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PREPARATION AND CHARACTERIZATION OF CYCLIC POLYOLEFIN COPPER(I) TRIFLUOROACETATE COMPLEXES

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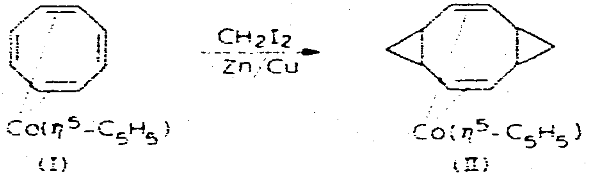
Summary

A series of polyolefin copper(I) trifluoroacetate complexes has been prepared with the following empirical formulae: $Cu(O_2CCF_3)$((*Z, E, E*)-1,5,9-cyclododecatriene); $Cu(O_2CCF_3)$(*endo*-dicyclopentadiene); $Cu(O_2CCF_3)$ (1,5-cyclooctadiene); $Cu_2(O_2CCF_3)_2$(1,5-cyclooctadiene); $Cu_2(O_2CCF_3)_2$(1,3,5,7-cyclooctatetraene); $Cu_4(O_2CCF_3)_4$(1,3,5,7-cyclooctatetraene); and $Cu_3(O_2CCF_3)_3$(1,3,5-cycloheptatriene). These complexes are soluble in polar organic solvents and have been characterized in solution by ^1H and ^{13}C NMR and molecular weight studies. Although the polyolefins are labile in solution, the NMR studies have shown which double bonds are coordinated to copper for the olefins with non-equivalent double bonds and how many of the equivalent double bonds are coordinated for the more symmetric olefins. In all cases only one double bond is bound to each copper. For all of the complexes studied, the molecular weights are highly concentration dependent, increasing at higher concentrations. For the cyclododecatriene complex, the molecular weight levels at 660 in benzene, the molecular weight corresponding to a dimer. Similarly, the $Cu_2(O_2CCF_3)_2$(1,3,5,7-cyclooctatetraene) complex levels of at a dimer at high concentration in THF. The other complexes which are less soluble show molecular weights between that of a monomer and dimer.

Introduction

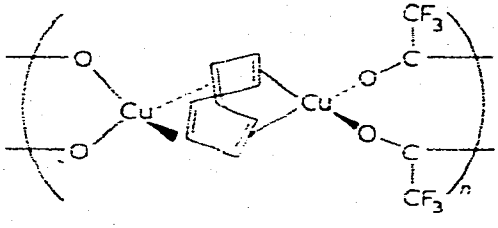
The ability to carry out chemical reactions at selected locations in polyfunctional compounds is of great importance in synthesis. Success in such reactions depends on the chemist's ability to enhance reactions at the desired sites or to block reactions at undesirable sites. We have recently begun an investigation into the use of transition metals as blocking and/or directing agents for carbon—carbon π bond addition reactions [1]. In particular, we have been able to prepare unusual polycyclic polyolefin complexes by directing methylene addition reactions with transition metals to uncoordinated double bonds in polyolefin metal complexes. For example, cyclooctatetraene-η^5-cyclopentadienyl cobalt (I) reacts with excess methylene generated from the Simmons—Smith reagent at the two uncoordinated double bonds and not at the coordinated double bonds as shown in eq. 1. In addition to preparing new metal complexes, this approach has potential for use in organic synthesis. Cleavage of the new ligand from complex II will yield a new organic compound of some interest, *syn*-dihomocyclooctatetraene. Although we are, at present, attempting to isolate this ligand from complex II, this is not a good route to large quantities of this compound because of the expense and difficulty of preparing the starting material. Thus, for the synthesis of polycyclic polyolefin compounds from this approach, a system is needed in which the metal complex can be prepared readily and in high yield and the new ligand cleaved from the metal in high yield after a metal directed reaction. Also, it would be advantageous if the metal was relatively selective in its coordination to particular double bonds in polyolefins.



(1)

It was felt that copper(I) olefin complexes with a strongly coordinating counterion would fit these requirements. A variety of copper(I) olefin complexes containing anions with a range of coordinating abilities are known [2—8]. Salomon and Kochi have carried out extensive studies on copper(I) olefin complexes containing the poorly coordinating trifluoromethanesulfonate (triflate) anion [2]. These complexes are soluble in polar organic solvents and have been used as homogeneous catalyst for the cyclopropanation [2c] and photocycloaddition of olefins [2d,e]. A series of copper(I) olefin complexes containing more strongly coordinating halide anions have also been prepared [3]. In general, these complexes have a lower coordinated double bond to copper(I) ratios than the corresponding triflate complexes because the anion competes for the copper coordination sites with the olefin. A number of copper(I) acetate complexes have also been prepared [4].

Copper(I) olefin complexes of the strongly coordinating trifluoroacetate anion seemed the most likely to have the properties described above. Dines has briefly reported three complexes of this type; two 1,5-cyclooctadiene complexes with hydrocarbon to copper salt ratios of 1 : 1 and 1 : 2 and a 1,3,5,7-cyclooctatetraene complex of ratio 1 : 2 [5]. No structural characterization was reported but the polymeric structure pictured below was proposed for the cyclooctatetraene complex:



Amma and Rodesiler have reported [6] the crystal structure of the benzene adduct of copper(I) trifluoroacetate and shown it to be tetrakis(copper trifluoroacetate)dibenzene in the solid state. They also reported that the weakly coordinated benzenes could be replaced in solution by simple olefins to yield complexes that had one coordinated double bond per copper. In addition, molecular weight studies indicate that the benzene complex is undergoing a dimer—tetramer equilibrium in solution [7].

This paper reports the synthesis and characterization of a series of copper(I) trifluoroacetate polyolefin complexes. These complexes are soluble in organic solvents and we have studied their ^1H and ^{13}C NMR spectra in detail as well as their solution molecular weights. The main emphasis has been on the characterization of the environment of the polyolefins in solution although we have determined stoichiometries and discuss the structure of the complexes in both the solid and solution phase.

Experimental

General

All reactions were carried out under prepurified nitrogen using freshly distilled degassed solvents. Proton NMR spectra were recorded in acetone-d_6 on either a Varian A-60 spectrometer or a Perkin—Elmer R-32 spectrometer. Carbon-13 NMR spectra were recorded on a Varian CFT 20 spectrometer. All ^{13}C NMR spectra were run with ^1H decoupling. Chemical shifts of proton and ^1H decoupled carbon-13 resonances are reported in δ(ppm) from TMS. IR spectra were recorded on a Perkin—Elmer model 337 spectrophotometer. Solid state IR spectra were recorded on fluorolube mulls on NaCl plates for the 1300—4000 cm^{-1} range and nujol mulls on KBr plates for the 400—1300 cm^{-1} range. Gas chromatograms were recorded on a F and M model 500 gas chromatograph using a 6 ft column packed with 10% Carbowax 20 M on Chromosorb W 60/80 regular support. Molecular weight data was obtained using a Hewlett Packard 302B vapor pressure osmometer. Melting and decomposition points were measured in sealed, evacuated capillaries. All melting points are uncorrected.

Trifluoroacetic acid was purchased from Columbia Organic Chemical Company. With the exception of dicyclopentadiene, olefins were purchased from Aldrich and Columbia Organic Chemicals and used without further purification. Dicyclopentadiene (technical), purchased from Eastman, was cracked, distilled, and allowed to redimerize before use.

Olefin competition reactions were carried out in 5 mm proton NMR tubes using acetone-d_6 as the solvent. A proton NMR spectrum of the $[Cu(O_2CCF_3)]_n$(olefin) (ca. 0.1 g) in acetone-d_6 (0.30 ml) was recorded after the addition of successive drops of the appropriate competing olefin.

Samples were prepared for gas chromatographic analysis by dissolving the complex (1.00 g) in CO saturated acetone (15 ml). Complete olefin displacement was ascertained by bubbling additional CO through the acetone solution for 5—10 minutes. The volume of the displaced olefin was estimated and an equal volume of a standard, which gave good chromatographic separation from the olefin, was added to the solution. The acetone solution was injected several times. A 1 : 1 (v/v) olefin/standard reference mixture was injected several times. The volume of the olefin in the sample was determined by comparing average olefin to standard peak height ratios for the sample and the reference.

Trifluoroacetic anhydride

P_4O_{10} (36 g) was placed in a 500 ml one neck flask. Trifluoroacetic acid (73 ml) was added carefully and trifluoroacetic anhydride was collected at 40° C by fractional distillation of this mixture.

$Cu_4(O_2CCF_3)_4 \cdot 2C_6H_6$

Cu_2O (2.0 g, 14 mmol) was placed in a 250 ml 3 neck flask equipped with a condenser and dried in vacuo for 15 minutes. Benzene (35 ml) and trifluoroacetic anhydride (7.5 g, 36 mmol) were added and the mixture was stirred and refluxed overnight. After cooling, the solution was filtered to remove unreacted Cu_2O. The filtered solution was concentrated in vacuo (to ca. 10 ml) and precipitation of $Cu_4(O_2CCF_3)_4 \cdot 2C_6H_6$ was induced by the dropwise addition of hexane (30 ml).

$Cu(O_2CCF_3)(C_{12}H_{18})$

A mixture of Cu_2O (1.0 g, 7.0 mmol), $(CF_3CO)_2O$ (3.75 g, 18 mmol), and benzene (35 ml) was refluxed and stirred overnight. The resulting solution was stirred vigorously at room temperature while (*Z,E,E*)-1,5,9-cyclododecatriene (6.0 ml) was added causing the solution to turn a pale blue color. The solution was concentrated in vacuo to ca. 10 ml and white crystals were precipitated by the dropwise addition of hexane (30 ml). The white crystals were collected, washed with hexane (2 × 10 ml), and dried in vacuo (3.45 g, 72.9%) m.p. 91° C, decomposition point 180° C. (Found: C, 49.40: H, 5.27. $C_{12}H_{18}CuF_3O_2$ calcd.: C, 49.64: H, 5.36%.) ^1H NMR spectrum of the olefin region: 5.67 (4, broad), 5.98 (2, broad). IR spectrum: $\nu(CO)$ 1680s, $\nu(C=C)$ 1447w, 1436w, 1422m, $\nu(C-F)$ 1100—1200s, $\nu(O_2C-CF_3)$ 840m. ^{13}C NMR spectrum of the olefin region (solvent, $CDCl_3$): C(5,6), 117.36; C(2,9), 125.65; C(1,10), 130.69.

$Cu(O_2CCF_3)(C_{10}H_{12})$

This compound was prepared as described for $Cu(O_2CCF_3)(C_{12}H_{18})$ except *endo*-dicyclopentadiene (3.72 g, 28.1 mmol) was the displacing olefin. The product was a white crystalline solid (3.77 g, 88%). Decomposition was noted at 177° C, total decomposition and melting occurred at 222° C. (Found: C, 46.90: H, 4.26. $C_{12}H_{12}CuF_3O_2$ calcd.: C, 46.67; H, 3.92%). ^1H NMR spectrum of the olefin region: H(3,4), 5.27 (2, broad singlet); H(8,9), 5.50 (2, broad singlet). IR spectrum: $\nu(CO)$ 1690vs, $\nu(C=C)$ 1450m, $\nu(C-F)$ 1100—1200vs, $\nu(O_2C-CF_3)$ 850m. ^{13}C NMR spectrum of the olefin region (solvent and reference, $CDCl_3$): C(2,3), 106.94, 110.46; C(7,8), 127.48, 128.38.

$Cu(O_2CCF_3)(C_8H_{12})$

This compound was prepared as described for $Cu(O_2CCF_3)(C_{12}H_{18})$ except 1,5-cyclooctadiene (1.63 g, 15 mmol) was the displacing olefin. The product was a white crystalline solid (3.62 g, 90.9%). Decomposition was noted at 170° C, total decomposition and melting occurred at 206° C. (Found: C, 42.36: H, 4.21. $Cu_{10}H_{12}CuF_3O_2$ calcd.: C, 42.18: H, 4.25%.) ^1H NMR spectrum: CH_2, 2.42 (2, singlet); CH, 5.70 (1, broad). IR spectrum: ν(CO) 1694vs, ν(C=C) 1439s, 1451s, 1490m, ν(C—F) 1100—1200vs, ν(O_2C—CF_3)847m. ^{13}C NMR spectrum (solvent and reference, $CDCl_3$): CH_2, 28.21; CH, 116.5.

$Cu_2(O_2CCF_3)_2(C_8H_{12})$

$Cu_4(O_2CCF_3)_4 \cdot 2C_6H_6$ (4.41 g, 5.11 mmol) was dissolved in benzene (40 ml). While stirring the benzene solution vigorously at room temperature 1,5-cyclooctadiene (1.10 g, 10.2 mmol) was added. A small amount of white solid precipitated from the solution. After stirring for several minutes, the benzene was reduced in vacuo to approximately 15 ml and hexane (30 ml) was added to precipitate the remaining solid. The white crystals were collected, washed with hexane (2 × 10 ml) and dried in vacuo (4.54 g, 96.2%), m.p. and total decomposition 204°C. (Found: C, 30.91; H, 2.63. $C_{12}H_{12}Cu_2F_6O_4$ calcd.: C, 31.23; H, 2.62%.) ^{1}H NMR spectrum: CH_2, 2.50 (2, singlet); CH, 5.68 (2, broad). IR spectrum: ν(CO) 1680vs, ν(C=C) 1465m, ν(C—F) 1100—1200vs, ν(O_2C—CF_3)853m. ^{13}C NMR spectrum (solvent and reference, acetone): CH_2, 28.0; CH, 109.7.

$Cu_2(O_2CCF_3)_2(C_8H_8)$

A mixture of Cu_2O (1.0 g, 7.0 mmol), $(CF_3CO)_2O$ (3.75 g, 18 mmol), and benzene (35 ml) was treated as described for $Cu(O_2CCF_3)(C_{12}H_{18})$. The filtered solution was stirred vigorously at room temperature while 1,3,5,7-cyclooctatetraene (1.8 g, 17 mmol) was added. Upon first addition of the olefin, a red color appeared. The solvent was removed leaving a light green solid, which was stirred and washed with hexane (2 × 10 ml) to yield a white crystalline solid (2.33 g, 73%). Melting and decomposition points of $Cu_2(O_2CCF_3)_2(C_8H_8)$ were measured as follows. The compound was placed under constant vacuum and heated until one half an equivalent of olefin was liberated and removed (125—145°C) as shown by a change in color from white to orange. Further heating was carried out under nitrogen at atmospheric pressure causing melting with total decomposition at 243°C. (Found: C, 31.43; H, 1.73. $C_{12}H_8Cu_2F_6O_4$ calcd.: C, 31.52; H, 1.76%). ^{1}H NMR: C_8H_8, 5.43 (singlet). IR spectrum: ν(CO) 1565vs, ν(C=C) 1451m, ν(CF) 1100—1200vs, ν(O_2C—CF_3) 853. ^{13}C NMR spectrum (solvent and reference, acetone-d_6): C_8H_8, 114.41. ^{13}C NMR spectrum of $Cu_2(O_2CCF_3)_2C_8H_8$ plus one drop of free C_8H_8 at −95°C (solvent and reference, acetone-d_6): C_8H_8, 116.8.

$Cu_4(O_2CCF_3)_4(C_8H_8)$

A mixture of Cu_2O (1.0 g, 7.0 mmol), $(CF_3CO)_2O$ (3.75 g, 18 mmol), and benzene (25 ml) was refluxed overnight. While refluxing, the solution turned a light green color and most of the brown solid Cu_2O disappeared. After cooling, the mixture was filtered to remove unreacted Cu_2O. The filtered green solution was stirred vigorously at room temperature while 1,3,5,7-cyclooctatetraene (0.364 g, 3.5 mmol) was added via syringe. Precipitation of bright orange crystals occurred upon addition of olefin. The crystals were filtered, washed with hexane (2 × 10 ml), and dried in vacuo (4.24 g, 75%), m.p. with decomposition at 242°C. (Found: C, 23.31; H, 1.05. $C_{16}H_8Cu_4F_{12}O_8$ calcd.: C, 23.71; H, 0.995). ^{1}H NMR spectrum consisted of one broad resonance at 4.94. IR spectrum: ν(CO) 1646s, ν(C=C) 1455m, ν(C—F) 1100—1250vs, ν(O_2C—CF_3) 852s. ^{13}C NMR spectrum (solvent and reference acetone-d_6): C_8H_8, 90.5. ^{19}F NMR spectrum (solvent acetone-d_6, reference C_6F_6): CF_3, 91.7 ppm downfield.

$Cu_3(O_2CCF_3)_3(C_7H_8)$

$Cu_4(O_2CCF_3)_4 \cdot 2C_6H_6$ (1.96 g, 2.27 mmol) was dissolved in acetone (15 ml). While stirring vigorously 1,3,5-cycloheptatriene (1.33 g, 14.5 mmol) was syringed into the acetone solution. Dropwise addition of hexane (30 ml) precipitated yellow crystals. The crystals were collected by filtration, washed with hexane (2 × 10 ml) and dried in vacuo (1.70 g, 90.4%). Decomposition of this solid was first noted at 239°C with total decomposition and m.p. at 250°C. (Found: C, 25.30; H, 1.35. $C_{13}H_8Cu_3F_9O_6$ calcd.: C, 25.10; H, 1.30%). ^1H NMR spectrum: CH_2, 3.01 (1, triplet, J 1.3 Hz); H(1,6) 5.25 (1, broad); H(2,5), 5.64 (1, broad); H(3,4) 5.75 (1, broad). IR spectrum: $\nu(CO)$ 1645 vs, $\nu(C{=}C)$ 1460m, $\nu(CF)$ 1100–1250 vs, $\nu(O_2C{-}CF_3)$ 855m. ^{13}C NMR spectrum (solvent and reference, DMSO): CH_2, 27.31; CH, 113.61, 118.48, 125.72

Results and discussion

The complex $Cu_4(O_2CCF_3)_4 \cdot 2C_6H_6$ can be prepared by refluxing a mixture of Cu_2O and trifluoroacetic anhydride in benzene solution [6]. This complex is a white crystalline solid. It has been shown in the solid state to have this tetrameric formula by X-ray crystallagraphy [6]. The benzenes can be displaced from solutions of $Cu_2(O_2CCF_3)_4 \cdot 2C_6H_6$ by olefins to form $Cu(O_2CCF_3)$ olefin complexes [6].

The synthesis of $Cu(O_2CCF_3)$ olefin complexes can be carried out quickly and easily since reaction occurs immediately upon olefin addition to the dissolved benzene complex at room temperature. In preparations where the benzene complex was isolated so that stoichiometric amounts of olefin could be added, yields around 96% based on olefin and $Cu_4(O_2CCF_3)_4 \cdot 2C_6H_6$ were common. For other preparations in which excess of olefin could be added, the benzene complex was not isolated, but prepared in solution and treated directly with olefin. Synthesis of olefin complexes by this method gave yields from 73 to 91%, based on Cu_2O. These yields seemed to depend upon how well the benzene complex formed in solution rather than the olefin used to displace benzene.

These $Cu(O_2CCF_3)$ olefin complexes all decompose readily in the presence of water. This property has been used to recover the olefin in ca. 95% yield by simply adding water to the complex and extracting the olefin with organic solvents.

Since these $Cu(O_2CCF_3)$ olefin complexes are soluble in polar organic solvents such as acetone and THF, each complex was studied by NMR as will be discussed in the following sections. Besides the specific information given by NMR for each complex, information on the complexes as a group was obtained.

The copper(I) trifluoroacetate olefin complexes we have prepared are labile as are the copper(I) triflate olefin complexes prepared by Salomon and Kochi [2a]. This property of the complexes is shown readily by NMR. An NMR spectrum of a $Cu(O_2CCF_3)$ olefin complex run in the presence of additional free olefin does not show resonances for free and complexed olefin, but rather only one average resonance for each type of carbon or hydrogen. In addition, for complexes like $Cu_2(O_2CCF_3)_2(C_8H_8)$ in which only two of the double bands are coordinated to the copper (vide infra), only one sharp resonance for the C_8H_8 ring was observed in either the ^1H or ^{13}C NMR and no line broadening was observed down to −95°C for this complex. It is interesting to note that the carbons of the trifluoroacetate group are not observed in the ^{13}C NMR spectrum of any of the complexes discussed here, even under conditions of ^{19}F decoupling. Also the ^{19}F NMR spectra for these complexes contain very broad resonances with half widths ca. 2.5 ppm.

Due to the lability of these complexes, olefin competition reactions could be studied by NMR. These studies showed the relative affinities of the various olefins for $Cu(O_2CCF_3)$ to be as follows:

In the case of the cyclooctadiene ligand, the first double bond to coordinate to copper is the one considered in this series. We have been able to prepare a complex in which both double bonds of the cyclooctadiene ligand are coordinated to a copper atom and any of the ligands listed will displace this second coordinated bond.

$Cu(O_2CCF_3)(C_{12}H_{18})$

Addition of excess (*Z,E,E*)-1,5,9-cyclododecatriene to benzene solutions of $Cu_4(O_2CCF_3)_4 \cdot 2C_6H_6$, followed by concentration in vacuo and dropwise addition of hexane, precipitates the white crystalline complex $Cu(O_2CCF_3)(C_{12}H_{18})$. This complex has a melting point of 91°C. Upon melting a clear colorless liquid is formed which can be recooled to the solid and melted again. Upon heating of this liquid to 180°C it decomposes, with liberation of olefin, just as the other complexes to be discussed do upon melting.

PMR shows a shift of all olefinic proton resonances upon complexation. In the ^{13}C NMR spectrum, the resonance for the *cis*-olefinic carbons has shifted 11–12 ppm upfield from the position of the *cis*-olefinic carbons on the free olefin, while the resonances for the *trans*-olefinic carbons have shifted 3–4 ppm in the same direction. This indicates that although all three double bonds in (*Z,E,E*)-1,5,9-cyclododecatriene coordinate to copper(I) in solution the *cis* double bond is somewhat preferred.

Solutions of $Cu(O_2CCF_3)(C_{12}H_{18})$ are quite stable in the air relative to most of the other complexes. Generally upon exposure to the air solutions of the complexes are oxidized within minutes to a dark green solution. Solutions of $Cu(O_2CCF_3)(C_{12}H_{18})$ can remain in the air for approximately 30 minutes without extensive discoloration. This complex is quite soluble in polar organic solvents such as acetone and THF. In addition, it is soluble in solvents such as benzene and methylene chloride.

Due to the solubility of $Cu(O_2CCF_3)(C_{12}H_{18})$ in solution, vapor pressure osmometry molecular weight data were obtained over a large concentration range as well as in solutions with two different solvents. Data collected on benzene solutions of this complex show a steady increase in molecular weight as concentration increases until the molecular weight reaches ca. 660 at a concentration of ca. 450

g solute/kg solvent. As shown in Fig. 1, past this point the molecular weight remains constant at ca. 650 as concentration is increased. The molecular weight of a dimer, $Cu_2(O_2CCF_3)_2(C_{12}H_{18})_2$ is 677. This data indicates that in benzene solution there is equilibrium between a monomer and a dimer at low concentration and that the complex is dimeric at high concentration. This data gives no evidence for a tetrameric species in solution as observed for solid $Cu_4(O_2CCF_3)_4 \cdot 2C_6H_6$ since molecular weights above 677 were not observed at any concentration.

Vapor pressure osmometry studies on $Cu(O_2CCF_3)(C_{12}H_{18})$ in THF show an increase in molecular weight as concentration increases; however, the molecular weight values are much lower than those obtained in benzene and no leveling off is observed within the concentration range possible. The highest molecular weight observed close to the solubility limit was 357. Thus, donor solvents substantially effect the position of the monomer—dimer equilibrium in favor of the monomer.

$Cu(O_2CCF_3)(C_{10}H_{12})$

Carbon—hydrogen analysis shows that excess dicyclopentadiene displaces benzene from $Cu_4(O_2CCF_3)_4 \cdot 2C_6H_6$ in benzene solutions to form a white crystalline complex with the stoichiometry $Cu(O_2CCF_3)(C_{10}H_{12})$. The proton NMR spectrum of this complex shows that the norbornene like carbon—carbon double bond (8,9) is complexed to the copper because the resonance for the protons at these positions show an upfield shift of 0.56 ppm from the free olefin, while the resonance for the protons at the cyclopentene like double bond (3,4) position show a shift of less than 0.10 ppm from that of the free olefin. The ^{13}C NMR spectrum supports this conclusion, the resonances for the norbornene like double bond carbons shift 28 ppm upon complex formation, while those for the cyclopentene like double bonds shift only 5 ppm. This 5 ppm shift could reflect either some coordination of the double bond or just a change in its environment when the 8,9 carbons coordinate to copper. The solid state IR spectrum of $Cu(O_2CCF_3)(C_{10}H_{12})$ shows that only one carbon—carbon double bond is complexed by the presence of a single peak in the coordinated olefin region (the uncoordinated olefin region is obscured by the $\nu(CO)$ of the trifluoroacetate).

Due to the effect on molecular weight for the $Cu(O_2CCF_3)(C_{12}H_{18})$ complex

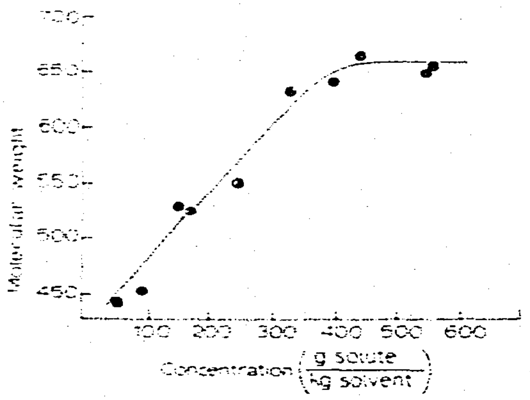


Fig. 1. Measured molecular weight versus concentration for $Cu(O_2CCF_3)(C_{12}H_{18})$.

in solutions of donor solvents, the ^{13}C NMR spectrum of $Cu(O_2CCF_3)(C_{10}H_{12})$ was obtained in a variety of solvents. Solvents used in this study were benzene, $CDCl_3$, CH_2Cl_2, acetone, THF, and DMSO. Spectra recorded in these solvents are essentially identical. This shows that the coordination of the olefin to copper(I) is not effected substantially by the solvent.

Since all of these $Cu(O_2CCF_3)$ olefin complexes are labile, it was important to determine if the free olefin concentration was building up in solution. In the equilibrium $Cu(O_2CCF_3)(C_{10}H_{12}) \rightleftharpoons Cu(O_2CCF_3) + C_{10}H_{12}$, as the ratio of $Cu(O_2CCF_3)$ to $C_{10}H_{12}$ is increased, if large amounts of free olefin are present under stoichiometric conditions, one would expect the equilibrium to shift toward the complex since there are additional copper atoms available to coordinate to carbon—carbon double bonds. The ^{13}C NMR spectra of $Cu_4(O_2CCF_3)_4 \cdot 2C_6H_6$ dissolved in THF with enough added $C_{10}H_{12}$ to displace 100, 75, 50, and 25% of the C_6H_6 were recorded. With increase in the ratio of copper/$C_{10}H_{12}$, very little shift in the resonances for carbons 8 and 9 was observed (ca. 1 ppm) while the resonances for carbons 3 and 4 shift substantially in the direction of complexed olefin (6 ppm upfield). The large change in the chemical shift of carbons 3 and 4 with the increased ratio of copper/$C_{10}H_{12}$ can be explained by increased coordination of the π bond between these carbons due to the availability of excess copper. The small shift of the resonances of the 8 and 9 carbons of dicyclopentadiene in the experiment described above is interpreted as showing that the equilibrium, $Cu(O_2CCF_3)(C_{10}H_{12}) \rightleftharpoons Cu(O_2CCF_3) + C_{10}H_{12}$, although fast on the NMR time scale, lies nearly completely to the left. This is substantiated, at least at high concentration, by our molecular weight data for the $Cu_2(O_2CCF_3)_2(C_8H_8)$ and $Cu(O_2CCF)(C_{12}H_{18})$ complexes which level off at dimer. If there was a build up of free olefin molecular weights would be lowered.

In addition to the above study, another investigation of the equilibrium $Cu(O_2CCF_3)(C_{10}H_{12}) \rightleftharpoons Cu(O_2CCF_3) + C_{10}H_{12}$, was carried out. The equilibrium will, of course, be concentration dependent. If large amounts of free olefin are present under stoichiometric conditions, at lower concentration this equilibrium would lie more to the right and thus the position of the resonance for the coordinated double bond should move in the direction of the free olefin. The ^{13}C NMR spectra of THF solutions of $Cu(O_2CCF_3)(C_{10}H_{12})$ recorded over an eight fold dilution showed only slight downfield shift (2 ppm) in the resonances for the coordinated carbon—carbon double bond. Surprisingly, the resonances for carbons 3 and 4, the uncoordinated double bond, shifted a larger amount (8 ppm downfield) upon dilution. These shifts are best explained by a change in the environment of the olefin due to the shift in the position of the monomer—dimer equilibrium which we have shown to be taking place by the molecular weight data discussed below. However, the small shift in the position of the carbon 8 and 9 resonances does show that a substantial concentration of free olefin is not present even in dilute solutions of the complex. An analogous study with $Cu(O_2CCF_3)(C_8H_{12})$ and $Cu(O_2CCF_3)(C_8H_8)$ mentioned below shows no changes in the location of the olefin resonance with a variation in concentration.

Vapor pressure osmometry molecular weight data collected on THF solutions of $Cu(O_2CCF_3)(C_{10}H_{12})$ showed a linear increase in molecular weight with concentration increase. The highest molecular weight obtained near the solubility limit was 410.

$Cu(O_2CCF_3)(C_8H_{12})$

A 1 : 1 complex, $Cu(O_2CCF_3)(C_8H_{12})$, and a 2 : 1 complex, $Cu_2(O_2CCF_3)_2(C_8H_{12})$, to be discussed below, have been reported previously by Dines [5]. He prepared these complexes by the reaction of the olefins with solutions of the $Cu(O_2CCF_3)$ salt. We have prepared $Cu(O_2CCF_3)(C_8H_{12})$ by displacing the benzene from a solution of $Cu_4(O_2CCF_3)_4 \cdot 2C_6H_6$ with excess C_8H_{12} followed by precipitation with hexane.

Upon coordination of 1,5-cyclooctadiene to $Cu(O_2CCF_3)$ the ^{13}C NMR resonance for the olefinic carbons shifts 12 ppm upfield from the position of the free olefin resonance. Although on the average only one carbon—carbon double bond in the 1,5-cyclooctadiene is coordinated, due to the lability discussed previously each double bond is spending equal time as a coordinated and uncoordinated double bond. Increasing the ratio of $Cu(O_2CCF_3)$ to C_8H_{12} increases the time each double bond spends coordinated to copper and further upfield shift of the olefinic resonance would be expected. This is observed in the ^{13}C NMR spectrum of the complex $Cu_2(O_2CCF_3)_2(C_8H_{12})$ to be discussed below.

$Cu(O_2CCF_3)(C_8H_{12})$ was sufficiently soluble to obtain vapor pressure osmometry molecular weight data in benzene as well as in THF. In both solvents the molecular weight increased linearly with concentration as with the previous complexes. As with the $Cu(O_2CCF_3)(C_8H_{12})$ complex, the molecular weights determined in THF were somewhat lower than those found in benzene. The highest molecular weight found for the complex in benzene, near the solubility limit of 160 g solute/kg solvent, was 510, while the molecular weight found in THF near 160 g solute/kg solvent was only 410. These molecular weights indicate again a monomer to dimer equilibrium.

$Cu_2(O_2CCF_3)_2(C_8H_{12})$

Addition of half an equivalent of 1,5-cyclooctadiene per copper to benzene solutions of $Cu_4(O_2CCF_3)_4 \cdot 2C_6H_6$ gives a white crystalline complex with two $Cu(O_2CCF_3)$ groups per olefin.

The ^{13}C NMR spectrum of $Cu_2(O_2CCF_3)_2(C_8H_{12})$ shows an upfield shift of 19 ppm for the olefinic resonance from the free position. This increase in shift over the 12 ppm observed for the $Cu(O_2CCF_3)(C_8H_{12})$ complex indicates the complexation of both carbon—carbon double bonds. Solid state IR shows that the carbon—carbon double bonds are coordinated symmetrically since only one peak appears in the coordinated carbon—carbon double bond region of the spectrum.

The solubility of this complex is very low in solvents such as benzene and dissolves substantially only in highly polar solvents such as THF and acetone.

As a result of the low solubility of this complex, vapor pressure osmometry molecular weight data could be collected over a limited range of concentration even in THF. The molecular weights observed increased linearly with concentration as with the other complexes. The highest molecular weight, determined near the solubility limit was 300.

$Cu_2(O_2CCF_3)_2(C_8H_8)$

Addition of excess 1,3,5,7-cyclooctatetraene to solutions of $Cu_4(O_2CCF_3)_4 \cdot 2C_6H_6$ yields a white compound of stoichiometry $Cu_2(O_2CCF_3)_2(C_8H_8)$, which was reported previously by Dines [5]. This stoichiometry was determined by carbon—

hydrogen analysis and VPC analysis of olefin displaced from copper.

Upon initial addition of C_8H_8 to the solution of $Cu_4(O_2CCF_3)_4 \cdot 2C_6H_6$, a red color appeared. This color disappears upon further addition of olefin. Dines has reported this behavior upon adding C_8H_8 to solutions of the salt $Cu(O_2CCF_3)$ [5]. We have found this red color to result from the precipitation of the complex of stoichiometry $Cu_4(O_2CCF_3)_4(C_8H_8)$ which will be discussed shortly.

The solid $Cu_2(O_2CCF_3)_2(C_8H_8)$ like the other complexes is reasonably stable to air and shows similar thermal stability decomposing only at 243°C. The $Cu_2(O_2CCF_3)_2(C_8H_8)$, however, shows unique properties upon initial heating in vacuo. At ca. 120°C the white crystalline complex begins to turn orange and C_8H_8 condenses on the side of the capillary tube. If heating is continued slowly and the liberated liquid is removed in vacuo, the crystals become completely orange and melt with total decomposition within 1°C of the decomposition point of the orange $Cu_4(O_2CCF_3)_4(C_8H_8)$ complex discussed below. This dramatic color change is caused by the solid phase reaction of $Cu_2(O_2CCF_3)_2(C_8H_8)$ liberating half an equivalent of C_8H_8 to form $Cu_4(O_2CCF_3)_4(C_8H_8)$.

The ^{13}C NMR spectrum of $Cu_2(O_2CCF_3)_2(C_8H_8)$ showed an upfield shift in the carbon resonance of 19 ppm from that of the free olefin. As with the 1 : 1 copper-C_8H_{12} complex, this resonance is an average of coordinated and uncoordinated carbon—carbon double bonds so upon further coordination of the two uncoordinated bonds to copper an additional shift of the carbon resonance might be expected and this is observed for $Cu_4(O_2CCF_3)_4(C_8H_8)$ in which all double bonds are coordinated. Attempts to slow the lability, relative to the NMR time scale, at low temperature failed. The ^{13}C NMR spectrum of $Cu_2(O_2CCF_3)_2(C_8H_8)$ at −95°C in acetone-d_6 remained as one sharp peak.

Upon dissolving in polar solvents, $Cu_2(O_2CCF_3)_2(C_8H_8)$ gives a deeply colored orange solution. These solutions are quite stable and could be prepared on the bench and left in the air for approximately an hour without apparent decomposition. Due to the stability of this complex in solution, very good molecular weight data was collected. Although $Cu_2(O_2CCF_3)_2(C_8H_8)$ is very insoluble in benzene, it is extremely soluble in THF. Solutions of concentration up to 484 g solute/kg solvent were prepared readily. As with the other complexes, molecular weights were found to increase linearly with concentration up to ca. 80 g solute/kg solvent where they began to level off. The molecular weights leveled off at ca. 460 and showed no futther increase even with increase of concentration to 484 g solute/kg solvent. These data shows undisputably that $Cu_2(O_2CCF_3)_2(C_8H_8)$ is dimeric in THF solutions at high concentrations and at lower concentrations is in equilibrium between a dimer and some lower molecular weight species. In light of this molecular weight data and our observation that $Cu(O_2CCF_3)$ coordinates to one carbon—carbon double bond, the solid structure proposed by Dines [5] seems unlikely, although a tetrameric structure similar to that found for the benzene complex [6] definitely cannot be ruled out in the solid state.

$Cu_4(O_2CCF_3)_4(C_8H_8)$

As described previously, $Cu_4(O_2CCF_3)_4(C_8H_8)$ drops out of benzene solution immediately upon addition of 1,3,5,7-cyclooctatetraene to a solution of $Cu_4(O_2CCF_3)_4 \cdot 2C_6H_6$. This orangish red crystalline complex which melts with total decomposition at 242°C can also be prepared as discussed above by heating and vacuuming away one half of an equivalent of C_8H_8 from $Cu_2(O_2CCF_3)_2(C_8H_8)$.

This complex dissolves to give solutions of the same color and similar stability as the $Cu_2(O_2CCF_3)_2(C_8H_8)$. The ^{13}C NMR spectrum of $Cu_4(O_2CCF_3)_4(C_8H_8)$ shows the resonance is shifted 43 ppm upfield from the resonance of the free olefin. This is roughly twice the shift observed when two of the carbon—carbon double bonds in C_8H_8 were coordinated in $Cu_2(O_2CCF_3)_2(C_8H_8)$. As with $Cu_2(O_2CCF_3)_2(C_8H_8)$, the solid state IR spectrum contains only one absorption in the coordinated carbon—carbon double bond stretching region.

Vapor pressure osmometry data collected on THF solutions of $Cu_4(O_2CCF_3)_4(C_8H_8)$ shows as with other complexes a linear increase in molecular weight with increase in concentration. The highest molecular weight values obtained were ca. 350.

$Cu_3(O_2CCF_3)_3(C_7H_8)$

When excess 1,3,5-cycloheptatriene is added to acetone solutions of $Cu_4(O_2CCF_3)_4 \cdot 2C_6H_6$, a complex with one copper per carbon—carbon double bond forms. This light yellow compound was soluble only in polar solvents such as THF and acetone.

Proton NMR indicates that all of the carbon—carbon double bonds are complexed to copper in solution as would be expected from the stoichiometry. Upon complexation the change in proton chemical shifts from the free position are as follows: 3 and 4 > 2 and 5 > 1 and 6. ^{13}C NMR spectra also show complexation of all carbon—carbon double bonds.

Vapor pressure osmometry measurements on $Cu_3(O_2CCF_3)_3(C_7H_8)$ in THF solutions, showed, as with the other complexes, a linear dependence of molecular weight upon concentration. The highest molecular weight obtained for this complex was ca. 390 found near the solubility limit of $Cu_3(O_2CCF_3)_3(C_7H_8)$ in THF.

Mixed olefin complexes

An attempt was made to prepare complexes with two different olefins present. In particular, and attempt was made to prepare a mixed complex of 1,5-cyclooctadiene and dicyclopentadiene by adding enough dicyclopentadiene to the $Cu_2(O_2CCF_3)_2(C_8H_{12})$ complex to displace one of the two double bonds in each 1,5-cyclooctadiene ring. In two attempts to do this in benzene solution, a non-stoichiometric material was precipitated with hexane. In one case the solid was rich in 1,5-cyclooctadiene and in the other rich in dicyclopentadiene as shown by VPC analysis of the olefins after displacement with CO. These solids are most likely mixtures of olefin copper complexes because they show melting points below that of either pure compound.

Conclusion

We have prepared a series of copper(I) trifluoroacetate polyolefin complexes with one carbon—carbon double bond coordinated to each $Cu(O_2CCF_3)$. Molecular weight data shows that these complexes are in a monomer—dimer equilibrium in solution. Although the olefins in these complexes are labile in solution, there is no appreciable build up of free olefin. The olefins are held quite tightly in the solid complex, liberated only upon decomposition in vacuo at temperatures in excess of 170°C with the exception of $Cu_2(O_2CCF_3)_2(C_8H_8)$ which undergoes a solid state reaction in vacuo starting around 120°C to give off one half an equivalent of C_8H_8 yielding $Cu_4(O_2CCF_3)_4(C_8H_8)$. The olefin can be cleaved from these complexes readily and collected in ca. 95% yield by addition of water and extraction with organic solvents.

The ease of synthesis, ease of ligand cleavage, and the solubility of these complexes in polar organic solvents, which appear to be general properties applicable to many olefins, give promise for this system for organic synthesis. Investigations into the use of copper(I) trifluoroacetate olefin complexes in several types of organic reactions are underway.

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