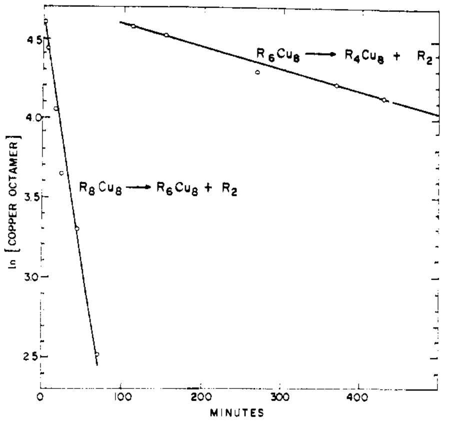

Figure 1. Plot of decomposition of 3.53×10^{-3} *M* *m*-trifluoromethylphenylcopper in benzene at 73.7°. The [copper octamer] plotted is the real concentration multiplied by 2.83×10^4 to equal 100 at time zero.

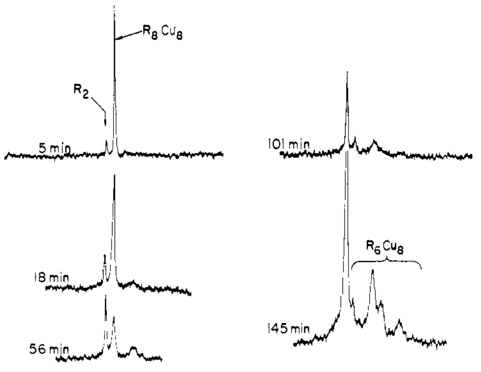

Figure 2. ^{19}F nmr of $[m\text{-}(CF_3)C_6H_4Cu]_8$ in dioxane at 70°.

Since at 73.7° in benzene $k_1/k_2 = 28$ ($k_1 = 55.0 \times 10^{-5}$ and $k_2 = 1.93 \times 10^{-5}$ sec^{-1}), it was possible to isolate the green R_6Cu_8 intermediate, **2**, by heating **1** for 2 hr, concentrating the solution to dryness, and triturating with hexane. **2** is more soluble than **1**, dissolving to the extent of 50 wt % in benzene. *Anal.* Calcd for $C_{42}H_{24}F_{18}Cu_8$: C, 36.58; H, 1.76; Cu, 36.86. Found: C, 36.08; H, 2.03; Cu, 37.34. **2** decomposes at 140–142° and has $\lambda_{\max}^{\text{benzene}}$ 620 nm (ϵ >1,400), which does not obey Beer's law, and a very broad ^{19}F nmr, indicating several environments for $-CF_3$ groups. The molecular weight of **2** was determined cryoscopically in benzene as 1757 under conditions where **1** was 276 higher. The difference between **1** and **2** closely corresponds to the loss of biaryl **3**, which has molecular weight 290. Both **1** and **2** hydrolyze quickly in 2 *N* HCl to benzotrifluoride and colorless aqueous solutions, and **2** additionally produces bright copper metal. Nmr studies show that **2** is diamagnetic.

The decomposition is nicely illustrated by ^{19}F nmr in dioxane (see Figure 2). After 101 min at 70° nearly all of **1** is gone, yet only a third of the fluorines are accounted for by **3**.

Further support for the above scheme is the failure to detect any free *m*-(trifluoromethyl)phenyl radicals during pyrolysis of **1**. Eventually **1** pyrolyzes to a near quantitative yield of biaryl **3** without giving any attack on benzene solvent to give 3-(trifluoromethyl)-biphenyl (0.1% could have been detected). *The m-(trifluoromethyl)phenyl groups are lost pairwise in a unimolecular reaction.* This may be a general mechanism in organocopper pyrolyses. For instance, Whitesides and Casey ruled out free radicals in the pyrolysis of vinylcoppers.[7]

The above data are consistent with an octamer cluster for **1**. Fackler, *et al.*, determined the crystal structure of $\{Cu_8[S_2CC(CN)_2]_6\}^{4-}$ phenyltrimethylammonium salt to have a central copper cube.[8] The equivalent $-CF_3$ groups in the room-temperature ^{19}F nmr of **1** could be explained if **1** similarly had a central copper cube with mobile-bridging benzotrifluoride groups. At −117° in ether, the nmr of **1** has two broad overlapping $-CF_3$ peaks which may result from solvent complexing or restricted benzotrifluoride motion. The green R_6Cu_8 species **2** could also have a central copper cube with benzotrifluoride groups on each face; however, its complex ^{19}F nmr would be hard to explain. These novel organocopper aggregates may be the first examples of a family of large copper clusters analogous to large gold clusters, including an Au_{11} cluster.[9]

Acknowledgments. The difficult molecular weight determinations were performed by Mrs. Flora C. Youngken. Synthetic preparations and physical organic studies were accomplished with the skillful assistance of Mr. Paul Davidson.

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Organocopper Cluster Compounds. II. Pentafluorophenylcopper and *o*-(Trifluoromethyl)phenylcopper Tetramers

Sir:

Until recently, organocoppers were thought to be polymeric because of their insolubility in organic solvents. Recently several group Ib cluster compounds have been described. These include, to mention a few, small copper clusters,[1] copper tetramer,[2,3] copper hexamer,[4] copper octamers,[3,5] silver tetramer,[6] and

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gold clusters up to Au_{11}.[7] One organocopper monomer has been reported.[8]

We wish to report the first examples of organocopper tetramers, pentafluorophenylcopper (**1**) and *o*-(trifluoromethyl)phenylcopper (**2**).

These were prepared from the corresponding aryl bromides *via* the Grignard in ether, metathesis with cuprous bromide, removal of magnesium bromide as its insoluble dioxane complex, isolation of the ether-soluble organocopper, and recrystallization from benzene.[9] These analyze well, have sharp infrared and ^{19}F nmr spectra that resemble those of other derivatives of pentafluorobenzene and *o*-benzotrifluorides, and like most organocoppers are easily oxidized by air and hydrolyze in water. All work was done in a nitrogen atmosphere.[10]

Compound **1**, which has been prepared by others in an impure state,[11] is a nearly white solid which melts and quickly decomposes at 210–220°, giving copper metal and decafluorobiphenyl. It is a mild Lewis acid, forming isolable complexes with σ bases such as dioxane, tri-*n*-butylamine, and benzonitrile, and π bases butyne-2 and 1,5-cyclooctadiene. **2** also is nearly white, decomposes at 200–205° giving 2,2′ bis(trifluoromethyl)biphenyl, and forms complexes less readily than **1**.

The aggregation of **1** in benzene was determined cryoscopically as 3.75–3.85, and by vapor pressure osmometry as 3.95. The mass spectrum of **1** was obtained by direct injection of a solid sample at 160–190° into a Consolidated Electrodynamics Corp. 21-110B high-resolution mass spectrometer at an ionizing voltage of 70 eV. The most abundant species other than decafluorobiphenyl is the parent ion for tetrameric **1**, *m/e* 920.[12] There were no fragments with more than four coppers. The relative abundances were *m/e* 920 (100), 753 (15), 690 (85), 523 (85), and 460 (40). Although significant quantities of trimer (*m/e* 690) and dimer (*m/e* 460) were detected, these much more volatile aggregates were less abundant[13] than tetramer. We consider that the mass spectrum is related to the composition of the solid, and that, taking into account volatility differences, the solid is almost all tetramer.[14]

The aggregation of **2** in benzene was found cryoscopically to be 3.82 and 4.28. The mass spectrum of **2** was obtained similarly at 130–190°. The relative abundance of *m/e* 832 (tetramer) was 100, 624 (trimer) and 416 (dimer) were both less than 1, and 208 (monomer) was less than 0.1. Surprisingly, a peak corresponding to $CF_3C_6H_4Cu_4F_2^+$ of *m/e* 435 was much more abundant (20) than monomer, dimer, and trimer. The tetramer **2** is very stable and much less contaminated by other oligomers than **1**. *Thus, the tetramers* **1** *and* **2** *are remarkably stable, not appreciably dissociating at 5° in benzene solution or at 190° under high vacuum in the mass spectrometer.*

We assume the tetramers have central copper tetrahedra as does $[CuS_2CN(C_2H_5)_2]_4$.[2d] Organolithiums likewise form tetramers[15] and $(CH_3Li)_4$ has a central Li_4 tetrahedron.[16] Organolithium clusters are quite thermally stable. The mass spectrum of ethyllithium has parent ions of $Et_5Li_6^+$ and $Et_3Li_4^+$ but no $Et_6Li_6^+$ or $Et_4Li_4^+$.[17] The aryl groups of **1** and **2** have ir and nmr spectra resembling those of normal covalently bound aryl groups even though they may be bridging copper atoms.

The ^{19}F nmr spectra of **1** and **2** vary with temperature. We feel that these changes may be due to changes in solvent complexes or rotamer populations.

Both **1** and **2** are much more thermally stable than the octameric meta isomer of **2** and undergo copper metal catalyzed decompositions without forming colored solutions. When **1** was decomposed in benzene with a copper catalyst, no $C_6F_5C_6H_5$ and thus no free C_6F_5 radicals were detected. On the other hand, the octamer decomposition is not copper catalyzed and forms a stable deep green R_6Cu_8 intermediate. The difference in stability of the organocopper clusters relative to size and structure is under study, and we are currently exploring cluster substitution reactions and ligand exchange upon mixing cluster compounds.

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(10) We have stored samples for 5 years in a Dry Ice chest with no change. Under these conditions organocoppers show no tendency to carboxylate.

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(12) Because of the ^{63}Cu, ^{65}Cu isotopes the pattern for the tetrameric species ranges from 920 to 928 in relative ratios expected from the isotopic abundances. Patterns corresponding to isotopic abundances are also found for other *m/e* positions.

(13) This crude approximation assuming equal ionization potentials for all aggregates undoubtedly is wrong. The conclusion that the less volatile tetramer is by far the most abundant species seems justified.

(14) Dimer and trimer might arise from dissociation of tetramer, but not the reverse. The spectrum does not change much with observation time. Interpretation is made difficult by continuous decomposition to decafluorobiphenyl. Some samples show peaks due to $(C_6F_5Cu)_4$-(C_6F_4). Occasionally the preparation of **1** goes awry, giving 3,4,5,6,-2′,3′,4′,5′,6′-nonafluorobiphenylcopper.

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Studies in Linear Dichroism. V.[1] Spectroscopic and Conformational Properties of the Benzyloxy Group

Sir:

Previously we have described a method[2,3] which enables correlation of the values of dichroic ratios (**d**$_0$) of compounds incorporated in stretched polyethylene films with the position of their chromophores relative to their longitudinal axis. This method is

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