Synthesis, Characterization, and Olefin/CO Exchange Reactions of Copper(I) Derivatives Containing Bidentate Oxygen Ligands

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New hexafluoroacetylacetonate (hfacac) and trifluoroacetato olefin complexes of copper(I) of the general formulas Cu(hfacac)(olefin) and $Cu(CF_3COO)$(olefin) have been prepared from Cu_2O/hfacacH/olefin or $Cu(CF_3COO)(toluene)_{0.5}$/olefin systems. The structures of [Cu(hfacac)(coe)], [Cu(hfacac)(van)], $[Cu(\mu\text{-}CF_3COO)(tbve)]_n$, and $[Cu(\mu\text{-}CF_3COO)(van)]_2\cdot C_7H_8$ have been determined by X-ray diffraction methods, where coe = cyclooctene, van = 4-vinylanisole, and tbve = *tert*-butyl vinyl ether. In the solid state, the 4-vinylanisole/trifluoroacetate complex $[Cu(CF_3COO)(van)]_2$ is dimeric with two carboxylato groups symmetrically bridging two copper atoms, while the *tert*-butyl vinyl ether derivative $[Cu(\mu\text{-}CF_3COO)(tbve)]_n$ is polymeric with single $[CF_3COO]^-$ bridges between adjacent copper atoms. Olefin hfacac complexes are monomeric, and considering the two oxygen atoms and the midpoint of the double bond of the coordinated olefin, the copper atom lies in a nearly trigonal-planar environment. The carbonylation reactions of $Cu(CF_3COO)$(olefin), (olefin = tbve, van; $2Cu(CF_3COO)(olefin) + 2CO \leftrightarrows [Cu(CF_3COO)(CO)]_2 + 2(olefin)$) and of Cu(hfacac)(olefin) (olefin = coe, 1,5-cyclooctadiene (cod), norbornene (nbe), van; $Cu(hfacac)(olefin) + CO \leftrightarrows Cu(hfacac)(CO) + olefin$) have been studied gas volumetrically, and the equilibrium constants for the displacement of the coordinated olefin by carbon monoxide have been determined at different temperatures. Some hypotheses on the copper−olefin bond have been formulated on the basis of structural, thermodynamic and spectroscopic (^{13}C NMR) data.

Introduction

In the general context of CO/olefin competition thermodynamics[1] (eq 1) we have recently investigated the effect of the olefin ligand on the CO/olefin exchange reaction of organometallic compounds containing early or late transition elements, namely $VCp_2(CO)$[1a] and $Cu(CF_3COO)(CO)$.[1b] The choice of the olefin was somewhat

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

limited by the fact that vanadocene does not coordinate olefins containing electron-releasing substituents[1a] and by the difficulties encountered in the preparation and the purification of copper(I) trifluoroacetato derivatives bearing electron-rich olefins, such as vinyl ethers and alkoxystyrenes.

In an effort to show how the electronic character of the coordinated olefin affects the stability of the olefin derivative Cu(L)(olefin) with respect to the carbonyl compound Cu(L)(CO), attempts have been made to obtain trifluoroacetato copper(I) complexes of electron-rich olefins. Moreover, to extend our knowledge about the thermodynamics of CO/olefin exchange equilibria, we have focused our attention on copper(I) hexafluoroacetylacetonate, Cu(hfacac), due to its ability to bind both carbon monoxide and alkenes.[2] Lewis base stabilized copper(I) β-diketonates of the general formula Cu(β-diketonate)(L) (L = alkenes, alkynes, phosphines) were extensively studied in the past as precursors for copper vapor deposition.[2−4]

In this paper we report the synthesis and full characterization of two new trifluoroacetato derivatives of copper(I) bearing electron-rich olefins, $[Cu(\mu\text{-}CF_3COO)(tbve)]_n$ and $[Cu(\mu\text{-}CF_3COO)(van)]_2$, and the thermodynamic parameters of their carbonylation reactions. The study of CO/olefin exchange equilibria has been extended to the copper(I) hexafluoroacetylacetonate sys-

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[1] (a) Calderazzo, F.; Guelfi, M.; Pampaloni, G. *Organometallics* **2004**, *23*, 1519. (b) Pampaloni, G.; Peloso, R.; Graiff, C.; Tiripicchio, A. *Organometallics* **2005**, *24*, 819.

[2] Doyle, G.; Eriksen, K. A.; Van Engen, D. *Organometallics* **1985**, *4*, 830.

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[4] (a) Chi, K.-M.; Hou, H.-C.; Hung, P.-T.; Peng, S.-M.; Lee, G.-H. *Organometallics* **1995**, *14*, 2641. (b) Rozenberg, G. G.; Steinke, J. H. G.; Gelbrich, T.; Hursthouse, M. B. *Organometallics* **2001**, *20*, 400. (c) Chen, T.-Y.; Vaissermann, J.; Doppelt, P. *Inorg. Chem.* **2001**, 40, 616. (d) Krisyuk, V. V.; Turgambaeva, A. E.; Rhee, S.-W. *Polyhedron* **2004**, *23*, 809. Herberhold, M.; Milius, W.; Akkus, N. *Z. Naturforsch., B* **2004**, *59*, 843.

10.1021/om050416r CCC: $30.25

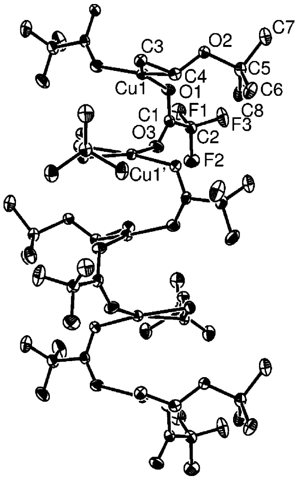

Figure 1. View of a fragment of the molecular structure of $[Cu(\mu\text{-}CF_3COO)(tbve)]_n$ with the atomic numbering scheme. The chain develops along the crystallographic 4_1 axis.

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

Cu(1)−O(1)	1.972(3)	Cu(1)−M(1)	1.967(5)
Cu(1)−O(3′)	2.020(3)	C(1)−O(1)	1.251(5)
Cu(1)−C(3)	2.001(4)	C(1)−O(3)	1.224(5)
Cu(1)−C(4)	2.159(3)	C(3)−C(4)	1.363(5)
O(1)−Cu(1)−O(3′)	95.10(13)	O(3′)-Cu(1)−M(1)	133.67(14)
O(1)−Cu(1)−M(1)	131.23(14)		

[a] M(1) is the midpoint of the C(3)−C(4) double bond. Symmetry transformations used to generate equivalent atoms: (′) $1 - y + 1$, $x - 1$, $z + 1/4$; (″) $y + 1$, $-x + 1$, $z - 1/4$.

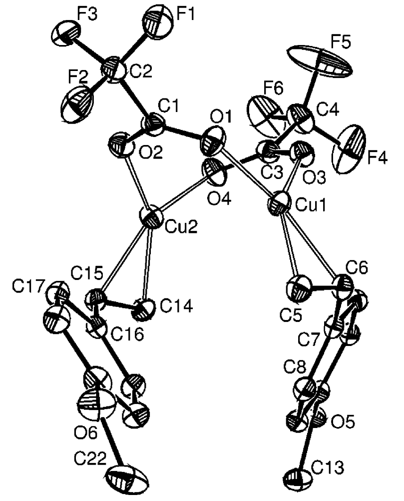

Figure 2. View of the molecular structure of $[Cu(\mu\text{-}CF_3COO)(van)]_2 \cdot C_7H_8$ with the atomic numbering scheme.

tem, and the parameters of the carbonylation equilibrium have been determined for [Cu(hfacac)(L)] (L = coe, nbe, van, cod). Moreover, the crystal structures of [Cu(hfacac)(coe)] and [Cu(hfacac)(van)] have been determined.

Results and Discussion

Synthesis and Structural Studies. Trifluoroacetato olefin complexes of copper(I) have been prepared from $Cu(CF_3COO)(toluene)_{0.5}$[5] by ligand exchange in toluene (eq 2). The olefin derivatives, soluble in aromatic

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

$$olefin = tbve, van, nbe$$

or chlorinated hydrocarbons, have been characterized (IR and NMR spectra and X-ray crystallography) as containing η^2-ligated olefins. Some difficulties have been encountered in the isolation of $Cu(CF_3COO)(tbve)$, due to its heat and light sensitivity. Although no particular conditions must be adopted during the preparation, the isolated complex darkens in the solid state with formation of unidentified compounds; for this reason, it has to be stored in the dark and at low temperature. No special precautions are necessary for the norbornene derivative, while storing of $Cu(CF_3COO)(van)$ in a refrigerator is highly recommended.

The structures of $[Cu(\mu\text{-}CF_3COO)(tbve)]_n$ and $[Cu(\mu\text{-}CF_3COO)(van)]_2 \cdot C_7H_8$ have been fully elucidated by X-ray crystallography. The structure of $[Cu(\mu\text{-}CF_3COO)(tbve)]_n$ is shown in Figure 1 together with the atomic numbering scheme; a selection of bond distances and angles is reported in Table 1. The complex is polymeric, with the trifluoroacetato ligand bridging two adjacent copper atoms (the Cu···Cu separation is 3.075(2) Å). On consideration of the two oxygen atoms of two $[CF_3COO]^-$ bridges and the midpoint of the C=C double bond of the coordinated olefin, the coordination at copper can be considered to be nearly trigonal planar. The copper atom is asymmetrically bound to the olefin double bond, the Cu−C bond distances being 2.001(4) and 2.159(3) Å.

The structure of $[Cu(\mu\text{-}CF_3COO)(tbve)]_n$ adds to the restricted family of structurally characterized vinyl ether complexes of transition elements[6] and represents the first example of a transition-metal complex of tbve[7] characterized by X-ray diffractometry. Moreover, at variance with most of the structurally characterized polymeric copper(I) trifluoroacetato compounds, which contain two bridging trifluoroacetates,[1b] the polymeric chain in $[Cu(\mu\text{-}CF_3COO)(tbve)]_n$ is obtained through single trifluoroacetate bridges between adjacent copper atoms. It is noteworthy that the polymeric chain runs around the crystallographic screw axis 4_1.

The copper(I) complex of van, $[Cu(\mu\text{-}CF_3COO)(van)]_2 \cdot C_7H_8$, crystallizes with one molecule of disordered toluene per dimeric unit. The molecular structure of $[Cu(\mu\text{-}CF_3COO)(van)]_2 \cdot C_7H_8$ is shown in Figure 2; the most significant bond distances and angles are listed in Table 2. The complex is dimeric, the two carboxylate ligands symmetrically bridging the two copper atoms to form an eight-membered ring. The copper···copper separation is 3.100(2) Å, slightly longer than that found

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(5) Belli Dell'Amico, D.; Alessio, R.; Calderazzo, F.; Della Pina, F.; Englert, U.; Pampaloni, G.; Passarelli, V. *Dalton Trans.* **2000**, 2067.

(6) Chang, T. C. T.; Foxman, B. M.; Rosenblum, M.; Stockman, C. *J. Am. Chem. Soc.* **1981**, *103*, 7361. Planas, J. G.; Marumo, T.; Ichikawa, Y.; Hirano, M.; Komiya, S. *Dalton Trans.* **2000**, 2613. Elder, R. C.; Pesa, F. *Acta Crystallogr., Sect. B* **1978**, *34*, 268. Sartori, F.; Leoni, L. *Acta Crystallogr., Sect. B* **1976**, *32,* 145.

(7) Only a few examples of tbve derivatives have been reported in the literature, namely *trans*-$PtCl_2L(tbve)$ (L = py, *p*-toluidine: Lazzaroni, R.; Uccello-Barretta, G.; Bertozzi, S.; Salvadori, P. *J. Organomet. Chem.* **1985**, *297*, 117. Lazzaroni, R.; Mann, B. E. *J. Organomet. Chem.* **1979**, *164*, 79), and $[MCl_2(tbve)]_2$ (M = Pt, Pd: Wakatsuki, Y.; Nozakura, S.; Murahashi, S. *Bull. Chem. Soc. Jpn.* **1972**, *45*, 3426. Wakatsuki, Y.; Nozakura, S.; Murahashi, S. *Bull. Chem. Soc. Jpn.* **1971**, *44*, 786).

Table 2. Selected Bond Distances (Å) and Angles (deg) in $[Cu(\mu\text{-}CF_3COO)(van)]_2 \cdot C_7H_8$[a]

Cu(1)−O(1)	1.961(2)	Cu(1)−C(5)	2.010(4)
Cu(1)−O(3)	1.977(3)	Cu(1)−C(6)	2.033(3)
Cu(2)−O(2)	1.984(3)	Cu(1)−M(1)	1.904(4)
Cu(2)−O(4)	1.991(3)	C(5)−C(6)	1.358(5)
C(1)−O(1)	1.246(4)	Cu(2)−C(14)	2.021(3)
C(1)−O(2)	1.242(4)	Cu(2)−C(15)	2.046(3)
C(3)−O(3)	1.245(4)	Cu(2)−M(2)	1.913(4)
C(3)−O(4)	1.233(4)	C(14)−C(15)	1.382(5)
O(1)−Cu(1)−O(3)	103.60(12)	O(2)−Cu(2)−O(4)	103.40(11)
M(1)−Cu(1)−O(1)	129.02(13)	M(2)-Cu(2)−O(2)	128.31(13)
M(1)−Cu(1)−O(3)	126.89(12)	M(2)-Cu(2)−O(4)	128.14(13)

[a] M(1) and M(2) are the midpoints of the C(5)−C(6) and C(14)−C(15) double bonds.

in $[Cu(\mu\text{-}CF_3COO)(coe)]_2$ (2.898(1) Å).[1b] On consideration of the two oxygen atoms of the $[CF_3COO]^-$ bridges and the midpoint of the olefin double bond, the coordination at copper can be considered as nearly trigonal planar. The Cu−C bond distances are in the range 2.010(4)–2.046(3) Å. The two ethereal oxygen atoms O5 and O6 are involved in weak interactions with the copper atoms of adjacent dimers (Cu2⋯O5 = 2.774(3) and Cu1⋯O6 = 2.881(3) Å), forming polymeric chains along the crystallographic *b* axis.

Hexafluoroacetylacetonato derivatives of copper(I) have been prepared by reaction of Cu_2O with hexafluoroacetylacetone in dichloromethane or THF in the presence of olefin or CO (eq 3).

$$Cu_2O + 2hfacacH + 2(olefin) \rightarrow 2Cu(hfacac)(olefin) + 2H_2O \quad (3)$$

$$L = \text{nbe, coe, van, cod}$$

Due to the tendency to disproportionation in the presence of basic solvents typical of copper(I) derivatives[8] (2Cu(I) → Cu + Cu(II)), and in particular of hexafluoroacetylacetonato derivatives,[2] the procedure described by Doyle and co-workers[2] has been modified in some cases and dichloromethane was used instead of THF. Nevertheless, some disproportionation (formation of a pale green solution and of a reddish solid) was always observed, the amount of copper(II) being almost negligible in the case of nbe and coe. On the other hand, a separation procedure of Cu(hfacac)(van) from the copper(II) complex $Cu(hfacac)_2(van)$, derived from the disproportionation reaction, had to be devised (see Experimental Section). The compound $Cu(hfacac)_2(van)$ was identified as containing an O-coordinated van ligand by analytical and infrared data (the $O-CH_3$ stretching vibration shifts from 1248 to 1163 cm^{-1} on complexation).

We have observed that the copper(I) disproportionation occurs to a large extent in THF during the preparation of Cu(hfacac)(cod),[2] with formation of $Cu(hfacac)_2(THF)_2$ (vide infra). Furthermore, we could not prepare tbve, diethyl fumarate, or methyl cinnamate derivatives, due to the fact that disproportionation of copper(I) was the main reaction even in hydrocarbon solutions. These reactions were not investigated further.

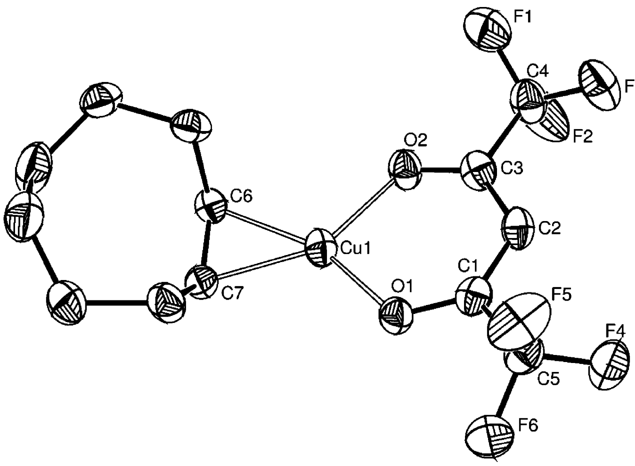

Figure 3. View of the molecular structure of [Cu(hfacac)(coe)] with the atomic numbering scheme.

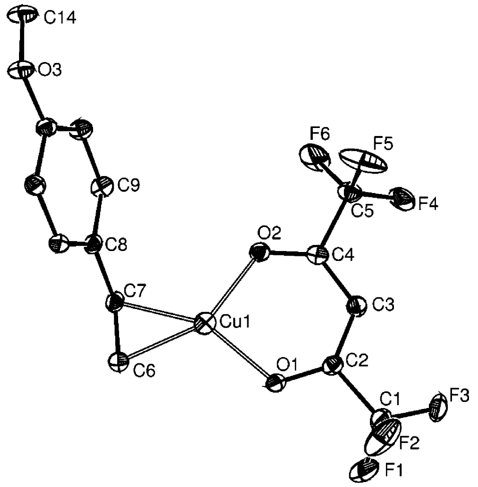

Figure 4. View of the molecular structure of [Cu(hfacac)(van)] with the atomic numbering scheme.

Table 3. Selected Bond Distances (Å) and Angles (deg) in [Cu(hfacac)(coe)][a]

Cu(1)−C(6)	2.017(4)	C(6)−C(7)	1.363(6)
Cu(1)−C(7)	2.013(4)	Cu(1)−O(2)	1.956(3)
Cu(1)-M(1)	1.904(4)	Cu(1)−O(1)	1.961(3)
O(2)−Cu(1)−O(1)	94.19(13)	O(2)−Cu(1)−M(1)	130.11(16)
O(1)−Cu(1)−M(1)	134.25(15)		

[a] M(1) is the midpoint of the C(6)−C(7) double bond.

The compounds Cu(hfacac)(L) (L = coe, nbe, van) have been characterized by single-crystal X-ray diffraction; due to the poor quality of the crystals of Cu(hfacac)(nbe), only the structures of [Cu(hfacac)(coe)] and of [Cu(hfacac)(van)] are described here, the structure of the norbornene derivative being substantially similar as far as coordination to copper is concerned.

Hexafluoroacetylacetonato olefin derivatives of copper(I) are monomeric compounds, with the copper atom lying in a nearly trigonal planar environment. The structures of [Cu(hfacac)(coe)] and [Cu(hfacac)(van)] are shown in Figures 3 and 4, and the most important bond distances and angles are listed in Tables 3 and 4, respectively. In [Cu(hfacac)(van)], two centrosymmetrically related molecules are joined as dimers through weak interactions between the ethereal oxygen atoms and the copper atoms (Cu1⋯O3 = 2.658(3) Å) and through face-to-face $\pi-\pi$ stacking (approximately 3.7

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[8] (a) Endicott, J. F.; Taube, H. *Inorg. Chem.* **1965**, *4*, 437. (b) Caulton, K. G.; Davies, G.; Holt, E. M. *Polyhedron* **1990**, *9*, 2319. (c) Jardine, F. H. *Adv. Inorg. Chem. Radiochem.* **1975**, *17*, 115. (d) Sloan, W. H. *J. Am. Chem. Soc.* **1910**, *32*, 972 (cited in ref 8c). (e) Anders, U.; Plambeck, J. A. *Can. J. Chem.* **1969**, *47*, 3055.

Table 4. Selected Bond Distances (Å) and Angles (deg) in [Cu(hfacac)(van)][a]

Cu(1)–C(6)	2.008(4)	C(6)–C(7)	1.379(5)
Cu(1)–C(7)	2.024(3)	Cu(1)–O(1)	1.975(3)
Cu(1)-M(1)	1.894(3)	Cu(1)–O(2)	1.970(3)
O(2)–Cu(1)–O(1)	94.06(12)	O(2)–Cu(1)–M(1)	130.61(13)
O(1)–Cu(1)–M(1)	134.49(13)		

[a] M(1) is the midpoint of the C(6)–C(7) double bond.

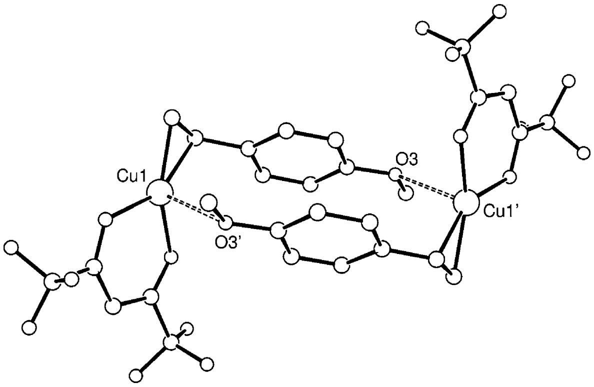

Figure 5. Schematic view of the centrosymmetric [Cu(hfacac)(van)]$_2$ dimeric units. Dashed lines indicate intermolecular contacts between copper and ethereal oxygen in adjacent molecules.

Å) between the aromatic rings of the olefins (see Figure 5). The Cu–C bond distances are almost identical in both [Cu(hfacac)(coe)] (2.013(4) and 2.017(4) Å) and [Cu(hfacac)(van)] (2.008(4) and 2.024(4) Å) and comparable to the corresponding distances found in the Cu(hfacac)(alkene) family (2.011(3) and 2.029(3) Å in Cu(hfacac)(7-*tert*-butoxy-2,5-norbornadiene)[4a] and 2.011(5) and 2.025(6) Å in Cu(hfacac)(vinyltrimethylsilane)).[9]

The preparation of the carbonyl derivative Cu(hfacac)(CO) deserves some additional comments. Attempts to isolate Cu(hfacac)(CO) from THF according to the procedure reported in the literature[2] (eq 2) were not successful, due to disproportionation and easy loss of CO during the isolation procedures (evaporation of the solvent in vacuo at room temperature or lower). Nevertheless, a strong IR carbonyl band ($\tilde{\nu}_{CO}$: 2120 cm^{-1} (toluene); 2131 cm^{-1} (CH_2Cl_2)) confirmed the presence of coordinated CO. During one preparation of Cu(hfacac)(CO), a *green* THF/heptane solution was cooled at −30 °C, but the compound which separated out consisted of pale green crystals of Cu(hfacac)$_2$(THF)$_2$, formed by disproportionation of copper(I) in THF, which was characterized by analysis, spectroscopy, and X-ray diffraction.[10]

Operating in the absence of basic species which may induce disproportionation of copper(I), and considering that water is formed in stoichiometric amounts according to eq 3, we attempted the preparation of Cu(hfacac)(CO) by reacting CuCl and Tl(hfacac)[11] in toluene under a CO atmosphere (eq 4). No disproportionation was

$$\mathrm{CuCl + Tl(hfacac) + CO \rightarrow Cu(hfacac)(CO) + TlCl} \tag{4}$$

observed under these experimental conditions, and cooling the solution to −30 °C afforded Cu(hfacac)(CO) as a colorless crystalline compound ($\tilde{\nu}_{CO}$: 2112 cm^{-1}, Nujol mull) which quickly decomposed into a green brown solid with loss of CO.

Table 5. ^{13}C NMR Resonances of the Olefinic Carbon Atoms in CuL(olefin) compounds (C_6D_6, T = 294 K)

		Cu(L)(olefin)			
		L = hfacac		L = CF_3CO_2	
olefin	uncomplexed olefin δ (ppm)	δ (ppm)	Δ[a]	δ (ppm)	Δ[a]
cod	128.8	115.1	13.7	115.7	13.1
coe	130.3	100.2	30.1	102.6	27.7
nbe	135.5	103.2	32.3	104.6	30.9
van	136.8 (*C*H=)	102.5	34.3	106.6	30.2
	111.4 (*C*H_2=)	72.2	39.2	76.5	34.2

[a] $\Delta = \delta_{\text{uncomplexed olefin}} - \delta_{\text{complexed olefin}}$, both measured in the same solvent under the same conditions.

^{13}C NMR Spectra and Some Ideas Concerning the Copper(I)–Alkene Bond. The availability of two classes of olefin copper(I) compounds (trifluoroacetates and hexafluoroacetylacetonates) and their high solubility in non polar solvents prompted us to study their ^{13}C NMR spectra. This study was of particular interest as far as the interpretation of the nature of the copper–alkene bond is concerned. Data are collected in Table 5. The general observation is that the resonances of the olefin carbon atoms show high-field shifts on coordination, thus suggesting a shielding of the carbon atoms on going from uncoordinated to ligated olefin. Similar results have been reported in former studies on copper(I) complexes of the same type.[12] The difference between the resonances of the olefinic carbon atoms of coordinated and uncoordinated cod (13.7 and 13.1 ppm for Cu(hfacac)(cod) and Cu(CF_3COO)(cod) complexes, respectively) is smaller than those observed for other olefins: it has been ascribed to fluxionality processes which average the chemical shifts of the coordinated and uncoordinated olefin.

According to former contributions on similar systems,[12] the Cu→olefin π-back-donation will cause a high-field shift of the ^{13}C NMR spectra of coordinated olefins with respect to the uncoordinated ones, whereas a low-field shift of the corresponding resonance will be expected due to olefin→Cu σ-donation. Therefore, the resulting NMR spectrum will be the combination of the two contributions and we would observe low-field shifts in the case of prevalence of the σ-contribution and high-field shifts when the π-contribution is dominant.

On the basis of these considerations, data reported in Table 5 suggest that the π-component dominates over the σ-component in our systems. Similar conclusions were obtained on cyclopentadienyl palladium(II) derivatives containing substituted styrenes.[13] The largest

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(9) Chen, T. Y.; Omnès, L.; Vaisserman, J.; Pascal, P. *Inorg. Chim. Acta* **2004**, *357*, 1299.

(10) As the structure of Cu(hfacac)$_2$(THF)$_2$ (green crystals from THF/heptane at −30 °C) is very similar to that of Cu(hfacac)$_2$(H_2O)$_2$ (Maverick, A. W.; Fronczek, F. R.; Maverick, E. F.; Billodeaux, D. R.; Cygan, Z. T.; Isovitsch, R. A. *Inorg. Chem.* **2002**, *41*, 6488) and the two THF molecules are severely disordered, crystal data have been submitted as Supporting Information.

(11) Hartmann, F. A.; Jacobi, P. L.; Wojcicki, A. *Inorg. Synth.* **1970**, *12*, 81.

(12) (a) Baum, T. H.; Larson, C. E.; May, G. *J. Organomet. Chem.* **1992**, *425*, 189. (b) Salomon, R. G.; Kochi, J. K. *J. Am. Chem. Soc.* **1973**, *95*, 1889. (c) Salomon, R. G.; Kochi, J. K. *J. Organomet. Chem.* **1974**, *64*, 135.

Table 6. Carbon−Carbon Double-Bond Distances of Olefins as Uncomplexed Species and in the Corresponding CuL(olefin) Derivatives

		complexed olefin	
olefin	uncomplexed olefin	L = hfacac	L = CF_3COO
cod	1.312[a]	1.367(11)[b]	1.377(4)[c]
coe	1.314[d]	1.363(6)[e]	1.367(7)[c]
van	1.303[f]	1.379(5)[e]	1.382(5), 1.358(5)[e]

[a] Reference 14. [b] Reference 3a. [c] Reference 1b. [d] Reference 15. [e] This work. [f] Reference 16.

high-field shift has been observed for Cu(L)(van) (L = CF_3COO, hfacac), thus suggesting a larger π-back-donation contribution in the case of this olefin than in the case of cod, nbe, and coe. In this connection, it is interesting to observe that the largest increase of the C═C bond distances on going from uncoordinated to complexed olefin (see Table 6) is observed for van with respect to cod and coe.

Table 6 data also suggest that the upfield shifts of the olefin carbon resonances for the trifluoroacetato derivatives are smaller than those found within the hexafluoroacetylacetonato analogues. This observation may be explained by considering that the π-component to the Cu−olefin bond increases on increasing the basicity of the ancillary ligand, which was reported to increase in the order triflate < trifluoroacetate < hexafluoroacetylacetonate < trifluoroacetylacetonate for Cu(I)(cod) complexes.[12]

Olefin/CO Exchange Reactions. In this section of the paper we will discuss the results obtained on the carbonylation reactions of trifluoroacetato and hexafluoroacetylacetonato olefin derivatives of copper(I).

Before presenting the results of the thermodynamic study, some comments are required concerning the nuclearity of the species present in solution. Since we used the same experimental conditions as in our previous research on this subject,[1b] we will consider olefin and carbonyl adducts of copper trifluoroacetate to be present in toluene solution as mononuclear and dinuclear species, respectively. On the other hand, on the basis of the fact that olefin adducts of copper(I) hexafluoroacetylacetonate are generally mononuclear in the solid state[2,3a,b,4,17] (vide infra), a mononuclear formulation for the diketonates (either olefin or carbonyl derivative) will be used in our calculations (Scheme 1). As additional support to this hypothesis, bridging diketonates have not been observed for copper, while the bridging disposition is rather common for carboxylate derivatives of transition elements.[18]

Scheme 1. Carbonylation of Cu(L)(olefin) Derivatives

$$2\mathrm{Cu(CF_3COO)(olefin)_{solv}} + 2\mathrm{CO_{solv}} \rightleftarrows \mathrm{Cu_2(CF_3CO_2)_2(CO)_{2,solv}} + 2(\mathrm{olefin})$$

$$K_{\mathrm{CF_3COO}} = [\mathrm{Cu_2(CF_3COO)_2(CO)_{2,solv}}][\mathrm{olefin_{solv}}]^2/[\mathrm{Cu(CF_3COO)(olefin)_{solv}}]^2[\mathrm{CO_{solv}}]^2$$

olefin = tbve, van

$$\mathrm{Cu(hfacac)(olefin)_{solv}} + \mathrm{CO_{solv}} \rightleftarrows \mathrm{Cu(hfacac)(CO)_{solv}} + \mathrm{olefin_{solv}}$$

$$K_{\mathrm{hfacac}} = [\mathrm{Cu(hfacac)(CO)_{solv}}][\mathrm{olefin_{solv}}]/[\mathrm{Cu(hfacac)(olefin)_{solv}}][\mathrm{CO_{solv}}]$$

olefin = coe, nbe, van

Data were collected by gas volumetric methods,[19] and the values of the equilibrium constants are reported in Table 7 together with the enthalpy and entropy of the reactions obtained from van't Hoff plots.

Data of Table 7 (which lists also our previous results on copper(I)[1b]) show the following.

(a) Reactions are exothermic; 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 equations reported in Scheme 1.

(b) On considering that the enthalpy of solution of olefins is generally small and not largely dependent on the nature of the olefin,[20] we can observe that the relative stability of the olefin complex with respect to CuL(CO) increases in the order meci[21] ≪ defu < tbve < van < coe < cod for L = trifluoroacetate and in the order van < coe < nbe < cod for L = hexafluoroacetylacetonate. The presence of some interactions between both the double bonds of cod and copper, observed either in the solid state[3a] or in the gas phase,[22] may explain the stability of Cu(hfacac)(cod) with respect to all of the other derivatives of the same class.

(c) Once the difference of stoichiometry of the carbonylation reactions is considered, the general trend is that the stability of the olefin complexes with respect to the corresponding carbonyl derivative depends on the anionic ligand as well; i.e., the enthalpy variation of the reactions reported in Scheme 1 is higher for trifluoroacetates than for the corresponding hexafluoroacetylacetonates.

Concluding Remarks

This paper deals with olefin derivatives of copper(I) containing fluorinated ancillary ligands. With respect to our previous paper, we have reported new data

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Table 7. Equilibrium Constants and Thermodynamic Parameters at 298 K for the CO/Olefin Exchange Reported in Scheme 1

L = CF_3COO

olefin	$K_{CF_3CO_2}$ (M^{-1})	ΔH (kJ mol^{-1})	ΔS (J mol^{-1} K^{-1})	ref
coe[a]	$(6.3 \pm 3.2) \times 10^2$	-71 ± 17	-189 ± 57	1b
cod	12.6 ± 2.4	-46 ± 4	-131 ± 14	1b
defu	$(1.1 \pm 0.7) \times 10^7$	-112 ± 20	-248 ± 65	1b
tbve	$(1.4 \pm 0.4) \times 10^4$	-110 ± 12	-285 ± 38	this work
van	$(5.3 \pm 1.0) \times 10^3$	-91 ± 7	-234 ± 25	this work

L = hfacac

olefin	K_{hfacac}	ΔH (kJ mol^{-1})	ΔS (J mol^{-1} K^{-1})	ref
coe	2.80 ± 0.40	-12.0 ± 0.2	-31.7 ± 0.7	this work
nbe	0.86 ± 0.15	-8.3 ± 0.7	-29 ± 2	this work
cod	0.40 ± 0.08	nd[b]	nd	this work
van	20 ± 3	-28 ± 2	-69 ± 7	this work

[a] Equilibrium constant at 293.2 K. [b] nd = not determined.

concerning hexafluoroacetylacetonato derivatives and trifluoroacetato copper(I) complexes containing electron-releasing olefins.

Mixed olefin trifluoroacetato derivatives have been prepared by starting from Cu(CF_3COO)(toluene)$_{0.5}$ according to a previously reported synthetic pathway. At variance with the previously reported copper(I) trifluoroacetato olefin derivatives, the solid-state structure of $[Cu(\mu\text{-}CF_3COO)(tbve)]_n$ consists of polymeric chains formed by single trifluoroacetato bridges. The preparation of the mixed olefin hfacac derivatives (from the readily available Cu_2O, hfacacH, and olefin) is complicated by the instability of Cu(hfacac), whose disproportionation to copper(0) and copper(II) may also be promoted by the water formed in the reaction (see Scheme 2). We have found that disproportionation becomes an important reaction with respect to olefin complexation in the case of alkenes containing electron-withdrawing substituents.

Scheme 2. Formation and Disproportionation Pathways of Copper Hexafluoroacetylacetonates

$$Cu_2O \xrightarrow[-H_2O]{L,\ hfacacH,\ solvent} 2Cu(hfacac)L \xrightarrow{L'} Cu + Cu(hfacac)_2L'_n$$

(a) L = nbe, coe; solvent = CH_2Cl_2; L′ = H_2O

(b) L = van; solvent = CH_2Cl_2; L′ = van

(c) L = cod; solvent = THF; L′ = THF

The availability of two copper(I) systems containing ancillary ligands featuring different electronic properties (trifluoroacetate and hexafluoroacetylacetonate) and the choice of alkenes containing electron-releasing or electron-withdrawing substituents have allowed some hypotheses on the nature of the copper(I) olefin bond to be formulated. In particular, we have added some new evidence to the suggestions reported in the literature[12] concerning the decrease of the stability of the copper olefin derivatives on increasing the Cu→olefin π-back-donation. As a matter of fact, we have found that Cu(hfacac)(van) is the least stable complex within the hfacac derivatives, whose spectral and X-ray data suggest that van behaves as a better π-acid ligand than coe, cod, and nbe. Moreover, the stability of the Cu(CF_3COO)(olefin) species decreases on increasing the electron-withdrawing power, i.e., the π-acceptor capability, of the olefin.

The smaller carbonylation enthalpy observed for the hfacac complexes with respect to the trifluoroacetates probably depends on the relative stabilities of Cu(hfacac)(CO) and Cu(CF_3CO_2)(CO). Due to the presence of the more donating hexafluoroacetylacetonate, the π-back-donation in Cu(hfacac)(CO) is likely larger than in Cu(CF_3CO_2)(CO), thus causing a decrease of stability of the former (Cu(hfacac)(CO) is unstable with respect to the CO loss). On the other hand, the stability of the olefin complexes may be less affected by the ancillary ligands, the alkenes behaving as better σ-donors than CO.

Experimental Section

General Procedures. 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 (Fluka), 1,5-cyclooctadiene (Aldrich), *cis*-cyclooctene (Aldrich), and 4-vinylanisole (Aldrich) were distilled under reduced pressure and stored at ca. −30 °C; *tert*-butyl vinyl ether (Aldrich) was distilled at atmospheric pressure and stored at ca. −30 °C; hfacacH (Aldrich), norbornene (Aldrich), and Cu_2O (Aldrich) were used as received. Cu(CF_3COO)(toluene)$_{0.5}$[5] and Tl(hfacac)[11] were prepared according to literature procedures. IR spectra were recorded on a FT-1725X instrument on Nujol or polychlorotrifluoroethylene (PCTFE) mulls prepared under rigorous exclusion of moisture and air. NMR spectra (^1H at 200 MHz and ^{13}C at 50.31 MHz, with TMS as reference; ^{19}F at 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.[19]

Preparation of Cu(CF_3COO)(L) (L = tbve, van, nbe). Only the preparation of Cu(CF_3COO)(tbve) is described in detail, the other preparations being performed similarly. A solution of Cu(CF_3COO)(toluene)$_{0.5}$ (1.83 g, 8.2 mmol) in toluene (40 mL) was added to tbve (0.91 g, 9.1 mmol). A pale yellow suspension formed. After 15 h of stirring at room temperature, the pale yellow suspension was added to heptane (150 mL). The colorless microcrystalline solid which separated out was recovered by filtration and dried in vacuo at room temperature, affording 1.62 g (71% yield) of Cu(CF_3COO)(tbve) as an air- and light-sensitive colorless solid, indefinitely stable in sealed tubes at −30 °C. Anal. Found: C, 33.9; H, 3.9. Calcd for $C_8H_{12}CuF_3O_3$: C, 34.7; H, 3.9. IR (Nujol and PCTFE): $\tilde{\nu}$/cm^{-1} 3079 w, 1670 vs, 1639 vs, 1631 vs, 1615 s, 1548 m, 1529 m, 1459 vs, 1406 m, 1264 m, 1198 vs, 1155 vs, 1002 s, 884 s, 847 m, 837 m, 789 m, 727 s. ^1H NMR (C_6D_6): δ 6.20 (s, 1 H), 4.20 (s, 1 H), 3.64 (s, 1 H). 1.01 (s, 9 H, CH_3).

Cu(CF_3COO)(van) was obtained as a colorless crystalline compound, sensitive to air, in 75% yield. Anal. Found: C, 42.8; H, 3.6. Calcd for $C_{11}H_{10}CuF_3O_3$: C, 42.5; H, 3.2. IR (Nujol and PCTFE): $\tilde{\nu}$/cm^{-1} 3138 w, 3096 w, 3072 w, 1867 w, 1679 vs, 1606 s, 1579 m, 1535 mw, 1507 s, 1500 s, 1456 vs, 1314 m, 1303 s, 1250 s, 1198 vs, 1172 vs, 1153 vs, 1041 w, 1024 s, 953 w, 928 s, 850 s, 845 s, 814 m, 788 m, 750 m, 724 s, 693 mw, 525 m. ^1H NMR (C_6D_6): δ 6.95 (d, 2H, J = 8.4 Hz, *m*-C*H*), 6.61 (d, 2H, J = 8.4 Hz, *o*-C*H*), 5.30 (dd, 1H, J_{trans} = 16.4 Hz, J_{cis} = 9 Hz, C*H*=CH_2), 4.13 (d, 1H, J_{trans} = 16.4 Hz, cis *H*), 3.53 (d, 1H, J_{cis}= 9 Hz, trans *H*). ^{13}C NMR (C_6D_6): δ 160.6 (*C*OCH_3), 128.3 (ring *C*H), 127.9 (*C*CH=CH_2), 114.7 (ring *C*H), 106.6 (*C*H=CH_2), 76.5 (CH=*C*H_2), 54.9 (O*C*H_3).

Cu(CF_3COO)(nbe) was obtained as a colorless crystalline compound, very sensitive to air, in 80% yield, Anal. Found:

C, 40.0; H, 3.6. Calcd for $C_9H_{10}CuF_3O_2$: C, 39.9; H, 3.7. IR (Nujol and PCTFE): $\tilde{\nu}/\mathrm{cm}^{-1}$ 3082 w, 3045 w, 1678 vs, 1455 s, 1325 m, 1295 mw, 1277 mw, 1211 vs, 1146 vs, 1122 s, 971 mw, 945 w, 902 w, 889 m, 850 m, 846 m, 789 m, 729 s, 673 w, 523 m, 451 m. ^{1}H NMR (C_6D_6): δ 4.47 (s, 2 H, C*H*=C*H*), 2.62 (s, 2 H, C*H*CH=CH), 1.40−0.90 (m, 3 H), (d, 1 H, J = 10 Hz), 0.70−0.30 (m, 3 H). ^{13}C NMR (C_6D_6): δ 104.6 (*C*H=*C*H), 45.4 (*C*HCH=), 43.1 (CH*C*H$_2$CH), 24.2 (*C*H$_2$*C*H$_2$).

Preparation of Cu(hfacac)(L) (L = coe, nbe). Only the preparation of Cu(hfacac)(coe) is described in detail, the other being performed similarly. A solution of hfacacH (2.94 g, 14.1 mmol) in dichloromethane (20 mL) was dropped into a well-stirred mixture of coe (1.59 g, 14.5 mmol) and Cu_2O (1 g, 7.0 mmol) in dichloromethane (50 mL). A yellow-green suspension was obtained, which was filtered. After elimination of the solvent in vacuo at room temperature, the yellow-green liquid residue was dissolved in heptane (5 mL) and the solution was cooled to ca. −30 °C. The pale yellow crystalline solid was recovered by filtration and dried in vacuo at room temperature, affording 2.8 g (53% yield) of Cu(hfacac)(coe). Anal. Found: C, 40.8; H, 3.5. Calcd for $C_{13}H_{15}CuF_6O_2$: C, 41.1; H, 3.7. IR (Nujol and PCTFE): $\tilde{\nu}/\mathrm{cm}^{-1}$ 1639 vs, 1598 m, 1553 s, 1526 s, 1473 vs, 1346 m, 1257 vs, 1207 vs, 1101 s, 984 w, 974 w, 799 s, 763 w, 743 w, 722 w, 672 s, 586 m, 528 w, 497 w. ^{1}H NMR (C_6D_6): δ 6.19 (s, 1 H, C*H*C=O), 4.35 (m, 2 H, C*H*=C*H*), 1.74 (s, 4 H, C*H*$_2$CH=), 1.12 (s, 8 H, (C*H*$_2$)$_4$). ^{13}C NMR (C_6D_6): δ 177.9 (q, J_{C-F} = 34 Hz, CF$_3$*C*=O), 118.4 (q, J_{C-F} = 286 Hz, *C*F$_3$C=O), 100.2 (*C*H=*C*H), 90 (*C*HC=O), 29.8 (*C*H$_2$CH=), 26.1 ((*C*H$_2$)$_4$).

Cu(hfacac)(nbe) was obtained as a yellow crystalline compound, slightly sensitive to air, in 60% yield. Anal. Found: C, 39.4; H, 3.0. Calcd for $C_{12}H_{11}CuF_6O_2$: C, 39.6; H, 2.8. IR (Nujol and PCTFE): $\tilde{\nu}/\mathrm{cm}^{-1}$ 3085 w, 3042 w, 1639 vs, 1598 m, 1554 s, 1526 s, 1473 vs, 1345 m, 1323 m, 1257 vs, 1207 vs, 1149 vs, 1101 s, 967 w, 944 w, 903 w, 892 w, 799 s, 743 w, 672 s, 586 m, 528 w, 457 w. ^{1}H NMR (C_6D_6): δ 6.19 (s, 1 H, C*H*C=O), 4.34 (s, 2 H, C*H*=C*H*), 2.53 (s, 2 H, C*H*CH=CH), 1.02 (d, 2 H, J = 7.4 Hz), 0.83 (d, 1 H, J = 10 Hz), 0.60−0.30 (m, 3 H). ^{13}C NMR (C_6D_6): δ 178.0 (q, J_{C-F} = 34 Hz, CF$_3$*C*=O), 118.4 (q, J_{C-F} = 286 Hz, *C*F$_3$C=O), 103.2 (*C*H=*C*H), 90.0 (*C*HC=O), 44.9 (*C*HCH=), 42.9 (CH*C*H$_2$CH), 24.9 (*C*H$_2$*C*H$_2$).

Preparation of Cu(hfacac)(van). A solution of hfacacH (5 g, 24.0 mmol) in dichloromethane (25 mL) was dropped over 30 min into a well-stirred mixture of van (3.23 g, 24.1 mmol) and Cu_2O (1.6 g, 11.2 mmol) in dichloromethane (25 mL). The green suspension was filtered to remove insoluble materials. After elimination of the solvent in vacuo at room temperature, a yellow-green solid was obtained, which was heated at 55 °C/10^{-2} mmHg. The compound Cu(hfacac)(van) was obtained as a yellow crystalline solid residue (6.13 g; 68%). Anal. Found: C, 40.8; H, 2.4. Calcd for $C_{14}H_{11}CuF_6O_3$: C, 41.5; H, 2.8. IR (Nujol and PCTFE): $\tilde{\nu}/\mathrm{cm}^{-1}$ 3271 w, 1642 vs, 1607 s, 1583 m, 1550 m, 1525 s, 1506 s, 1486 s, 1442 s, 1342 m, 1313 m, 1256 vs, 1243 s, 1202 vs, 1186 s, 1177 vs, 1147 vs, 1095 s, 1044 m, 1023 s, 957 m, 911 m, 833 s, 797 s, 751 w, 741 w, 709 mw, 672 s, 587 m, 550 mw, 523 m, 453 w. ^{1}H NMR (C_6D_6): δ 7.00 (d, 2H, J = 7.4 Hz, *m*-C*H*), 6.58 (d, 2H, J = 7.4 Hz, *o*-C*H*), 6.02 (s, 1H, C*H*C=O), 5.45 (dd, 1H, J_{trans} = 16.0 Hz, J_{cis} = 9.6 Hz, C*H*=CH$_2$), 4.11 (d, 1H, J_{trans} = 16.0 Hz, cis *H*), 3.46 (d, 1H, J_{cis} = 9.6 Hz, trans *H*). ^{13}C NMR (C_6D_6): δ 177.8 (q, J_{C-F} = 34 Hz, CF$_3$*C*=O), 160.6 (*C*−OCH$_3$), 128.3 (ring *C*H), 118.3 (q, J_{C-F} = 286 Hz, *C*F$_3$C=O), 114.6 (ring *C*H), 102.5 (*C*H=CH$_2$), 90.0 (*C*HC=O), 72.2 (CH=*C*H$_2$), 54.7 (O*C*H$_3$).

The green sublimate (ca. 300 mg) was identified as Cu(hfacac)$_2$(van). Anal. Found: C, 36.8, H, 1.6. Calcd for $C_{19}H_{12}CuF_{12}O_5$: C, 37.3; H, 2.0. IR (Nujol and PCTFE): $\tilde{\nu}/\mathrm{cm}^{-1}$ 3251 w, 3082 w, 1640 vs, 1608 s, 1561 s, 1530 s, 1511 s, 1366 m, 1300 m, 1257 vs, 1211 vs, 1163 s, 1148 vs, 1110 m, 1043 m, 986 m, 832 s, 802 s, 769 w, 722 s, 680 s, 596 m, 528 mw. Magnetic measurement: $\chi_M^{corr} = 1.70 \times 10^{-3}$ cgsu; diamagnetic correction -286.40×10^{-6} cgsu; μ_{eff}(294 K) = 2.01 μ_B.

Table 8. Carbonylation Reactions of Cu(L)(olefin) Complexes

T (K)	10^3[Cu(CF$_3$COO)(tbve)]$_i$	CO/Cu	$10^3K_{CF_3COO}$ (M^{-1})
288.4	9.25	0.977	150
298.2	13.21	0.919	14
308.5	6.98	0.881	3
317.5	10.19	0.791	1
332.0	10.38	0.689	0.3
T (K)	10^3[Cu(CF$_3$COO)(van)]$_i$	CO/Cu	$10^3K_{CF_3COO}$ (M^{-1})
278.5	12.69	0.585^a	70.9
288.3	5.12	0.953	18.2
298.2	18.70	0.859	5.3
308.3	8.36	0.863	2.5
318.0	8.96	0.729	0.42
T (K)	10^3[Cu(hfacac)(coe)]$_i$	CO/Cu	K_{hfacac}
278.6	16.22	0.723	4.09
288.5	11.37	0.748	3.35
298.3	12.78	0.703	2.80
308.0	11.14	0.703	2.47
317.8	18.52	0.593	2.13
T (K)	10^3[Cu(hfacac)(nbe)]$_i$	CO/Cu	K_{hfacac}
278.6	16.79	0.496	1.09
288.5	17.62	0.461	0.93
298.3	23.65	0.403	0.86
308.0	20.51	0.401	0.73
317.8	25.71	0.362	0.70
T (K)	10^3[Cu(hfacac)(van)]$_i$	CO/Cu	K_{hfacac}
278.5	11.96	0.717^b	43
288.4	14.48	0.934	25
298.3	19.09	0.887	20
307.9	13.95	0.880	12
318.0	19.03	0.823	10

^{a} [olefin]$_i$ = 0.16 M. ^{b} [olefin]$_i$ = 0.12 M.

Preparation of Cu(hfacac)(cod). The preparation has been performed by a modification of the literature procedure.[2] A solution of hfacacH (5.44 g, 26.1 mmol) in THF (30 mL) was added dropwise over 30 min into a well-stirred mixture of cod (2.82 g, 26.1 mmol) and Cu_2O (1,87 g, 13.1 mmol) in THF (50 mL). After 18 h of stirring, the green suspension was filtered to remove copper and unreacted Cu_2O. After elimination of the solvent in vacuo at room temperature, a yellow-green solid was obtained, which was heated at 70 °C/10^{-2} mmHg. The green sublimate was identified as Cu(hfacac)$_2$(THF)$_2$ by IR spectroscopy (vide infra). Cu(hfacac)(cod) was obtained as a yellow crystalline solid residue (3.29 g; 33%). ^{1}H NMR (C_6D_6): δ 6.16 (s, 1H, C*H*C=O), 5.05 (s, 4H, C*H*=C*H*), 1.77 (s, 8H, C*H*$_2$). ^{13}C NMR (C_6D_6): δ 177.7 (q, J_{C-F} = 34 Hz, CF$_3$*C*=O), 118.6 (q, J_{C-F} = 286 Hz, *C*F$_3$C=O), 115.1 (*C*H=*C*H), 89.0 (*C*HC=O), 28.1 (*C*H$_2$).

Attempted Preparation of Cu(hfacac)(CO): Preparation of Cu(hfacac)$_2$(THF)$_2$. According to the literature procedure,[2] a solution of hfacacH (4.7 g, 22.6 mmol) in THF (25 mL) was dropped over 30 min under CO into a well-stirred suspension of Cu_2O (1.56 g, 10.9 mmol) in CO-saturated THF (15 mL). The mixture was then filtered under CO to remove metallic copper from the green solution. The volume of the solution was reduced to 10 mL in vacuo at room temperature, and heptane (50 mL) was added. The green solution was saturated with CO and kept at −30 °C, affording Cu(hfacac)$_2$(THF)$_2$ as pale green crystals. Anal. Found: C, 33.9; H, 2.6. Calcd for $C_{18}H_{18}CuF_{12}O_6$: C, 34.8; H, 2.9. IR (Nujol and PCTFE): $\tilde{\nu}/\mathrm{cm}^{-1}$ 3289 w, 3148 w, 1640 vs, 1602 s, 1559 s, 1532 s, 1488 vs, 1464 s, 1353 s, 1257 vs, 1219 vs, 1201 vs, 1149 vs, 1107 s, 1050 s, 953 w, 918 m, 888 s, 815 m, 802 vs, 771 w, 745 m, 721 w, 679 vs, 594 s, 528 w. Magnetic measurement: χ_M^{corr} = 1.23×10^{-3} cgsu; diamagnetic correction -262.30×10^{-6} cgsu, μ_{eff}(294 K) = 1.71 μ_B.

Table 9. Crystallographic Data for the Compounds $[Cu(\mu\text{-}CF_3COO)(tbve)]_n$, $[Cu(\mu\text{-}CF_3COO)(van)]_2\cdot C_7H_8$, [Cu(hfacac)(coe)], and [Cu(hfacac)(van)]

	$[Cu(\mu\text{-}CF_3COO)(tbve)]_n$	$[Cu(\mu\text{-}CF_3COO)(van)]_2\cdot C_7H_8$	[Cu(hfacac)(coe)]	[Cu(hfacac)(van)]
formula	$C_8H_{12}CuF_3O_3$	$C_{22}H_{20}Cu_2F_6O_6\cdot C_7H_8$	$C_{13}H_{15}CuF_6O_2$	$C_{14}H_{11}CuF_6O_3$
formula wt	276.72	713.59	380.79	404.77
cryst syst	tetragonal	triclinic	orthorhombic	triclinic
space group	$P4_1$	$P\bar{1}$	*Pbca*	$P\bar{1}$
a, Å	9.495(3)	12.714(5)	20.574(5)	9.926(4)
b, Å	9.495(3)	13.467(5)	13.856(3)	10.517(5)
c, Å	12.168(5)	9.236(3)	10.607(3)	9.211(4)
α, deg	90	99.23(5)	90	102.71(5)
β, deg	90	101.09(5)	90	106.81(5)
γ, deg	90	95.04(5)	90	112.72(5)
V, Å^3	1097.0(7)	1520.2(10)	3023.8(13)	786.8(6)
Z	4	2	8	2
D_{calcd}, g cm^{-3}	1.675	1.559	1.673	1.708
$F(000)$	560	724	1536	404
μ, cm^{-1}	31.37	24.18	27.10	14.63
no. of rflns collected	4153	5725	2622	6003
no. of unique rflns	1092 ($R_{int} = 0.0603$)	5710 ($R_{int} = 0.0522$)	2622 ($R_{int} = 0.000$)	2949 ($R_{int} = 0.0537$)
no. of obsd rflns ($I > 2\sigma(I)$)	1071	4456	2204	2889
no. of params	184	454	200	272
final R indices ($I > 2\sigma(I)$)[a]	R1 = 0.0295, wR2 = 0.0742	R1 = 0.0496, wR2 = 0.1345	R1 = 0.0557, wR2 = 0.1650	R1 = 0.0535, wR2 = 0.1518
final R indices (all data)[a]	R1 = 0.0301, wR2 = 0.0748	R1 = 0.0643, wR2 = 0.1445	R1 = 0.0643, wR2 = 0.1839	R1 = 0.0545, wR2 = 0.1527

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

Attempted Isolation of Cu(hfacac)(CO). A thin-walled sealed glass container containing CuCl (0.36 g, 3.6 mmol) was introduced into an Erlenmeyer flask equipped with a lateral stopcock containing a solution of Tl(hfacac) (1.5 g, 3.6 mmol) in toluene (50 mL). The system was connected to a gas volumetric buret and saturated with CO at 292.3 K at 753 mmHg of total pressure. The container was broken by mechanical stirring, and the CO absorption was measured. After 3 days of stirring, the absorption of CO had become very slow and corresponded to a CO/Cu molar ratio of 0.7. An IR spectrum of the solution in the carbonyl stretching region showed a strong absorption at 2120 cm^{-1}. Solids (containing ca. 30% of the copper introduced) were filtered off, and the solution was partially evaporated in vacuo at room temperature. After saturation with CO, the solution turned colorless and a strong absorption at 2120 cm^{-1} was present in the infrared spectrum. The concentrated solution was then cooled at ca. −30 °C, affording a small amount of colorless crystals ($\tilde{\nu}_{CO}$, Nujol = 2112 cm^{-1}) which quickly decomposed with CO loss.

Carbonylation Reactions of Cu(L)(olefin) (L = CF_3CO_2, olefin = tbve, van; L = hfacac, olefin = coe, nbe, van). IMPORTANT: In the case of a carbonylation reaction largely shifted to the right such as in the cases of $Cu(CF_3CO_2)(van)$ and Cu(hfacac)(van) at 278.5 K, a certain amount of olefin, $[olefin]_i$, was added to the solution. In the following, the carbonylation in the absence of added olefin is described. 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 glass 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.[1a] The gas volumetric experiments were repeated twice, thus obtaining consistent $CO_{absorbed}$/Cu molar ratios. The details of the experiments together with the measured $CO_{absorbed}$/Cu molar ratios (CO/Cu) at equilibrium, respectively, are reported in Table 8.

X-ray Structure Determination of $[Cu(\mu\text{-}CF_3COO)(tbve)]_n$, $[Cu(\mu\text{-}CF_3COO)(van)]_2\cdot C_7H_8$, [Cu(hfacac)(coe)], and [Cu(hfacac)(van)]. Crystals were grown from toluene/heptane ($[Cu(\mu\text{-}CF_3COO)(tbve)]_n$, $[Cu(\mu\text{-}CF_3COO)(van)]_2\cdot C_7H_8$, [Cu(hfacac)(van)]) or by sublimation at 35 °C/10^{-2} mmHg ([Cu(hfacac)(coe)]). Data were collected at 173 K on an Enraf-Nonius CAD 4 single-crystal diffractometer (Cu Kα radiation, $\lambda = 1.54183$ Å). Details of the X-ray data collections are collected in Table 9. The structures were solved by Patterson and by direct methods with SHELXS-97 and refined against F^2 with SHELXL-97,[23] with anisotropic thermal parameters for all non-hydrogen atoms. In $[Cu(\mu\text{-}CF_3COO)_2(van)]_2\cdot C_7H_8$ the toluene molecule was disordered in two positions with an occupancy factor of 0.5. The fluorine atoms of one of the two trifluoroacetate groups in $[Cu_2(\mu\text{-}CF_3COO)_2(van)]_2\cdot C_7H_8$ and those of the hfacac anion in [Cu(hfacac)(van)] were disordered and distributed over two positions.

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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 the compounds $[Cu(\mu\text{-}CF_3COO)(tbve)]_n$, $[Cu(\mu\text{-}CF_3COO)(van)]_2\cdot C_7H_8$, [Cu(hfacac)(coe)], [Cu(hfacac)(van)], and $[Cu(hfacac)_2(THF)_2]$; X-ray data are also available as CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

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[23] Sheldrick, G. M., SHELX-97: Programs for Crystal Structure Analysis (Release 97-2); University of Göttingen, Göttingen, Germany, 1997.