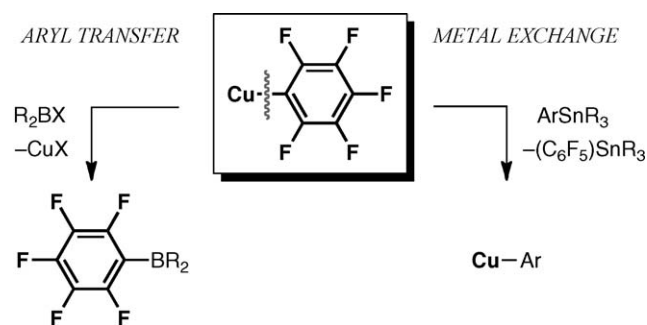
We have an ongoing interest in the development of ferrocene-based chiral Lewis acids as reagents and catalysts for stereoselective transformations. In this regard, we are currently exploring heteronuclear bidentate Lewis acids, in which an organotin and an organoborane Lewis acid group are attached adjacent to one another at one of the Cp rings of ferrocene [15], as well as planar chiral 2-naphthylferrocenylborane species [10,16]. We describe here the preparation of a planar chiral 2-naphthylferrocenylcopper species and its reactivity toward boron halides.

2. Results and discussion

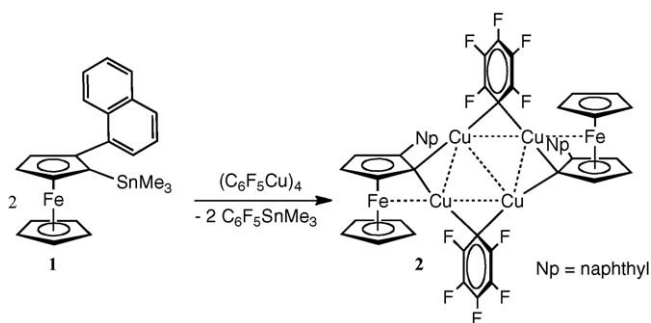
We decided to attempt the synthesis of an enantiomerically pure 2-naphthylferrocenyl copper reagent by tin-copper exchange [7] of (*S*_p-2-naphthylferrocenyl)trimethyltin (**1**) with pentafluorophenyl copper. Treatment of **1** with 0.5 equiv of (CuC₆F₅)₄ at RT resulted in highly selective formation of the arylcopper heteroaggregate **2** (Scheme 2), which was isolated in 77% yield after crystallization from a mixture of toluene and hexanes. Compound **2** features 2-naphthylferrocenyl (NpFc) as well as pentafluoro-

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Scheme 1. Schematic illustration of the reactivity of “C₆F₅Cu” in metal–metal exchange and aryl group transfer reactions.



Scheme 2. Synthesis of the *S_p*-2-naphthylferrocenylcopper heteroaggregate **2**.

phenyl groups according to ¹H and ¹⁹F NMR analysis. The ¹H NMR spectrum revealed the typical pattern of a 1,2-disubstituted ferrocene with four signals in an intensity ratio of 5:1:1:1, none of which showed tin satellites as would be expected upon quantitative replacement of the Me₃Sn groups. The ¹⁹F NMR spectrum displayed three resonances for the C₆F₅ groups at δ –108.2, –148.9, and –160.1. They are significantly shifted relative to those of the starting material (CuC₆F₅)₄ (δ –104.1, –141.5, and –158.1) [17], suggesting a different chemical environment.

The X-ray crystal structure revealed **2** to form an aggregate (Fig. 1), which is composed of two planar chiral NpFcCu and two C₆F₅Cu units. The NpFc moieties exhibit *S_p* planar chirality, consistent with the chiral information of the starting material, which demonstrates that substitution of the SnMe₃ group for Cu proceeded through an *ipso*-destannylation process with retention of stereochemistry. Complex **2** is otherwise structurally similar to the achiral species [(FcCu)₂(C₆F₅Cu)₂] [7] and features the ferrocene moieties at opposite corners of the Cu₄C₄ core. Unlike (C₆F₅Cu)₄ itself, which forms a tetrameric structure with square planar geometry in the solid state [17], **2** adopts a distorted parallelogram geometry.

An unusual aspect of the structure of **2** is the orientation of the naphthyl groups, both of which point into the same direction with respect to the Cu₄C₄ core. This effect is a result of the identical *S_p* planar chirality of the NpFc moieties. Favorable π-stacking interactions of the C₆F₅ moieties with the naphthyl groups may also play a role. Moreover, weak Fe···Cu interactions are apparent based on the relatively short Fe···Cu distances of 2.6046(19) and 2.7147(19) Å. These contacts are in a similar range as those of 2.7011(9) Å in the related complex [(FcCu)₂(C₆F₅Cu)₂] [7] and considerably shorter than the distances of 2.945(5) Å reported for the homoleptic complex [2-FcCH₂NMe₂Cu]₄ [18]. As another consequence of the short Fe···Cu contacts, the Cp rings of the ferrocenes are considerably tilted with interplanar angles of 9.8° and 8.2°.

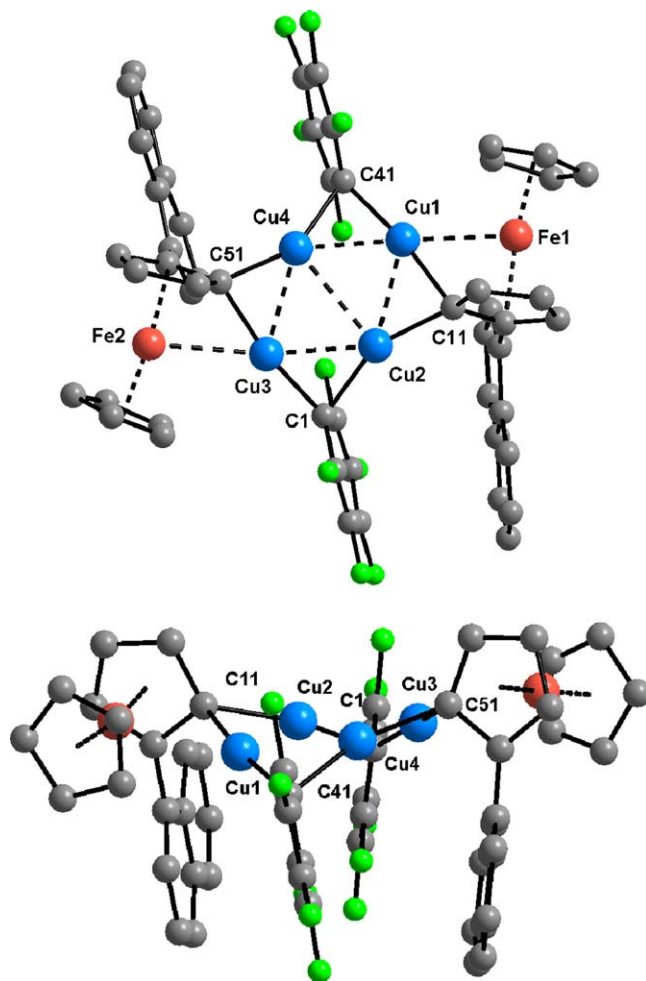


Fig. 1. Two different views of the X-ray crystal structure of **2**; hydrogen atoms are omitted for clarity. Selected interatomic distances (Å): Cu(1)–C(11) 2.010(10), Cu(1)–C(41) 1.983(10), Cu(2)–C(1) 2.048(11), Cu(2)–C(11) 1.961(9), Cu(3)–C(1) 1.993(11), Cu(3)–C(51) 1.986(10), Cu(4)–C(41) 2.043(10), Cu(4)–C(51) 1.970(10), Cu(2)···Cu(4) 2.7971(17), Cu(1)···Fe(1) 2.6046(19), Cu(3)···Fe(2) 2.7147(19).

In earlier work we found that (C₆F₅Cu)₄ and (MesCu)_{*n*} (Mes = 2,4,6-trimethylphenyl; *n* = 4, 5) can serve as mild reagents for the transfer of aryl groups to boron [3,8]. In fact, the reagent (C₆F₅Cu)₄ has been successfully employed in areas ranging from molecular Lewis acid chemistry [9,10] to polymeric Lewis acids [11], conjugated materials [12], and even amphiphilic borate block copolymers [13]. With the ultimate goal of developing new chiral naphthylferrocenylborane Lewis acids, we decided to explore the reactivity of the heteroaggregate **2** with boron halides. Initially, in an NMR scale reaction, we treated **2** with BBr₃ in CDCl₃ at –35 °C. However, it quickly became clear that the number of possible products is exceedingly large due to the unselective reactivity of the “C₆F₅Cu” component of **2** with BBr₃; (C₆F₅Cu)₄ is known to lead to a mixture of (C₆F₅)BBr₂, (C₆F₅)₂BBr, and (C₆F₅)₃B along with unreacted BBr₃ [8]. Indeed, we were able to identify BBr₃, (C₆F₅)BBr₂, (C₆F₅)₂BBr, and (C₆F₅)₃B in the reaction mixture in a ratio of ca. 3:1:0.5:1 based on ¹⁹F and ¹¹B NMR spectroscopy. Given this complexity, it was surprising to only find two major ferrocene-containing products in the ¹H NMR spectrum. Although the “(NpFc)Cu” component of **2** should be able to give a large number of different species (NpFc)BBR_{*x*}(C₆F₅)_{2–*x*} with *x* = 0, 1, 2, we identified only compounds of type (NpFc)BBR₂ (**3**, Chart 1). A possible explanation is that reaction of the “(NpFc)Cu” component with BBr₃ is relatively fast, but subsequent substitution of a second Br with either a C₆F₅ or a ferrocenyl group is less favorable due to

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