ORGANOMETALLICS

Volume 18, Number 19, September 13, 1999

## Communications

# $Cu(CO)_2(N(SO_2CF_3)_2)$. The First Structurally Characterized Copper(I) Polycarbonyl

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*Received March 19, 1999*

*Summary: The title compound contains a three-coordinate $Cu^+$ ion bonded to the sulfonamide nitrogen atom and to two CO ligands with long Cu−C bonds (1.90 and 1.91 Å) and a C−Cu−C bond angle of 122°. The two ν(CO) IR bands for this compound are at 2158 (s) and 2184 (m) $cm^{-1}$.*

Copper(I) carbonyls have long been of interest to chemists.[1] They are formed in many catalytic transformations of $CO^2$ and in the purification of CO from steam-methane-reforming gases.[3] In addition, CO is used as a probe ligand for studying reduced copper-containing proteins and enzymes.[4] Finally, the ν(CO) values of copper(I) carbonyls can be either higher or lower than 2143 $cm^{-1}$, the value for gaseous CO. This makes copper(I) carbonyls of pivotal importance in understanding and refining the distinction between classical and nonclassical metal carbonyls.[5]

Virtually all copper(I) carbonyl complexes studied to date have a stoichiometry Cu:CO = 1:1.[6] Nevertheless, there are some important exceptions. In a seminal paper in 1976, Souma and co-workers reported that $Cu^+$ ions dissolved in strong protic acids could absorb up to 4

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10.1021/om990196f CCC: $18.00

equiv of CO, the exact stoichiometry being dependent on temperature, pressure, and the conjugate base of the strong acid.[7] Armentrout and co-workers identified the species $Cu(CO)_2^+$, $Cu(CO)_3^+$, and $Cu(CO)_4^+$ in the gas phase.[8] Borokov and Karge, Iwamoto and Hoshino, Kurodo et al.,[9] and Zecchina et al.[10] have reported that the copper ions in copper(I) zeolites can form di- and tricarbonyl species under certain conditions of pressure and temperature.[9,10] We have reported the IR spectrum of $Cu(CO)_2(CF_3SO_3)(s)$ and the IR and Raman spectra of $Cu(CO)_2(AsF_6)(s)$ and $Cu(CO)_3(AsF_6)(s)$.[11] The spectra indicated that the $Cu(CO)_2^+$ and $Cu(CO)_3^+$ cations in the two $AsF_6^-$ salts have $D_{\infty h}$ and $D_{3h}$ symmetry, respectively. The two $AsF_6^-$ salts were the only crystalline copper(I) polycarbonyl compounds isolated before this work, and neither has been structurally characterized. We herein report the synthesis and IR spectra of three new copper(I) carbonyls, $Cu(CO)(N(SO_2CF_3)_2)$ (**I**), $Cu(CO)_2(N(SO_2CF_3)_2)$ (**II**), and $Cu(CO)_3(N(SO_2CF_3)_2)$ (**III**), and the structural characterization of **II**, which is the first isolable three-coordinate dicarbonyl complex of any metal and the first structurally characterized copper(I) polycarbonyl. It is abundantly clear that $Cu^+$ has an extensive polycarbonyl chemistry waiting to be explored with the use of superweak[12] anions.

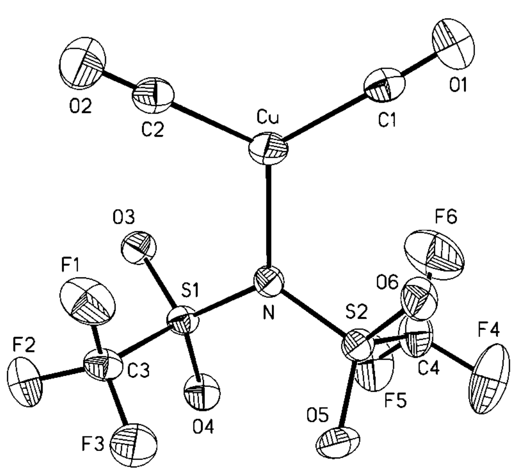

**Figure 1.** Structure of $Cu(CO)_2(N(SO_2CF_3)_2)$ (50% probability ellipsoids). Selected interatomic distances (Å) and angles (deg): Cu−C1 = 1.895(6) Å; Cu−C2 = 1.906(6) Å; Cu−N, 2.030(4); C1−O1, 1.130(7); C2−O2, 1.115(7); Cu−C1−O1, 177.7(5); Cu−C2−O2, 177.1(5); C1−Cu−C2 = 122.0(2); C1−Cu−N, 118.4(2); C2−Cu−N, 118.1(2).

**II** was prepared by treating a dichloromethane solution of mesitylcopper(I)[13] with the superacid[14] $HN(SO_2CF_3)_2$ under a nitrogen atmosphere.[15] When the resulting solution was treated with 1.3 atm CO and cooled to 0 °C, crystals of **II** were formed (63% yield):

$$\mathrm{Cu(mes)} + \mathrm{HN(SO_2CF_3)_2} \xrightarrow[\mathrm{CO}]{\mathrm{CH_2Cl_2}} \mathrm{mesH} + \mathbf{II}$$

The structure of **II** is shown in Figure 1.[16] Distances and angles within the $N(SO_2CF_3)_2^-$ anion are normal.[17] The copper(I) dicarbonyl moiety is bent, in contrast with the linear $Cu(CO)_2^+$ moiety in $Cu(CO)_2(AsF_6)$,[11] with Cu−C1 = 1.895(6) Å, Cu−C2 = 1.906(6) Å, and C1−Cu−C2 = 122.0(2)°. The $CuC_2N$ coordination unit is essentially trigonal planar. There are two very weak intermolecular Cu···O(S) interactions at >2.7 Å, one above and one below the trigonal plane. For comparison, the sum of van der Waals radii for copper and oxygen is 2.9 Å,[18] and the Cu−O(S) bond distances in $Cu(CO)(C_2H_5SO_3)$ are 2.050(4), 2.060(3), and 2.068(3) Å.[6i] The Cu−CO bonds in **II** are considerably longer, and presumably weaker, than the Cu−CO bonds in $[Cu(CO)(OAr)]_2$ (1.78(1)−1.79(1) Å),[6a] the Cu−CO bond in Cu(CO)(Tp′) (1.808(4) Å),[6b] or the Cu−CO bond in $Cu(CO)(C_2H_5SO_3)$ (1.784(8) Å).[6i] This is due to two reasons. First, the $N(SO_2CF_3)_2^-$ anion is a much weaker base than either $OAr^-$, $(Tp')^-$, or $CF_3SO_3^-$. This results in less Cu → CO $\pi$ back-bonding, and hence weaker and longer Cu−CO bonds, in **II** than in $[Cu(CO)(OPh)]_2$, Cu(CO)(Tp′), or $Cu(CO)(CF_3SO_3)$. Second, the two CO ligands in **II** compete with each other for the d$\pi$ electron density of the $Cu^+$ ion, which should make the Cu−CO bonds in **II** longer than the single Cu−CO bond distance in the monocarbonyl complex **I** as well as in other copper(I) monocarbonyl complexes.

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[15] The compounds $HN(SO_2CF_3)_2$ (1.54 g, 5.5 mmol) and Cu(mesityl) (1.00 g, 5.5 mmol) were each dissolved in 25 mL of dichloromethane. The solution of acid was slowly added to the solution of the copper complex under a dinitrogen atmosphere. The resulting mixture was a bright pink color with a small amount of a white solid. The mixture was filtered. When the pink filtrate was treated with hexane under 1.3 atm of CO, the white microcrystalline monocarbonyl $Cu(CO)N(SO_2CF_3)_2$ precipitated and was isolated in 86% yield. Crystals of the dicarbonyl $Cu(CO)_2N(SO_2CF_3)$ suitable for diffraction were grown by cooling a saturated dichloromethane solution under 1.3 atm of CO and isolating the crystals at −78 °C (to avoid decarbonylation).

[16] Crystal data for **II**: $C_4CuF_6NO_6S_2$, $M_r$ = 399.71 Da, orthorhombic, $P2_12_12_1$, $a$ = 6.0219(3) Å, $b$ = 11.3523(6) Å, $c$ = 17.191(1) Å, $V$ = 1175.2(1) Å$^3$, $Z$ = 4. Data were collected at −109(2) °C on a Siemens SMART System with Mo Kα radiation to a maximum $2\theta$ = 56.32°, giving 7739 unique reflections; the structure was solved by direct methods (Sheldrick, G. M. SHELXTL, vers. 5.03, 1994) with full-matrix least-squares refinement on $F^2$, yielding $R_1 = 0.052$ ($I > 2\sigma(I)$), $wR_2 = 0.131$ (all data).

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**Table 1. Solid-State $\nu$(CO) IR Data for Copper(I) Polycarbonyl Compounds $Cu(CO)_nX$**

| $X^-$ | $n$ | $Cu(CO)_n{}^+$ fragment idealized symmetry | $\nu$(CO), $cm^{-1}$ | av $\nu$(CO), $cm^{-1}$ |
|---|---|---|---|---|
| $N(SO_2CF_3)_2{}^-$ [a] | 1 | $C_{\infty v}$ | 2162 | 2162 |
| | 2 | $C_{2v}$ | 2158(s), 2184(m) | 2171 |
| | 3 | $C_{3v}$ | 2172(s), 2190(m) | 2178 |
| zeolite $Y^-$ [b] | 1 | $C_{\infty v}$ | 2160 | 2160 |
| | 2 | $C_{2v}$ | 2150(s), 2178(m) | 2164 |
| zeolite $MFI^-$ [c] | 1 | $C_{\infty v}$ | 2158 | 2158 |
| | 2 | $C_{2v}$ | 2151(s), 2177(m) | 2164 |
| zeolite $MOR^-$ [d] | 1 | $C_{\infty v}$ | 2160 | 2160 |
| | 2 | $C_{2v}$ | 2153(s), 2177(m) | 2165 |
| | 3 | $C_{3v}$ | 2165(s), 2190(m) | 2173 |
| zeolite ZSM-$5^-$ [e] | 1 | $C_{\infty v}$ | 2157 | 2157 |
| | 2 | $C_{2v}$ | 2151(s), 2178(m) | 2165 |
| | 3 | $C_{3v}$ | 2167(s), 2192(m) | 2175 |
| $CF_3SO_3{}^-$ [f] | 1 | $C_{\infty v}$ | 2131 | 2131 |
| | 2 | $C_{2v}$ | 2143(s), 2171(m) | 2165 |
| $AsF_6{}^-$ [g] | 1 | $C_{\infty v}$ | 2178 | 2178 |
| | 2 | $D_{\infty h}$ | 2164 [2177[h]] | 2171[i] |
| | 3 | $D_{3h}$ | 2179 [2206[h]] | 2188[i] |

[a] This work. [b] Ref 9a. [c] Ref 9b. [d] Refs 10b,c. [e] Ref 10a. [f] Ref 11b. [g] Ref 11a. [h] From Raman spectrum. [i] Weighted average of IR and Raman band positions.

IR spectra of **II** under 1 atm CO exhibited two $\nu$(CO) bands at 2158 (s) and 2184 (m) $cm^{-1}$ (solid state) or at 2157 (s) and 2181 (m) $cm^{-1}$ ($CH_2Cl_2$). The integrated intensity ratio $I(2184)/I(2158) \approx 0.47$ suggests that the $Cu(CO)_2{}^+$ moiety in **II** has $C_{2v}$ symmetry in solution as well as in the solid state, with the C−Cu−C angle > 90°.[19] These IR bands are compared in Table 1 with bands for related copper(I) di- and tricarbonyls. All of the $\nu$(CO) values in Table 1 are $\geq 2143$ $cm^{-1}$, indicating less extensive $\pi$ back-bonding for $Cu(CO)_2{}^+$ species than for the vast majority of dicarbonyl moieties of other metals.[19,20] Complex **I** ($\nu(CO) = 2162$ $cm^{-1}$) formed quickly when **II** was placed under vacuum (cf. 2178 $cm^{-1}$ for $[Cu(CO)][AsF_6]$,[10,21] 2160 $cm^{-1}$ for Cu(CO)(NaY),[9] 2157 $cm^{-1}$ for Cu(CO)(ZSM-5),[10] and 2131 $cm^{-1}$ for $Cu(CO)(CF_3SO_3)$[11a]). Loss of CO from **I** was very slow at 24 °C but occurred over several hours at 80 °C. A gas-adsorption isotherm (Figure S-1, Supporting Information) revealed that the equilibrium pressure of CO necessary to transform **I** into **II** at 24 °C is $85 \pm 5$ Torr. When a Fluorolube mull of **II** was placed under 2000 psi CO, two new bands appeared in the IR spectrum at 2172 (s) and 2190 (m) $cm^{-1}$; we attribute these bands to the $C_{3v}$-symmetry tricarbonyl complex **III**.

The vibrational data in Table 1 demonstrate that $\nu(CO)_{av}$ is higher, by 7−17 $cm^{-1}$, for all three $Cu(CO)_3X$ species than for the corresponding $Cu(CO)_2X$ species. A decrease in $\nu(CO)_{av}$ for the transformation $LM(CO)_n \rightarrow LM(CO)_{n-1}$ is the hallmark of classical metal polycarbonyls, i.e., those with significant $\pi$ back-bonding[5a,b,d,e] (in contrast, $\nu$(CO) is 7 $cm^{-1}$ *lower* for $Ag(CO)_3(Nb(OTeF_5)_6)$ than for $Ag(CO)_2(Nb(OTeF_5)_6)$[5j,22]). This is a very interesting observation. Since there is $\pi$ back-bonding in $Cu(CO)_2X$ species, it would seem that substituting a more basic $X^-$ ligand would induce more $\pi$ back-bonding, which would strengthen the two Cu−CO bonds and stabilize the dicarbonyl species $Cu(CO)_2X$ with respect to CO dissociation to the monocarbonyl species Cu(CO)X. Nevertheless, the opposite behavior is observed. Only $Cu^+$ salts of weakly basic $X^-$ anions such as $AsF_6{}^-$, $N(SO_2CF_3)_2{}^-$, and framework zeolites form polycarbonyls. Copper(I) monocarbonyls such as Cu(CO)Cl ($\nu(CO) = 2127$ $cm^{-1}$)[23] and $Cu(CO)(OC(CH_3)_3)$ ($\nu(CO) = 2063$ $cm^{-1}$)[24] show no tendency to form dicarbonyls, even at CO pressures up to 2000 psi.[25]

The observation that copper(I) polycarbonyls are "classical" by the $LM(CO)_n \rightarrow LM(CO)_{n-1}$ criterion and "nonclassical" by the $\nu(CO) > 2143$ $cm^{-1}$ criterion does not diminish the usefulness of the classical/nonclassical distinction. It does, however, require a richer lexicon than previously appreciated[5a,b] (an analogy is that most metal oxides are classified as either acidic or basic, but some must be classified as amphoteric). More than any other group of compounds, copper(I) carbonyls have helped us to refine our ideas about the classical/nonclassical distinction and have caused us to consider the interesting case of "borderline" behavior.

**Acknowledgment.** This research was supported by a grant from the National Science Foundation (CHE-9628769) and by Air Products and Chemicals, Inc. We thank Dr. S. V. Ivanov for experimental assistance.

**Supporting Information Available:** Figure S-1, a CO adsorption isotherm for the transformation of **I** into **II**; Tables S-1, S-2, S-3, and S-4, listing crystallographic parameters, atomic coordinates, bond distances and angles, and thermal parameters for **II**. This material is available free of charge via the Internet at http://pubs.acs.org.

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