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Olefin Trifluoroacetato Derivatives of Copper(I) and Their Olefin/CO Exchange Reactions

Guido Pampaloni,*[,†] Riccardo Peloso,[†] Claudia Graiff,[‡] and Antonio Tiripicchio[‡]

Dipartimento di Chimica e Chimica Industriale, Università di Pisa, Via Risorgimento 35, I-56126 Pisa, Italy, and Dipartimento di Chimica Generale ed Inorganica, Chimica Analitica, Chimica Fisica, Università di Parma, Parco Area delle Scienze 17/A, I-43100 Parma, Italy

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Compounds of the general formula Cu(CF_3COO)(olefin) (olefin = cyclooctene (coe), 1,5-cyclooctadiene (cod), diethylfumarate (defu), methylcinnamate (meci)) have been prepared, and the molecular structures have been solved by X-ray diffraction for olefin = coe, defu, meci. The complexes feature a dimeric [$Cu_2(\mu\text{-}CF_3COO)_2(olefin)_2$] core with bridging trifluoroacetates and a η^2-bonded olefin. In the case of the defu and meci complexes, [$Cu_2(\mu\text{-}CF_3COO)_2(olefin)_2$] dimeric units are linked by the oxygen atom of a carbonyl group of the ester to give polymeric chains. The compound [$Cu_2(\mu\text{-}CF_3COO)_2(meci)_2$]$_n$ is the first structurally characterized example of a metal-bonded methylcinnamate. By recrystallization of [$Cu_2(CF_3COO)_2(cod)_2$], a derivative featuring a cod/Cu molar ratio of 0.5 has been isolated and structurally characterized as [$Cu_2(\mu\text{-}CF_3COO)_2(\mu\text{-}cod)$]$_n$, which represents the first example of a polymeric metal complex containing a bridging cod ligand. The carbonylation reaction of [Cu(CF_3COO)(olefin)]$_2$ (olefin = coe, cod, defu; 2Cu(CF_3COO)(olefin) + 2CO $\rightleftarrows$ [Cu(CF_3COO)(CO)]$_2$ + 2(olefin)) has been studied gas volumetrically, and the equilibrium constants are 12.6 ± 2.4 M^{-1} (298.3 K, cod), (6.3 ± 3.2) × 10^2 M^{-1} (293.2 K, coe), and (1.1 ± 0.7) × 10^7 M^{-1} (293.2 K, defu). The enthalpy changes, obtained from variable-temperature experiments, are −46 ± 4 (olefin = cod), −71 ± 17 (coe), and −112 ± 20 kJ mol^{-1} (defu). These data for copper(I) are compared with those obtained for the $3d^3$ V(II) and $5d^{10}$ Au(I) systems VCp_2(CO) and AuCl(CO).

Introduction

Copper(I) trifluoroacetate, Cu(CF_3COO), has long been known[1] for its ability to coordinate olefins or carbon monoxide[2] to afford complexes notable for both their structural and reactivity characteristics. (Trifluoroacetato)copper(I) complexes containing olefins such as (*Z,E,E*)-cyclododecatriene, *endo*-dicyclopentadiene, and 1,5-cyclooctadiene (cod)[2c] have been studied in solution (equilibria involving compounds of different nuclearity have been observed), but to date the solid-state structures are limited to the η^2-benzene adduct, a tetranuclear species of formula $Cu_4(\mu\text{-}CF_3COO)_4(\eta^2\text{-}benzene)_2$.[2d] Regarding carbonyl derivatives, it has been reported that copper(I) trifluoroacetate undergoes carbonylation at atmospheric pressure to afford Cu(CF_3COO)(CO),[2h] which dimerizes to [Cu(CO)(CF_3COOH)(μ-CF_3COO)]$_2$[2f] in the presence of excess trifluoroacetic acid. Molecular weight data in solution suggest that an equilibrium exists between dinuclear and tetranuclear species.[2h]

We have had a general interest in the thermodynamics of the CO/olefin competition reactions[3] (eq 1) and thought that copper(I) trifluoroacetate could be an interesting substrate to investigate this equilibrium, due to its well-established ability to give stable compounds with both olefins and carbon monoxide. The literature

$$ML(olefin) + CO \leftrightarrows ML(CO) + olefin \qquad (1)$$

suggests that the carbonyl derivative is generally more stable than the corresponding olefin complex for VCp_2(CO),[3] $Co_2(CO)_8$,[4] Rh(acac)$(CO)_2$,[5] [PdMe(phenanthroline)CO]$^+$,[6] $PtX_2(CO)_2$,[7] and Cu[hydridotris(1-pyr-

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* To whom correspondence should be addressed. E-mail: pampa@dcci.unipi.it. Tel: int. code + 050 2219 219. Fax: int. code +050 2219 246.

[†] Università di Pisa.

[‡] Università di Parma.

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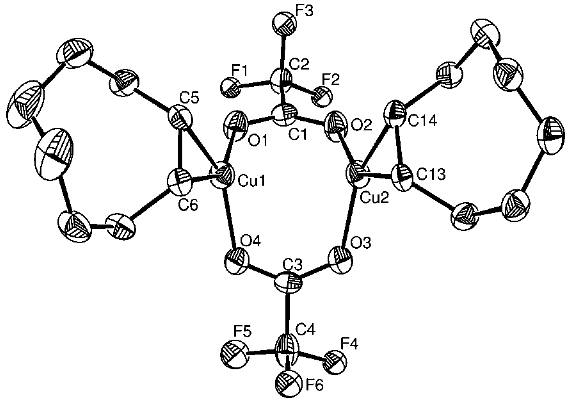

Figure 1. View of the molecular structure of $[Cu(\mu\text{-}CF_3COO)(coe)]_2$ with the atomic numbering scheme.

azolyl)borate](CO).[8] Nevertheless, the opposite trend is observed for the $5d^{10}$ gold(I) system AuCl(CO), the equilibrium constant for the displacement of ligated CO by the olefin being 4 at 294.6 K (AuCl(CO) + norbornene $\leftrightarrows$ AuCl(norbornene) + CO).[9] The study of the thermodynamics of the olefin/CO exchange for a $3d^{10}$ Cu(I) system would be useful in order to determine horizontal and vertical trends that operate in carbonyl and olefin derivatives.

In this paper we report the isolation and the characterization of olefin derivatives of copper(I) trifluoroacetate and their crystal structures, including that of the first example of a metal-bonded methyl cinnamate and of a polymeric compound with cod behaving as a bridging ligand. We also report olefin/CO exchange data involving copper(I) trifluoroacetate derivatives of cod, coe, meci, and defu. Olefins have been selected to cover a wide spectrum as far as the electronic properties are concerned: a cyclic monoolefin (coe), a cyclic diolefin (cod), and two ester derivatives, diethyl fumarate and methyl cinnamate, the latter containing a double-bond-conjugated phenyl ring and only one ester functionality.

Results and Discussion

Synthesis and Structural Studies. The olefin complexes of copper(I) have been prepared by reaction of $Cu(CF_3COO)(toluene)_{0.5}$[2g] with the olefin (eq 2); the compounds, soluble in aromatic hydrocarbons, have been characterized (IR and NMR spectra and X-ray diffraction methods for coe, meci, and defu) as containing η^2-ligated olefins.

$$Cu(CF_3COO)(toluene)_{0.5} + \text{olefin} \rightarrow Cu(CF_3COO)(\text{olefin}) + 0.5(\text{toluene}) \quad (2)$$

$$\text{olefin} = \text{coe, cod, meci, defu}$$

The structure of $[Cu(\mu\text{-}CF_3COO)(coe)]_2$ is shown in Figure 1 together with the atomic numbering scheme; a selection of bond distances and angles are reported in Table 1. The complex is dimeric, with the two carboxylic groups of the trifluoroacetate ligands symmetrically bridging the two copper atoms through the oxygen atoms to form an eight-membered ring. The copper–copper separation is 2.898(1) Å. Each copper atom is also involved in a η^2 interaction with the double bond of cyclooctene; if the midpoints (M1 and M2) of the double bonds are considered as coordination sites, the copper atoms lie in a nearly trigonal-planar environment. The Cu–O bond distances are in the range 1.963(4)–1.983(4) Å. The Cu–C bond lengths range from 2.031(5) to 2.043(5) Å to be compared to the values of 2.024(6)–2.074(6) Å observed in the copper(I) derivative *catena*-Cu(*μ*-Cl)(coe).[10]

Table 1. Selected Bond Distances (Å) and Angles (deg) in $[Cu(\mu\text{-}CF_3COO)(coe)]_2$[a]

Cu(1)–M(1)	1.919(5)	Cu(2)–M(2)	1.921(5)
Cu(1)–C(5)	2.043(5)	Cu(2)–C(13)	2.038(5)
Cu(1)–C(6)	2.031(5)	Cu(2)–C(14)	2.037(5)
Cu(1)–O(1)	1.964(4)	Cu(2)–O(2)	1.963(4)
Cu(1)–O(4)	1.973(4)	Cu(2)–O(3)	1.983(4)
O(1)–Cu(1)–O(4)	103.54(17)	O(2)–Cu(2)–O(3)	102.10(16)
O(1)–Cu(1)–M(1)	128.64(16)	O(2)–Cu(2)–M(2)	129.06(16)
O(4)–Cu(1)–M(1)	126.15(16)	O(3)–Cu(2)–M(2)	128.55(19)

[a] M(1) and M(2) are the midpoints of the C(5)–C(6) and C(13)–C(14) double bonds.

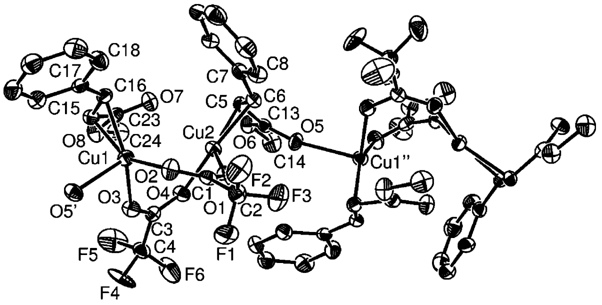

Figure 2. View of a fragment of the molecular structure of $[Cu_2(\mu\text{-}CF_3COO)_2(meci)_2]_n$ with the atomic numbering scheme.

Dimeric units, similar to those found in $[Cu(\mu\text{-}CF_3COO)(coe)]_2$, are also present in the structures of the ester derivatives $[Cu_2(\mu\text{-}CF_3COO)_2(meci)_2]_n$ and $[Cu_2(\mu\text{-}CF_3COO)_2(defu)_2]_n$, the latter having a crystallographically imposed C_2 symmetry. Due to the presence of the ester groups, the methyl cinnamato and the diethyl fumarato derivatives are arranged in infinite chains with oxygen bridges between the dimeric units. Views of the structures of the two ester complexes are shown in Figures 2 and 3, while selections of bond distances and angles are given in Tables 2 and 3. In $[Cu_2(\mu\text{-}CF_3COO)_2(meci)_2]_n$ only one of the two ester groups is involved in the interaction with the copper atom of an adjacent unit through its carbonylic oxygen atom. In the defu derivative both esters interact with the copper atom of an adjacent unit through only one of the two C(=O)OEt fragments, and infinite chains are obtained via two oxygen bridges.

Structurally characterized complexes showing such polynuclear structures are not common in the literature, an example being the copper(I) chloro methyl acrylate derivative $[Cu_2(\mu\text{-}Cl)_2(C_4H_6O_2)]_n$.[11] Due to the presence of a different number of oxygen bridges between the dimeric units, the coordination at copper is different within the two ester derivatives. In the defu complex both copper atoms display a trigonal-pyramidal coordi-

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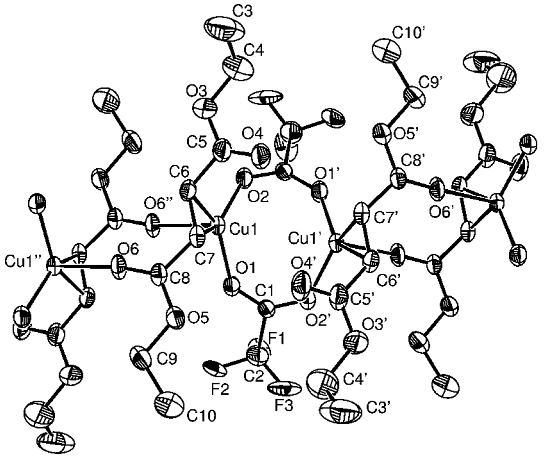

Figure 3. View of a fragment of the molecular structure of $[Cu_2(\mu\text{-}CF_3COO)_2(defu)_2]_n$ with the atomic numbering scheme.

Table 2. Selected Bond Distances (Å) and Angles (deg) in $[Cu_2(\mu\text{-}CF_3COO)_2(meci)_2]_n$[a]

Cu(1)−M(1)	1.919(6)	Cu(2)−M(2)	1.940(6)
Cu(1)−C(15)	2.017(6)	Cu(2)−C(5)	2.066(6)
Cu(1)−C(16)	2.061(5)	Cu(2)−C(6)	2.055(6)
Cu(1)−O(2)	1.969(5)	Cu(2)−O(1)	1.974(5)
Cu(1)−O(3)	1.998(4)	Cu(2)−O(4)	1.986(4)
Cu(1)−O(5′)	2.266(4)	C(13)−O(5)	1.207(7)
C(23)−O(7)	1.207(8)		
O(2)−Cu(1)−O(3)	101.7(2)	O(1)−Cu(2)−O(4)	99.42(19)
O(2)−Cu(1)−M(1)	130.86(18)	O(1)−Cu(2)−M(2)	116.68(17)
O(3)−Cu(1)−M(1)	125.12(18)	O(4)−Cu(2)−M(2)	140.09(17)
O(2)−Cu(1)−O(5′)	91.99(19)	C(13)−O(5)−Cu(1″)	167.5(4)
O(3)−Cu(1)−O(5′)	89.74(17)		
M(1)−Cu(1)−O(5′)	101.82(18)		

[a] M(1) and M(2) are the midpoints of the C(15)−C(16) and C(5)−C(6) double bonds. Symmetry transformations used to generate equivalent atoms: (′) $x + 1/2, -y + 3/2, -z + 2$; (″) $x - 1/2, -y + 3/2, -z + 2$.

Table 3. Selected Bond Distances (Å) and Angles (deg) in $[Cu_2(\mu\text{-}CF_3COO)_2(defu)_2]_n$[a]

Cu(1)−M(1)	1.914(4)	Cu(1)−O(2)	1.975(3)
Cu(1)−C(6)	2.028(4)	Cu(1)−O(6″)	2.303(3)
Cu(1)−C(7)	2.031(4)	C(5)−O(4)	1.208(6)
Cu(1)−O(1)	1.943(3)	C(8)−O(6)	1.195(5)
O(1)−Cu(1)−O(2)	109.54(15)	O(2)−Cu(1)−O(6″)	89.54(13)
O(1)−Cu(1)−M(1)	124.76(18)	M(1)−Cu(1)−O(6″)	102.68(14)
O(2)−Cu(1)−M(1)	124.32(18)	C(8)−O(6)−Cu(1″)	160.8(3)
O(1)−Cu(1)−O(6″)	88.12(13)		

[a] M(1) is the midpoint of the C(6)−C(7) double bond. Symmetry transformation used to generate equivalent atoms: (″) $-x + 1/2, -y + 1/2, -z + 1$.

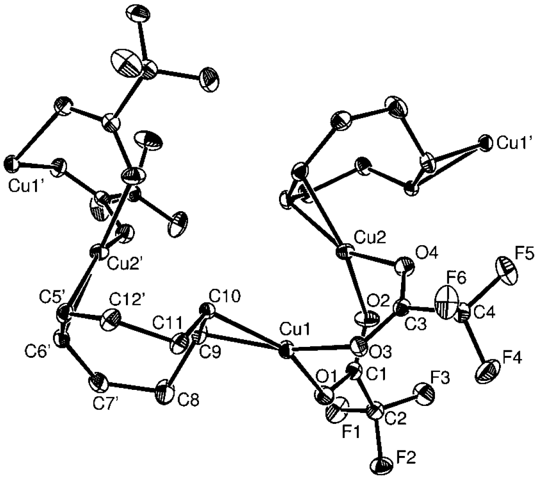

Figure 4. View of a fragment of the molecular structure of $[Cu_2(\mu\text{-}CF_3COO)_2(\mu\text{-}cod)]_n$ with the atomic numbering scheme.

Table 4. Selected Bond Distances (Å) and Angles (deg) in $[Cu_2(\mu\text{-}CF_3COO)_2(\mu\text{-}cod)]_n$[a]

Cu(1)−M(1)	1.902(3)	Cu(2)−M(2)	1.931(3)
Cu(1)−C(9)	2.011(3)	Cu(2)−C(5)	2.047(3)
Cu(1)−C(10)	2.034(3)	Cu(2)−C(6)	2.054(3)
Cu(1)−O(3)	1.969(2)	Cu(2)−O(4)	1.985(2)
Cu(1)−O(1)	1.979(2)	Cu(2)−O(2)	1.993(2)
O(3)−Cu(1)−O(1)	99.16(10)	O(4)−Cu(2)−O(2)	98.29(11)
O(3)−Cu(1)−M(1)	132.52(11)	O(4)−Cu(2)−M(2)	128.82(12)
O(1)−Cu(1)−M(1)	128.17(12)	O(2)−Cu(2)−M(2)	132.25(13)

[a] M(1) and M(2) are the midpoints of the C(9)−C(10) and C(5)−C(6) double bonds.

nation while, in the meci complex, one copper atom (Cu(2)) shows a nearly trigonal-planar arrangement of ligands and the other one (Cu(1)), involved in the carbonylic oxygen bridge, a trigonal-pyramidal coordination. The Cu−$O_{CF_3CO\mathit{O}}$ bond distances do not differ significantly (1.943(3)−1.998(4) Å) for both tri- and tetracoordinated copper atoms in the two complexes, whereas the Cu−$O_{C(=\mathit{O})OR}$ bond distances are 2.266(4) Å in the meci complex and 2.303(3) Å in the defu complex. In both the defu and meci derivatives the C−O bond lengths involving the coordinated carbonyls (C8−O6 (olefin = defu) and C13−O5 (olefin = meci)) are in the range 1.195(5)−1.207(7) Å and do not change significantly with respect to the lengths in the uncoordinated species (C5−O4 (olefin = defu) and C23−O7 (olefin = meci)), as already observed for other copper(I) complexes containing esters.[12] The C=C bond distance of 1.350(6) Å observed in the defu complex is significantly shorter than those observed in $Fe(CO)_3(PPh_3)$(defu) (1.423(6) Å),[13] VCp_2(defu) (1.468(11) Å),[14] and $Pt(PPh_3)_2$(defu) (1.467(5) Å),[15] thus suggesting a lower degree of Cu→olefin π-back-donation in the case of the copper(I) derivative.

The cod derivative, as isolated from the workup of the reaction mixture, shows a 1:1 metal to ligand stoichiometry;[2c] on the other hand, the crystalline compound which slowly separates out by layering heptane on a diluted CH_2Cl_2 solution of $Cu(CF_3COO)$(cod) is in fact $Cu(CF_3COO)(cod)_{0.5}$; i.e., it contains cod and copper in a 0.5:1 molar ratio.[2c] Its molecular structure has been fully elucidated by X-ray diffraction methods.

As in the previously discussed complexes, the structure of $Cu(CF_3COO)(cod)_{0.5}$ (see Figure 4 and Table 4) consists of dimeric units with bridging trifluoroacetates: copper atoms display a nearly trigonal-planar coordination involving two oxygen atoms of two different trifluoroacetate ligands and the midpoint of one of the two C=C bonds of cod. The values of Cu−O and Cu−C bond distances are in the ranges 1.969(2)−1.993(2) and 2.011(3)-2.054(3), respectively, comparable to those

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observed in the other olefinic complexes described in this paper. In the cod derivative polymeric chains of the dimers are obtained through the η^2 interaction of the second double bond of the cod ligand with the copper atom of the adjacent dimer. Although some examples have been reported of dinuclear complexes containing cod bonded to two metal centers through both its double bonds,[15] to the best of our knowledge, $[Cu_2(\mu\text{-}CF_3COO)_2(\mu\text{-cod})]_n$ is the first structurally reported example of a coordination polymer in which the infinite chain is built up through the bidentate cod ligand. It has to be noted that the 1,5-cyclooctadiene rhodium(I) complexes $\{[RhL(cod)]X\}_n$ (L = 1,4-bis(2-pyridyl)butadiyne, 1,4-bis(4-pyridyl)butadiyne, X = BF_4, PF_6; *trans*-1,2-bis(4-pyridyl)ethylene, X = BF_4)[17] form 1-D coordination polymers but the rhodium centers are joined by the ligand L: the diolefin behaves as a bidentate chelating ligand for rhodium and is not involved into the infinite chains.

The isolation of the 2:1 derivative $Cu(CF_3COO)(cod)_{0.5}$ from a solution of the 1:1 complex suggests that a cod exchange equilibrium is attained within the system (eq 3). Due to the presence of fluxionality even at the lowest

$$Cu(CF_3COO)(cod) \leftrightarrows Cu(CF_3COO)(cod)_{0.5} + 0.5(cod) \tag{3}$$

temperature (183 K) we could reach before a solid separated out, a solution of Cu(CF$_3$COO)(cod) in $C_6D_5CD_3$ shows only two broad signals at 5.35 and 1.92 ppm. Nevertheless, the broad resonances of $Cu(CF_3COO)(cod)_{0.5}$ at 4.49 and 1.59 ppm shift to those observed in the spectrum of $Cu(CF_3COO)(cod)$ (see above) on addition of cod.

Olefin/CO Exchange Reactions. To present the results of the thermodynamic study, some comments are required about the nuclearity of the species involved. Reger and Dukes[2c] reported that the molecular weight of the 1:1 adduct between copper(I) trifluoroacetate and cod near the solubility limit of 60 g/kg of benzene (ca. 0.2 M) was intermediate between the values corresponding to a mononuclear and a dinuclear formulation, thus suggesting a monomer/dimer equilibrium. Due to the fact that concentrations as low as 0.01 M have been used in the gas volumetric measurements, we have used a mononuclear formulation for the cod compound in our equilibrium calculations. The same considerations apply to the cyclooctene and defu derivatives, which are described for the first time. On the basis of the molecular weight data reported by Rodesiler and Amma,[2h] a dinuclear formula for the carbonyl derivative is used in our calculations (Scheme 1).

Scheme 1. Carbonylation of $Cu(CF_3COO)$(olefin) Derivatives

$$2Cu(CF_3COO)(\text{olefin}) + 2CO \rightleftarrows Cu_2(CF_3COO)_2(CO)_2 + 2(\text{olefin})$$

$$K = [Cu_2(CF_3COO)_2(CO)_2][\text{olefin}]^2/[Cu(CF_3COO)(\text{olefin})]^2[CO]^2$$

olefin = cod, coe, defu

Data were collected by gas volumetric methods,[18] and the values of the equilibrium constants are reported in Table 5 together with the enthalpy and entropy of the reactions obtained from van't Hoff plots.

Table 5. Equilibrium Constants and Thermodynamic Parameters for the CO/Olefin Exchange Reported in Scheme 1

olefin	K (M^{-1})	ΔH (kJ mol^{-1})	ΔS (J mol^{-1}K^{-1})
cod[a]	12.6 ± 2.4	-46 ± 4	-131 ± 14
coe[b]	$(6.3 \pm 3.2) \times 10^2$	-71 ± 17	-189 ± 57
defu[b]	$(1.1 \pm 0.7) \times 10^7$	-112 ± 20	-248 ± 65

[a] Equilibrium constant at 298.3 K. [b] Equilibrium constant at 293.2 K.

The data in Table 5 show that the carbonyl derivative is the thermodynamically favored compound at 1 atm pressure of CO. A qualitative similar result was obtained by Sterling and Kutal for the Cu[hydridotris(1-pyrazolyl)borate](CO)/norbornadiene system,[8] but no characterization of the olefinic compound was described and no equilibrium constant was reported. The reactions are exothermic, especially in the case of defu, an olefin containing two electron-withdrawing ester groups. The negative values of the reaction entropy are in agreement with the decreasing number of gaseous species on going from left to right in the equation reported in Scheme 1.

It is interesting to observe that, at variance with the other olefinic complexes, the meci derivative is quantitatively carbonylated *in the solid state*. This observation suggests that the stability of the olefin complexes of copper(I) studied decreases in the sequence cod > cyclooctene > defu > meci, the quantitative carbonylation of $Cu(CF_3COO)$(meci) likely being a consequence of the weakening of the Cu−olefin bond due to the aromatic ring/C=C conjugation in methyl cinnamate.

Concluding Remarks

In this paper we have shown that $Cu(CF_3COO)(\text{toluene})_{0.5}$, as obtained from $Cu_2O/CF_3COOH/(CF_3CO)_2O$ in heptane−toluene, is a easy-to handle and readily available starting material for the preparation of mixed carboxylato−olefin derivatives of copper(I).

The copper(I) olefin derivatives contain a dimeric $[Cu_2(\mu\text{-}CF_3COO)_2]$ core; in the case of the ester derivatives (defu and meci), the dimeric units $[Cu_2(\mu\text{-}CF_3COO)_2(\text{olefin})_2]$ are arranged in polymeric chains through coordination of the oxygen atoms of an ester carbonyl group to a copper atom of an adjacent unit. In the case of cod, infinite chains form through olefin bridges, providing the first example of a crystallographically characterized coordination polymer in which the chain is propagated by 1,5-cyclooctadiene.

The high solubility of the compounds in toluene, due to the presence of the fluorinated carboxylate, allowed a study of the CO/olefin exchange reaction (Scheme 1) to be performed in a solvent of low polarity, thus reducing solvation effects by the medium.

The results with a variety of olefinic ligands (cyclooctene, a cyclic monoolefin; 1,5-cyclooctadiene, a cyclic

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diolefin; diethyl fumarate, with two −COOEt groups, and methyl cinnamate, containing a double-bond-conjugated phenyl ring and only one ester functionality) indicate that the electronic properties of the olefin are important in determining the overall stability of the complex. For example, methyl cinnamate is quantitatively displaced by CO, while an equilibrium situation is attained in the case of the other olefinic complexes.

From a more general point of view, the reported study of the CO/olefin exchange reaction with copper(I) trifluoroacetate, a $3d^{10}$ system, demonstrates that (i) at variance with the $5d^{10}$ system AuCl(CO), the carbonyl derivative $Cu(CF_3COO)(CO)$ is more stable than the corresponding olefin compound $Cu(CF_3COO)$(olefin); (ii) the stability of the $Cu(CF_3COO)$(olefin) compound decreases on increasing the electron-withdrawing power of the substituents on the olefin, at variance with the vanadium(II) derivative, $VCp_2(CO)$, a typical $3d^3$ transition-metal organometallic compound, which does not coordinate olefins such as cyclooctene or norbornene.[3] These observations suggest that a horizontal and a vertical trend is operating as far as the relative stability of carbonyl and olefin metal complexes are concerned. Moreover, the position of the equilibrium between an olefin and a carbonyl derivative seems to depend on the $M \rightarrow CO$ back-donation, which increases in the sequence Au(I) < Cu(I) < V(II).

Experimental Section

General Considerations. Unless otherwise stated, all of the operations were carried out under an atmosphere of prepurified argon. Solvents were dried by conventional methods prior to use. Diethyl fumarate (defu, Fluka), 1,5-cyclooctadiene (Aldrich), and *cis*-cyclooctene (Aldrich) were distilled under reduced pressure and stored at ca. −30 °C; methyl cinnamate (Aldrich) was used as received. IR spectra were recorded on a FT-1725X instrument as Nujol or polychlorotrifluoroethylene (PCTFE) mulls prepared under rigorous exclusion of moisture and air. NMR spectra (^{1}H, 200 MHz; ^{13}C, 50.31 MHz, with TMS as reference; ^{19}F, 188 MHz with C_6F_6 as reference) were recorded with a Varian Gemini 200BB spectrometer. The gas volumetric measurements were performed with the apparatus described by Calderazzo and Cotton.[18]

Preparation of $Cu(CF_3COO)$(coe). A solution of $Cu(CF_3COO)(toluene)_{0.5}$ (1.99 g, 9.0 mmol) in toluene (50 mL) was added to *cis*-cyclooctene (1.18 g, 10.7 mmol) at room temperature. After 15 h of stirring, the solution was partially evaporated in vacuo and heptane was added, affording a colorless solid which was recovered by filtration, washed with heptane (2 × 5 mL), and dried in vacuo to give $Cu(CF_3CO_2)$(coe) (1.66 g; 64% yield) as an air-sensitive solid. Anal. Found: C, 41.6; H, 4.9. Calcd for $C_{10}H_{14}CuF_3O_2$: C, 41.9; H, 4.9. IR (Nujol): $\tilde{\nu}$/cm^{-1} 3141 w, 3095 w, 1693 vs, 1644 m, 1463 vs, 1210 vs, 1175 s, 1148 vs, 991 w, 852 m, 847 m, 729 s. ^{1}H NMR (C_6D_6): δ 4.66 (2H), 1.90 (4H), 1.15 (8H). ^{19}F NMR (C_6D_6): δ −73.8.

Preparation of $Cu(CF_3COO)$(meci). A solution of *trans*-PhCH=CHCO$_2$Me (1.28 g, 7.9 mmol) in 50 mL of toluene (50 mL) was added to solid $Cu(CF_3COO)(toluene)_{0.5}$ (1.61 g, 7.2 mmol). After 15 h of stirring at room temperature, the volume of the solution was reduced to ca. 10 mL. Addition of heptane (70 mL) caused the separation of a pale yellow solid, which was recovered by filtration, washed with heptane (2 × 5 mL), and dried in vacuo at room temperature, affording 2.0 g (77% yield) of a pale yellow solid that is very sensitive to air. Anal. Found: C, 42.1; H, 3.2. Calcd for $C_{12}H_{10}CuF_3O_4$: C, 42.3; H, 3.0. IR (Nujol): $\tilde{\nu}$/cm^{-1} 3087 w, 1690 vs, 1666 m, 1632 s, 1598 m, 1581 m, 1537 s, 1491 m, 1460 vs, 1451 vs, 1436 s, 1333 s, 1313 s, 1292 m, 1267 m, 1201 vs, 1147 vs, 1074 m, 1009 m, 984 mw, 976 mw, 931 m, 869 m, 849 m, 843 m, 792 m, 769 s, 725 s, 691 s, 614 w, 577 mw, 525 m. ^{1}H NMR (C_6D_6): δ 7.70 (1H, d, J = 15.4 Hz), 7.15−6.92 (5H, m), 6.34 (1H, d, J = 15.4 Hz), 3.48 (3H, s). ^{19}F NMR (C_6D_6): δ −73.7.

Carbonylation Reaction of $Cu(CF_3COO)$(meci). A thin-walled sealed glass container containing *solid* $Cu(CF_3COO)$(meci) (0.257 g, 0.76 mmol) was introduced into an Erlenmeyer flask equipped with a lateral stopcock. The system was connected to a gas volumetric buret thermostated at 308 K and filled with CO. The container was broken by mechanical stirring, and absorption of gas up to a CO$_{\text{absorbed}}$/Cu molar ratio of 0.99 was observed within 10 min.

Preparation of $Cu(CF_3COO)$(defu). A solution of $Cu(CF_3COO)(toluene)_{0.5}$ (2.00 g, 9 mmol) in toluene (50 mL) was added to defu (2.63 g, 15.2 mmol). A pale yellow solid formed. After 15 h of stirring at room temperature, the microcrystalline solid was recovered by filtration, washed with toluene (2 × 3 mL), and dried in vacuo at room temperature, affording 2.64 g (84% yield) of $Cu(CF_3COO)$(defu) as a solid stable in air for hours in the solid state. Anal. Found: C, 33.5; H, 3.4. Calcd for $C_{10}H_{12}CuF_3O_6$: C, 33.4; H, 3.5. IR (Nujol): $\tilde{\nu}$/cm^{-1} 3045 m, 1727 vs, 1704 vs, 1665 vs, 1540 s, 1462 s, 1311 s, 1208 s, 1152 s, 1029 s, 847 m, 789 mw, 725 s, 664 m. ^{1}H NMR (C_6D_6): δ 6.87 (2H, s), 3.88 (4H, q, J = 7 Hz), 0.87 (6H, t, J = 7 Hz). ^{19}F NMR (C_6D_6): δ −73.5.

Preparation of $Cu(CF_3COO)$(cod). The preparation of this compound was performed according to a modification of the procedure reported in the literature.[2c] A solution of $Cu(CF_3COO)(toluene)_{0.5}$ (1.93 g, 8.7 mmol) in toluene (40 mL) was added to 1,5-cod (1.85 g, 17.8 mmol). After 15 h of stirring at room temperature, the volume of the solution was reduced to ca. 15 mL. After addition of heptane (50 mL), the solid was recovered by filtration, washed with heptane (2 × 10 mL), and dried in vacuo at room temperature, affording 1.98 g (80% yield) of $Cu(CF_3COO)$(cod) as a colorless solid sensitive to air. Anal. Found: C, 42.0; H, 4.2. Calcd for $C_{10}H_{12}CuF_3O_2$: C, 42.2; H, 4.3. IR (Nujol): $\tilde{\nu}$/cm^{-1} 3129 w, 3092 w, 1811 w, 1686 vs, 1619 m, 1580 m, 1543 m, 1481 m, 1463 vs, 1452 vs, 1206 vs, 1141 vs, 998 s, 842 s, 789 s, 741 s, 724 vs, 674 m, 655 m, 523 mw. ^{1}H NMR (C_6D_6): δ 5.35 (4H), 1.92 (8H). ^{13}C NMR (C_6D_6): δ 163.6 (q, J_{C-F} = 37 Hz), 117.5 (q, J_{C-F} = 288 Hz), 115.6, 28.1. ^{19}F NMR: δ −74.6.

Preparation of $Cu_2(CF_3COO)_2$(cod). A solution of $Cu(CF_3COO)$(cod) (0.53 g, 1.9 mmol) in dichloromethane (10 mL) was layered with heptane (30 mL). Single crystals of $[Cu_2(\mu\text{-}CF_3COO)_2(\mu\text{-cod})]_n$ (0.32 g, 75% yield) were obtained within 5 days, which were recovered, briefly dried in vacuo at room temperature, and used for the X-ray structural study. Anal. Found: C, 30.8; H, 2.2. Calcd for $C_6H_6CuF_3O_2$: C, 31.2; H, 2.6. IR (neat solid): $\tilde{\nu}$/cm^{-1} 3093 w, 2923 w, 1782 w, 1673 vs, 1605 m, 1530 w, 1517 w, 1481 w, 1462 m, 1428 w, 1363 w, 1201 vs, 1141 vs, 1080 m, 1008 m, 1000 m, 990 m, 906 w, 850 s, 819 w, 789 s, 727 vs. ^{1}H NMR (C_6D_6): δ 4.49 (4H), 1.59 (8H).

X-ray Structure Determination of $[Cu(\mu\text{-}CF_3COO)(\text{coe})]_2$, $[Cu_2(\mu\text{-}CF_3COO)_2(\text{meci})_2]_n$, $[Cu_2(\mu\text{-}CF_3COO)_2(\text{defu})_2]_n$, and $[Cu_2(\mu\text{-}CF_3COO)_2(\mu\text{-cod})]_n$. Crystals of $[Cu(\mu\text{-}CF_3COO)(\text{coe})]_2$, $[Cu_2(\mu\text{-}CF_3COO)_2(\text{meci})_2]_n$, and $[Cu_2(\mu\text{-}CF_3COO)_2(\text{defu})_2]_n$ were grown from toluene/heptane. A mixture of CH_2Cl_2 and heptane was used to grow crystals of $[Cu_2(\mu\text{-}CF_3COO)_2(\mu\text{-cod})]_n$. Data were collected on Bruker AXS SMART 1000 ($[Cu_2(\mu\text{-}CF_3COO)_2(\text{defu})_2]_n$ and $[Cu(\mu\text{-}CF_3COO)(\text{coe})]_2$; Mo K$\alpha$ radiation, λ = 0.710 73 Å) and on a Enraf-Nonius CAD 4 ($[Cu_2(\mu\text{-}CF_3COO)_2(\text{cod})]_n$ and $[Cu_2(\mu\text{-}CF_3COO)_2(\text{meci})_2]_n$; Cu K$\alpha$ radiation, λ = 1.541 83 Å) single-crystal diffractometers. Details of the X-ray data collections are collected in Table 6. The structures were solved by Patterson and direct methods with SHELXS-97 and refined against F^2 with SHELXL-97,[19]

Table 6. Crystallographic Data for the Compounds $[Cu(\mu\text{-}CF_3COO)(coe)]_2$, $[Cu_2(\mu\text{-}CF_3COO)_2(meci)_2]_n$, $[Cu_2(\mu\text{-}CF_3COO)_2(defu)_2]_n$, and $[Cu_2(\mu\text{-}CF_3COO)_2(\mu\text{-}cod)]_n$

	$[Cu(\mu\text{-}CF_3COO)\text{-}(coe)]_2$	$[Cu_2(\mu\text{-}CF_3COO)_2\text{-}(meci)_2]_n$	$[Cu_2(\mu\text{-}CF_3COO)_2\text{-}(defu)_2]_n$	$[Cu_2(\mu\text{-}CF_3COO)_2\text{-}(\mu\text{-}cod)]_n$
formula	$Cu_2F_6O_4C_{20}H_{28}$	$Cu_2F_6O_8C_{24}H_{20}$	$CuF_3O_6C_{10}H_{12}$	$Cu_2F_6O_4C_{12}H_{12}$
formula wt	573.50	677.48	348.74	461.30
cryst syst	orthorhombic	orthorhombic	monoclinic	monoclinic
space group	*Pcab*	$P2_12_12_1$	*C*2/*c*	$P2_1/n$
a, Å	10.284(3)	16.142(5)	13.138(3)	11.606(5)
b, Å	21.386(5)	16.712(5)	15.135(5)	11.067(5)
c, Å	22.061(5)	9.861(3)	15.729(5)	11.864(5)
β, deg			112.78(5)	94.89(5)
V, Å^3	4852(2)	2660(1)	2884(2)	1518(1)
Z; D_{calcd}, g cm^{-3}	8; 1.570	4; 1.692	8; 1.607	4; 2.018
F(000)	2336	1360	1408	912
μ, cm^{-1}	18.21	27.86	15.68	42.76
temp, K	293(2)	233(2)	293(2)	173(2)
no. of rflns collected	23577	2249	8439	3014
no. of unique rflns	4267 ($R_{int} = 0.067$)	2249 ($R_{int} = 0.000$)	3189 ($R_{int} = 0.027$)	2872 ($R_{int} = 0.037$)
no. of rflns obsd ($I > 2\sigma(I)$)	1862	1873	1597	2537
no. of params	307	417	235	217
final *R* indices ($I > 2\sigma(I)$)[a]	R1 = 0.0466 wR2 = 0.1070	R1 = 0.0356 wR2 = 0.0876	R1 = 0.0436 wR2 = 0.1300	R1 = 0.0338 wR2 = 0.0895
final R indices (all data)[a]	R1 = 0.1197 wR2 = 0.1251	R1 = 0.0470 wR2 = 0.0949	R1 = 0.0905 wR2 = 0.1543	R1 = 0.0401 wR2 = 0.0975

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

with anisotropic thermal parameters for all non-hydrogen atoms, excluding the fluorine atoms of the trifluoroacetate groups in $[Cu(\mu\text{-}CF_3COO)(coe)]_2$. The fluorine atoms of the trifluoroacetate ions are disordered in three positions in $[Cu(\mu\text{-}CF_3COO)(coe)]_2$ and $[Cu_2(\mu\text{-}CF_3COO)_2(defu)_2]_n$ and in two positions in $[Cu_2(\mu\text{-}CF_3COO)_2(meci)_2]_n$. Idealized geometries were assigned to the hydrogen atoms.

Carbonylation Reactions of $Cu(CF_3COO)$(olefin). (a) olefin = defu. A solution of defu in toluene (50 mL) and a thin-walled sealed glass container containing the copper(I) derivative were introduced into an Erlenmeyer flask equipped with a lateral stopcock. The system was connected to a gas volumetric buret and saturated with CO at atmospheric pressure at the temperature of the experiment. The container was then broken by mechanical stirring, and the absorption of gas was measured. The concentration of CO in toluene is assumed to be 7.5×10^{-3} M in the range of temperature studied.[3] The temperature of the experiment, the starting molar concentrations of $Cu(CF_3COO)$(defu), $[Cu(CF_3COO)(defu)]_i$, and defu, $[defu]_i$, and the measured $CO_{absorbed}$/Cu molar ratios (CO/Cu) at equilibrium, respectively, are

$$T = 283.5\text{ K}, [Cu(CF_3COO)(defu)]_i = 0.011; [defu]_i = 0.33; CO/Cu = 0.94$$

$$T = 293.2\text{ K}, [Cu(CF_3COO)\ (defu)]_i = 0.010; [defu]_i = 0.19; CO/Cu = 0.94$$

$$T = 303.3\text{ K}, [Cu(CF_3COO)(defu)]_i = 0.011; [defu]_i = 0.21; CO/Cu = 0.87$$

$$T = 313.1\text{ K}, [Cu(CF_3COO)(defu)]_i = 0.011; [defu]_i = 0.20; CO/Cu = 0.83$$

$$T = 323.0\text{ K}, [Cu(CF_3COO)(defu)]_i = 0.009; [defu]_i = 0.05; CO/Cu = 0.80$$

(b) olefin = cod, coe. The experimental procedure is substantially the same as in (a), the main difference being the absence of added olefin, due to the fact that the equilibrium was not as shifted to the right as in the case of defu. The temperature of the experiment, the starting molar concentrations of $Cu(CF_3COO)$(olefin), $[Cu(CF_3COO)(olefin)]_i$, and the measured $CO_{absorbed}$/Cu molar ratios (CO/Cu) at equilibrium, respectively, are, for olefin = cod

$$T = 278.6\text{ K}, [Cu(CF_3COO)(cod)]_i = 0.015; CO/Cu = 0.48$$

$$T = 288.5\text{ K}, [Cu(CF_3COO)(cod)]_i = 0.012; CO/Cu = 0.45$$

$$T = 298.3\text{ K}, [Cu(CF_3COO)(cod)]_i = 0.013; CO/Cu = 0.35$$

$$T = 308.1\text{ K}, [Cu(CF_3COO)(cod)]_i = 0.014; CO/Cu = 0.33$$

$$T = 317.2\text{ K}, [Cu(CF_3COO)(cod)]_i = 0.017; CO/Cu = 0.25$$

and for olefin = coe

$$T = 283.5\text{ K}, [Cu(CF_3COO)(coe)]_i = 0.006; CO/Cu = 0.91$$

$$T = 293.2\text{ K}, [Cu(CF_3COO)(coe)]_i = 0.011; CO/Cu = 0.75$$

$$T = 303.3\text{ K}, [Cu(CF_3COO)(coe)]_i = 0.009; CO/Cu = 0.73$$

$$T = 313.1\text{ K}, [Cu(CF_3COO)(coe)]_i = 0.008; CO/Cu = 0.74$$

$$T = 322.8\text{ K}, [Cu(CF_3COO)(coe)]_i = 0.008; CO/Cu = 0.55$$

The gas volumetric experiments were repeated twice, thus giving consistent $CO_{absorbed}$/Cu molar ratios.

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Supporting Information Available: A full table of equilibrium data at different temperatures (including van't Hoff plots) and X-ray crystallographic data for [Cu(μ-CF$_3$COO)(coe)]$_2$, [Cu$_2$(μ-CF$_3$COO)$_2$(meci)$_2$]$_n$, [Cu$_2$(μ-CF$_3$COO)$_2$(defu)$_2$]$_n$, and [Cu$_2$(μ-CF$_3$COO)$_2$(μ-cod)]$_n$; X-ray data are also available in electronic form as CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

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