Infrared and Manometric Evidence for the Formation of the $[Ag(CO)_3]^+$ Complex Ion at High P_{CO}

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At high pressures of CO, the Ag^+ salt of the weakly coordinating anion $[Nb(OTeF_5)_6]^-$ takes up three equiv. CO reversibly both in the solid state and in 1,1,2-$C_2Cl_3F_3$ solution; the CO ligands can be removed from $[Ag(CO)_3][Nb(OTeF_5)_6]$ under vacuum at 25 °C but none are removed at −78 °C; IR ν(CO) values are 2192 cm^{-1} for $[Ag(CO)_3]^+$, 2198 cm^{-1} for $[Ag(CO)_2]^+$, and 2208 cm^{-1} for $[AgCO]^+$.

Until recently, isolable silver(I) carbonyls were unknown. Manchot and coworkers reported that a solution of Ag_2SO_4 in conc. H_2SO_4 reversibly absorbed carbon monoxide. A limiting Ag : CO stoichiometry of 2 : 1 was achieved when $T = 0$ °C and $P_{CO} =$ *ca.* 1 atm (1 atm = 101.3 kPa).[1,2] Later, Souma and coworkers found that this phenomenon was general for a variety of Ag^+ salts in a variety of strong protic acids (*e.g.* HSO_3F, $BF_3{\cdot}H_2O$).[3,4] These authors were able to achieve a Ag : CO stoichiometry of 1 : 2, but only at low temperatures (*e.g.* −40 °C at 1 atm) or high pressures (*e.g.* 19 atm at 24 °C). In neither Manchot's nor Souma's work were silver carbonyls isolated from solution.

Using a variety of weakly coordinating anions,[5] we have recently isolated a number of compounds containing the $[AgCO]^+$ and $[Ag(CO)_2]^+$ ions, and have structurally characterized two of them, $[AgCO][B(OTeF_5)_4]$[6] and $[Ag(CO)_2][B(OTeF_5)_4]$.[7] Based on structural and vibrational spectroscopic data, we suggested that there is little or no Ag → CO π-backbonding in these cationic carbonyls, a conclusion that has now been supported by Veldkamp and Frenking using calculations at the MP2 level of theory.[8,9] These authors also predicted the existence of a weakly bound D_{3h} $[Ag(CO)_3]^+$ ion: the first Ag–CO dissociation energies for $[AgCO]^+$, $[Ag(CO)_2]^+$ and $[Ag(CO)_3]^+$ were calculated to be 20, 24 and 11 kcal mol^{-1} (1 cal = 4.184 J), respectively, at 298 K. Here, we report on the formation, characterization, and stability of the cationic tricarbonyl complex $[Ag(CO)_3]^+$.

Our expectation was that the preparation of $[Ag(CO)_3]^+$ would require a pressure of CO well above 1 atm. Furthermore, the silver(I) carbonyls $[AgCO]^+$ and $[Ag(CO)_2]^+$ are labile with respect to loss of CO, at least at room temperature.[6,7] These factors preclude measuring the Ag : CO stoichiometry for a $[Ag(CO)_n]^+$ complex ($n > 2$) by gas buret titration or by a simple mass increase. Therefore, the following procedure was used: a weighed sample of solid $AgNb(OTeF_5)_6$[10] (*ca.* 0.3 g) was subjected to 13 atm CO for 4 h at 25 °C. After cooling the sample to −78 °C for 30 min, it was placed under vacuum until the pressure in the steel bomb containing the sample reached 10^{-5} Torr. The bomb was cooled to −196 °C and ~5 ml toluene were added. The mixture was then warmed to 25 °C and the CO evolved was collected, through a series of −196 °C traps, with a Toepler pump. The number of equiv. CO collected per equiv. Ag in two separate determinations was 3.05 and 3.06, confirming the formation of $[Ag(CO)_3]^+$. The tricarbonyl complex of Ag^+ is apparently not labile at −78 °C.

It was previously found that any solvent that dissolved $[AgCO][B(OTeF_5)_4]$ or $[Ag(CO)_2][B(OTeF_5)_4]$ displaced the CO ligands.[6,7,11] Complete displacement occurred in solvents such as toluene and dichloromethane as well as in acetone and nitromethane. Only chlorofluorocarbon solvents could be used to grow crystals of these labile carbonyls, and even here solvent molecules compete with CO for coordination to Ag^+. Fig. 1 shows IR spectra of $AgNb(OTeF_5)_6$ dissolved in 1,1,2-$C_2Cl_3F_3$ at 25 °C under pressures of CO that range from 1 to 100 atm.[12] At 1 atm, ν(CO) bands are observed for both $[AgCO]^+$ [shoulder at 2210 cm^{-1}; solid-state (Nujol mull) value 2208 cm^{-1} at < 10 Torr CO] and $[Ar(CO)_2]^+$ (2198 cm^{-1}; solid-state value 2198 cm^{-1} at 1 atm CO). As the pressure increases, the band at *ca.* 2210 cm^{-1} disappears and the band at 2198 cm^{-1} appears to shift to lower energy. All spectral changes were fully reversible as a function of pressure. Our interpretation is that the equilibria shown in eqn. (1) are shifted to the right as the CO pressure increases

$$[AgCO]^+ \underset{-CO}{\overset{+CO}{\rightleftharpoons}} [Ag(CO)_2]^+ \underset{-CO}{\overset{+CO}{\rightleftharpoons}} [Ag(CO)_3]^+ \qquad (1)$$

and that the band at *ca.* ~2195 cm^{-1} at 100 atm is the convolution of ν(CO) bands for linear $[Ag(CO)_2]^+$ (Σ_u^+ normal mode) and $[Ag(CO)_3]^+$ (E' normal mode assuming D_{3h} symmetry).

This conclusion was confirmed by recording IR spectra of solid-state samples of $AgNb(OTeF_5)_6$ at varying pressures of CO. Fig. 2 shows IR spectra of a Fluorolube mull of $AgNb(OTeF_5)_6$ under 1.6 and 13 atm CO at 25 °C.[13] Note that a separate and distinct band for the tricarbonyl complex is observed at 2192 cm^{-1} at 13 atm CO. This band is assigned to the E' ν(CO) normal mode of $[Ag(CO)_3]^+$. The shoulder at

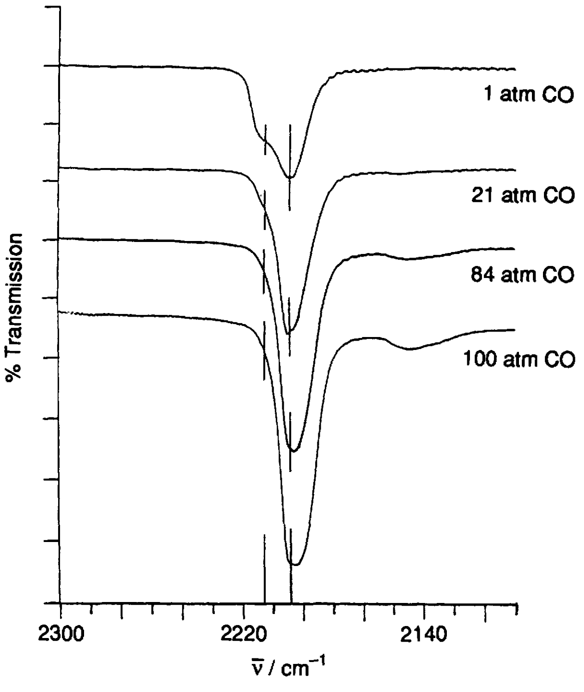

Fig. 1 IR spectra of $AgNb(OTeF_5)_6$ dissolved in 1,1,2-$C_2Cl_3F_3$ at varying pressures of CO at 25 °C. Vertical lines have been drawn at 2210 and 2198 cm^{-1}. The weak band at 2142 cm^{-1} in the 84 and 100 atm spectra is due to dissolved CO (incomplete spectral subtraction) and the wavelike baseline in the 2200–2100 cm^{-1} region in some of the spectra is due to bubbles of CO gas adhering to the silicon crystal of the cylindrical internal reflectance cell.

ca. 2200 cm^{-1} in the 13 atm spectrum may be due to the A_1' ν(CO) mode of D_{3h} $[Ag(CO)_3]^+$ rendered IR active by site symmetry lowering. Note that the formation of $[Ag(CO)_3]^+$ is complete at 13 atm CO pressure in the solid state (*i.e.* in the absence of potentially coordinating solvent molecules), whereas in 1,1,2-$C_2Cl_3F_3$ solution, the formation of $[Ag(CO)_3]^+$ seems to be far from complete even at 100 atm CO pressure.

The formation of $[Ag(CO)_3]^+$, a weakly bound species with little or no π-backbonding, suggests that carbonyls of the d^{10} metal cations Zn^{2+}, Cd^{2+}, and Hg^{2+}, and possibly the $d^{10}s^2$ metal cations Tl^+ and Pb^{2+}, might be prepared and isolated using high pressure techniques.

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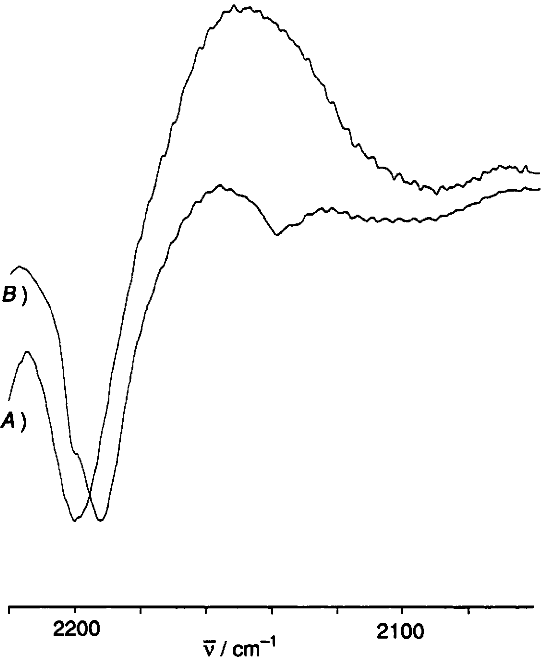

Fig. 2 IR spectra of a Fluorolube mull of $AgNb(OTeF_5)_6$ under 1.6 atm (*A*) and 13 atm (*B*) CO at 25 °C. Spectrum *A* has been expanded vertically by a factor of 2. The peak at 2199 cm^{-1} in *A* is assigned to the Σ_u^+ symmetry ν(CO) mode of linear $[Ag(CO)_2]^+$. The peak at 2192 cm^{-1} in spectrum *B* is assigned to the *E'* symmetry ν(CO) mode of $[Ag(CO)_3]^+$. The weak band at 2138 cm^{-1} in spectrum *B* is due to CO gas dissolved in Fluorolube (confirmed by control experiments) and the wave-like baseline in the 2200–2160 cm^{-1} region of both spectra is due to a very small amount of CO gas in the beam path. The intensity of the most intense peak in each spectrum is equivalent to ~1% transmittance.

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