Notes

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Formation and Properties of Group 1B Metal Carbonyl Cations

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It is known that copper(I) compounds absorb carbon monoxide under various conditions with a Cu:CO ratio of 1:1. The copper carbonyl complexes such as CuCOX (X = Cl, Br, I),[1] $CuCOCF_3COO$,[2] and $CuCO$-π-C_5H_5[3] are unstable. Recently the preparations of the stable copper(I) carbonyl complexes such as $HB(pz)_3CuCO$ (pz = pyrazolyl) and *t*-BuOCuCO were reported by Bruce[4-6] and Tsuda.[7] On the other hand, the formation of copper polycarbonyl cations such as $Cu(CO)_3^+$ or $Cu(CO)_4^+$ in acidic media have been reported.[8,9] These copper(I) polycarbonyl cations are used as catalysts for carbonylation reactions of olefins,[10] alcohols,[11] and saturated hydrocarbons.[12] The existence of a silver carbonyl cation has also been reported.[13,14] The silver carbonyl cation has a similar catalytic activity to copper(I) carbonyl cations for carbonylation reactions in acid solution.[15]

This paper describes the formation of group 1B metal polycarbonyl cations such as $Cu(CO)_3^+$, $Cu(CO)_4^+$, and $Ag(CO)_2^+$ in strong acid media and spectral properties such as carbonyl stretching frequencies and ^{13}C NMR chemical shifts for the carbonyl groups.

Experimental Section

Materials. Cu_2O and Ag_2O were extra pure reagents and were used without further purification. H_2SO_4 was of analytical grade. FSO_3H and CF_3SO_3H were reagents for spectral analysis. HF was purified by trap to trap distillation using a vessel of Daiflon (poly(trifluorochloroethylene), Daikin). $BF_3 \cdot H_2O$ was prepared by treating BF_3 gas with water.

Preparation of Copper(I) Carbonyl Cation. In a 300-ml three-necked flask, equipped with a thermometer and carbon monoxide gas buret, 572 mg of Cu_2O and 20 ml of the strong acid were placed. The apparatus was evacuated after which carbon monoxide was introduced from the gas buret. The mixture of Cu_2O and strong acid was then stirred vigorously. The amount of absorbed CO was measured by a gas buret.

Preparation of Silver(I) Carbonyl Ion. The method was the same as that used for copper(I) carbonyl cation. However, 928 mg of Ag_2O and 20 ml of the strong acid were used.

Infrared Spectra Measurement. Infrared absorptions were recorded using a JASCO IRA-1 spectrophotometer. Measurement was carried out at ca. 10 °C with two sheets of polyethylene film. Spectra of $Ag(CO)_2^+$ and $Cu(CO)_3^+$ in H_2SO_4 were measured in a NaCl pressure cell under 5 atm of CO.

^{13}C NMR Spectra Measurement. The spectra were obtained using the pulse Fourier transform technique with a JEOL PS 100 instrument, FT-100 FT unit, DP-1 pulse programmer, and EC-100 computer, operating at a resonance frequency of 25.15 MHz. Proton noise decoupling was normally used. Chemical shifts are reported in ppm downfield from external TMS standard.

Results and Discussion

Under a CO atmosphere Cu_2O and Ag_2O absorbed CO to form colorless copper(I) carbonyl and silver(I) carbonyl cations in H_2SO_4, $BF_3 \cdot H_2O$, FSO_3H, CF_3SO_3H, and HF. The system in H_2SO_4 was a heterogeneous suspension whereas the systems in other acids were homogeneous. The copper(I) or silver carbonyl cations will exist as a form of $[S_mM(CO)_n]^+$-[counteranion]$^-$ (M = Cu or Ag, S = solvent); however, for the sake of brevity, the simple $M(CO)_n^+$ formulations will be used in the discussions below. In this report, the amounts of absorbed CO by Cu^+ or by Ag^+ were measured. The amount of absorbed CO increased with decreasing temperature. The results are shown in Figures 1 and 2. In dilute solutions of acids such as H_2SO_4, HCl, CH_3COOH, HCOOH, $HClO_4$, and H_3PO_4, $Cu(CO)^+$ is known to be comparatively stable, as described in a previous report.[8] It is stable even at 80 °C but decomposes to a Cu(I) salt by pumping away CO from the solution. The formation of $Cu(CO)_3^+$ is known in 98% H_2SO_4 at 7 atm of CO.[8] The formation of $Cu(CO)_4^+$ was found here in strong acids such as FSO_3H, CF_3SO_3H,

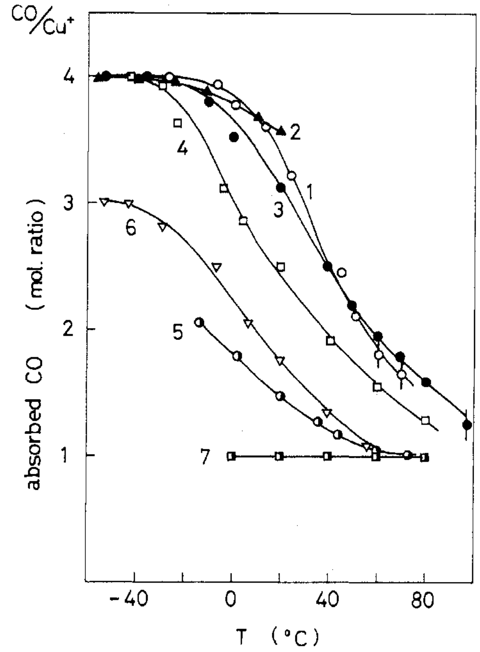

Figure 1. Formation of $Cu(CO)_n^+$ in strong acids: 1, $BF_3 \cdot H_2O$; 2, HF; 3, FSO_3H; 4, CF_3SO_3H; 5, H_2SO_4 (98%); 6, 1.0:0.3 FSO_3H–H_2SO_4; 7, H_2SO_4 (80%), 36% HCl, 60% $HClO_4$, HCOOH, CH_3COOH, H_3PO_4.

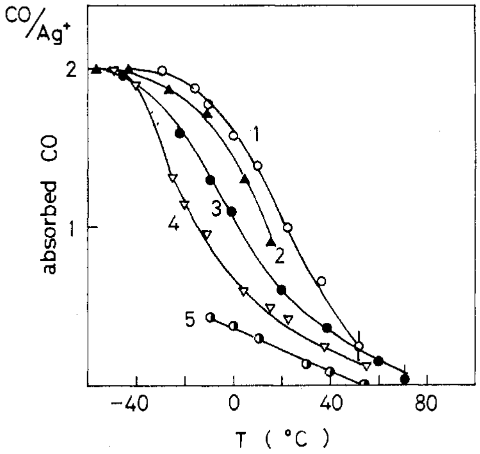

Figure 2. Formation of $Ag(CO)_2^+$ in strong acids: 1, $BF_3 \cdot H_2O$; 2, HF; 3, FSO_3H; 4, CF_3SO_3H; 5, H_2SO_4 (98%).

Table I. Carbonyl Stretching Frequencies $\nu_{C=O}$ of $Cu(CO)_n^+$ and $Ag(CO)_2^+$ in Strong Acids

	$\nu_{C=O}$, cm^{-1}			
Solvent	$Cu(CO)^+$	$Cu(CO)_3^+$	$Cu(CO)_4^+$	$Ag(CO)_2^+$
H_2SO_4	2140	2175		2186
1.0:0.3 FSO_3H–H_2SO_4	2150	2177		
CF_3SO_3H	2150		2180	2188
FSO_3H	2152		2183	2190
HF	2156		2184	2192
$BF_3 \cdot H_2O$	2160		2186	2193

$BF_3 \cdot H_2O$, and HF below −30 °C. In this complex cation the copper(I) carbonyl cation has the maximum coordination number. The amount of absorbed CO decreases when H_2SO_4 is added to the FSO_3H solution, and the number of coordinated CO groups is descreased to 3, i.e., $Cu(CO)_3^+$ as shown in Figure 1. This observation may be taken to suggest that the solvation tendency of Cu^+ in H_2SO_4 is a little greater than the other acids, therefore limiting the coordination of CO to Cu^+ in the presence of H_2SO_4. Among some acid solvents, the coordination tendency of CO to Cu^+ seems to decrease with the increase of solvation tendency of acid. On this assumption, the following order of solvation tendency can be given: $H_2SO_4 > CF_3SO_3H > FSO_3H > HF, BF_3 \cdot H_2O$. This order was also observed with Ag^+.

Both $Cu(CO)_3^+$ and $Cu(CO)_4^+$ are unstable and easily release CO with the increase of temperature and exist in equilibrium with $Cu(CO)^+$ in strong acids, i.e.

$$Cu(CO)_4^+ \rightleftharpoons Cu(CO)_3^+ + CO$$

$$Cu(CO)_3^+ \rightleftharpoons Cu(CO)^+ + 2CO$$

The formation of $Ag(CO)_2^+$ in H_2SO_4 at 20 atm of CO has been reported.[14] We have also observed this carbonyl cation in FSO_3H, CF_3SO_3H, $BF_3 \cdot H_2O$, and HF at −30 °C and even under atmospheric pressure of CO. $Ag(CO)_2^+$ is unstable and releases CO with increase in temperature, decomposing to Ag^+ and CO at 80 °C

$$Ag(CO)_2^+ \rightleftharpoons Ag^+ + 2CO$$

In carbonylation reactions of olefin and alcohol, $Cu(CO)_3^+$, $Cu(CO)_4^+$, and $Ag(CO)_2^+$ are the active catalytic species whereas $Cu(CO)^+$ exhibits no catalytic activity.[10,11] It seems that catalytic activity of the group 1B metal carbonyl cations depends upon the ease of releasing CO.

The copper(I) carbonyl and silver carbonyl cations reported in this paper are too unstable to be isolated in the pure state. Therefore, infrared spectra and ^{13}C NMR chemical shifts were measured in acid solutions.

The carbonyl stretching frequencies of $Cu(CO)_n^+$ and $Ag(CO)_2^+$ are given in Table I.

The carbonyl stretching frequencies vary in several acid solvents. The $\nu_{C=O}$ was highest in $BF_3 \cdot H_2O$ and lowest in H_2SO_4. The increasing order of $\nu_{C=O}$ (see Table I) was the same as the decreasing order of solvating tendency.

Among $Cu(CO)^+$, $Cu(CO)_3^+$, and $Cu(CO)_4^+$ $\nu_{C=O}$ becomes higher with increase in number of CO ligands. When the solvation tendency of acid becomes smaller, the electron density of Cu^+ becomes lower; hence the tendency for CO coordination becomes higher. The increase of $\nu_{C=O}$ in copper(I) carbonyl cations with increase in coordination number may be due to the positive charge on the copper.

In another acid solution such as $HClO_4$, HCOOH, CH_3COOH, and HCl, copper compounds absorb CO to form Cu(CO)X (X = anion). The $\nu_{C=O}$ of Cu(CO)X varies in each solution, as shown in Table II. The value of $\nu_{C=O}$ decreases with the decrease of acidity of solvents or with the increase of Cl^- concentration.

Table II. $\nu_{C=O}$ of CuCOX in Solution

CuCOX	$\nu_{C=O}$, cm^{-1}	Soln
$CuCOHSO_4$	2136	80% H_2SO_4
$CuCOHSO_4$	2128	50% H_2SO_4
$CuCOClO_4$	2130	60% $HClO_4$
CuCOHCOO	2119	95% HCOOH
$CuCOCH_3COO$	2109	95% CH_3COOH
CuCOCl[a]	2128	1.3% $HClO_4$
$CuCOCl \cdot 2H_2O$[a]	2126	White ppt
$CuCOCl_2^-$ [a]	2103	7%, 36% HCl

[a] CuCl was used to prepare CuCOX.

Table III. ^{13}C NMR Chemical Shifts of the Group 1B Metal Carbonyl Cations

	δ[a]			
Solvent	$Cu(CO)^+$ [b]	$Cu(CO)_3^+$ [c]	$Cu(CO)_4^+$ [c]	$Ag(CO)_2^+$ [b]
H_2SO_4	168.5			172.9
1.0:0.3 H_2SO_4–FSO_3H	169.0	169.2		
CF_3SO_3H	168.3		168.4	170.0
FSO_3H	169.2		171.1	172.2
$BF_3 \cdot H_2O$	169.0		169.5	173.4
HCl	170.7			

[a] Ppm downfield from external TMS. [b] Measured at 30 °C. [c] Measured at −30 to −60 °C.

In preparations containing $Cu(CO)_3^+$ or $Cu(CO)_4^+$, the characteristic absorptions of $Cu(CO)^+$ were always observed, because these cations exist as an equilibrium mixture. During the repeated measurements on one sample, the absorption of $Cu(CO)_3^+$ or $Cu(CO)_4^+$ diminished gradually with the rise of temperature, and the absorption of $Cu(CO)^+$ remained.

The ^{13}C NMR chemical shifts of the group 1B metal carbonyl cations are given in Table III.

The carbonyl resonances of copper(I) carbonyl and silver(I) carbonyl cations were observed as singlets in the carbonyl region. The signals of copper(I) carbonyl cations were broad owing to the quadrupole broadening effect of the nucleus.[29] In the case of silver(I) carbonyl cations, coupling constants J_{Ag-C} were not observed, though both ^{107}Ag and ^{109}Ag have $^1/_2$ spin. We suggest that exchange of CO is very rapid.

The measurements of the ^{13}C NMR spectra of $Cu(CO)_3^+$ and $Cu(CO)_4^+$ were carried out at −30 to −60 °C. The ^{13}C NMR signals of $Cu(CO)_3^+$ and $Cu(CO)_4^+$ were broader than the signals of $Cu(CO)^+$ at 30 °C.[30] The clear differences between the carbonyl chemical shifts for $Cu(CO)^+$, $Cu(CO)_3^+$, and $Cu(CO)_4^+$ were not found, although the high-field shifts were anticipated in $Cu(CO)_3^+$ and $Cu(CO)_4^+$ in parallel with the increase of $\nu_{C=O}$. NMR spectra were obtained for various samples in which the ratio of $Cu(CO)_4^+$ to $Cu(CO)^+$ was varied. This was done in a temperature range of −30 to −60 °C. In the measurements, we covered the region of carbonyl chemical shifts from 300 to 130 ppm. If $Cu(CO)_4^+$ and $Cu(CO)^+$ were to have different chemical shifts, the data would have shown scattered chemical shifts corresponding to their average carbonyl environment, but the observed shifts were virtually the same in every measurement (i.e., 168.4–171.1 ppm). Here it is important to note that an HCl solution of only $Cu(CO)^+$ gives a chemical shift value of 170.1 ppm. Thus the chemical shifts of $Cu(CO)_n^+$ (n = 3, 4) were almost the same as the value obtained for $Cu(CO)^+$ in HCl solution. Therefore we concluded that the chemical shift values for $Cu(CO)^+$, $Cu(CO)_3^+$, and $Cu(CO)_4^+$ were approximately the same and that the total electron density around the carbon atom seems not to change in these three species. We suggest that the bonding between Cu^+ and CO (π back-bonding and σ dative bonding) changed with the increase of the coordinated number of CO.

Table IV. ^{13}C NMR Carbonyl Chemical Shifts and Stretching Frequencies in Transition Metal Carbonyl Compounds

Compd	δ, ppm	Ref	$\nu_{C=O}$, cm^{-1}	Ref
CO	181.5	17	2143	22
$Cu(CO)^+$	169.0		2160	*a*
$Cu(CO)_3^+$	169.2		2177	*b*
$Cu(CO)_4^+$	169.5		2185	*a*
$Ag(CO)_2^+$	173.4		2193	*a*
$Ni(CO)_4$	191.1	18	2057	23
$Co_2(CO)_8$	203.8	19	2070, 2043, 2025	24
$Fe(CO)_5$	211.9	20	2045, 2027	25
$Cr(CO)_6$	212.3	21	2100, 2020	26
$V(CO)^-$	225.7	16	1850	27
$V_2(CO)_{12}$			1980	28

[a] This work—data in $BF_3 \cdot H_2O$. [b] This work—data in 1.0:0.3 H_2SO_4–FSO_3H.

The comparison of ^{13}C NMR chemical shifts and ir stretching frequencies in transition metal carbonyl compounds is shown in Table IV. The $\nu_{C=O}$ in 1B metal carbonyl compounds is larger than in free CO or other metal carbonyl compounds. The ^{13}C NMR chemical shifts of 1B metal carbonyl compounds are observed at higher field than in other carbonyl compounds. This may be due to the shortening of C—O bond caused by the C→M dative bond.

Bodner et al. have observed a correlation between ^{13}C NMR carbonyl chemical shifts and the stretching frequencies for a series of (π-arene)tricarbonylchromium complexes and suggested that the ^{13}C chemical shift is deshielded with increasing π back-donation.[16] From Table IV, the decrease of π back-donation in the order $V(CO)_6^- > Cu(CO)_4^+$ is suggested from the increase in $\nu_{C=O}$ and in the shielding of the ^{13}C NMR chemical shift. A linear relationship is found between ^{13}C NMR chemical shift and the carbonyl stretching frequency.

Registry No. $Cu(CO)^+$, 28410-99-3; $Cu(CO)_3^+$, 28990-05-8; $Cu(CO)_4^+$, 41697-87-4; $Ag(CO)_2^+$, 49694-96-4.

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(29) The half-bandwidths of $Cu(CO)^+$ were 38, 33, 8, 10, and 10 Hz in H_2SO_4, CF_3SO_3H, FSO_3H, $BF_3 \cdot H_2O$, and HCl solutions, respectively. On the other hand, the half-bandwidths of $Ag(CO)_2^+$ were 6 Hz in all of the above solutions.
(30) The half-bandwidths of $Cu(CO)_4^+$ in FSO_3H solution were 52 Hz at −30 °C and 133 Hz at −60 °C. In $BF_3 \cdot H_2O$ solution the values were 15 Hz at −30 °C and 37 Hz at −45 °C.

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Niobium–Dinitrogen Complexes Studied by Infrared Matrix Isolation Spectroscopy[1a]

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Nitrogen had long been thought to have no affinity for transition metals on the basis of the inertness of gaseous nitrogen itself. This view has changed drastically in the last few years which have seen the preparation of a large number of transition metal complexes containing molecular nitrogen[2] following the initial synthesis[3] of $[Ru(NH_3)_5(N_2)]^{2+}$. More recently binary metal–dinitrogen complexes including those of Li,[4] Ni and Pd,[5] Cr and Cu,[6] Pt,[7] Co,[8] and Rh[9] have been synthesized in noble gas matrices at low temperatures. It is the purpose of this Note to present some results of experiments in which Nb atoms were cocondensed with N_2 in Ar matrices at 14 K.

Experimental Section

Metal atoms were produced by a sputtering source[10] with a Nb metal (Research Organic/Inorganic Chemical Corp.) cathode using Ar as the sputtering gas as well as the matrix gas. Experimental procedures were similar to those described previously in the study of Pt–N_2 complexes.[7a] The estimated Ar:Nb ratio was 10^4:1 in the matrix. Due to the breadth of most of the observed peaks, the frequency accuracy is ±1 cm^{-1} above 2000 cm^{-1} and ±0.5 cm^{-1} below 2000 cm^{-1}.

Results

Compared to the corresponding spectra obtained[7a] by cocondensing Pt and N_2, the spectra obtained by cocondensing Nb and N_2 are strikingly different in two ways. First, the number of absorption peaks observed is much greater in the case of Nb + N_2 which suggests that a larger number of complexes are formed. Second, the frequency range of these peaks (1850–2200 cm^{-1}) extends to considerably lower frequency in the case of Nb + N_2. This suggests the Nb–N_2 interaction is stronger than that of Pt–N_2 (or any other reported metal–dinitrogen complex with the possible exception of Li, for which the assigned[4] N–N stretch of LiN_2 is 1800 cm^{-1}) if one interprets the difference between the frequency of gaseous N_2 and that of the complex as a measure of the strength of interaction.

In order to determine the nature of the absorbers responsible for these peaks, several experiments were performed. The spectrum of Nb in an Ar matrix, taken in the absence of N_2, demonstrated that no major absorption peak in the frequency range of interest was due to an impurity in the Nb, in the Ar, or in the background gas. A study of the products of the condensation of Nb with CO in Ar matrices[11] has specifically shown that none of the major absorptions can be attributed to $Nb(CO)_x$ or $Nb(CO)_x(N_2)_y$ complexes. Further evidence that all of the peaks can be assigned to the N–N stretches of various Nb–N_2 complexes is contained in Table I which compares the frequencies observed in different experiments using $^{14}N_2$ to their counterparts when $^{15}N_2$ was used. When the Cotton–Kraihanzel force-field approximation[12] is applied to metal–dinitrogen complexes, it is predicted that at least one N–N stretching mode of a $M(^{15}N_2)_x$ complex should show