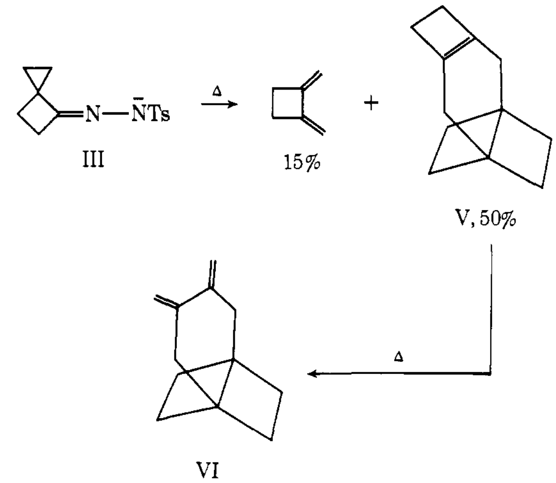
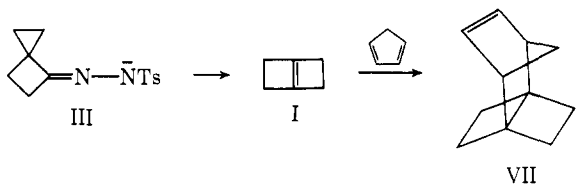


hydrocarbon, VII, was isolated. Its mass spectrum and elementary analysis corresponded to a 1:1 adduct between I and cyclopentadiene. The nmr spectrum indicated two olefinic protons (τ 3.8) coupled to two allylic protons (τ 7.4) and a complex multiplet of ten protons (τ 7.55–8.75). The ir spectrum had no C=C band suggesting a symmetrically substituted double bond.[12] These data strongly suggest that hydrocarbon VII is the Diels–Alder adduct of cyclopentadiene with bicyclo[2.2.0]hexene.



Finally, the product derived by heating III was distilled at low pressure and low temperature into an nmr tube containing deuteriomethylene chloride. The nmr spectrum at *ca.* −52°[13] showed the presence of 1,2-dimethylenecyclobutane (τ 4.86 (2 H), 5.30 (2 H), and 7.43 (4 H)) and a sharp singlet at τ 6.76. The latter, as well as the dimethylenecyclobutane peaks, slowly disappeared at −20° giving the spectrum of the dimer. The singlet must then correspond to $\Delta^{1,4}$-bicyclo[2.2.0]hexene (I). It is now easily prepared, and has at least moderate thermal stability.

[12] Dicyclopentadiene has two C=C bands at 1640 and 1620 cm^{-1} and therefore the two possible Diels–Alder adducts between cyclopentadiene and dimethylenecyclobutane should have an infrared band. The latter adducts also could not account for the observed nmr spectrum.

[13] CDHCl$_2$ (τ 4.70) was used as an internal standard. The chemical shifts of dimethylenecyclobutane appear to vary somewhat with temperature.

[14] National Institutes of Health Predoctoral Fellow (1968–1970).

[15] National Science Foundation Postdoctoral Fellow (1970–1971).

* Address correspondence to this author.

Kenneth B. Wiberg,* George J. Burgmaier,[14] Philip Warner[15]
Department of Chemistry, Yale University
New Haven, Connecticut 06520

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Organocopper Cluster Compounds. I. *m*-(Trifluoromethyl)phenylcopper Octamer and Its Pyrolysis Product, [*m*-(CF$_3$)C$_6$H$_4$]$_6$Cu$_8$

Sir:

Since the first organocopper was prepared by Reich[1] in 1923, very little structural work has been reported. Most workers have assumed polymeric structures (RCu)$_n$ based on the low solubility of many organocoppers. Camus and Marsich find arylcoppers to be low molecular weight[2] and Costa, *et al.*, find they form a bewildering array of complexes, some containing more than one copper by elemental analysis.[3] An X-ray study shows (C$_6$H$_5$)$_3$PCuC$_5$H$_5$ to be a monomer.[4]

We have found that fluorinated arylcoppers exist as discrete stable tetramers and octamers[5] and report here on the determination of the structure of *m*-(trifluoromethyl)phenylcopper as an octamer **1** and its novel pyrolysis to [*m*-(CF$_3$)C$_6$H$_4$]$_6$Cu$_8$, **2**, a stable Cu(0)–Cu(I) cluster compound.

Compound **1** was prepared by the metathetical reaction of *m*-(trifluoromethyl)phenylmagnesium bromide or iodide and cuprous bromide or iodide. The brown solid analyzes for C$_7$H$_4$F$_3$Cu, melts and decomposes at 158°, and has an ir spectrum typical of meta-substituted benzotrifluorides and uv $\lambda_{\max}^{\text{benzene}}$ 565 nm (ϵ 146), which does not obey Beer's law. It is soluble in ethereal solvents and less soluble in benzene. Its ^{19}F nmr spectrum at room temperature in ether is a sharp singlet. Like most organocoppers it oxidizes in air and hydrolyzes with water.

We first became suspicious of its structure while studying its thermal decomposition. When **1** is heated in benzene, it quickly forms a deep green solution and up to 50% yield of 3,3′-bis(trifluoromethyl)biphenyl (**3**) *before copper metal appears.* The formation and stability of the green color and the rate of formation of biaryl **3** are not altered by added copper powder, ruling out colloidal copper as the green species. Instead, we believe the green color is due to the formation of the stable Cu(0)–Cu(I) cluster compound **2**.

The aggregation of **1** was determined cryoscopically in benzene under a nitrogen atmosphere to be 7.7–10.7 and by vapor pressure osmometry as 9.0–10.6.[6] No copper-containing fragments were detected by mass spectrometry at 100–200° under conditions where (C$_6$F$_5$Cu)$_4$ was easily detected.[5c] This probably rules out the presence of monomer, dimer, and trimer.

Studies of the thermal decomposition of **1** by cryoscopic molecular weight in benzene, assay both for biaryl **3** and hydrolyzable benzotrifluoride groups, and direct nmr observation in dioxane show that decomposition slows drastically when 25% biaryl **3** has formed (*i.e.*, **2** is more stable than **1**), the decomposition is unimolecular, and the average size of the copper aggregate stays about the same during the pyrolysis. The kinetic data were plotted for several large aggregates but only fit the following scheme (see Figure 1).

$$\underset{\mathbf{1}}{\mathrm{R_8Cu_8}} \xrightarrow{k_1} \underset{\mathbf{3}}{\mathrm{R_2}} + \underset{\mathbf{2}}{\mathrm{R_6Cu_8}} \xrightarrow{k_2} \mathrm{R_2} + \mathrm{R_4Cu_8}$$

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[1] R. Reich, *C. R. Acad. Sci.*, 177, 322 (1923).

[2] A. Camus and N. Marsich, *J. Organometal. Chem.*, **14**, 441 (1968).

[3] G. Costa, A. Camus, N. Marsich, and L. Gatti, *ibid.*, **8**, 339 (1967).

[4] F. A. Cotton and J. Takats, *J. Amer. Chem. Soc.*, **92**, 2353 (1970).

[5] (a) A. Cairncross and W. A. Sheppard, *ibid.*, **90**, 2186 (1968); (b) for preliminary accounts of this, see A. Cairncross and W. A. Sheppard, Abstracts, 157th National Meeting of the American Chemical Society, Minneapolis, Minn., April 1969, No. ORGN 118; Abstracts, 4th International Conference on Organometallic Chemistry, Bristol, England, July 1969, No. E1; (c) A. Cairncross, H. Omura, and W. A. Sheppard, *J. Amer. Chem. Soc.*, **93**, 248 (1971).

[6] The molecular weights were hard to determine because **1** reacts with traces of oxygen and water. Unfortunately, **1** is not very soluble in benzene. These problems caused us to erroneously report **1** as a trimer.[5a]

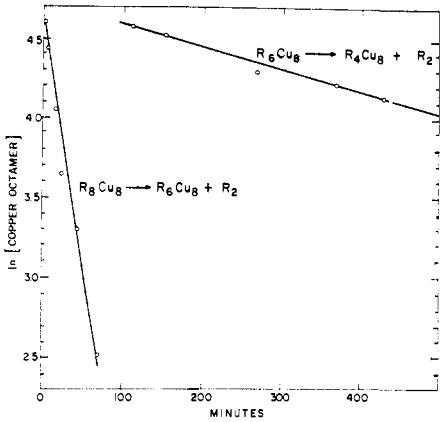

Figure 1. Plot of decomposition of 3.53×10^{-3} *M* *m*-trifluoromethylphenylcopper in benzene at 73.7°. The [copper octamer] plotted is the real concentration multiplied by 2.83×10^4 to equal 100 at time zero.

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 $\lambda_{max}^{benzene}$ 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

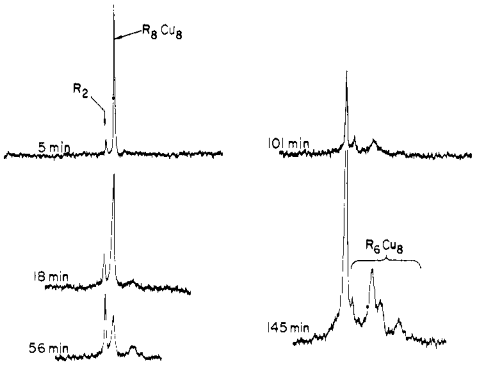

Figure 2. ^{19}F nmr of $[m-(CF_3)C_6H_4Cu]_8$ in dioxane at 70°.

−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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[7] G. M. Whitesides and C. P. Casey, *J. Amer. Chem. Soc.*, **88**, 4541 (1966).

[8] L. E. McCandlish, E. C. Bissell, D. Coucouvanis, J. P. Fackler, and K. Knox, *ibid.*, **90**, 7357 (1968).

[9] M. McPartlin, R. Mason, and L. Malatesta, *Chem. Commun.*, 334 (1969).

Allan Cairncross,* William A. Sheppard
Contribution No. 1739, Central Research Department
Experimental Station, E. I. du Pont de Nemours and Company
Wilmington, Delaware 19898

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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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[1] (a) A. Camus and N. Marsich, *J. Organometal. Chem.*, **14**, 441 (1968); (b) G. Costa, A. Camus, N. Marsich, and L. Gatti, *ibid.*, **8**, 339 (1967).

[2] (a) A. F. Wells, *Z. Kristallogr., Kristallgeometrie, Kristallchem., Kristallphys.*; **94**, 447 (1936); (b) F. A. Cotton, *Quart. Rev., Chem. Soc.*, **20**, 389 (1966); (c) J. Lewis, *Pure Appl. Chem.*, **10**, 11 (1965); (d) R. Hesse, *Ark. Kemi*, **20**, 481 (1963).

[3] This work was preliminarily reported by A. Cairncross and W. A. Sheppard, Abstracts, 157th National Meeting of the American Chemical Society, Minneapolis, Minn., April 1969, No. ORGN 118; Abstracts, 4th International Conference on Organometallic Chemistry, Bristol, England, July 1969, No. E1; 5th International Symposium on Fluorine Chemistry, Moscow, USSR, July 1969.

[4] R. Hesse and U. Aava, *Acta Chem. Scand.*, **24**, 1355 (1970).

[5] (a) A. Cairncross and W. A. Sheppard, *J. Amer. Chem. Soc.*, **93**, 247 (1971); (b) L. E. McCandlish, E. C. Bissell, D. Coucouvanis, J. P. Fackler, and K. Knox, *ibid.*, **90**, 7357 (1968).

[6] W. T. Miller, Jr., *et al.*, 5th International Symposium on Fluorine Chemistry, Moscow, USSR, July 1969.