Structural Diversity of Pentafluorophenylcopper Complexes. First Evidence of π-Coordination of Unsupported Arenes to Organocopper Aggregates

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The binding behavior of arenes toward pentafluorophenylcopper was investigated. Crystallization of pentafluorophenylcopper from a mixture of 1,2-dichloroethane and cyclohexane affords the homoleptic tetrameric complex $[Cu(C_6F_5)]_4$, whereas a π-complex, $[Cu(C_6F_5)]_4(\eta^2\text{-toluene})_2$, is obtained from toluene solution. The unique coordination of two toluene molecules in $[Cu(C_6F_5)]_4(\eta^2\text{-toluene})_2$ leads to major structural changes as the regular square planar tetramer is distorted toward a butterfly structure with one short and one long diagonal Cu···Cu distance of 2.5935(3) and 3.955(1) Å, respectively. The toluene molecules are bound in an unsymmetrical η^2-coordination mode with the shortest contacts observed between copper and the *meta* carbon atoms ($d(\text{Cu}-\text{C}) = 2.271(2), 2.298(2)$ Å) and slightly longer distances to the *para* positions ($d(\text{Cu}-\text{C}) = 2.339(2), 2.455(4)$ Å). Multinuclear NMR studies show that complexation to the intact tetrameric cluster species also occurs in neat solution of the aromatic species. Strongly coordinating solvents such as acetonitrile or DMSO, however, lead to aggregate breakdown.

Introduction

Studies on π-arene complexes of d10 transition metals have recently resulted in important new findings that, for example, suggest their use as catalysts for deuterium-exchange reactions[1] and show their potential as components of supramolecular assemblies and of luminescent materials.[2,3] Evidence of such species as intermediates in electrophilic aromatic substitution has also been presented.[4] However, although the structures of a number of organomercury complexes with arenes have been reported,[2,5] thus far no crystallographic evidence has been presented for similar interactions between organocopper compounds and unsupported arenes, i.e., of complexes in which chelation does not lead to stabilization of the copper−arene bonding.

We are currently studying arylcopper species as part of our efforts directed at the development of new multidentate and polymeric Lewis acids.[6,7] Of particular interest in this area is the development of convenient isolable reagents for transfer of aryl groups with strongly electron-withdrawing substituents. A potential candidate for these purposes is pentafluorophenylcopper, which can readily be synthesized through metathesis reaction of pentafluorophenyl organometallic reagents with cuprous halides.[8−10] Pentafluorophenylcopper is most conveniently prepared from the Grignard reagent and isolated as a dioxane complex, from which dioxane may subsequently be removed by careful heating to 130 °C.[10] The resulting material has been shown by cryoscopy and vapor pressure osmometry in benzene and by EI-mass spectrometry of a solid sample at 160−190 °C to consist primarily of tetrameric aggregates.[9] The reported formation of a dioxane complex is surprising as, for example, the related complexes mesitylcopper,[11] pentamethylphenylcopper,[12] and thienylcopper[13] co-

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crystallize with THF molecules that are not coordinated to the copper centers. Furthermore, 2-vinylphenylcopper does not show an interaction between the olefinic moiety and the copper centers.[14] The coordination behavior of pentafluorophenylcopper toward dioxane indicates that the electron-withdrawing nature of the pentafluorophenyl group may allow the isolation and structural characterization of unusual Lewis base adducts of organocopper species that otherwise would either not form or would be thermally unstable.

We report here on new aspects of the intriguing binding properties of pentafluorophenylcopper, including the first crystallographic and multinuclear NMR studies on the binding of unsupported arenes to organocopper species.

Results and Discussion

Preparation of $[Cu(C_6F_5)]_4$ (1) and Arene Complex $[Cu(C_6F_5)]_4(\eta^2\text{-toluene})_2$ (2). Pentafluorophenylcopper was prepared from the Grignard reagent and CuCl in diethyl ether according to the procedure described by Cairncross and Sheppard.[10] The carefully dried product was recrystallized from a mixture of 1,2-dichloroethane and cyclohexane (ca. 50:50) at 60 °C. Colorless crystals of **1** were obtained and found to contain half a molecule of 1,2-dichloroethane per $[(C_6F_5)Cu]_4$ unit according to ^1H NMR and elemental analysis. Repeated recrystallization of **1** from toluene at −37 °C yielded large colorless plates of the novel toluene complex **2**.[15] Both complexes are stable to ca. 160 °C.

Solid-State Structures of 1 and 2. An X-ray crystal structure determination of **1** revealed the formation of a homoleptic tetrameric complex similar to those described previously such as (2-dimethylaminomethylferrocenyl)copper,[16] (2,4,6-triisopropylphenyl)copper,[17] mesitylcopper,[11] pentamethylphenylcopper,[12] and thienylcopper[13] (Figure 1a). The copper atoms show a distorted square-planar arrangement with deviations for the individual atoms of only ca. ±0.01 Å from the Cu_4 plane and Cu−Cu−Cu angles ranging from 85.27(1)° to 94.78(1)°. The pentafluorophenyl substituents stand orthogonally to the Cu_4 plane but are dislocated from the Cu_4 plane as illustrated in Figure 1b. This leads to puckering of the Cu_4C_4 ring with a mean deviation of the individual atoms from an ideal plane of ca. 0.25 Å.

Although the toluene complex **2** also consists of a tetranuclear aggregate, all structural parameters are distinct from those of **1** and other homoleptic tetranuclear organocopper complexes that lack interactions with donor molecules (Figure 2). The most striking difference between **2** and **1** is that the four copper atoms in **2** do not lie in a plane but rather form an unusual butterfly structure[18] with an angle between the (Cu1Cu3Cu2) and the (Cu1Cu4Cu2) planes of 37.53°. Consequently, the eight-membered Cu_4C_4 ring in **2** is much more strongly puckered, with a mean deviation of the individual atoms from an ideal plane of ca. 0.66 Å. The four Cu⋯Cu distances between adjacent copper atoms in **2** range from 2.4404(4) to 2.4729(4) Å and are only slightly longer than those in **1** with 2.4286(3)−2.4534(3) Å. However, in contrast to the nearly regular square planar arrangement in **1** with long diagonal distances of 3.307 and 3.584 Å, the separation between opposite corners in **2** is much smaller for Cu1⋯Cu2 with 2.5935(3) Å than for Cu3⋯Cu4 with 3.955(1) Å. Although this is a typical feature of tetranuclear copper species with two copper atoms coordinated by donor ligands,[19,20] the Cu⋯Cu distances in **2** are the shortest observed thus far. All Cu−C distances in **1** are within a close range from 1.962(2) to 2.007(2) Å, as expected for a symmetrical bridging situation of the pentafluorophenyl groups. In contrast, the Cu−C distances vary

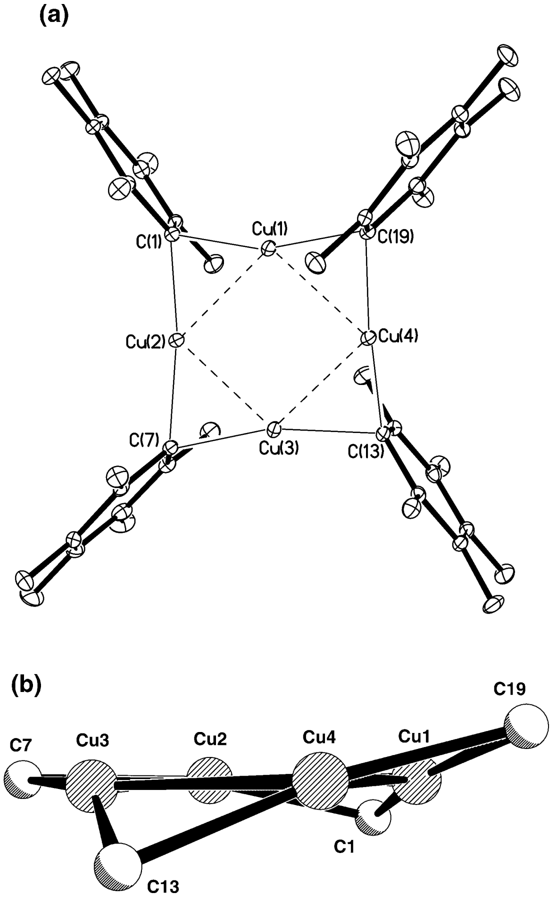

Figure 1. (a) The molecular structure of **1**; the cocrystallized molecule of 1,2-dichloroethane is omitted for clarity. (b) View of the puckered central Cu_4C_4 ring in **1**.

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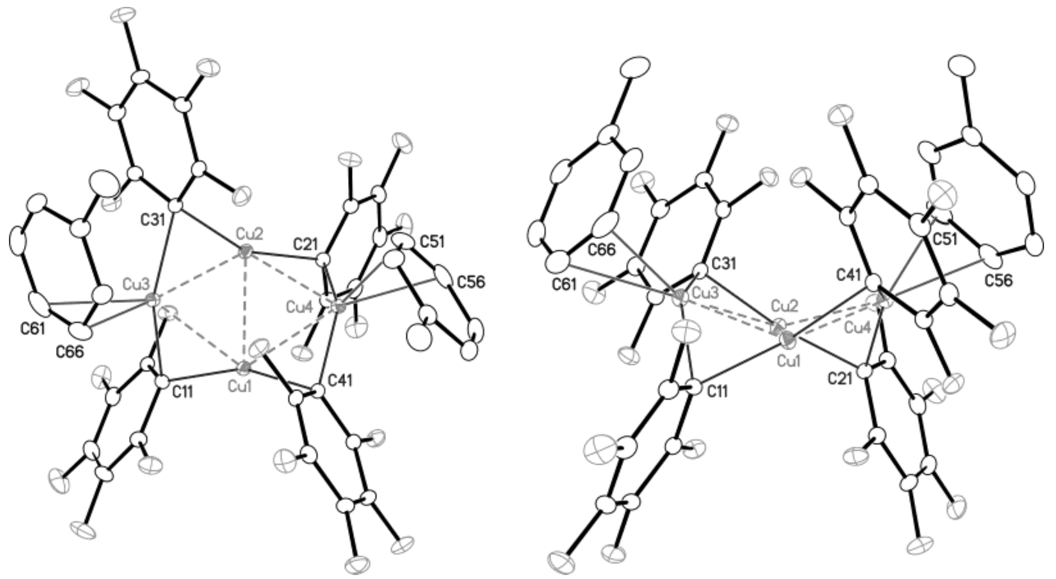

Figure 2. Two views of the molecular structure of **2**. Thermal ellipsoids are at the 20% level; hydrogen atoms are omitted for clarity.

Table 1. Selected Bond Lengths [Å], Interatomic Distances [Å], and Angles [deg] for 1 and 2

1	2
Cu(1)−Cu(2) 2.4413(3)	Cu(1)−Cu(3) 2.4672(4)
Cu(1)−Cu(4) 2.4286(3)	Cu(1)−Cu(4) 2.4404(4)
Cu(2)−Cu(3) 2.4301(3)	Cu(2)−Cu(3) 2.4522(4)
Cu(3)−Cu(4) 2.4534(3)	Cu(2)−Cu(4) 2.4729(4)
Cu(1)−C(1) 2.002(2)	Cu(1)−C(11) 1.957(2)
Cu(1)−C(19) 1.998(2)	Cu(1)−C(41) 2.006(2)
Cu(2)−C(1) 1.984(2)	Cu(2)−C(31) 2.001(2)
Cu(2)−C(7) 1.995(2)	Cu(2)−C(21) 1.978(2)
Cu(3)−C(7) 1.991(2)	Cu(3)−C(11) 2.145(2)
Cu(3)−C(13) 2.007(2)	Cu(3)−C(31) 2.070(2)
Cu(4)−C(13) 1.962(2)	Cu(4)−C(21) 2.119(2)
Cu(4)−C(19) 1.979(2)	Cu(4)−C(41) 2.034(2)
Cu(4)−Cu(1)−Cu(2) 94.78(1)	Cu(4)−Cu(1)−Cu(3) 107.38(1)
Cu(2)−Cu(3)−Cu(4) 94.43(1)	Cu(3)−Cu(2)−Cu(4) 106.83(1)
Cu(1)−Cu(4)−Cu(3) 85.27(1)	Cu(2)−Cu(3)−Cu(1) 63.63(1)
Cu(3)−Cu(2)−Cu(1) 85.51(1)	Cu(1)−Cu(4)−Cu(2) 63.72(1)
C(19)−Cu(1)−C(1) 164.09(8)	C(11)−Cu(1)−C(41) 153.47(9)
C(7)−Cu(3)−C(13) 157.34(8)	C(21)−Cu(2)−C(31) 155.94(9)
C(13)−Cu(4)−C(19) 170.52(8)	C(31)−Cu(3)−C(11) 140.79(8)
C(1)−Cu(2)−C(7) 165.02(8)	C(41)−Cu(4)−C(21) 140.99(8)
C(19−24)//Cu(1)Cu(2)Cu(3)Cu(4) 88.2	C(11−16)//Cu(1)Cu(2)Cu(3) 98.7
C(7−12)//Cu(1)Cu(2)Cu(3)Cu(4) 88.3	C(21−26)//Cu(1)Cu(2)Cu(4) 101.5
C(13−18)//Cu(1)Cu(2)Cu(3)Cu(4) 86.0	C(31−36)//Cu(1)Cu(2)Cu(3) 85.7
C(1−6)//Cu(1)Cu(2)Cu(3)Cu(4) 82.2	C(41−46)//Cu(1)Cu(2)Cu(4) 79.5
Cu(1)C(1)Cu(2)//Cu(1)Cu(2)Cu(3)Cu(4) −20.7	Cu(1)C(41)Cu(4)//Cu(1)Cu(2)Cu(4) 21.7
Cu(1)C(7)Cu(2)//Cu(1)Cu(2)Cu(3)Cu(4) 2.2	Cu(2)C(31)Cu(3)//Cu(1)Cu(2)Cu(3) 18.0
Cu(1)C(13)Cu(2)//Cu(1)Cu(2)Cu(3)Cu(4) −25.6	Cu(2)C(21)Cu(4)//Cu(1)Cu(2)Cu(4) −60.3
Cu(1)C(19)Cu(4)//Cu(1)Cu(2)Cu(3)Cu(4) 17.2	Cu(1)C(11)Cu(3)//Cu(1)Cu(2)Cu(3) −57.4

from 1.957(2) to 2.145(2) Å in **2**. Remarkably, the Cu−C distances involving Cu3 and Cu4 (average 2.092 Å) in **2** are significantly longer than those involving Cu1 and Cu2 (average 1.986 Å), indicating a highly unsymmetrical bridging mode of the aryl groups. A similar bond alternation is not observed for $[Cu_4Mes_4](THT)_2$ (THT = tetrahydrothiophene)[19] and is less pronounced in other sulfide complexes.[20]

Copper−Arene Interaction in the Solid-State Structure of 2. A number of examples of arene π-complexes of copper(I) salts such as $[Cu(benzene)]AlCl_4$,[21] $[Cu(benzene)_{0.5}]$triflate,[22] $[Cu(benzene)]_2ZrCl_6$,[23] and the paracyclophane complex $\{[Cu(p\text{-}C_6H_4CH_2CH_2CH_2)_2)]GaCl_4\}_n$[24] have been reported. Moreover, several cationic copper(I) complexes in which π-interaction between copper and an aromatic group is supported by chelation have been described.[25] However, π-coordination of unsupported arenes to organocopper species has not been previously observed.[26] Both toluene molecules

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in **2** are coordinated to the copper centers in an unsymmetrical η^2-coordination mode with short contacts of the *meta* carbon atoms C51 and C66 (Cu4−C51 = 2.298(2) Å; Cu3−C66 = 2.271(2) Å) and slightly longer contacts between the *para* carbon atoms C56 and C61 and the copper centers (Cu4−C56 = 2.339(2) Å; Cu3−C61 = 2.455(3) Å). These distances are only marginally longer than the Cu−C bonds to the pentafluorophenyl groups; they are comparable with those observed in inorganic Cu(I)X−benzene complexes ranging from 2.09 to 2.30 Å. The toluene molecules are bound in an unsymmetrical fashion with differences in the pairs of Cu−C distances of $\Delta = 0.04$ and 0.18 Å (for Cu(I)X complexes $\Delta = 0.03-0.15$ Å). It is interesting to note that all previously characterized copper−arene complexes show short contacts of copper to the *ipso* and *ortho* carbon atoms, whereas in **2** the *meta* position is closest to the copper centers.[27] This feature can most likely be attributed to effects related to the binding of toluene in the pocket formed by two adjacent pentafluorophenyl groups. Indeed, the observed arrangement of the toluene molecules parallel to the pentafluorophenyl groups at distances of ca. 3.3 Å is typical of strong arene−arene π-stacking interactions.[28] The distances for the copper-bound C−C bonds C51−C56 and C61−C66 of 1.373(5) and 1.380(5) Å are qualitatively slightly shorter than those for the adjacent C_m-C_p bond distances for C51−C52 and C61−C62 of 1.396(4) and 1.398(5) Å, respectively. A similar effect has been observed for the benzene ring in $[Cu(benzene)]_2ZrCl_6$[23] and was attributed to a dearomatization of the benzene ring as a result of metal-to-ligand charge transfer.[29] The close resemblance of the structural parameters of the toluene complex **2** and the previously described arene complexes of copper salts and the long copper−carbon bonds at Cu3 and Cu4 indicate a pronounced cationic character of the toluene-bound copper atoms. These observations support a description of **2** as a contact ion pair consisting of an assembly of two $[(C_6F_5)_2Cu]^-$ cuprate anions bridged by two toluene-stabilized copper cations via the *ipso* carbon atoms of the pentafluorophenyl rings, as previously suggested by van Koten and co-workers for other donor-supported tetrameric arylcopper species.[30]

Extended Solid-State Structure. It is interesting to point out that **1** forms an extended structure with channels along the crystallographic *b*-axis (Figure 3). These channels are filled with cocrystallized solvent molecules (1,2-dichloroethane), which do not show any significant interactions with the organocopper tetramers. A similar situation is met for **2**, in which the covalently bound toluene molecules are located in channels along the crystallographic *c*-axis (see Supporting Information). Consequently, when **2** was stirred in hexanes for 24 h and thoroughly washed with hexanes, toluene was quantitatively removed from the crystals according to ^{1}H NMR spectroscopy. The described procedure provides a convenient method for the generation of solvent-free **1**, which is a highly suitable base-free reagent for the transfer of the pentafluorophenyl group to other transition metals or main group elements.[7,31] The solvent-free complex **1** thus obtained was also used in the following studies on the coordination behavior of different π and σ donors toward pentafluorophenylcopper in solution.

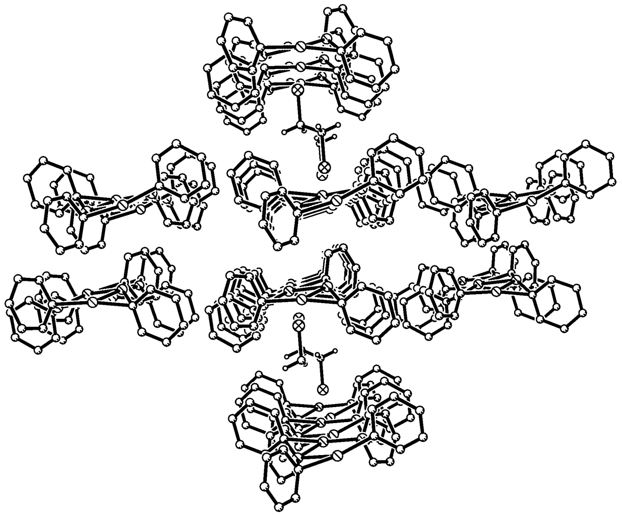

Figure 3. View of a fragment of the crystal packing of **1** along the crystallographic *b*-axis.

Structure of 1 in Solution. Cairncross and Sheppard determined the aggregation number of **1** in benzene to 3.75−3.85 by cryoscopy and to 3.95 by vapor pressure osmometry, suggesting that a tetrameric aggregate also is present in solution.[10] We have determined the ^{19}F and ^{13}C NMR spectra of **1** in toluene and a variety of other noncoordinating and potentially coordinating solvents in order to investigate a possible interaction between the aromatic solvent and the tetramer. We found that the separation between the ^{19}F NMR chemical shifts for the *para* and *meta* fluorine atoms, $\Delta\delta_{m,p}$, the chemical shifts of the copper-bound carbon atoms, $\delta(^{13}C_{ipso})$,[32] and the coupling constant $^2J(^{13}C_{ipso}, ^{19}F_o)$ to the *ortho* fluorine atoms are especially useful in assessing the coordination state of the copper centers (Table 2).

It is evident from Table 2 that the chemical shift difference, $\Delta\delta_{m,p}$, strongly depends on the choice of solvent. The largest $\Delta\delta_{m,p}$ of 16.6 ppm was observed in chloroform, which corresponds to the noncoordinated

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(26) π-Coordination has been encountered for arylcopper species in which chelation places the aryl group close to the Cu(I) center, thereby supporting the bonding interaction. This motif is present in the dimeric structure of (2,6-dimesitylphenyl)copper and the related trimer (2,6-diphenylphenyl)copper. Interestingly, the trimeric (2,6-diphenylphenyl)copper cocrystallizes with deuterated benzene, but the latter does not show any close contacts to the copper centers: Niemeyer, M. *Organometallics* **1998**, *17*, 4649.

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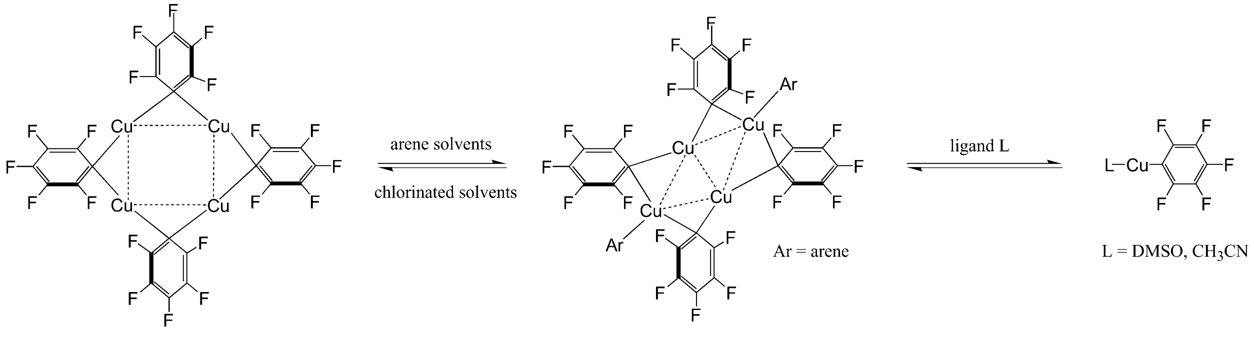
Scheme 1. Proposed Equilibrium between Oligonuclear and Mononuclear Arylcopper Complexes



1 **2** **3**

Table 2. ^{19}F and ^{13}C NMR Data of 1 in Coordinating and Noncoordinating Solvents (ca. 100 mg/mL)[a]

solvent	$\delta(F_o)$ (ppm)	$\delta(F_p)$ (ppm)	$\delta(F_m)$ (ppm)	$\Delta\delta_{m,p}$ (ppm)	$\delta(^{13}C_{ip})$ (ppm)	$^2J(^{13}C,^{19}F)$ (Hz)
$CDCl_3$	−104.1	−141.5	−158.1	16.6	98.7	52
$CDCl_3$[b]	−104.1	−141.5	−158.1	16.6	98.7	52
C_6D_6	−106.0	−146.2	−159.9	13.7	102.2	55
toluene-d_8[c]	−105.9	−147.0	−160.2	13.2	102.6	56
mesitylene	−105.4	−148.1	−160.2	12.1	d	d
DMSO-d_6	−109.9	−161.4	−162.6	1.2	126.7	77
acetonitrile-d_3	−113.4	−164.0	−165.3	1.3	129.3	78

[a] Data were acquired at room temperature unless otherwise noted. [b] Measurement of the toluene complex **2**. [c] The chemical shifts did not significantly vary within the temperature range from −35 to +60 °C. [d] ^{13}C NMR data in mesitylene were not acquired.

tetrameric species found in the solid-state structure of **1**. The chemical shift difference $\Delta\delta_{m,p}$ in the π-donor solvents benzene, toluene, and mesitylene ranges from 13.7 to 12.1 ppm and decreases as the aromatic species becomes more electron-rich, which is consistent with coordination of solvent molecules to **1**. A broadening of the ^{19}F NMR signals in aromatic solvents suggests a fast exchange between coordinated and noncoordinated arene molecules (Scheme 1). Such an exchange is likely further complicated by intra- and interaggregate exchange processes.[33] However, only one set of signals was observed in toluene within the temperature range from −35 to +60 °C, indicating that the observed dynamic process is very fast on the NMR time scale.[34] Coordination of arenes in solution is also evident from a distinct downfield shift of the copper-bound *ipso* carbon atom from $\delta = 98.7$ in $CDCl_3$ to $\delta = 102.2$ and 102.6 in benzene and toluene, respectively. Furthermore, a change in the coordination state of copper is reflected in an increase of the coupling constant $^2J(^{13}C_{ipso}, {}^{19}F)$ from 52 Hz in $CDCl_3$ to 55 Hz in benzene and 56 Hz in toluene solution. In contrast, dissolution of the toluene complex **2** in the noncoordinating solvent $CDCl_3$ gave rise to a large $\Delta\delta_{m,p}$ of 16.6 ppm, identical to that of toluene-free **1**. This indicates that the toluene molecules are readily released from the copper complex **2** in solution. Further evidence for this behavior was gathered from solution IR spectroscopy. The spectrum of **2** in CH_2Cl_2 shows bands corresponding to free toluene and the uncomplexed copper tetramer **1**.

Preliminary results in our laboratory suggest that whereas intact tetrameric complexes are the predominant species in aromatic solvents, smaller aggregates are readily formed in more strongly coordinating solvents. Dissolution of **1** in acetonitrile or dimethyl sulfoxide led to sharp ^{19}F NMR signals with a very small $\Delta\delta_{m,p}$ of 1.2−1.3 ppm (Table 2). The copper-bound *ipso* carbon atoms are strongly downfield shifted to $\delta = 126.7$ in DMSO and $\delta = 129.3$ in acetonitrile. This shift is accompanied by a large increase of the coupling constant $^2J(^{13}C_{ipso}, {}^{19}F)$ to 77−78 Hz. Small values for $\Delta\delta_{m,p}$ of 3.6 and 3.5 have been reported for the mononuclear complexes C_6F_5Au(3-Pic) (3-Pic = 3-methylpyridine)[35] and C_6F_5Au(3-FcPy) (3-FcPy = 3-ferrocenylpyridine),[36] and a downfield shift of the *ipso* carbon atoms was found by Bertz and Power to be characteristic of the formation of smaller aggregates of phenylcopper.[32] Aggregate breakdown and formation of mononuclear complexes C_6F_5CuL (**3**, L = DMSO, CH_3CN) as shown in Scheme 1 is therefore likely to account for the observation of small $\Delta\delta_{m,p}$ values and of large shifts for the *ipso* carbon atoms of **1** in coordinating solvents. However, contribution of an ion pair as in the structurally characterized cuprate complexes $[CuMes_2]^-[Cu(dppe)_2]^+$ (dppe = 1,2-bis(diphenylphosphino)ethane; Mes = 2,4,6-trimethylphenyl) and $[CuMe_2]^-[Cu(PMe_3)_4]^+$ formed through ligand redistribution in solution must also be taken into consideration.[37]

Summary and Conclusions

We found that **1** readily forms complexes with arenes that function as weakly coordinating π-donor molecules and do not cause breakdown of the tetranuclear structure. However, complexation of toluene molecules results in major structural changes within the tetrameric aggregate. Most notably, the four copper centers that are in a slightly distorted square planar arrangement in **1** form an unusual butterfly structure with a very short diagonal Cu1⋯Cu2 distance of 2.5935(3) Å in **2**. Indeed, a highly unsymmetrical bridging mode of the

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(33) For solution NMR studies of dynamic processes in organocopper aggregates, see: van Koten, G.; James, S. L.; Jastrzebski, J. T. B. H. In *Comprehensive Organometallic Chemistry*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon Press: Oxford, 1995; Vol. 3, Chapter 2. Also note that arene solvents have been found to catalyze the equilibration of $[CuMes]_5$ to a mixture of $[CuMes]_5$ and $[CuMes]_4$ upon dissolution; see ref 19b.

(34) Fast dynamic processes have also been observed for aryllithium species; see for example: Reich, H. J.; Green, D. P.; Medina, M. A.; Goldenberg, W. S.; Gudmundsson, B. O.; Dykstra, R. R.; Phillips, N. H. *J. Am. Chem. Soc.* **1998**, *120*, 7201.

(35) Jones, P. G.; Ahrens, B. *Z. Naturforsch. B* **1998**, *53*, 653.

(36) Barranco, E. M.; Crespo, O.; Gimeno, M. C.; Jones, P. G.; Laguna, A.; Villacampa, M. D. *J. Organomet. Chem.* **1999**, *592*, 258.

(37) (a) Leoni, P.; Pasquali, M.; Ghilardi, C. A. *J. Chem. Soc., Chem. Commun.* **1983**, 240. (b) Dempsey, D. F.; Girolami, G. S. *Organometallics* **1988**, *7*, 1208.

pentafluorophenyl groups supports a description of **2** as a contact ion pair consisting of an assembly of two $[(C_6F_5)_2Cu]^-$ cuprate anions bridged by two toluene-stabilized copper cations. Considering that toluene or even THF cocrystallize with mesitylcopper and other arylcopper species without complexation to the copper centers, we conclude that the electron-poor pentafluorophenyl group significantly enhances the Lewis acidity of the copper centers.

^{19}F and ^{13}C NMR spectroscopy serve as valuable tools for structural studies of arylcopper species in solution. A strongly reduced $\Delta\delta(^{19}F_{m,p})$, a downfield-shift of C_{ipso}, and an increase in the coupling constant ^2J ($^{13}C_{ipso}$, ^{19}F) to fluorine in aromatic solvents together with the observed broadening in the ^{19}F NMR spectrum of the toluene complex **2** at low temperature all suggest that a fast equilibrium between complexed and uncomplexed tetramers is established in solution. It is interesting to point out in this context that Gambarotta and coworkers have observed an accelerating effect of aromatic solvents on the equilibration of $[CuMes]_5$ to give a mixture of $[CuMes]_5$ and $[CuMes]_4$.[19] Our results suggest that coordination of the aromatic solvent molecules may indeed play an important role in stabilizing the intermediates in this process.

The equilibrium between the homoleptic complex **1** and the toluene solvate **2** is shifted strongly toward the side of **1** in noncoordinating solvents such as dichloromethane. In contrast, more strongly coordinating σ-donor ligands such as acetonitrile or DMSO lead to aggregate breakdown. We are currently investigating the nature of the resulting donor complexes in detail. We are also studying applications of the base-free complex **1** as a convenient and mild reagent for transfer of the C_6F_5 moiety to other metal and metalloid centers.

Experimental Section

Materials and General Methods. Pentafluorophenylcopper was prepared according to a literature procedure[10] and repeatedly recrystallized from toluene. All reactions and manipulations were carried out under an atmosphere of prepurified nitrogen using either Schlenk techniques or an inert-atmosphere glovebox (Innovative Technologies). Ether solvents were distilled from Na/benzophenone prior to use. Hydrocarbon and chlorinated solvents were purified using a solvent purification system (Innovative Technologies); chlorinated solvents were subsequently degassed via several freeze pump thaw cycles. All 500 MHz ^{1}H NMR spectra, 125.7 MHz ^{13}C NMR spectra, and 470.2 MHz ^{19}F NMR spectra were recorded on a Varian INOVA NMR spectrometer operating at 499.91 MHz. The 400 MHz ^{1}H NMR spectra, 100.5 MHz ^{13}C NMR spectra, and 376.2 MHz ^{19}F NMR spectra were recorded on a Varian VXR-S spectrometer. All solution ^{1}H and ^{13}C NMR spectra were referenced internally to the solvent signals. ^{19}F NMR spectra were referenced externally to α,α′,α″-trifluorotoluene (0.05% in C_6D_6; $\delta = -63.73$). The abbreviation Pf is used for pentafluorophenyl. Decomposition temperatures were determined in sealed capillary tubes and are not corrected. UV−visible absorption data were acquired on a Varian Cary 500 UV−vis/NIR spectrophotometer. Solutions (ca. 5×10^{-5} M) were prepared using a microbalance (±0.1 mg) and volumetric glassware and then charged into quartz cuvettes with sealing screw caps (Starna) inside the glovebox. Elemental analyses were performed by Schwarzkopf, Woodside, NY.

Table 3. IR Data of 1 and 2 (in CH_2Cl_2, Region from 1700 to 900 cm^{-1})

1	2	toluene
1630 w	1630 m	
	1603 w	1604 m
1505 s	1502 s	1496 s
1455 m	1461 m	1467 m
	1381 w	1381 w
1342 w	1341 m	
1075 m	1076 m	1082, 1031 w
965 m	967 w	

Table 4. Experimental Data for X-ray Diffraction Studies of 1 and 2

	1	2
empirical formula	$C_{25}H_2ClCu_4F_{20}$	$C_{38}H_{16}Cu_4F_{20}$
MW	971.88	1106.67
T, K	100(2)	173(2)
wavelength, Å	0.71073	0.71073
crystal system	triclinic	monoclinic
space group	P-1	$P2_1/c$
a, Å	10.3875(6)	15.2253(9)
b, Å	10.8479(6)	15.3381(9)
c, Å	12.1005(6)	15.8026(9)
α, deg	86.908(1)	90
β, deg	88.685(1)	91.716(1)
γ, deg	79.922(1)	90
V, Å^3	1340.6(1)	3688.7(4)
Z	2	4
ρ_{calc}, g cm^{-3}	2.408	1.993
μ(Mo Kα), mm^{-1}	3.389	2.407
F(000)	930	2160
crystal size, mm	0.33 × 0.29 × 0.15	0.40 × 0.30 × 0.30
limiting indices	$-13 \leq h \leq 13$ $-14 \leq k \leq 6$ $-15 \leq l \leq 15$	$-15 \leq h \leq 20$ $-18 \leq k \leq 20$ $-21 \leq l \leq 20$
θ range, deg	1.69−27.52	1.89−28.26
reflns collected	8428	23498
independent reflns	5871 [R(int) = 0.0173]	8720 [R(int) = 0.0212]
absorption corrctn	SADABS	SADABS
refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2
data/restraints/ parameters	5871/0/459	8720/0/559
goodness-of-fit on F^2	1.032	1.115
final R indices [$I > 2\sigma(I)$][a]	$R1 = 0.0240$ $wR2 = 0.0666$	$R1 = 0.0306$ $wR2 = 0.0831$
R indices (all data)[a]	$R1 = 0.0262$ $wR2 = 0.0676$	$R1 = 0.0372$ $wR2 = 0.0869$
peak/hole (e Å^{-3})	0.779 and −0.504	0.410 and −0.445

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

NMR spectroscopic data for **1** in coordinating and noncoordinating solvents: ^{13}C NMR (100.5 MHz, $CDCl_3$, 20 °C) δ 154.7 (dd, $^{1,2}J$ (F, C) = 244 Hz/22 Hz, Pf-C2,6), 145.7 (dm, ^1J (F, C) = 262 Hz, Pf-C4), 137.2 (dm, ^1J (F, C) = 260 Hz, Pf-C3,5), 98.7 (t, ^2J (F, C) = 52 Hz, Pf-C1); ^{13}C NMR (100.5 MHz, C_6D_6, 60 °C) δ 153.8 (dd, $^{1,2}J$ (F, C) = 236 Hz/24 Hz, Pf-C2,6), 144.2 (dm, ^1J (F, C) = 259 Hz, Pf-C4), 137.7 (dm, ^1J (F, C) = 259 Hz, Pf-C3,5), 102.2 (t, ^2J (F, C) = 55 Hz, Pf-C1); ^{13}C NMR (100.5 MHz, C_7D_8, 20 °C) δ 153.5 (dd, $^{1,2}J$ (F, C) = 230 Hz/27 Hz, Pf-C2,6), 143.9 (dm, ^1J (F, C) = 257 Hz, Pf-C4), 137.7 (dm, ^1J (F, C) = 258 Hz, Pf-C3,5), 102.6 (t, ^2J (F, C) = 56 Hz, Pf-C1); ^{13}C NMR (125.7 MHz, CD_3CN, 25 °C) δ 150.9 (dd, $^{1,2}J$ (F, C) = 218 Hz/32 Hz, Pf-C2,6), 139.4 (dm, ^1J (F, C) = 240 Hz, Pf-C4), 137.1 (dm, ^1J (F, C) = 250 Hz, Pf-C3,5), 129.3 (t, ^2J (F, C) = 78 Hz, Pf-C1); ^{13}C NMR (125.7 MHz, d_6-DMSO, 25 °C) δ 148.5 (dd, $^{1,2}J$ (F, C) = 218 Hz/30 Hz, Pf-C2,6), 136.9 (dm, ^1J (F, C) = 241 Hz, Pf-C4), 135.2 (dm, ^1J (F, C) = 252 Hz, Pf-C3,5), 126.7 (t, ^2J (F, C) = 77 Hz, Pf-C1). Elemental Analyses: for **1**·0.5 $ClCH_2CH_2Cl$ calcd C 30.89, H 0.21; found C 30.41, H 0.21; for **2** calcd C 41.24, H 1.46; found C 40.03, H 1.40. Compare to CuC_6F_5: calcd C31.25; H 0.00. UV−vis of complex **1** ($CHCl_3$): $\lambda_{max} = 275$ nm ($\epsilon = 42\,000$ L mol^{-1} cm^{-1}), 292 nm (sh, $\epsilon = 37\,000$ L mol^{-1} cm^{-1}). UV−vis of **2** ($CHCl_3$): $\lambda_{max} = 276$ nm ($\epsilon = 38\,000$ L mol^{-1} cm^{-1}), 292 nm (sh, $\epsilon = 32\,000$ L mol^{-1} cm^{-1}). UV/vis of **2** ($CHCl_3$): $\lambda_{max} = 285$ nm

($\epsilon = 28\ 000$ L mol^{-1} cm^{-1}), 325 nm (sh, $\epsilon = 5\ 600$ L mol^{-1} cm^{-1}). IR absorption bands of **1** and **2** are summarized in Table 3.

Crystal Structure Determinations. Data were collected on a Bruker Smart Apex CCD diffractometer. The structures were solved by direct methods and refined by full-matrix least squares (SHELXTL V5.1; G. Sheldrick, Siemens XRD, Madison, WI) based on F^2 with all reflections. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms in **1** were found on the F-map and refined isotropically; in **2** they were included in calculated positions. Atomic coordinates, bond lengths and angles, and thermal parameters for **1** and **2** have been deposited at the Cambridge Crystallographic Data Centre (CCDC) as supplementary publications no. 215021 and 215022, respectively. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033. email: deposit@ccdc.cam.ac.uk).

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Supporting Information Available: Crystallographic data for compounds **1** and **2** including tables of crystal data, atomic coordinates, bond lengths and angles, and anisotropic thermal parameters and a cell plot of **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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