Ferrocene Aggregates

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Mono- and Dimetalated Ferrocenylcopper Complexes by Tin–Copper Exchange**

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Metalated ferrocenes have received tremendous interest owing to their importance as reagents in the preparation of other ferrocene derivatives and their often intriguing structural features.[1] For instance, lithioferrocene and 1,1′-dilithioferrocene are key intermediates for a variety of ferrocene derivatives, including ferrocene-based ligands for catalysis and ferrocene-containing polymers.[1] The pentamethyldiethylenetriamine (pmdeta) complex of 1,1′-dilithioferrocene[2] has been confirmed to be a dimer with the lithium atoms bridging the two cyclopentadienyl (Cp) rings of one ferrocene and another Cp ring of a neighboring ferrocene. Complexation with tetramethylethylenediamine (tmeda) leads to a trimeric structure in which the Cp rings of one of the ferrocene moieties are doubly bridged by lithium.[3] Similarly unusual multiply deprotonated species with sodium and magnesium have been reported recently.[4] Although organocopper compounds play an increasingly important role as reagents in organic and organometallic synthesis,[5] the respective ferrocenylcopper derivatives have received comparatively less attention and little is known about their structural features. The only crystallographically characterized derivative of ferrocenylcopper to date is the tetrameric *ortho*-substituted derivative $[2\text{-FcCH}_2\text{NMe}_2\text{Cu}]_4$ (Fc = $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\eta^5\text{-C}_5\text{H}_3)$).[6] Polymeric structures are presumably formed in the absence of the dimethylaminomethyl groups,[5c] and these break up in the presence of donor solvents and can only be solubilized in the form of the adducts.[7]

Herein we describe a new approach taking advantage of the facile and highly selective formation of heteroleptic copper complexes in a novel reaction between aryltin species and pentafluorophenylcopper.[8] The resulting soluble aggregates provide a rare insight into the structural complexity of highly aggregated arylenedicopper species. We also discuss possible interactions between the iron atom of ferrocene and the pendant Lewis acidic organocopper substituents. The ability of the central metal to form dative bonds to other Lewis acidic metals is an intriguing feature of metallocenes that has direct implications for the mechanism of electrophilic aromatic substitution with metallocenes.[9] In the case of ferrocene, bonding metal–metal interactions were first discovered for adducts with mercury salts[10,11] and have since been confirmed for [3]ferrocenophanes, such as $[\text{Fe}(\text{C}_5\text{H}_4\text{S})_2\text{M}(\text{PR}_3)]$ (M = Ni, Pd, Pt)[12] and $[\{\text{Fe}(\text{C}_5\text{H}_4\text{NSiMe}_3)_2\text{TiCl}\}_2]^{2+}$[13] and are broadly debated for other ferrocene species.[2,3,14,15] We report on the discovery of an intriguing ferrocene complex in which the iron atom appears to interact simultaneously with two Lewis acidic metal centers.

A solution of $[\text{FcSnMe}_3]$ (**1**) in hexanes was treated with half an equivalent of $[\text{C}_6\text{F}_5\text{Cu}]_4$[16,17] in toluene at ambient temperature (Scheme 1).[18] The color of the mixture gradually changed from yellow to orange. Crystallization at −35 °C yielded the arylcopper complex **2** as an orange crystalline solid in 83 % yield. In contrast to the reported insolubility of $[\text{FcCu}]_n$,[5c] complex **2** was found to be very soluble in noncoordinating solvents. The incorporation of both ferrocenyl and pentafluorophenyl groups in the product was evident from the ^{1}H and ^{19}F NMR spectra. The typical signal pattern for a monosubstituted ferrocene was observed in the ^{1}H NMR spectrum, with two pseudo-triplets corre-

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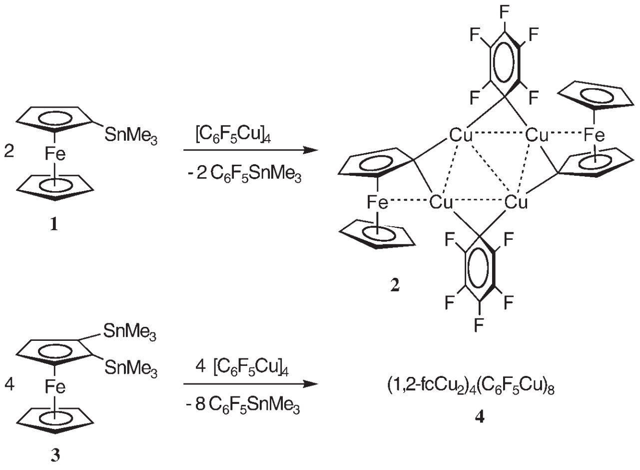

Scheme 1. Synthesis of **2** and **4** by tin–copper exchange. fc = $(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_3)$.

sponding to the α- and β-protons ($\delta = 4.13$ and 4.82 ppm, respectively) and a singlet for the free Cp ring ($\delta = 3.99$ ppm). The chemical shift difference between the α- and β-protons ($\Delta\delta = 0.69$ ppm) is remarkable and reminiscent of that typically found for ring-tilted ferrocenophanes and/or metallocenes in which the metal is acting as a donor to other Lewis acidic metal centers.[11–13,15] The ^{19}F NMR spectrum of **2** shows a set of three slightly broadened resonances at $\delta = -106.9$, -148.9, and -160.2 ppm, which are in a similar range to those of $[C_6F_5Cu]_4$ (in $CDCl_3$: $\delta = -104.1$, -141.5, and -158.1 ppm),[17] thereby confirming the incorporation of "C_6F_5Cu" units into the product. However, the chemical shift difference ($\Delta\delta_{m,p} = 11.3$ ppm) between the *meta*- and *para*-fluorine substituents is considerably smaller than that observed for $[C_6F_5Cu]_4$ ($\Delta\delta_{m,p} = 16.6$ ppm).[17] This result indicates an increase in electron density at the copper sites owing to the presence of the ferrocenyl moieties. We have observed similar effects upon coordination of aromatic solvents, such as toluene or mesitylene, to $[C_6F_5Cu]_4$.[17]

A single-crystal X-ray analysis of **2** confirmed the formation of a rare example of a heteroleptic arylcopper complex with two ferrocene and two pentafluorophenyl units (Figure 1).[18] The ferrocene moieties are *trans* to each other and the central Cu_4 core in **2** shows a parallelogram geometry with one small and one large diagonal Cu···Cu distance (2.9631(12) and 3.9275(13) Å, respectively). These features are typical of tetrameric structures of arylcopper species in which two of the copper centers are coordinated by an additional donor ligand.[7,17] In contrast, the noncoordinated complexes $[2\text{-}FcCH_2NMe_2Cu]_4$[6] and $[C_6F_5Cu]_4$[16,17] adopt a square-planar geometry. The ferrocene moieties appear to act as additional coordinating groups, with Fe–Cu distances of 2.7011(9) Å that are close to the sum of the covalent radii of Cu and Fe (2.53 Å[19]) and considerably shorter than the Fe–Cu distances of 2.945(5) Å in $[2\text{-}FcCH_2NMe_2Cu]_4$.[6] The Cp rings are no longer parallel in **2**, presumably a result of the short Fe–Cu contacts, and show a tilt angle of 10.7° (for $[2\text{-}FcCH_2NMe_2Cu]_4$: 6.5°). Bending of metallocenes is known to lead to distinct changes in the frontier orbitals[20] and enhancement of the basicity of the central metal, which favors complex formation.[11] A comparison with a recent study by Enders et al. is noteworthy. They used quinolyl substituents in the 1,1′-positions of ferrocene and ruthenocene to support the binding of Cu and Zn salts to the metal center.[21] A short Ru···Cu contact of 2.633(1) Å was observed for the ruthenocene complex $[1,1'\text{-}Rc(quin)_2Cu]BF_4$ (Rc = ruthenocene, quin = 8-quinolyl) and the tilt angle between the Cp planes was found to be 7.6°.[22]

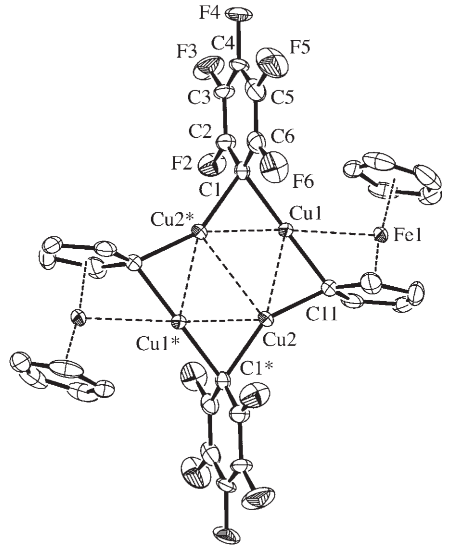

Figure 1. Molecular structure of **2**; hydrogen atoms and cocrystallized toluene molecules have been omitted for clarity. Selected interatomic distances [Å] and angles [°]: Cu1–Cu2 2.4865(8), Cu1–Cu2* 2.4331(8), Cu2–Cu2* 2.9631(12), Cu1–C1 2.018(5), Cu1–C11 1.971(5), Cu2–C11 1.969(5), Cu2–C1* 2.031(5), Cu1–Fe1 2.7011(9); C1–Cu1–C11 170.5(2), C11–Cu2–C1* 150.7(2), Cu1–Cu2–Cu1* 105.94(3), Cu2–Cu1–Cu2* 74.06(3), Cu1–Cu2–Cu2* 52.14(2), Cu1*–Cu2–Cu2* 53.79(2), Cu2–Cu1–Fe1 101.69(3), Cu2*–Cu1–Fe1 174.99(3). Symmetry operator for generating equivalent atoms (*): 1−*x*, 1−*y*, 1−*z*.

To investigate the possibility of multiple interactions[23] of Lewis acidic copper centers with the iron atom of ferrocene we treated the distannylated species $[1,2\text{-}fc(SnMe_3)_2]$ (**3**)[24] with $[C_6F_5Cu]_4$ (Scheme 1).[18] Treatment of a solution of **3** in hexanes with one equivalent of $[C_6F_5Cu]_4$ in toluene at ambient temperature led to a gradual change of the color of the mixture from light orange to wine red. Crystallization of the mixture at −35 °C yielded the arylcopper complex **4** as a dark-red crystalline solid in 77 % yield. The thermal stability of **4** ($T_{\text{decomp.}} = 153$ °C) is similar to that of $[C_6F_5Cu]_4$, but **4** is comparatively less sensitive to air and moisture according to ^{1}H NMR studies.

The ^{1}H NMR spectrum of **4** shows one resonance for the free Cp rings at $\delta = 4.60$ ppm and three strongly downfield shifted signals of equal intensity for the substituted Cp rings at $\delta = 6.05$ (d), 5.77 (t), and 4.64 ppm (d), which suggests that the two α-hydrogen aroms are in different environments. Four doublets for the *ortho*-F, two triplets for the *para*-F, and four overlapping multiplets for the *meta*-F are observed in the ^{19}F NMR spectrum. This pattern is consistent with the presence of two different types of C_6F_5 groups in the product, where hindered rotation of the C_6F_5 groups leads to nonequivalent *ortho*- and *meta*-F atoms. This result suggests the presence of a highly rigid molecular framework, in contrast to the commonly observed fluxionality of copper aggregates in solution.[7]

Dark-red single crystals of [**4**(toluene)$_x$] (x is approximately 4 according to integration of the ^{1}H NMR spectrum) were obtained by recrystallization from toluene at low temperature. While the toluene molecules are highly disordered and were therefore removed using the "Squeeze" routine, the copper aggregate **4** itself showed no disorder and refined well (Figure 2a).[18] The crystal-structure analysis reveals that **4** is one of the most highly aggregated copper complexes to date, consisting of four 1,2-fcCu$_2$ and eight CuC$_6$F$_5$ groups for a total of 16 copper and four iron atoms.

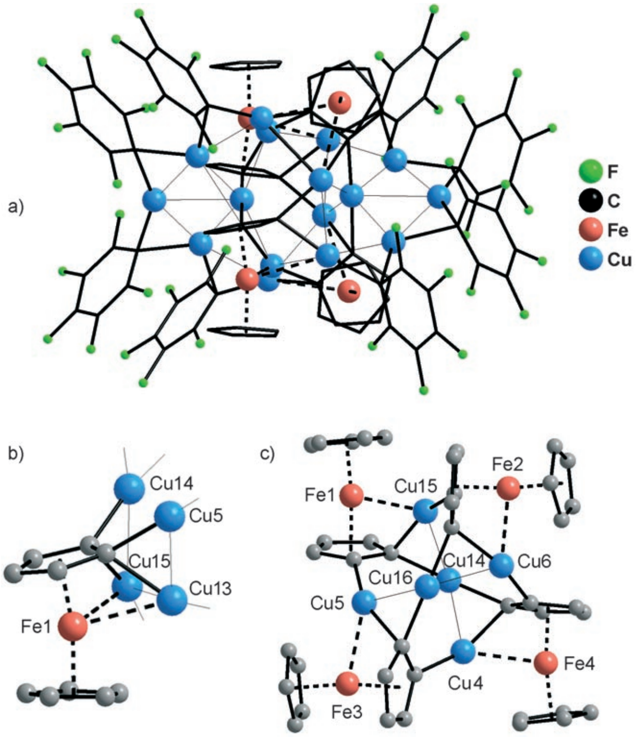

Figure 2. a) Molecular structure of **4**; hydrogen atoms have been omitted for clarity. Selected geometric parameters are provided in the Supporting Information. b) View of one ferrocene moiety with all Cu substituents; c) view of the [fc$_4$Cu$_6$]$^{2-}$ core.

Each ferrocene moiety is bound to four bridging copper centers, two of which are located above the Cp plane with the other two bound from the *endo* side (Figure 2b). However, in contrast to the arrangement in **2**, the ferrocene moieties are directly linked by copper atoms ("fc-Cu-fc" fragments in Figure 2c). Among the four copper atoms attached to each ferrocene moiety, three are involved in bridging interactions with other ferrocene units, which leads to a core of four ferrocene units and six copper centers. The fourth copper atom only bridges C$_6$F$_5$ groups. This arrangement results in the formation of two interlocked crown-like substructures, each of which consists of four CuC$_6$F$_5$ moieties (Figure 2a).

The Fe–Cu contacts in **4** range from 2.5702(9) to 2.6963(10) Å, and are thus even shorter than those in **2**. Interestingly, one shorter (2.5702(9)–2.5757(9) Å) and one longer Fe–Cu contact (2.6365(10)–2.6963(10) Å) are observed for each ferrocene moiety. Most closely related are the trianionic clusters (Bu$_4$N)$_3$[Cu$_5$(Fe(CO)$_4$)$_n$] (n = 3,5),[25] in which n Fe(CO)$_4$ fragments are covalently bound to a Cu$_n$ fragment, and the neutral clusters [Fe$_2$(CO)$_8$(μ-CuPR$_3$)$_2$] (R = *t*Bu, cyclohexyl).[26] The Fe–Cu contacts in **4** are close to or within the range of bonding Fe–Cu distances in these clusters (2.394–2.638 Å). Additional support for bonding interactions in **4** is provided by the strong bending of the *endo* Cu atoms toward Fe, which is reflected in small Cp$_{\text{centroid}}$–C–Cu angles that range from 132.28(2) to 124.78(2)° (*exo* Cu atoms: 150.61(2)–161.02(2)°). Moreover, the Cp rings in **4** are highly tilted, with interplanar angles of 15.4°, 15.5°, 16.7°, and 16.8° for the four ferrocene units (Figure 2b). A considerable deviation from linear geometry is observed for the Cu atoms that are close to Fe (C···Cu···C 153.8(2)–161.5(2)°), thus suggesting coordination by the Fe atoms, while Cu14 and Cu16 show a nearly linear arrangement (C···Cu···C 176.7(2)° and 179.5(2)°) (Figure 2c). Finally, it is noteworthy that the two Cu atoms in the *endo* positions are in close proximity to one another, with Cu···Cu distances (2.7180(9)–2.8255(9) Å) that are considerably smaller than those of the Cu pairs in the *exo* position (3.403–3.433 Å) and close to those in reported "FeCu$_2$" cluster fragments (2.582–2.691 Å).[25] The Cu–Fe–Cu angles of 62.06(3)–65.59(3)° compare favorably with the H–Mo–H angle of 75.5° in the related complex [Cp$_2$Mo(H)$_2$], which displays a similar bent geometry and has been shown to involve a set of suitable metallocene orbitals of 4a$_1$, 2b$_1$, and 3a$_1$ symmetry in bonding to the hydrogen atoms.[20,27]

The NMR spectroscopic data and geometric parameters of **2** and **4** suggest the possibility for (multiple) Fe–Cu interactions, which should also be reflected in the UV/Vis spectra. For instance, unusually strong absorption bands at 380 nm for the [2]ferrocenophane adduct [(C$_5$H$_4$CH$_2$)$_2$Fe]Hg(ClO$_4$)$_2$[11] and at 330 nm (ε = 35000 M^{-1}cm^{-1}) for the ruthenocene (Rc) complex [Rc-Hg-Rc](ClO$_4$)$_2$[28] have been reported. The UV/Vis spectra of orange **2** and dark-red **4** in CH$_2$Cl$_2$ are shown in comparison to those of ferrocene and [C$_6$F$_5$Cu]$_4$ in Figure 3. A strong enhancement and red-shift of the ferrocene absorption band at 438 nm (ε = 77) to 465 nm (ε = 450) for **2** and 457 nm (ε = 15750) for **4** is evident, and the intense red color of **4** can be attributed to tailing of the band

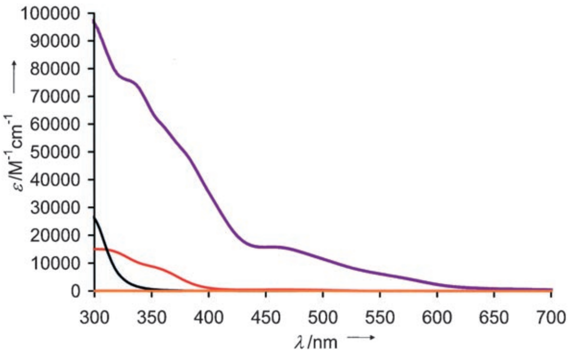

Figure 3. The UV/Vis spectra of **4** (purple), **2** (red), [C$_6$F$_5$Cu]$_4$ (black), and ferrocene (orange).

to about 650 nm. In addition, a very strong high-energy absorption band is found at 332 nm ($\varepsilon = 75\,500$) for **4**.

In conclusion, we have reported a new synthetic route to organocopper species by reaction of arylstannanes with pentafluorophenylcopper. The reaction offers an exceptionally mild route to heteroleptic complexes of organocopper species that are otherwise not easily accessible. Complex **4** provides a first insight into the structural complexity of multimetallic arylcopper species $ArCu_n$, which typically form polymeric aggregates and hence have evaded detailed structural characterization. Finally, the first structural and spectroscopic evidence that the iron atom in ferrocene may interact simultaneously with multiple transition-metal sites is presented. Further studies on the binding of multiple Lewis acid centers to ferrocene and other metallocenes are currently in progress.

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