plexes with 2,2'-bipyrimidine, the unbridged germacarborane complexes produced in the present investigation could be complexed further with either stanna- or plumbacarboranes by utilizing the uncoordinated N-donor atoms of the Ge-bound 2,2'-bipyrimidine to produce novel, bridged heterobimetallacarborane complexes. Such an endeavor is currently underway in our laboratories.

Supplementary Material Available: Listings of IR absorptions (Table S-1) of I–VI and of anisotropic displacement coefficients (Table S-2), bond angles and torsion angles (Table S-3), and H atom coordinates and isotropic displacement coefficients of I, IVA, and IVB (Table S-4) (15 pages); listings of structure factors of I, IVA, and IVB (Table S-5) (34 pages). Ordering information is given on any current masthead page.

Synthesis and Characterization of Copper(I) Trifluoroacetate Alkyne Complexes of the Type $Cu_4(\mu\text{-}O_2CCF_3)_4(\mu\text{-alkyne})_2$ and $Cu_2(\mu\text{-}O_2CCF_3)_2(\text{alkyne})_2$

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The complex $Cu_4(\mu\text{-}O_2CCF_3)_4(\mu\text{-EtC}{\equiv}\text{CEt})_2$ (**1**) is prepared from 3-hexyne and $Cu_4(\mu\text{-}O_2CCF_3)_4(C_6H_6)_2$ followed by recrystallization from hexane. Recrystallization from hexane containing added 3-hexyne yields $Cu_2(\mu\text{-}O_2CCF_3)_2(\text{EtC}{\equiv}\text{CEt})_2$ (**2**). Molecular weight studies show these stoichiometries are retained in solution. Low-temperature NMR spectra show that complex **2** is in equilibrium with **1** and free 3-hexyne, whereas **2** is not observed in solutions of **1**. The tetranuclear complexes $Cu_4(\mu\text{-}O_2CCF_3)_4(\mu\text{-RC}{\equiv}\text{CCO}_2\text{Me})_2$ (R = CO_2Me (**3**), Me (**4**)), analogous to **1**, form in reactions of $Cu_4(\mu\text{-}O_2CCF_3)_4(C_6H_6)_2$ and $MeO_2CC{\equiv}CCO_2Me$ or $MeC{\equiv}CCO_2Me$, respectively. In contrast, only the dinuclear complex $Cu_2(\mu\text{-}O_2CCF_3)_2(\text{PhC}{\equiv}\text{CPh})_2$ (**5**), analogous to **2**, forms in the reaction with diphenylacetylene. Competition studies indicate that the affinity of these alkynes for copper(I) in this system is similar for 3-hexyne, $MeO_2CC{\equiv}CCO_2Me$, and $MeC{\equiv}CCO_2Me$, but diphenylacetylene has a lower affinity.

Introduction

Continuing our interest in η^2-alkyne complexes of the transition metals,[1] we have initiated an investigation of alkyne complexes of copper(I). We began our investigations with the synthesis of alkyne complexes of copper(I) trifluoroacetate because similar $[Cu(\mu\text{-}O_2CCF_3)(\text{alkene})]_n$ complexes had been prepared previously and are quite stable.[2] Prior to our work, the only copper(I) acetate alkyne complex that had been definitively characterized was the dinuclear complex $Cu_2(\mu\text{-}O_2CPh)_2(\text{PhC}{\equiv}\text{CPh})_2$.[3]

In our first report in this area, we communicated the synthesis and solid-state structure of the unusual tetranuclear complex $Cu_4(\mu\text{-}O_2CCF_3)_4(\mu\text{-EtC}{\equiv}\text{CEt})_2$ (**1**). Complex **1** contains two alkyne ligands bridging copper atoms not directly bridged by other ligands.[4] A very recent publication has reported additional examples of the analogous tetranuclear, 2-substituted copper(I) benzoate complexes $Cu_4(\mu\text{-}O_2CC_6H_4\text{-}2\text{-X})_4(\mu\text{-RO}_2CC{\equiv}CCO_2R)_2$ (X = H, Cl, Br; R = Me, Et).[5] We report here the synthesis of a series of alkyne complexes of copper(I) trifluoroacetate. With 3-hexyne, careful control of the purification procedures can lead to the synthesis of the dinuclear complex $Cu_2(\mu\text{-}O_2CCF_3)_2(\text{EtC}{\equiv}\text{CEt})_2$ (**2**). In addition, we show that the copper to alkyne stoichiometry (either 4:2 or 2:2) can also be controlled by the choice of alkyne.

Experimental Section

General Procedure. All operations were carried out under a nitrogen atmosphere with use of either standard Schlenk techniques or a Vacuum Atmospheres HE-493 drybox. All solvents were dried, degassed, and distilled prior to use. Infrared spectra were recorded on a Perkin-Elmer 781 spectrophotometer. The ^1H and ^{13}C NMR spectra were recorded on Bruker AM-300 and AM-500 spectrometers using a 5-mm broad-band probe. Proton and carbon chemical shifts are reported in ppm downfield from TMS with use of the solvents CD_3COCD_3 ($\delta(H) = 2.04$ ppm, $\delta(C) = 29.8, 206.0$ ppm), C_6D_6 ($\delta(H) = 7.15$ ppm, $\delta(C) = 128$ ppm), and $C_6D_5CD_3$ ($\delta(H) = 2.09$ ppm, $\delta(C) = 20.4$ ppm) as internal standards. All spectra were recorded at room temperature unless otherwise indicated. Elemental analyses were performed by Robertson Laboratories, Inc. Mass spectra were run on a Finnigan 4521 GC–mass spectrometer. The clusters assigned to specific ions show the appropriate patterns as calculated for the atoms present. $Cu_4(\mu\text{-}O_2CCF_3)_4(C_6H_6)_2$[2a] was prepared by published methods. Molecular weights were determined by freezing point depression measurements in an apparatus similar in basic design to that described by Shriver.[6] The cell contains a Fenwal GB41P2 10-kΩ thermistor, balanced against a Leeds & Northrup bridge circuit. A working calibration curve of molality versus ΔT was obtained by using known concentrations of doubly sublimed ferrocene. Data acquisition and processing were automated by interfacing the apparatus to a WYSE 286 computer. Typically, the mass of a sample was determined on a benchtop analytical

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(2) (a) Rodesiler, P. F.; Amma, E. L. *J. Chem. Soc., Chem. Commun.* 1974, 599. (b) Reger, D. L.; Dukes, M. D. *J. Organomet. Chem.* 1976, *113*, 173.

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(5) Aalten, H. L.; van Koten, G.; Riethorst, E.; Stam, C. H. *Inorg. Chem.* 1989, *28*, 4140.

(6) Shriver, D. F.; Drezdzon, M. A. *The Manipulation of Air-Sensitive Compounds*, 2nd ed.; Wiley: New York, 1986; p 38.

balance and the sample then quickly transported into the drybox. The solute and the solvent were then introduced to the cryoscopy cell under the nitrogen atmosphere. For each sample, the measurement was carried out in duplicate and the results averaged.

Bis(μ-3-hexyne)tetrakis[(μ-trifluoroacetato)copper(I)], $Cu_4(\mu\text{-}O_2CCF_3)_4(\mu\text{-}EtC\equiv CEt)_2$ **(1).** $Cu_4(\mu\text{-}O_2CCF_3)_4(C_6H_6)_2$ (1.02 g, 1.18 mmol) was dissolved in C_6H_6 (50 mL). 3-Hexyne (0.27 mL, 0.19 g, 2.4 mmol) was added via syringe. The light green solution was stirred for 3 h. This solution was reduced to dryness by evaporation of solvent in vacuo. After drying in vacuo, the green powder was dissolved in hexane (10 mL, 60 °C). Cooling this solution to 4 °C yields colorless clear crystals (0.69 g, 67%), mp 138–140 °C. ^1H NMR spectrum (C_6D_6, δ): 1.88 (4, q, J = 7 Hz, CH_2); 0.64 (6, t, J = 7 Hz, Me). ^1H NMR spectrum (CD_3COCD_3, δ): 2.62 (4, q, CH_2); 1.28 (6, t, Me). ^1H NMR spectrum (–77 °C, $C_6D_5CD_3$, δ): 1.70 (4, q, CH_2); 0.55 (6, t, Me). ^1H NMR spectrum (–76 °C, CD_3COCD_3, δ): 2.58 (4, br, CH_2); 1.22 (6, br, Me). ^{13}C NMR spectrum (C_6D_6, δ): 89.2 ($C\equiv$); 13.8 (CH_2); 13.4 (Me). ^{13}C NMR spectrum (–77 °C, $C_6D_5CD_3$, δ): 164.8 (q, J_{C-F} = 39 Hz, CO); 117.1 (q, J_{C-F} = 287 Hz, CF_3); 88.8 ($C\equiv$); 20.7 (CH_2); 14.2 (Me). IR (Nujol mull, cm^{-1}): 1678 (ν(CO)); 1130–1220 (ν(CF_3)). Mass spectrum (m/e): 434 ([$Cu(O_2CCF_3)$]$_2$(3-hexyne)); 352 ([$Cu(O_2CCF_3)$]$_2$); 239 ($Cu_2(O_2CCF_3)$); 82 (3-hexyne). Anal. Calcd for $Cu_4C_{20}H_{20}O_8F_{12}$: C, 27.59; H, 2.30. Found: C, 28.15; H, 2.30. Cryoscopic molecular weight (benzene solution, formula weight 870 (observed molality, observed molecular weight)): 0.0376, 943; 0.0646, 952; 0.0889, 957.

Bis(3-hexyne)bis[(μ-trifluoroacetato)copper(I)], $Cu_2(\mu\text{-}O_2CCF_3)_2(EtC\equiv CEt)_2$ (2). $Cu_4(\mu\text{-}O_2CCF_3)_4(C_6H_6)_2$ (1.00 g, 1.16 mmol) was dissolved in benzene (25 mL). 3-Hexyne (0.53 mL, 0.38 g, 4.6 mmol) was added to the stirred solution via syringe. After the mixture was stirred for ca. 2 h, it was reduced to dryness by evaporation of solvent in vacuo. After it was dried in vacuo for 1 h, the residue was dissolved in a mixture of hexane (4 mL) and 3-hexyne (1 mL) at 60 °C. Cooling this solution to 4 °C yields white crystals (0.87 g, 73%), mp 94–98 °C. ^1H NMR spectrum (C_6D_6, δ): 1.97 (2, q, J = 7.5 Hz, CH_2); 0.84 (3, t, J = 7.5 Hz, Me). ^1H NMR spectrum (CD_3COCD_3, δ): 2.44 (4, q, CH_2); 1.20 (6, t, Me). ^1H NMR spectrum (–77 °C, $C_6D_5CD_3$, δ): 1.90 (4, q, CH_2); 1.70 (0.2, q, CH_2 from 1); 0.83 (6, t, Me); 0.56 (0.3, t, Me from 1). ^{13}C NMR spectrum (C_6D_6, δ): 88.3 ($C\equiv$); 15.8 (CH_2); 13.9 (Me). ^{13}C NMR spectrum (–77 °C, $C_6D_5CD_3$, δ): 164.3 (q, J = 38 Hz, CO); 117.5 (q, J = 287 Hz, CF_3); 88.8 ($C\equiv$ from 1); 88.2 ($C\equiv$); 15.9 (CH_2); 14.3 (Me); 14.2 (Me from 1). IR (Nujol mull, cm^{-1}): 2070 (w, $C\equiv C$); 1670 (s, br, $C=O$); 845 (m, O_2CCF_3). Mass spectrum (m/e): 239 ($Cu_2O_2CCF_3$); 352 ([$Cu(O_2CCF_3)$]$_2$). Anal. Calcd for $Cu_2C_{16}H_{20}O_4F_6$: C, 37.17; H, 3.90. Found: C, 37.05; H, 3.68. Cryoscopic molecular weight(benzene solution, formula weight 517 (observed molality, observed molecular weight)): 0.0331, 476; 0.0782, 486.

Bis(μ-dimethyl acetylenedicarboxylate)tetrakis[(μ-trifluoroacetato)copper(I)], $Cu_4(\mu\text{-}O_2CCF_3)_4(\mu\text{-}MeO_2CC\equiv CCO_2Me)_2$ (3). $Cu_4(\mu\text{-}O_2CCF_3)_4(C_6H_6)_2$ (1.00 g, 1.16 mmol) was dissolved in benzene (15 mL). Dimethyl acetylenedicarboxylate (0.29 mL, 0.33 g, 2.3 mmol) was added slowly via syringe. The color of the solution changed to a reddish orange. This mixture was stirred for 2 h. The mixture was filtered to collect the light pink powder. The product was washed with hexane (3 × 5 mL) and dried overnight in vacuo (1.06 g, 92%); mp 134–136 °C. ^1H NMR spectrum (C_6D_6, δ): 3.08 (s). IR (Nujol mull, cm^{-1}): 1730 (s, C=O from alkyne); 1670 (s, C=O from acetate); 850 (m, O_2CCF_3). Mass spectrum (m/e): 352 ([$Cu(O_2CCF_3)$]$_2$); 239 ($Cu_2(O_2CCF_3)$); 142 ($MeO_2CC\equiv CCO_2Me$). Anal. Calcd for $Cu_4C_{20}H_{12}O_{16}F_{12}$: C, 24.30; H, 1.22. Found: C, 24.45; H, 1.32.

Bis(μ-methyl 2-butynoate)tetrakis[(μ-trifluoroacetato)copper(I)], $Cu_4(\mu\text{-}O_2CCF_3)_4(\mu\text{-}MeC\equiv CCO_2Me)_2$ (4). $Cu_4(\mu\text{-}O_2CCF_3)_4(C_6H_6)_2$ (1.00 g, 1.16 mmol) was dissolved in benzene (15 mL). Methyl 2-butynoate (0.23 mL, 0.23 g, 2.3 mmol) was added via syringe to the stirred solution. The mixture was allowed to stir for 1 h. The light pink powder was isolated via filtration, washed with hexane (3 × 5 mL), and dried overnight in vacuo (0.61 g, 58%); mp 167–170 °C. ^1H NMR spectrum (C_6D_6, δ): 3.24 (3, s, OMe); 1.11 (3, s, Me). ^{13}C NMR spectrum (CD_3COCD_3, δ): 53.5 (OMe); 94.2 ($\equiv CCO_2Me$); 154.7 (C=O). ^{13}C NMR spectrum (–93 °C, toluene and toluene-d_8 mix, δ): 164.9 (m, O=CCF_3); 117 (m, CF_3); 152.7 (C=O); 94.7 ($\equiv CCO_2Me$); 72.5 ($\equiv CMe$); 54.1

(OMe); 10.5 (Me). IR (Nujol mull, cm^{-1}): 2038 (m, $C\equiv C$); 1700 (br, s, overlapping C=O's): 850 (m, O_2CCF_3). Mass spectrum (m/e): 352 ([$Cu(O_2CCF_3)$]$_2$); 239 ($Cu_2O_2CCF_3$); 98 ($MeC\equiv CCO_2Me$). Anal. Calcd for $Cu_4C_{18}H_{12}O_{12}F_{12}$: C, 23.97; H, 1.34. Found: C, 23.93; H, 1.36. Cryoscopic molecular weight (benzene solution, formula weight 902 (observed molality, observed molecular weight)): 0.0223, 734; 0.0207, 926.

Bis(diphenylacetylene)bis[(μ-trifluoroacetato)copper(I)], $Cu_2(\mu\text{-}O_2CCF_3)_2(PhC\equiv CPh)_2$ (5). $Cu_4(\mu\text{-}O_2CCF_3)_4(C_6H_6)_2$ (0.50 g, 0.58 mmol) was dissolved in benzene (25 mL), and diphenylacetylene (1.24 g, 6.97 mmol) in benzene (15 mL) was added to this stirred solution. After 1 h, the solution was reduced to ca. 20 mL. Hexane (45 mL) was added to precipitate the pure white powder. The product was washed with hexane (3 × 10 mL) and dried in vacuo (0.55 g, 67%); mp 156–160 °C. ^1H NMR spectrum (C_6D_6, δ): 7.20–6.80 (m, phenyl region). ^{13}C NMR spectrum (C_6D_6, δ): 131.4, 129.1, 128.6, 122.8 (phenyl region); 91 ($C\equiv$). ^{13}C NMR spectrum (–93 °C, toluene and toluene-d_8 mix, δ): 164.5 (q, CO_2, J_{C-F} = 38 Hz); 117.5 (q, CF_3, J_{C-F} = 287 Hz); 95.7 ($C\equiv$); phenyl region obscured by toluene. IR (Nujol mull, cm^{-1}): 1680 (s, C=O); 840 (m, O_2CCF_3). Anal. Calcd for $Cu_2C_{32}H_{20}O_4F_6$: C, 54.17; H, 2.84. Found: C, 53.91; H, 2.83. Cryoscopic molecular weight (benzene solution, formula weight 709 (observed molality, observed molecular weight)): 0.0183, 751.

Results

Two (trifluoroacetato)copper(I) complexes of 3-hexyne, $Cu_4(\mu\text{-}O_2CCF_3)_4(\mu\text{-}EtC\equiv CEt)_2$ (1) and [$Cu(\mu\text{-}O_2CCF_3)$–($EtC\equiv CEt$)]$_2$ (2), can be isolated, depending on the reaction conditions and isolation procedures. The alkyne-deficient complex 1 forms in reactions of $Cu_4(\mu\text{-}O_2CCF_3)_4(C_6H_6)_2$ and excess 3-hexyne, but the product is generally contaminated with 2. Crystallization from hexane yields pure 1. 1 is best prepared directly from a reaction of $Cu_4(\mu\text{-}O_2CCF_3)_4(C_6H_6)_2$ and 3-hexyne in which the copper:alkyne ratio is 4:2 followed by crystallization from hexane. Complex 2 is formed in a reaction of Cu_4-($\mu\text{-}O_2CCF_3$)$_4(C_6H_6)_2$ and 3-hexyne in which the copper:alkyne ratio is at least 2:2 followed by crystallization from hexane *containing an excess of 3-hexyne*.

As communicated earlier,[4] the tetranuclear nature of 1 in the solid state has been determined by X-ray crystallography. The structure contains two $Cu_2(\mu\text{-}EtC\equiv CEt)$ units held together by four bridging trifluoroacetate ligands. Each $Cu_2(\mu\text{-}3\text{-hexyne})$ unit has a typical butterfly arrangement of the two copper atoms and the bridging acetylenic carbon atoms.[7] The two $Cu_2(\mu\text{-}3\text{-hexyne})$ units within each molecule are oriented perpendicular with respect to each other.

1
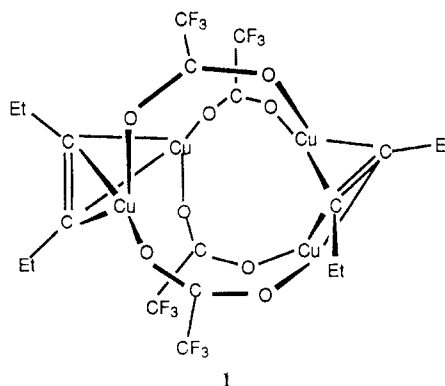
We have now determined from molecular weight studies that 1 is also tetranuclear in benzene solution. In addition, ^1H NMR studies indicate that a single form of the complex

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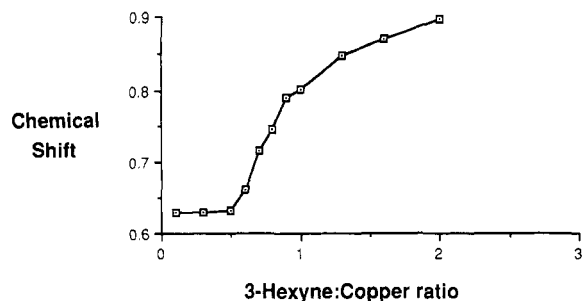
Figure 1. Plot of the chemical shift in benzene-d_6 for the methyl resonance of 3-hexyne as a function of the 3-hexyne:copper ratio.
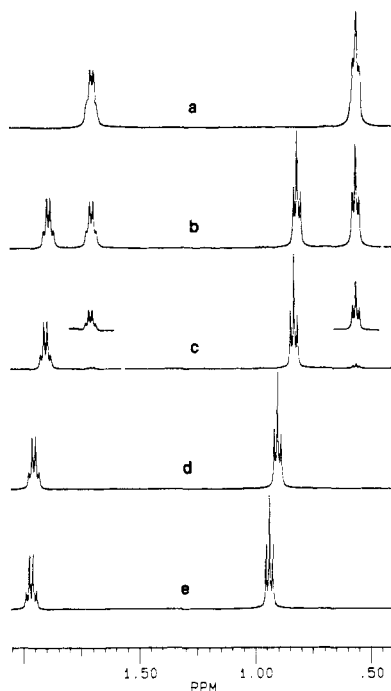

Figure 2. ^{1}H NMR spectra in toluene-d_8 at -77 °C for (a) 1, (b) a mixture of 1 and 2, (c) 2, (d) 2 plus added 3-hexyne, and (e) 3-hexyne. The offset in (c) is a 10-fold magnification of the resonances for 1 present in low concentration.

exists in solution. At ambient temperature, both 1 and 2 exchange the 3-hexyne ligand rapidly with each other and with added excess 3-hexyne. Figure 1 shows a plot of the chemical shift of the methyl resonance of 3-hexyne at ambient temperature as a function of the alkyne:copper ratio. For low, copper-rich ratios up to 0.5, the chemical shift is constant and equal to that observed for pure 1. Above a ratio of 0.5, the signal shifts toward the direction of the free alkyne. At all ratios, only a single resonance is observed for the methyl group.

Figure 2 shows a series of ^{1}H spectra at -77 °C of solutions containing various 3-hexyne:copper ratios. Only a single set of resonances is observed in the spectrum of pure 1. At this temperature, addition of 2 or free alkyne to a solution of 1 leads to the observation of two sets of alkyne resonances, one set with the same chemical shifts as observed in solutions of pure 1 and a second set of resonances that are shifted in the direction of the free alkyne. The low-temperature spectrum of pure 2 shows a predominance of this second set of resonances but also shows the resonances for 1. In toluene, the solvent used for the spectra shown in Figure 2, the ratio of 1:2 is 1:20, and in acetone it is 1:4. Addition of free alkyne to a solution of 2 causes the second set of resonances to move closer to the position of the free alkyne. In toluene, the resonance for 1 is no longer observed under these conditions, but in acetone it

is still observed *at the same position* with the intensity of the signal diminished from that observed in the spectrum of pure 2. A separate resonance for free 3-hexyne is not observed in any of the spectra. Thus, in low-temperature solutions containing a 2:2 stoichiometry of Cu:3-hexyne, there is a low concentration of 1 that does *not exchange rapidly with free 3-hexyne on the NMR time scale and an averaged signal for 2 and free 3-hexyne (which must be present if 1 is observed). It is not possible to measure a spectrum of a solution containing only 2. These observations were confirmed by low-temperature ^{13}C NMR spectroscopy. In these spectra, the alkyne resonance for 2 is slightly broadened, presumably indicating the onset of exchange with free alkyne on the NMR time scale.

Two other interesting points are observed in these NMR spectra. First, the direction of the shifts for coordinated versus free 3-hexyne in the ^{1}H spectra are solvent-dependent. In both solvents the shifts are greater for 1, but the direction is upfield in toluene (Figure 2) or benzene and downfield in acetone. The shifts in the ^{13}C spectra for the alkyne carbon atoms are the same, downfield, in both solvents. Second, in the low-temperature ^{13}C spectra, the two resonances for the acetate carbon atoms are clearly observed. These resonances are not observed at ambient temperature, even in high-quality spectra, for either these alkyne complexes or the cycloalkene complexes studied earlier.[2b] This difficulty is overcome by lowering the temperature.

Molecular weight determinations of 2 in benzene show that it is approximately a dimer in solution. This assumes that the small concentration of 1 observed in solutions of 2 by the low-temperature ^{1}H NMR experiment in toluene does not substantially increase in the benzene solution. The low concentration of 1 (ca. 5%) that is present does not greatly influence the molecular weight determination for 2 because two molecules of 2 convert to one molecule of 1 and two alkyne molecules. The slightly low determined values (average of 481 versus a calculated value of 517) may reflect the small amount of 1 and free alkyne present in solutions of 2.

For the alkynes $MeO_2CC\equiv CCO_2Me$ and $MeC\equiv CCO_2Me$, it is only possible to isolate the 4:2 copper:alkyne complexes of the presumed formula $Cu_4(\mu\text{-}O_2CCF_3)_4(\mu\text{-}RC\equiv CCO_2Me)_2$ (R = CO_2Me (3), Me (4)). Molecular weight studies with 4 had to be carried out in relatively dilute solution because of solubility problems but indicate that it is tetranuclear in solution. It was not possible to determine the molecular weight of 3 due to its low solubility in benzene. We assume it is also tetranuclear. The IR spectra of both complexes show the absorption for the ester groups of the alkyne to be essentially unchanged. Thus, the ester group does not appear to interact with the copper atom.

For the alkyne $PhC\equiv CPh$, only the 2:2 complex $Cu_2(\mu\text{-}O_2CCF_3)_2(PhC\equiv CPh)_2$ (5) can be isolated. Molecular weight studies show this complex to be dinuclear in benzene solution. ^{13}C NMR spectra of low-temperature toluene solutions containing $Cu:PhC\equiv CPh$ ratios of 2:1 show only resonances of the 2:2 complex.

Competition studies monitored by ^{1}H NMR spectroscopy aimed at determining the relative affinity of each alkyne for copper(I) are complicated by the alkyne-deficient stoichiometry of 1, 3, and 4. Addition of 3-hexyne (1 equiv/Cu) to a solution of 5 results in the displacement of diphenylacetylene with the formation of 2. Mixing solutions of 2 and 5 of equal concentrations leads to the *formation of 1 and free diphenylacetylene.* Clearly, coordination of the copper trifluoroacetate group to 3-hexyne

to form either **1** or **2** is favored over coordination to diphenylacetylene to form **5**. Addition of either $MeO_2CC\equiv CCO_2Me$ or $MeC\equiv CCO_2Me$ to a solution of **1** causes the signals for both 3-hexyne and the added alkyne to move the same percentage in the direction of the free alkyne resonances.

Finally, in the solid state these complexes are stable under an inert atmosphere and decompose only slowly in air. Solutions of all of these complexes slowly decompose in the absence of air, and decomposition is rapid in air.

Discussion

The most important results of these studies is the surprising tendency for the formation of tetranuclear complexes with a copper:alkyne ratio of 4:2, $Cu_4(\mu\text{-}O_2CCF_3)_4(\mu\text{-alkyne})_2$, even in the presence of excess alkyne. We initially anticipated that the reaction of $Cu_4(\mu\text{-}O_2CCF_3)_4(C_6H_6)_2$ with an excess of an internal alkyne would yield complexes of the general formula $[Cu(O_2CCF_3)(\text{alkyne})]_n$, analogous to the cycloalkene complexes that we had prepared previously.[2] The first definitive indication of the stability of the tetranuclear unit was our crystal structure of **1**.[4] This tendency for alkyne complexes of copper(I) acetate to form tetranuclear units is supported by the syntheses of **3** and **4** and the syntheses by van Koten of the complexes $Cu_4(\mu\text{-}O_2CC_6H_4\text{-}2\text{-}X)_4(\mu\text{-}RO_2CC\equiv CCO_2R)_2$ (X = H, Cl, Br; R = Me, Et).[5] Molecular weight studies with **1** and **3** and low-temperature NMR studies with **1** indicate that this tetranuclear structure is preserved in solution. There is no indication of the formation of a dinuclear species, $Cu_2(\mu\text{-}O_2CCF_3)_2(\mu\text{-alkyne})$, a reasonable possibility, in solution.

The stoichiometry of the products obtained in the reactions of $Cu_4(\mu\text{-}O_2CR)_4(C_6H_6)_2$ with alkynes is dependent on the alkyne. With diphenylacetylene, dinuclear complexes form with a copper:alkyne ratio of 2:2, $Cu_2(\mu\text{-}O_2CR)_2(PhC\equiv CPh)_2$. The solid-state structure has been determined crystallographically for R = Ph (**6**).[3] Molecular weight studies show that **5** (R = CF_3) is also dinuclear in solution.

With the alkyne 3-hexyne, we have been able to isolate complexes of both stoichiometries. Formation of the 4:2 complex **1** is favored, but the 2:2 complex **2** can be obtained by crystallization from hexane containing excess 3-hexyne. For the ester-substituted alkynes $MeO_2CC\equiv CCO_2Me$ and $MeC\equiv CCO_2Me$, only tetranuclear 4:2 complexes form.

The driving force behind the formation of these 4:2 copper:alkyne complexes in favor of 2:2 complexes is not
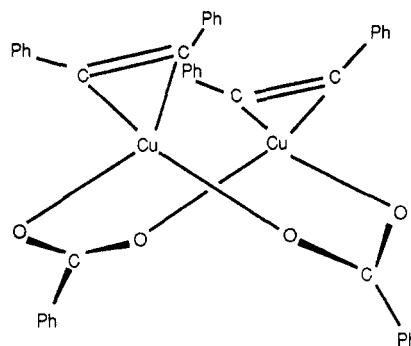
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clear. It is not just that the 4:2 complexes crystallize in preference to 2:2 complexes, because in solutions of **2**, low-temperature NMR studies show that **2** is in equilibrium with **1** and free alkyne. In contrast, with diphenylacetylene, there is no indication of formation of a 4:2 complex, even in solutions that contain a copper:alkyne ratio of 4:2. The present trends are that with alkynes substituted with one or two electron-withdrawing ester groups, the tetranuclear, 4:2 complexes form. With π-electron-donating phenyl substituents on the alkyne, the dinuclear, 2:2 complex forms. For 3-hexyne, both types of complexes can be isolated. It has been suggested that ester-substituted alkynes lead to the formation of tetranuclear complexes in reactions with $Cu_4(\mu\text{-}O_2CR)_4(C_6H_6)_2$ because these alkynes are not strong enough donor ligands to break the tetranuclear cage of the starting material.[5] Other factors must be important because recrystallization of dinuclear **2** in the absence of excess 3-hexyne leads to the isolation of tetranuclear **1**. Also, the alkyne competition studies demonstrate that diphenylacetylene has the weakest affinity for coordination to copper, but it exclusively forms the dinuclear 2:2 complex. The fact that a solution prepared from a mixture of the dinuclear 2:2 complexes **2** and **5** contains tetranuclear **1** and free diphenylacetylene is additional evidence of the strong driving force for the formation of these tetranuclear 4:2 complexes.