

Mono-, Di-, Tri-, and Tetracarbonyls of Copper(I), Including the Structures of $\text{Cu}(\text{CO})_2(1\text{-Bn-CB}_{11}\text{F}_{11})$ and $[\text{Cu}(\text{CO})_4][1\text{-Et-CB}_{11}\text{F}_{11}]$

Svetlana M. Ivanova,^{1a} Sergei V. Ivanov,^{1a,b} Susie M. Miller,^{1a} Oren P. Anderson,^{1a} Konstantin A. Solntsev,^{*,1b} and Steven H. Strauss^{*,1a}

Department of Chemistry, Colorado State University, Fort Collins, Colorado 80523, and Institute of General and Inorganic Chemistry, Russian Academy of Sciences, Moscow 117907, Russia

Received March 19, 1999

Copper(I) carbonyls, first generated in solution nearly 150 years ago,² are species of scientific and technological importance. We recently reviewed the pivotal roles they play in refining the distinction between classical and nonclassical metal carbonyls, in several industrially important catalytic reactions involving CO as a feedstock, in the purification of CO from steam–methane–reforming gases, and in protein biochemistry.³

The discovery that copper(I) could bind more than one CO ligand in strongly acidic media (e.g., neat FSO_3H) was first reported by Souma and co-workers in 1976.⁴ We⁵ and others^{6,7} have recently shown that a strongly acidic medium is not required for the generation of copper(I) polycarbonyls. What is required is the virtual absence of counteranion basicity, and a superacid medium is only one way to achieve this. Other ways include (i) using weakly coordinating (i.e., superweak) counteranions such as AsF_6^- and $\text{N}(\text{SO}_2\text{CF}_3)_2^-$,⁵ (ii) using weakly basic sites in zeolite host lattices as counteranions,⁶ and (iii) using the gas phase to form $\text{Cu}(\text{CO})_n^+(\text{g})$ species by eliminating the need for counteranions.⁷ We recently reported the synthesis of a new class of superweak⁸ anions, 1-R- $\text{CB}_{11}\text{F}_{11}^-$.⁹ In this paper we report that copper(I) salts of the R = benzyl (**I**[−]) and R = ethyl (**II**[−]) undecafluorocarborane anions will absorb up to four CO ligands per Cu^+ ion. The new compounds $\text{Cu}(\text{CO})_2(\text{I})$ and $[\text{Cu}(\text{CO})_4](\text{II})$, which were crystallized from solution under 1 atm of CO, were structurally characterized. The former compound is the third isolable copper(I) dicarbonyl¹⁰ and only the second one to be structurally characterized.^{5a} The latter compound is the first isolable copper(I) tetracarbonyl. The tetrahedral species $\text{Cu}(\text{CO})_4^+$ is the newest member of the series of isolable 3d¹⁰ metal tetracarbonyls $\text{Cr}(\text{CO})_4^{4-}$, $\text{Mn}(\text{CO})_4^{3-}$, $\text{Fe}(\text{CO})_4^{2-}$, $\text{Co}(\text{CO})_4^-$, and $\text{Ni}(\text{CO})_4$, the only member of the series that is cationic, and the only member with $\nu(\text{CO}) > 2143\text{ cm}^{-1}$.

The compounds $\text{Cu}(\text{CO})_2(\text{I})$ and $[\text{Cu}(\text{CO})_4](\text{II})$ were prepared by treating a 5-fold excess of CuCl with either Ag(**I**) or Ag(**II**),¹⁰

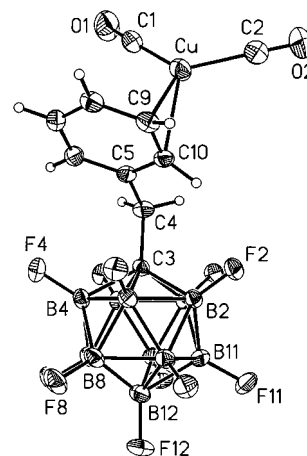


Figure 1. Structure of $\text{Cu}(\text{CO})_2(1\text{-Bn-CB}_{11}\text{F}_{11})$ ($\text{Cu}(\text{CO})_2(\text{I})$; 50% probability ellipsoids except for hydrogen atoms, which are shown as spheres of arbitrary size). Selected interatomic distances (Å) and angles (deg): Cu–C1, 1.916(3); Cu–C2, 1.915(3); Cu–C9, 2.218(2); Cu–C10, 2.303(2); C1–Cu–C2, 124.1(1); O1–C1–Cu, 177.7(2); O2–C2–Cu, 177.4(3); C1–Cu–C9, 119.2(1), C2–Cu–C9, 116.4(3); Cu–C9–C10, 75.2(1); Cu–C10–C9, 68.6(1).

respectively, in dichloromethane at 24 °C for 1 month under an atmosphere of CO. Excess CuCl and AgCl were separated by filtration. When the supernatant from either reaction was treated with 1 atm of CO and cooled to 0 °C, X-ray quality crystals of $\text{Cu}(\text{CO})_2(\text{I})$ and $[\text{Cu}(\text{CO})_4](\text{II})$ were formed. The structure of $\text{Cu}(\text{CO})_2(\text{I})$ is shown in Figure 1.¹¹ The copper(I) dicarbonyl moiety is bent, with Cu–C1 = 1.916(3) Å, Cu–C2 = 1.915(3) Å, and C1–Cu–C2 = 124.1(1)°. As was the case with $\text{Cu}(\text{CO})_2(\text{N}(\text{SO}_2\text{CF}_3)_2)$,^{5a} the Cu–CO bonds are considerably longer, and presumably much weaker, than the 1.806(6) Å Cu–CO bond in $\text{Cu}(\text{CO})(\text{en})(\text{BPh}_4)$,¹² the 1.78(1)–1.79(1) Å Cu–CO bonds in $[\text{Cu}(\text{CO})(\text{OPh})_2]_2$,¹³ or the 1.808(4) Å Cu–CO bond in $\text{Cu}(\text{CO})(\text{Tp})$.¹⁴ The structure of $[\text{Cu}(\text{CO})_4](\text{II})$,¹⁵ shown in Figure 2,

- (1) (a) Colorado State University. (b) Russian Academy of Sciences.
- (2) (a) Leblanc, F. C. *R. Acad. Sci. Paris* **1850**, 30, 483. (b) Berthelot, M. *Ann. Chim. Phys.* **1856**, 346, 477.
- (3) (a) Strauss, S. H. *Chemtracts: Inorg. Chem.* **1997**, 10, 77. (b) Rack, J. J.; Strauss, S. H. *Catal. Today* **1997**, 36, 99.
- (4) Souma, Y.; Iyoda, J.; Sano, H. *Inorg. Chem.* **1976**, 15, 968.
- (5) (a) $\text{Cu}(\text{CO})_{1.2,3}(\text{N}(\text{SO}_2\text{CF}_3)_2)$: Polyakov, O. G.; Ivanova, S. M.; Gaudinski, C. M.; Miller, S. M.; Anderson, O. P.; Strauss, S. H. Submitted for publication. (b) $\text{Cu}(\text{CO})_{1.2,3}(\text{AsF}_6)$: Rack, J. J.; Webb, J. D.; Strauss, S. H. *Inorg. Chem.* **1996**, 35, 277.
- (6) (a) Zecchina, A.; Bordiga, S.; Salvalaggio, M.; Spoto, G.; Scarano, D.; Lamberti, C. *J. Catal.* **1998**, 173, 540. (b) Iwamoto, M.; Hoshino, Y. *Inorg. Chem.* **1996**, 35, 6918. (c) Borokov, V. Y.; Karge, H. G. *J. Chem. Soc., Faraday Trans.* **1995**, 91, 2035.
- (7) Meyer, F.; Chen, Y.-M.; Armentrout, P. B. *J. Am. Chem. Soc.* **1995**, 117, 4071.
- (8) Lupinetti, A. J.; Strauss, S. H. *Chemtracts: Inorg. Chem.* **1998**, 11, 565.
- (9) Ivanov, S. V.; Rockwell, J. J.; Polyakov, O. G.; Gaudinski, C. M.; Anderson, O. P.; Solntsev, K. A.; Strauss, S. H. *J. Am. Chem. Soc.* **1998**, 120, 4224.
- (10) Ivanov, S. V.; Lupinetti, A. J.; Ivanova, S. M.; Anderson, O. P.; Solntsev, K. A.; Strauss, S. H. Manuscript in preparation.

- (11) $\text{Cu}(\text{CO})_2(1\text{-Bn-CB}_{11}\text{F}_{11})$ ($\text{Cu}(\text{CO})_2(\text{I})$): monoclinic, $P2_1/n$, $a = 9.4374(1)$ Å, $b = 16.1261(2)$ Å, $c = 13.3018(1)$ Å, $\beta = 99.160(1)^\circ$, $V = 1998.56(4)$ Å³, $Z = 4$. Data were collected at $-117(2)$ °C on a Siemens SMART System with Mo K_α radiation to $2\theta_{\text{max}} = 56.54^\circ$, giving 4817 unique reflections; the structure was solved by direct methods (Sheldrick, G. M. SHELXTL, version 5.03, 1994) with full-matrix least-squares refinement on F^2 , yielding $R1 = 0.040$ ($I > 2\sigma(I)$), $wR2 = 0.107$ (all data).
- (12) Pasquali, M.; Floriani, C.; Gaetani-Manfredotti, A. *Inorg. Chem.* **1980**, 19, 1191.
- (13) Lopes, C.; Håkansson, M.; Jagner, S. *Inorg. Chem.* **1997**, 36, 3232.
- (14) Dias, H. V. R.; Lu, H.-L. *Inorg. Chem.* **1995**, 34, 5380 (Tp' = hydridotris-(3,5-bis(trifluoromethyl)pyrazolyl)borate).
- (15) $[\text{Cu}(\text{CO})_4][1\text{-Et-CB}_{11}\text{F}_{11}]$ ($[\text{Cu}(\text{CO})_4](\text{II})$): orthorhombic, $P2_12_12_1$, $a = 10.6593(2)$ Å, $b = 13.3400(2)$ Å, $c = 13.8868(3)$ Å, $V = 1974.63(6)$ Å³, $Z = 4$. Data were collected at $-108(2)$ °C as described in ref 11: $2\theta_{\text{max}} = 56.64^\circ$; 4786 unique reflections; the structure was solved as described in ref 11: $R1 = 0.026$ ($I > 2\sigma(I)$); $wR2 = 0.083$ (all data).

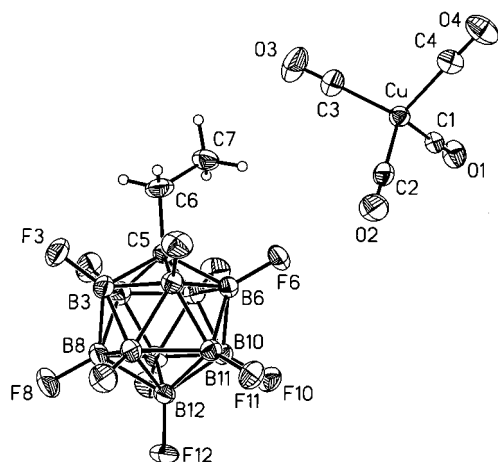


Figure 2. Structure of $[\text{Cu}(\text{CO})_4][1\text{-Et-CB}_{11}\text{F}_{11}]$ ($[\text{Cu}(\text{CO})_4][\text{I}]$; 50% probability ellipsoids except for hydrogen atoms, which are shown as spheres of arbitrary size). Selected interatomic distances (Å) and angles (deg): Cu–C1, 1.968(3); Cu–C2, 1.961(3); Cu–C3, 1.962(3); Cu–C4, 1.968(3); C–Cu–C, 104.3(1)–112.1(1); O–C–Cu, 174.8(3)–178.4(3).

consists of $\text{Cu}(\text{CO})_4^+$ cations and $1\text{-Et-CB}_{11}\text{F}_{11}^-$ anions that are essentially noninteracting. The closest $\text{F}\cdots\text{Cu}$ or $\text{F}\cdots\text{C}(\text{O})$ contacts are >3.1 and >2.8 Å, respectively. The six C–Cu–C bond angles span the range 104.3(1)–112.8(1)°, demonstrating only minor distortions from idealized T_d symmetry for the tetracarbonyl cation. The Cu–C bond distances, at 1.961(3)–1.968(3) Å, are by far the longest ever reported for a copper(I) carbonyl complex and are similar to the recent MP2-predicted distance of 1.932 Å.¹⁶

In the past, X-ray structures of metal carbonyls were rarely of sufficient precision that derived $R(\text{CO})$ values were significantly different (i.e., $\pm 3\sigma$) than 1.1282 Å, the distance in free CO.¹⁷ However, $R(\text{CO})$ values for $\text{Cu}(\text{CO})_2(\text{I})$, 1.109(3) and 1.115(3) Å, and for $[\text{Cu}(\text{CO})_4][\text{I}]$, 1.110(3), 1.114(3), 1.109(4), and 1.111(4) Å, are all significantly shorter than 1.1282 Å (a related example is $\text{Pd}(\text{CO})_2(\text{SO}_3\text{F})_2$,¹⁸ in which one of the two $R(\text{CO})$ values, 1.102(6) Å, was found to be significantly shorter than 1.1282 Å). Compare, for example, the significantly longer $R(\text{CO})$ values in two recently published “classical” metal carbonyl structures, $[\text{H}(\text{quinuclidine})][\text{Co}(\text{CO})_4]$, with $R(\text{CO}) = 1.150(2)$ – $1.153(2)$ Å, and $[\text{NEt}_4][\text{Cr}(\text{CO})_4(\text{NHMeCH}_2\text{CO}_2)]$, with $R(\text{CO}) = 1.154(3)$ – $1.165(3)$ Å.¹⁹

A solid-state IR spectrum of $\text{Cu}(\text{CO})_2(\text{I})$ under 1 atm of CO exhibited two $\nu(\text{CO})$ bands at 2166 (s) and 2184 (m) cm^{-1} , in harmony with the C_{2v} structure and a C–Cu–C angle $>90^\circ$ for the $\text{Cu}(\text{CO})_2^+$ moiety. The positions of these bands can be compared with the IR bands for $\text{Cu}(\text{CO})_2(\text{N}(\text{SO}_2\text{CF}_3)_2)$ (2158 (s), 2184 (m) cm^{-1} ; C–Cu–C = 122.0(2)°),^{5a} for $\text{Cu}(\text{CO})_2(\text{ZSM-5})$

(2151 (s), 2178 (m) cm^{-1}),^{6a} for $\text{Cu}(\text{CO})_2(\text{MFI-zeolite})$ (2151 (s), 2177 (m) cm^{-1}),^{6b} for $\text{Cu}(\text{CO})_2(\text{NaY})$ (2150 (s), 2178 (m) cm^{-1}),^{6c} and for $\text{Cu}(\text{CO})_2(\text{CF}_3\text{SO}_3)$ (2151 (s), 2178 (m) cm^{-1}).²⁰ Note that all of these $\nu(\text{CO})$ values are higher than 2143 cm^{-1} , suggesting that there is less π back-bonding for $\text{Cu}(\text{CO})_n^+$ species than for most metal carbonyl complexes, a conclusion reached many years ago by others.²¹ At CO pressures higher than 1 atm, new bands at 2172 (s) and 2190 (m) cm^{-1} appear at the expense of the 2166 and 2184 cm^{-1} bands. These are tentatively assigned as the E and A_1 $\nu(\text{CO})$ bands of the tricarbonyl complex $\text{Cu}(\text{CO})_3(\text{I})$ (cf. $\text{Cu}(\text{CO})_3(\text{N}(\text{SO}_2\text{CF}_3)_2)$, 2172 (s) and 2190 (m) cm^{-1} ,^{5a} and $\text{Cu}(\text{CO})_3(\text{ZSM-5})$, 2167 (s) and 2192 (m) cm^{-1}).^{6a} At a CO pressure of 1500 psi, a single band at 2185 cm^{-1} replaced the bands at 2172 and 2190 cm^{-1} . We believe that the band at 2185 cm^{-1} is the T_2 $\nu(\text{CO})$ band of the tetracarbonyl complex $[\text{Cu}(\text{CO})_4][\text{I}]$ (see below).

A solid-state IR spectrum of $[\text{Cu}(\text{CO})_4][\text{I}]$ under ~ 5 atm of CO exhibited one $\nu(\text{CO})$ band at 2184 cm^{-1} (there was a weak shoulder at ca. 2170 cm^{-1} ; see below), which is assigned as the T_2 $\nu(\text{CO})$ band for the idealized T_d $\text{Cu}(\text{CO})_4^+$ cation in this compound. For comparison, the T_2 $\nu(\text{CO})$ bands for $\text{Ni}(\text{CO})_4$, $\text{Co}(\text{CO})_4^-$, $\text{Fe}(\text{CO})_4^{2-}$, $\text{Mn}(\text{CO})_4^{3-}$, and $\text{Cr}(\text{CO})_4^{4-}$ are 2040, 1890, 1729, 1670, and 1462 cm^{-1} , respectively.²² The $\text{Cu}(\text{CO})_4^+$ cation is the first member of this isoelectronic series that is nonclassical according to the $\nu(\text{CO}) > 2143$ cm^{-1} definition. When the CO pressure above the sample of $[\text{Cu}(\text{CO})_4][\text{I}]$ was lowered from ~ 5 atm to ~ 0 atm in stages, bands tentatively assigned to “ C_{3v} ” $\text{Cu}(\text{CO})_3(\text{II})$, at 2173 (s) and 2187 (m) cm^{-1} , “ C_{2v} ” $\text{Cu}(\text{CO})_2(\text{II})$, at 2168 (s) and 2189 (m) cm^{-1} , and $\text{Cu}(\text{CO})(\text{II})$, at 2178 cm^{-1} , were observed. Interestingly, the removal of CO from the monocarbonyl complex $\text{Cu}(\text{CO})(\text{II})$ at 10^{-4} Torr was very slow (weeks at 25 °C), in contrast to the rapid removal of CO from the as-yet-unobserved monocarbonyl complex $\text{Cu}(\text{CO})(\text{I})$. It is possible that the presence of the relatively strongly coordinating phenyl substituent in $1\text{-Bn-CB}_{11}\text{F}_{11}^-$ promotes the rapid scission of the Cu–CO bond in $\text{Cu}(\text{CO})(\text{I})$. More detailed spectroscopic and structural studies are in progress.

Acknowledgment. This research was supported by Grant CHE-9628769 from the NSF. We also thank Air Products and Chemicals, Inc. and DuPont for financial support and the NIH Shared Instrumentation Grant Program for the SMART X-ray system.

Supporting Information Available: Tables S–1 to S–10, listing crystallographic parameters and results for $\text{Cu}(\text{CO})_2(\text{I})$ and $[\text{Cu}(\text{CO})_4][\text{I}]$. This material is available free of charge via the Internet at <http://pubs.acs.org>.

IC990321F

- (16) Lupinetti, A. J.; Jonas, V.; Thiel, W.; Frenking, G.; Strauss, S. H. Submitted for publication.
 (17) Gilliam, O. R.; Johnson, C. M.; Gordy, W. *Phys. Rev.* **1950**, *78*, 140.
 (18) Wang, C.; Willner, H.; Bodenbinder, M.; Batchelor, R. J.; Einstein, F. W. B.; Aubke, F. *Inorg. Chem.* **1994**, *33*, 3521.
 (19) $[\text{H}(\text{quinuclidine})][\text{Co}(\text{CO})_4]$: Brammer, L.; Mareque Rivas, J. C.; Zhao, D. *Inorg. Chem.* **1998**, *37*, 5512. $[\text{NEt}_4][\text{Cr}(\text{CO})_4(\text{NHMeCH}_2\text{CO}_2)]$: Darensbourg, D. J.; Draper, J. D.; Reibenspies, J. H. *Inorg. Chem.* **1997**, *36*, 3648.

- (20) Rack, J. J.; Polyakov, O. G.; Gaudinski, C. M.; Hammel, J. W.; Kasperbauer, P.; Hochheimer, H. D.; Strauss, S. H. *Appl. Spectrosc.* **1998**, *52*, 1035.
 (21) (a) Calderazzo, F. *J. Organomet. Chem.* **1990**, *400*, 303. (b) Pasquali, M.; Floriani, C. In *Copper Coordination Chemistry: Biochemical and Inorganic Perspectives*; Karlin, K. D., Zubieta, J., Eds.; Adenine Press: New York, 1983; p 311. (c) Bruce, M. I. *J. Organomet. Chem.* **1972**, *44*, 209.
 (22) Ellis, J. E. *Adv. Organomet. Chem.* **1990**, *31*, 1.