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# 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 $(C_6F_5Cu)_4$ 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.

## 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 $C_6F_5$ 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 $H_2$ [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 $(CuC_6F_5)_4$ 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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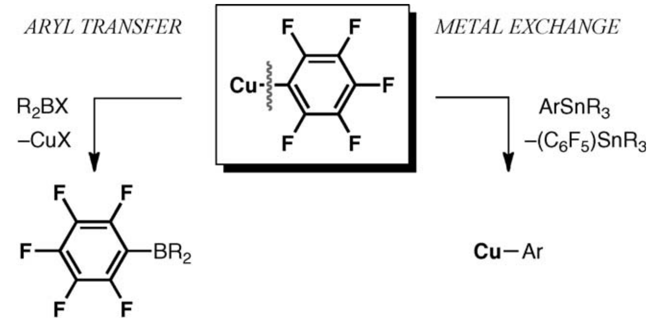
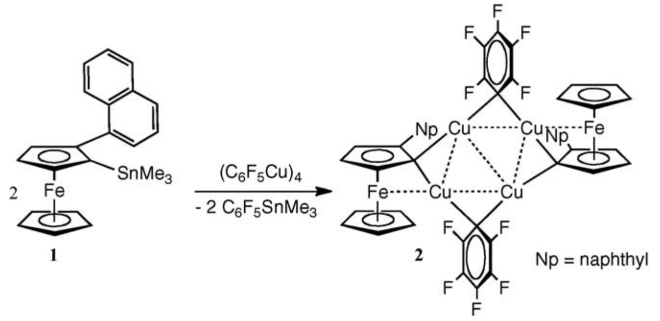


**Scheme 1.** Schematic illustration of the reactivity of "$C_6F_5Cu$" in metal–metal exchange and aryl group transfer reactions.



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

phenyl groups according to $^1H$ and $^{19}F$ 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 $Me_3Sn$ groups. The $^{19}F$ NMR spectrum displayed three resonances for the $C_6F_5$ groups at $\delta$ −108.2, −148.9, and −160.1. They are significantly shifted relative to those of the starting material $(CuC_6F_5)_4$ ($\delta$ −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 $C_6F_5Cu$ units. The NpFc moieties exhibit $S_p$ planar chirality, consistent with the chiral information of the starting material, which demonstrates that substitution of the $SnMe_3$ group for Cu proceeded through an *ipso*-destannylation process with retention of stereochemistry. Complex **2** is otherwise structurally similar to the achiral species $[(FcCu)_2(C_6F_5Cu)_2]$ [7] and features the ferrocene moieties at opposite corners of the $Cu_4C_4$ core. Unlike $(C_6F_5Cu)_4$ 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 $Cu_4C_4$ core. This effect is a result of the identical $S_p$ planar chirality of the NpFc moieties. Favorable $\pi$-stacking interactions of the $C_6F_5$ 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 $[(FcCu)_2(C_6F_5Cu)_2]$ [7] and considerably shorter than the distances of 2.945(5) Å reported for the homoleptic complex $[2\text{-}FcCH_2NMe_2Cu]_4$ [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°.

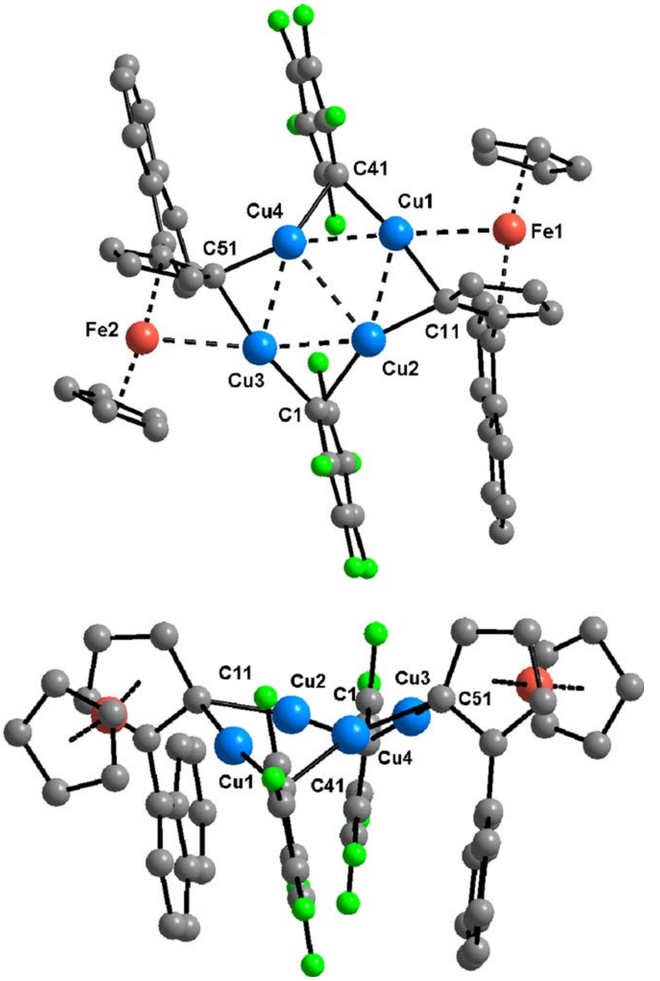


**Fig. 1.** Two different views of the X-ray crystal structure of **2**; hydrogen atoms are omitted for clarity. Selected interatomic distances (Å): Cu(1)–C(11) 2.010(10), Cu(1)–C(41) 1.983(10), Cu(2)–C(1) 2.048(11), Cu(2)–C(11) 1.961(9), Cu(3)–C(1) 1.993(11), Cu(3)–C(51) 1.986(10), Cu(4)–C(41) 2.043(10), 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 $(C_6F_5Cu)_4$ 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 $(C_6F_5Cu)_4$ 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 $BBr_3$ in $CDCl_3$ at −35 °C. However, it quickly became clear that the number of possible products is exceedingly large due to the unselective reactivity of the "$C_6F_5Cu$" component of **2** with $BBr_3$; $(C_6F_5Cu)_4$ is known to lead to a mixture of $(C_6F_5)BBr_2$, $(C_6F_5)_2BBr$, and $(C_6F_5)_3B$ along with unreacted $BBr_3$ [8]. Indeed, we were able to identify $BBr_3$, $(C_6F_5)BBr_2$, $(C_6F_5)_2BBr$, and $(C_6F_5)_3B$ in the reaction mixture in a ratio of ca. 3:1:0.5:1 based on $^{19}F$ and $^{11}B$ 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 $(NpFc)BBr_x(C_6F_5)_{2-x}$ with $x$ = 0, 1, 2, we identified only compounds of type $(NpFc)BBr_2$ (**3**, Chart 1). A possible explanation is that reaction of the "(NpFc)Cu" component with $BBr_3$ is relatively fast, but subsequent substitution of a second Br with either a $C_6F_5$ or a ferrocenyl group is less favorable due to

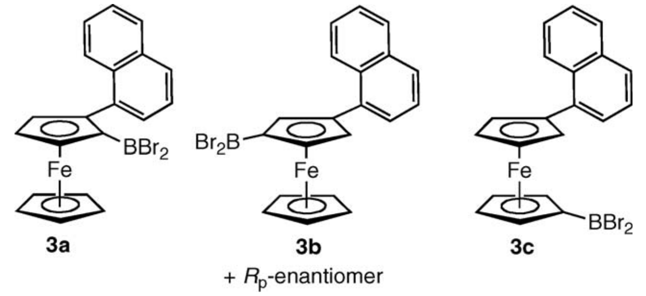
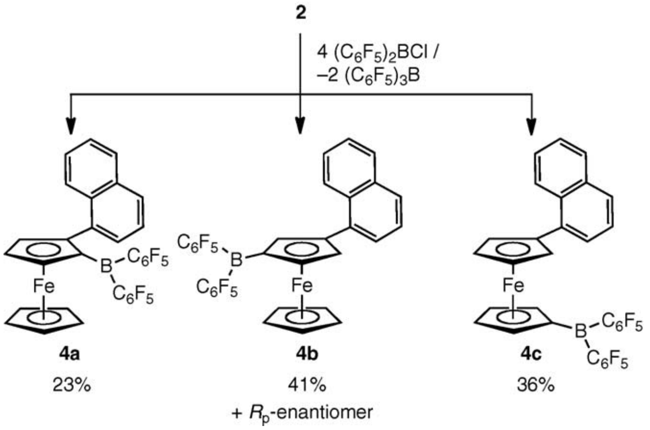


**Chart 1.** Possible ferrocenylborane regio-isomers from reaction of **2** with $BBr_3$.

the steric and electronic effect of the electron-rich ferrocenyl substituent, which is known to significantly reduce the Lewis acidity of boranes [19]. Further examination of the peak patterns in the $^1$H NMR spectrum revealed that not the expected 1,2-isomer **3a**, but a mixture of the 1,3- and 1,1′-isomers **3b** and **3c** in a 45:55 ratio was obtained. The different isomers were identified by comparison with literature data [10].

The formation of different regio-isomers of **3** depends on the reaction pathway: (a) *ipso*-substitution at the copper-bound Cp carbon with retention of stereochemistry should give rise to species **3a** ($R_p$-planar chirality of the product), which was not observed; (b) attack of the borane in the 3- or 4-position with subsequent proton transfer and elimination of CuBr would result in **3b** (racemic mixture of $R_p$- and $S_p$-isomers), while (c) attack at the unsubstituted Cp ring and subsequent proton transfer to the substituted Cp ring would result in the 1,1′-disubstituted ferrocene species **3c** (Chart 1). Rearrangements of this type with migration of protons from one Cp ring to another have been observed previously in the reaction of 1,1′-bis(trimethylstannyl)ferrocene with $BCl_3$ and other boron halides [15,20]. However, to our knowledge, they are unprecedented in the case of metalated ferrocene derivatives with more strongly polarized metal–carbon bonds.

We next decided to study the reactivity of **2** toward $(C_6F_5)_2BCl$, which was thought to be a milder and more selective reagent than $BBr_3$. In this case, species $(NpFc)B(C_6F_5)_2$ (**4**) are the only possible ferrocene-containing products. The reaction was again performed in $CDCl_3$ at −35 °C and the product mixture studied by $^1$H and $^{19}$F NMR spectroscopy. Formation of all three regio-isomers of $(NpFc)B(C_6F_5)_2$ (23% **4a**, 41% **4b**, 36% **4c**), along with an equimolar amount of $B(C_6F_5)_3$ was evident (Scheme 3). The individual isomers of **4** are easily distinguished based on their characteristic patterns in the Cp region of the $^1$H NMR spectrum. For **4a**, a singlet is observed at 4.61 ppm for the free Cp ring and the substituted Cp ring gives rise to three signals, one of which (Cp-H4) is a pseudotriplet at 5.28 ppm with a relatively large coupling constant of 2.5 Hz due to $^3J$ coupling with the two adjacent protons H3 and H5. While the pattern for the 1,3-isomer **4b** appears to be quite similar with $\delta$ 5.63 (dd, $J$ = 2.5, 1.5 Hz, 1H); 4.76 (br, 1H); 4.56 (br, 1H); 4.40 (s, 5H), the pseudotriplet for the proton between the boryl and naphthyl substituents ($\delta$ 4.76) is expected to show a significantly smaller $^4J$ coupling constant; the latter was not resolved in the present case. An entirely different pattern is found for the 1,1′-isomer **4c**, which shows four pseudotriplets of equal intensity at $\delta$ 5.16, 5.09, 4.66, 4.25. Consistent is also that three corresponding sets of $^{19}$F NMR signals were observed with intensities that match the isomer ratios determined by $^1$H NMR.



**Scheme 3.** Reaction of heteroaggregate **2** with $(C_6F_5)_2BCl$.

These unexpected results suggest that ferrocenylcopper species do not necessarily react with boron halides via *ipso*-substitution, which is generally assumed to be the preferred pathway for organolithium species. Instead, rearrangement reactions are observed that are reminiscent of the chemistry of ferrocenyltin compounds with boron halides. This could be because of a more covalent character of the bonding in ferrocenylcopper in comparison to ferrocenyllithium species. However, we need to also consider the possibility that in weakly coordinating solvents organolithium species might react in similarly unexpected ways.

## 3. Conclusion

A chiral 2-naphthylferrocenylcopper heteroaggregate (**2**) was prepared in high yield by reaction of ($S_p$-2-naphthylferrocenyl)-trimethyltin (**1**) with $(C_6F_5Cu)_4$. The reaction proceeded under mild conditions and with perfect retention of stereochemistry and no indication of isomerization. In contrast, subsequent reactions of the ferrocenylcopper species **2** with boron halides led to formation of all possible isomers, the 1,2-, 1,3-, and 1,1′-disubstituted naphthylferrocenylboranes. The identification of reaction conditions that allow for selective formation of one preferred isomer in the reaction of ferrocenylcopper compounds with boron halides is the subject of future studies.

## 4. Experimental

### *4.1. Reagents and general methods*

Enantiomerically pure **1** [10], $(C_6F_5)_2BCl$ [21], and $(C_6F_5Cu)_4$ [2,17,22] were prepared according to literature procedures. $BBr_3$ (99+%) was obtained from Aldrich and distilled prior to use. **Caution!** *$BBr_3$ is toxic and highly corrosive and should be handled appropriately with great care*. All reactions and manipulations were carried out under an atmosphere of prepurified nitrogen using either Schlenk techniques or an inert-atmosphere glove box (MBraun). Hydrocarbon solvents were purified using a solvent purification system (Innovative Technologies; alumina/copper columns).

The 499.9 MHz $^1$H NMR, 470.4 MHz $^{19}$F NMR, 125.7 MHz $^{13}$C NMR, and 160.3 MHz $^{11}$B NMR spectra were recorded on a Varian INOVA NMR spectrometer (Varian Inc., Palo Alto, CA) equipped with a 5 mm dual broadband gradient probe (Nalorac, Varian Inc., Martinez, CA). $^1$H and $^{13}$C NMR spectra were referenced internally to the residual solvent signal; $^{19}$F NMR and $^{11}$B NMR spectra were referenced externally to $\alpha,\alpha',\alpha''$-trifluorotoluene (0.05% in $C_6D_6$; $\delta = -63.73$) and $BF_3{\cdot}OEt_2$ ($\delta = 0$) in $C_6D_6$, respectively. The following abbreviations are used for signal assignments; Pf = pentafluorophenyl, Cp = cyclopentadienyl, dd = double doublet, pst = pseudotriplet, m = multiplet, dm = doublet of multiplet, br = broad unresolved signal.

UV/vis absorption data were acquired on a Varian Cary 500 UV/vis-NIR spectrophotometer. Solutions were prepared using a microbalance (±0.1 mg) and volumetric glassware and then charged into a quartz cuvette with a sealing screw cap inside the glove box.

The elemental analysis was performed by Quantitative Technologies Inc., Whitehouse, NJ.

### *4.2. Synthesis of [(NpFc)$_2$(C$_6$F$_5$)$_2$Cu$_4$] (2)*

To a solution of **1** (30.6 mg, 64.4 μmol) in hexanes (4 mL) was added $(C_6F_5Cu)_4$ (29.6 mg, 32.1 μmol) in toluene (2 mL) and the resulting mixture was kept for 4 days at −35 °C. The orange crystalline product obtained was washed with hexanes and dried under high vacuum. Yield: 29.8 mg (77%). $^1$H NMR (499.9 MHz, $CDCl_3$, 25 °C) $\delta$ 7.87 (d, $J$ = 8.0 Hz, 2H, Np), 7.83 (d, $J$ = 8.0 Hz, 2H, Np), 7.46–7.35 (m, 8H, Np), 7.22 (pst, $J$ = 7.5 Hz, 2H, Np), 5.07 (br, 2H, Cp), 4.96 (br, 2H, Cp), 4.15 (s, 10H, free Cp), 4.08 (br, 2H, Cp). $^{13}$C NMR (125.69 MHz, $CDCl_3$, 25 °C) $\delta$ 151.4 (dm, $^1J$(F, C) = 241 Hz, Pf-C$_o$), 142.0 (dm, $^1J$(F, C) = 254 Hz, Pf-C$_p$), 136.4 (Np), 136.0 (dm, $^1J$(F, C) = 260 Hz, Pf-C$_m$), 133.1, 132.9, 129.7, 128.3, 127.8, 125.7, 125.5, 125.4, 125.0 (Np), 106.6 (t, $^2J$ (F, C) = 58 Hz, Pf-C1) 103.1, 77.6, 77.3, 75.8, 70.8 (substituted Cp), 68.2 ($C_5H_5$). $^{19}$F NMR (470.4 MHz, $CDCl_3$, 25 °C) $\delta$ −108.2 (br d, J(F,F) = 18 Hz, F$_o$), −148.9 (br t, J(F,F) = 15 Hz, F$_p$), −160.1 (very br, F$_m$). UV–vis ($CH_2Cl_2$, $1.05 \times 10^{-4}$ M): $\lambda_{max}$ = 470 nm ($\varepsilon$ = 580). Elemental analysis for $C_{52}H_{30}Cu_4F_{10}Fe_2$, calcd. C 51.58, H 2.49, found C 51.49, H 2.39%.

### *4.3. NMR scale reaction of 2 with BBr$_3$*

To a solution of **2** (25.0 mg, 20.7 μmol) in $CDCl_3$ (0.8 mL) was added a solution of $BBr_3$ (20.7 mg, 82.6 μmol) in $CDCl_3$ (0.2 mL) at −35 °C. The mixture was stirred for 30 min. The color of the solution turned from yellow to dark red with precipitation of a white powder (CuBr). The supernatant was examined my multinuclear NMR spectroscopy, which revealed the presence of **3b** and **3c** in a ratio of 45:55 based on $^1$H NMR integration. In addition, the $^{19}$F and $^{11}$B NMR data revealed the presence of $C_6F_5BBr_2$, $(C_6F_5)_2BBr$, $(C_6F_5)_3B$, and $BBr_3$ in a ratio of ca. 1:0.5:1:3. The individual components were identified by comparison of the NMR data with literature values [8,10].

### *4.4. NMR scale reaction of 2 with (C$_6$F$_5$)$_2$BCl*

To a solution of **2** (23.0 mg, 19.0 μmol) in $CDCl_3$ (0.8 mL) was added $(C_6F_5)_2BCl$ (28.8 mg, 75.7 μmol) in $CDCl_3$ (0.2 mL) at −35 °C. A gradual color change to dark red and formation of a precipitate was observed. The supernatant was studied by $^1$H and $^{19}$F NMR spectroscopy. The expected by-product $B(C_6F_5)_3$ and the 1,2-isomer **4a** were identified by comparison with the data reported in the literature [8,10]; the other isomers were identified based on the characteristic patterns in the ferrocene region. The ratio of 1,2- to 1,3- to 1,1′-isomer according to $^1$H NMR integration of the Cp resonances is ca. 23:41:36. *NMR data for the 1,3 and 1,1′-isomers*: $^1$H NMR (499.9 MHz, $CDCl_3$, 25 °C) Np region (**4b** and **4c**; signal assignments were not possible): $\delta$ 8.47 (d), 8.27 (m), 7.91 (d), 7.85 (d), 8.80 (d), 7.63 (d), 7.55–7.45 (m), 7.4–7.3 (m), 8.1–7.8 (m); Cp region of 1,3-isomer **4b**: $\delta$ 5.63 (dd, $J$ = 2.5, 1.5 Hz, 1H, Cp-5), 4.76 (br, 1H, Cp-4), 4.56 (br, 1H, Cp-3), 4.40 (s, 5H, $C_5H_5$); Cp region of 1,1′-isomer **4c**: $\delta$ 5.16 (pst, $J$ = 1.8 Hz, 2H, Cp), 5.09 (pst, $J$ = 1.8 Hz, 2H, Cp), 4.66 (br, 2H, Cp), 4.25 (br, 2H, Cp). $^{19}$F NMR (470.4 MHz, $CDCl_3$, 25 °C) for 1,3-isomer **4b**: $\delta$ −134.1 (br d, F$_o$), −157.5 (br t, J(F,F) = 20 Hz, F$_P$), −166.7 (m, F$_m$); for 1,1′-isomer **4c**: $\delta$ −134.4 (m, J(F,F) = 18 Hz, F$_o$), −158.0 (t, J(F,F) = 20 Hz, F$_p$), −166.9 (m, F$_m$).

### *4.5. Crystallography*

Data for **2** were collected on a STOE IPDS II two-circle-diffractometer at 173 K. The structure was solved by direct methods and refined by full-matrix least squares based on $F^2$ with all reflections (SHELX 97; G. Sheldrick, Siemens XRD, Madison, WI) [23]. Details of the structure analysis are provided in Table 1. Non-hydrogen atoms were refined with anisotropic displacement coefficients, and hydrogen atoms were treated as idealized contribution. CCDC-775725 contains the supplementary crystallographic data for **2**. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; email: deposit@ccdc.cam.ac.uk).

**Table 1**
Details of the X-ray crystal structure analysis of complex **2**.

| Compound | **2** |
|---|---|
| Empirical formula | $C_{52}H_{30}Cu_4F_{10}Fe_2$ |
| MW | 1210.62 |
| *T*, K | 173(2) |
| Wavelength, Å | 0.71073 |
| Crystal system | Orthorhombic |
| Space group | $P2_12_12_1$ |
| *a*, Å | 12.9410(11) |
| *b*, Å | 13.5429(9) |
| *c*, Å | 25.0456(18) |
| *V*, Å$^3$ | 4389.5(6) |
| *Z* | 4 |
| $\rho_{calc}$, g cm$^{-3}$ | 1.832 |
| $\mu$ (Mo K$_\alpha$), mm$^{-1}$ | 2.627 |
| *F*(000) | 2400 |
| Crystal size, mm | 0.08 × 0.07 × 0.05 |
| $\theta$ range,° | 1.63–24.87 |
| Limiting indices | $-13 \le h \le 15$<br>$-14 \le k \le 15$<br>$-29 \le l \le 29$ |
| Reflns collected | 17380 |
| Independent reflns | 7550 [*R*(int) = 0.1205] |
| Absorption correction | Multi-scan |
| Refinement method | Full-matrix least square on $F^2$ |
| Data/restraints/parameters | 7550/0/613 |
| Goodness-of-fit on $F^2$ | 0.862 |
| Final *R* indices [$I > 2\sigma(I)$]$^a$ | *R*1 = 0.0583, w*R*2 = 0.0868 |
| *R* indices (all data)$^a$ | *R*1 = 0.1081, w*R*2 = 0.1009 |
| peak$_{max}$/hole$_{min}$ (e Å$^{-3}$) | 0.412/−0.553 |
| Absolute structure parameter | −0.01(3) |

$^a R1 = \Sigma||F_o| - |F_c||/\sum|F_o|$; $wR2 = \{\sum[w(F_o{}^2 - F_c{}^2)^2]/\sum[w(F_o{}^2)^2]\}^{1/2}$.

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