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Nonclassical Metal Carbonyls: $[Ag(CO)]^+$ and $[Ag(CO)_2]^+$ †

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Abstract: The synthesis and characterization of salts of the cationic silver(I) carbonyl complexes $[Ag(CO)]^+$ and $[Ag(CO)_2]^+$ are reported. The counterions used include $OTeF_5^-$ and the weakly coordinating anions $B(OTeF_5)_4^-$, $Zn(OTeF_5)_4^{2-}$, $Nb(OTeF_5)_6^-$, and $Ti(OTeF_5)_6^{2-}$. Despite the fact that carbon monoxide is reversibly bound to silver(I), these compounds are stable enough to be isolated as crystalline solids under a CO atmosphere or at low temperatures. Two of the new compounds, $[Ag(CO)][B(OTeF_5)_4]$ and $[Ag(CO)_2][B(OTeF_5)_4]$, were studied by single-crystal X-ray diffraction. A combination of manometric, spectroscopic, and diffraction results suggests little or no Ag → CO π-back-bonding in these complexes, which makes them rare examples of σ-only metal carbonyls (and for which we propose the name nonclassical metal carbonyls). The data include the following: $\nu(CO)$ values, which range from 2189 to 2220 cm^{-1}; solid-state $\delta(^{13}C)$ values, which are ~ 171; $J_{^{109}Ag^{13}C}$ values, which range from 190 to 284 Hz; chemical shift anisotropies, which range from $-45(5)$ to $-76(5)$ ppm for $\sigma_{\|}$ and from 280(5) to 295(5) ppm for $\sigma_{\perp}$; Ag–C and C–O bond distances for $[Ag(CO)][B(OTeF_5)_4]$, which are 2.10(1) and 1.077(16) Å, respectively; and Ag–C and C–O bond distances for the three unique cations in $[Ag(CO)_2][B(OTeF_5)_4]$, which range from 2.06(5) to 2.20(4) Å and from 1.07(5) to 1.09(6) Å, respectively. For $[Ag(CO)][B(OTeF_5)_4]$, monoclinic, $P2_1/n$: $a = 10.001(2)$ Å, $b = 16.180(4)$ Å, $c = 12.235(3)$ Å, $\beta = 100.48(2)°$, $Z = 4$, $T = -125$ °C, $R = 0.040$. For $[Ag(CO)_2][B(OTeF_5)_4]$, triclinic, $P\bar{1}$: $a = 10.367(5)$ Å, $b = 13.146(7)$ Å, $c = 16.56(1)$ Å, $\alpha = 87.77(5)°$, $\beta = 76.38(4)°$, $\gamma = 89.06(4)°$, $Z = 4$, $T = -100$ °C, $R = 0.078$. The structure of $[(CH_3)_2CHCO][SbCl_6]$ was redetermined at low temperature by single-crystal X-ray diffraction. The C–O distance in the acylium cation was found to be 1.101(4) Å, significantly shorter than the 1.12822(7) Å bond distance in gaseous CO. For $[(CH_3)_2CHCO][SbCl_6]$, orthorhombic, $Pnma$: $a = 19.368(1)$ Å, $b = 7.055(1)$ Å, $c = 9.108(1)$ Å, $Z = 4$, $T = -130$ °C, $R = 0.020$.

Introduction

Carbon monoxide is without a doubt one of the most important ligands in transition metal chemistry. Many industrial processes, from hydroformylation and the Fischer–Tropsch synthesis to the synthesis of acetic acid and the water–gas shift reaction, employ CO as a reagent and transition metal compounds as heterogeneous or homogeneous catalysts and involve the intermediacy of metal carbonyls.[2] Carbon monoxide is used to stabilize transition metals in low, even negative, oxidation states.[3] It is also used as a probe ligand in fields such as surface chemistry, organometallic chemistry, and biochemistry. There are many thousands of citations in the literature that include the keyword phrase "metal carbonyl".[4]

The classical picture of metal–carbonyl bonding is well understood and is probably one of the best-remembered concepts in the inorganic chemistry curriculum. The metal–carbonyl interaction involves synergistic bonding, with carbon monoxide acting as a σ-donor and a π-acceptor for d-block metals.[5,6] However, this picture may not be accurate for all d-block metals. While there are many thousands of stable, isolable transition metal carbonyl complexes, there are few or none known for the metals at the extreme fringes of the d-block. For example, the group 3 d^0 ions Sc^{3+}, Y^{3+}, and La^{3+} have not yielded any isolable carbonyl complexes, presumably because their lack of d electrons precludes π-back-bonding and synergistic bonding. In addition, no isolable carbonyls are known for the group 12 d^{10} ions Zn^{2+} and Cd^{2+}, presumably because their effective nuclear charges are too high to permit effective metal → carbon d → π^* π-back-bonding. (The first isolable carbonyl complex of Hg^{2+}, $[Hg(CO)_2][Sb_2F_{11}]_2$, was reported very recently.[7]) Groups 4 and 11 are better represented. Isolable carbonyls are known for some of the elements of these groups, with the greatest number known for Cu^+. Examples include $[Ti(CO)_6]^{2-}$,[3] $[Zr(\eta^5\text{-}C_5Me_5)_2(CH_3CO)(CO)]^+$,[8] $Cu(CO)Cl$,[9] $[Cu_2(CO)(dcmpz)_2(py)_2]$ (Hdcmpz = 3,5-dicarbomethoxypyrazole),[10] $Au(CO)Cl$,[11] and $[Au(CO)_2][Sb_2F_{11}]$.[12] Significantly, before this work was started, there

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† Dedicated to Professor D. F. Shriver, teacher, scholar, and friend, on the occasion of his 60th birthday.

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were no known isolable carbonyl complexes of Ag^+, despite the fact that silver(I) carbonyls have been shown to exist in solution[13] and in the solid state[14,15] and have been implicated in a number of catalytic processes.[16]

Based on the existence of simple Lewis acid/base adducts such as HCO^+,[17] CH_3CO^+,[18] and BH_3CO,[19] an entire class of metal carbonyls should be stable for d-block metal ions that cannot, for whatever reason, participate in π-back-bonding. We propose the name *nonclassical metal carbonyls* for this growing class. Since CO is an extremely weak base,[20] our approach to the synthesis of nonclassical, σ-only metal–carbonyl complexes is to use new weakly coordinating anions[21] to make certain metal ions more Lewis acidic than has been previously possible. It is within this framework that we are studying the CO coordination chemistry of the metal ions of groups 3, 4, 11, and 12. Our isolation and characterization of the elusive group 11 d^{10} complexes $[Ag(CO)]^+$ and $[Ag(CO)_2]^+$ are reported in this paper.[22,23]

Results

Synthesis of $[Ag(CO)_n]^+$ Complexes and Determination of *n*. Solid samples of the extremely hygroscopic compounds $AgOTeF_5$, $AgB(OTeF_5)_4$, $Ag_2Zn(OTeF_5)_4$, $AgNb(OTeF_5)_6$, and $Ag_2Ti(OTeF_5)_6$ reversibly absorbed CO gas at less than 1 atm at 25 °C. For pressures up to and including 1 atm, the silver(I) ion in $AgOTeF_5$ formed only a 1:1 complex, $[Ag(CO)][OTeF_5]$. The other salts formed 1:1 $[Ag(CO)]^+$ complexes at low pressures and 1:2 $[Ag(CO)_2]^+$ complexes at pressures approaching 1 atm. The compound $AgB(OTeF_5)_4$ slowly decomposes to $AgOTeF_5$ and volatile $B(OTeF_5)_3$,[24,25] but as long as CO gas was present the compounds $[Ag(CO)][B(OTeF_5)_4]$ and $[Ag(CO)_2][B(OTeF_5)_4]$ were stable indefinitely. The compounds AgCl, $AgClO_4$, and $AgSbF_6$ did not absorb any measurable amount of CO under these conditions.

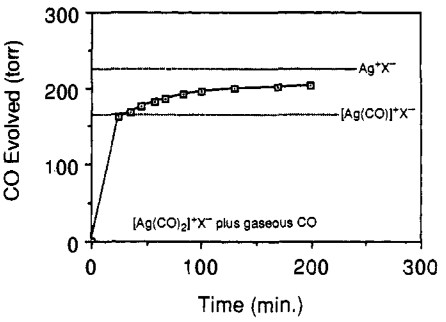
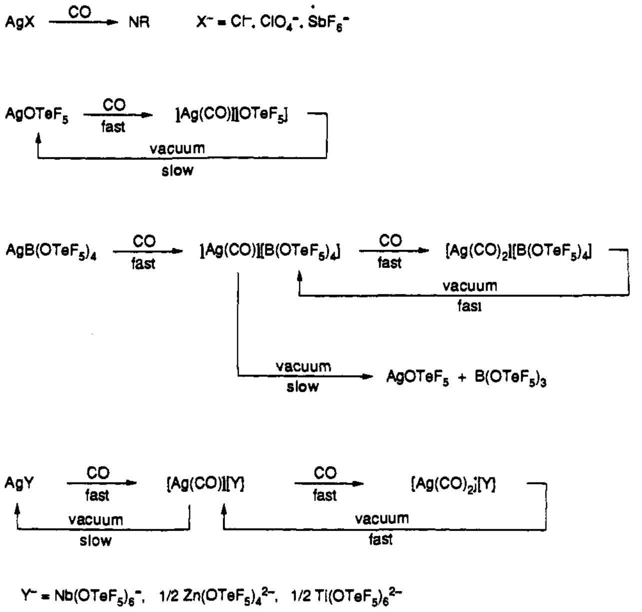


Figure 1. Pressure of carbon monoxide evolved from $[Ag(CO)_2][B(OTeF_5)_4]$ vs time ($X^- = B(OTeF_5)_4^-$). The sample was equilibrated at 183 Torr CO, at which pressure the formation of $[Ag(CO)_2][B(OTeF_5)_4]$ was >90% complete. The sample container was then evacuated with a Toepler pump for 3.5 h, and the amount of CO evolved was measured periodically. The data show that 1 equiv of CO is evolved rapidly (minutes) from $[Ag(CO)_2]^+$ and that CO is evolved slowly (hours) from $[Ag(CO)]^+$.

Scheme 1



The uptake of gaseous CO by the silver(I) salts was rapid: most reactions were complete within minutes. When the pressure of CO above the solid samples was reduced to zero by placing the samples under vacuum, 1 equiv of CO was lost from the $[Ag(CO)_2]^+$ cation within minutes, and the remaining equivalent was lost over a period of hours. This is shown graphically in Figure 1 for a sample of $[Ag(CO)_2][B(OTeF_5)_4]$ that was originally under 183 Torr of CO. These results are summarized in Scheme 1.

Vibrational Spectroscopy. As will be discussed later, even weakly coordinating solvents such as nitromethane, toluene, diethyl ether, and dichloromethane competed with CO for

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(23) We define a carbonyl complex as a stoichiometric $ML_x(CO)_y$ compound with at least one demonstrable M–C≡O linkage. In this vein, complexes such as $Pt(CO)(AuPPh_3)_8Ag(NO_3)_3$[23a] and $Cp(CO)_2Mo(\mu\text{-}Ag(PPh_3))(\mu\text{-}PPh_2)\text{-}Mn(CO)_4$,[23b] with all Ag–C(O) distances ≥2.7 Å, are not silver(I) carbonyls: (a) Kanters, R. P. F.; Schlebos, P. P. J.; Bour, J. J.; Bosman, W. P.; Smits, J. M. M.; Beurskens, P. T.; Steggerda, J. J. *Inorg. Chem.* **1990**, *29*, 324. (b) Horton, A. D.; Mays, M. J.; Adatia, T.; Henrick, K.; McPartlin, M. *J. Chem. Soc., Dalton Trans.* **1988**, 1683.

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Table 1. Vibrational Spectral Data[a]

cation	anion	medium	ν(CO), cm^{-1}
$[Ag(CO)]^+$	$OTeF_5^-$	Nujol mull	2189 (IR)
			2193 (Raman)
	$B(OTeF_5)_4^-$	Nujol mull	2204[b]
	$Zn(OTeF_5)_4^{2-}$	Nujol mull	2203
	$Ti(OTeF_5)_6^{2-}$	Nujol mull	2207
	$Nb(OTeF_5)_6^-$	Nujol mull	2208
		powder	2204 (IR)
			2206 (Raman)
		1,1,2-$C_2Cl_3F_3$ soln	~2209[c]
$[Ag(CO)_2]^+$	$B(OTeF_5)_4^-$	Nujol mull	2198
	$Zn(OTeF_5)_4^{2-}$	Nujol mull	2197
	$Ti(OTeF_5)_6^{2-}$	Nujol mull	2197
	$Nb(OTeF_5)_6^-$	Nujol mull	2198
		powder	2196 (IR)
			2220 (Raman)
		1,1,2-$C_2Cl_3F_3$ soln	2197

[a] All data from IR spectra unless otherwise noted. Peak positions are ±1 cm^{-1}. [b] ν(CO) for $[Ag^{13}CO][B(OTeF_5)_4]$ = 2154 cm^{-1}. [c] Shoulder; see Figure 4.

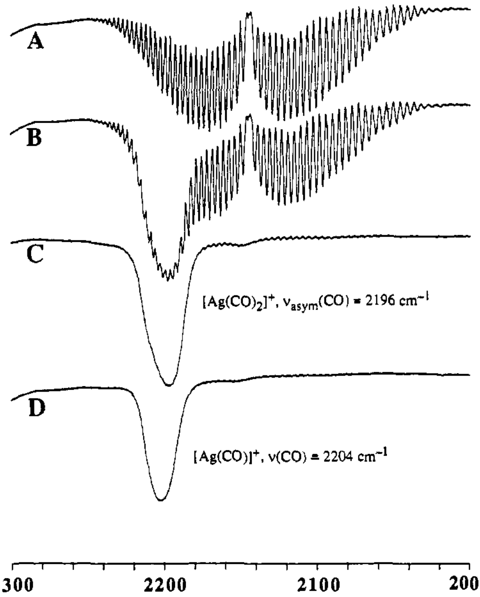

Figure 2. IR spectra taken with a 1.6 cm path length gas-phase cell with AgBr windows: (A) 501 Torr of CO, ν(CO) = 2143 cm^{-1}; (B) solid $AgNb(OTeF_5)_6$ deposited on the inside of both windows (no mulling agent) plus 501 Torr of CO; (C) spectrum A subtracted from spectrum B—the peak at 2196 cm^{-1} is assigned to ν_{asym}(CO) for $[Ag(CO)_2]^+$; (D) the sample for spectrum B placed under vacuum for ~10 min—the peak at 2204 cm^{-1} is assigned to ν(CO) for $[Ag(CO)]^+$.

coordination to Ag^+. Therefore, most vibrational data reported here are for solid samples (powders, Nujol mulls, or Fluorolube mulls). In most cases, spectra were recorded at 25 °C using mulls of the compounds spread on the inside surfaces of one or both AgBr windows of a short path length (1.6-cm) gas IR cell assembled in the glovebox. A vacuum-tight seal was made by pressing the windows against O-rings that fit into grooves machined into the body of the brass cell. In another experiment, a 1,1,2-$C_2Cl_3F_3$ solution of $AgNb(OTeF_5)_6$ was added dropwise to one surface of both cell windows inside the glovebox. Following evaporation of the solvent, the cell was assembled and spectra of the powdered sample were recorded in the presence and absence of CO. This was done so that IR and Raman spectra for at least one compound could be recorded on dry powdered samples (i.e., no mulling agent present). The results are listed in Table 1. The presence of a mulling agent resulted in small shifts in ν(CO) bands. IR and Raman spectra for $[Ag(CO)_n][Nb(OTeF_5)_6]$ (n = 1, 2) in the CO region are shown in Figures 2 and 3. The IR spectrum of a 1,1,2-$C_2Cl_3F_3$ solution of $AgNb(OTeF_5)_6$ under a partial atmosphere of CO was also recorded. This spectrum is shown in Figure 4. IR spectra in the region 600–200 cm^{-1} (polyethylene windows) did not reveal any bands attributable to ν(AgC).

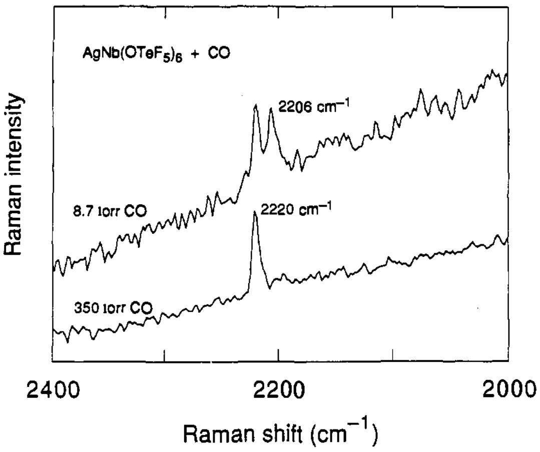

Figure 3. Raman spectra of $AgNb(OTeF_5)_6$ under 8.7 and 350 Torr of CO (1054 nm excitation). The peaks at 2220 and 2206 cm^{-1} in the 8.7 Torr spectrum are assigned as ν_{sym}(CO) for the $[Ag(CO)_2]^+$ ion and ν(CO) for the $[Ag(CO)]^+$ ion, respectively.

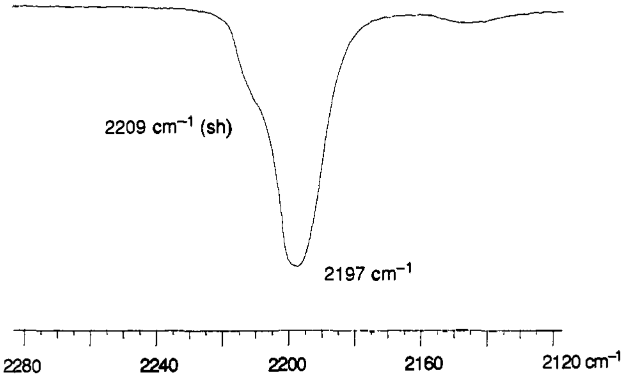

Figure 4. IR spectrum of a solution of $AgNb(OTeF_5)_6$ dissolved in 1,1,2-$C_2Cl_3F_3$ under ~1 atm of CO. The peaks at ca. 2209 and 2198 cm^{-1} are assigned as ν_{asym}(CO) for the $[Ag(CO)_2]^+$ ion and ν(CO) for the $[Ag(CO)]^+$ ion, respectively.

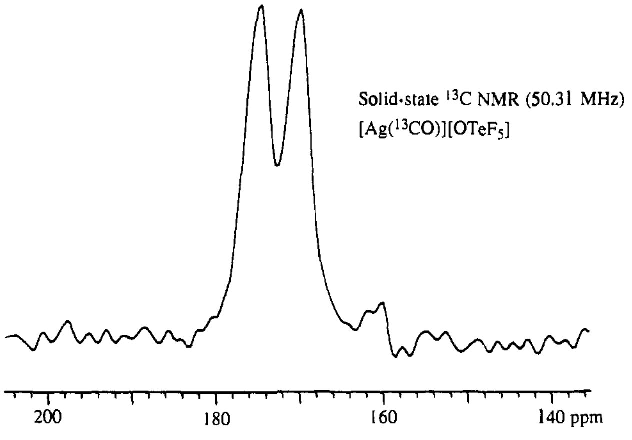

Figure 5. Solid-state ^{13}C MAS NMR spectrum of $[Ag(^{13}CO)][OTeF_5]$ in the δ_{iso} region (50.31 MHz). The splitting is due to $Ag^{13}C$ coupling (individual lines for $^{109}Ag^{13}C$ and $^{107}Ag^{13}C$ couplings are not resolved).

NMR Spectroscopy. Room temperature ^{13}C NMR spectra of dichloromethane solutions of a mixture of ^{13}CO and $AgB(OTeF_5)_4$ exhibited only one resonance at δ ~174 (i.e., no silver–carbon coupling was observed; a single resonance at δ 184 was observed for ^{13}CO dissolved in dichloromethane).[26] Since our silver compounds bind CO reversibly, a reasonble conclusion is that $[Ag(CO)_n]^+$ complexes are labile in solution and that free and

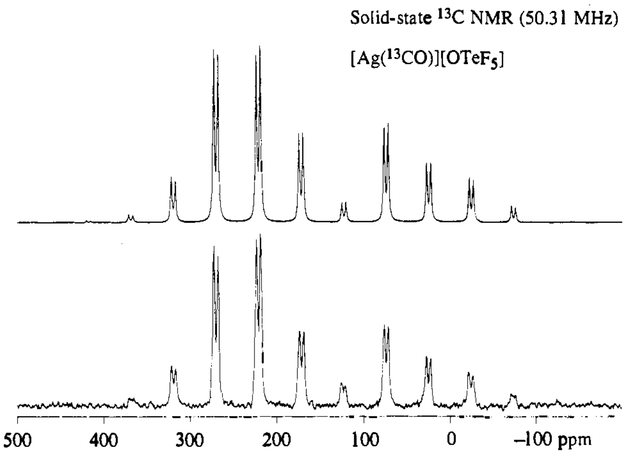

Figure 6. Experimental (bottom) and calculated (top) solid-state ^{13}C MAS NMR spectra of $[Ag(^{13}CO)][OTeF_5]$ (50.31 MHz). The splittings are due to $Ag^{13}C$ coupling (individual lines for $^{109}Ag^{13}C$ and $^{107}Ag^{13}C$ couplings are not resolved).

Table 2. Solid-State ^{13}C MAS NMR Spectral Data[a]

			CSA,[d] ppm	
compd	$\delta(^{13}C)$[b]	$J_{^{109}Ag^{13}C}$ (Hz)[c]	σ_{zz}	σ_{xx} ($=\sigma_{yy}$)
$[Ag(CO)][OTeF_5]$	172.8(2)	265(12)	−76(10)	295(10)
$[Ag(CO)]_2[Zn(OTeF_5)_4]$	171.4(2)	284(12)	−45(10)	280(10)
$[Ag(CO)]_2[Ti(OTeF_5)_6]$	170.8(2)	263(12)		
$[Ag(CO)_2]_2[Zn(OTeF_5)_4]$	172.3(2)	203(12)	−66(10)	291(10)
$[Ag(CO)_2]_2[Ti(OTeF_5)_6]$	171.7(2)	190(12)		

[a] 37.70 MHz. Numbers in parentheses are estimated errors. [b] ppm from external adamantane (δ 29.7, 38.7). [c] $J_{^{109}Ag^{13}C} = (1.0748)$(peak-to-peak separation); $1.0748 = 1 + (^1/_2)[[\gamma(^{109}Ag)/\gamma(^{107}Ag)] - 1]$. [d] Chemical shift anisotropies were calculated using the intensities of spinning sidebands.

bound CO were undergoing rapid exchange in these experiments. To slow down the exchange, we recorded solid-state ^{13}C NMR spectra of five silver carbonyl compounds. The spectrum of $[Ag(^{13}CO)][OTeF_5]$, a typical spectrum consisting of two broad resonances, is shown in Figure 5. The splitting is assigned as $J_{Ag^{13}C}$. The possibility that the two resonances are due to two different CO environments in the samples was ruled out by recording spectra of $[Ag(^{13}CO)][OTeF_5]$ at two different frequencies, 37.70 and 50.31 MHz. In both spectra, the same splitting was observed to within experimental error, 265(12) and 254(10) Hz, respectively. Since ^{107}Ag and ^{109}Ag are nearly equally abundant and the ratio of their magnetogyric ratios is 0.870,[27] we conclude that the expected four-line spectra are partially unresolved and that the observed peak-to-peak separations correspond to the average of $J_{^{107}Ag^{13}C}$ and $J_{^{109}Ag^{13}C}$. For three samples, the signal-to-noise ratio was sufficiently high to measure ^{13}C chemical shift anisotropies by the spinning sideband method (axial symmetry was assumed). Calculated and experimental spectra for $[Ag(^{13}CO)][OTeF_5]$ are shown in Figure 6. All of the NMR data are listed in Table 2.

X-ray Crystallography. Experimental parameters for the crystallographic study of $[Ag(CO)][B(OTeF_5)_4]$, $[Ag(CO)_2][B(OTeF_5)_4]$, and $[(CH_3)_2CHCO][SbCl_6]$ are listed in Table 3. Selected interatomic distances and angles for $[Ag(CO)][B(OTeF_5)_4]$ and $[Ag(CO)_2][B(OTeF_5)_4]$ are listed in Table 4. Selected interatomic distances and angles for $[(CH_3)_2CHCO][SbCl_6]$ are listed in Table 5 and are compared with the corresponding results from a previous structure determination at room temperature.[28] Complete tables of atomic coordinates and equivalent isotropic thermal parameters, interatomic distances and angles, and anisotropic thermal parameters for $[Ag(CO)][B(OTeF_5)_4]$, $[Ag(CO)_2][B(OTeF_5)_4]$, and $[(CH_3)_2CHCO][SbCl_6]$ are available as supplementary material. In both silver(I) carbonyl structures, the $B(OTeF_5)_4^-$ anions are unremarkable and have structural parameters similar to those observed in three previous structures of this anion.[24,29] The asymmetric unit and the silver ion coordination sphere of $[Ag(CO)][B(OTeF_5)_4]$ are shown in Figures 7 and 8, respectively. The coordination spheres of the three unique silver ions in $[Ag(CO)_2][B(OTeF_5)_4]$ are shown in Figure 9. The asymmetric unit of $[(CH_3)_2CHCO][SbCl_6]$ is shown in Figure 10.

The structure of $[Ag(CO)][B(OTeF_5)_4]$ has a nearly linear Ag–C–O moiety (176(1)°) and a planar O1–O2–Ag–C framework (the maximum deviation from the least-squares plane of these four atoms is 0.019 Å for Ag). The $[Ag(CO)]^+$ ion has four Ag···F contacts ranging in distance from 2.959(6) to 3.076(8) Å. The closest C···F contacts are greater than 3 Å. For comparison, the Ag–F distances in $AgSbF_6$[30] and AgF[31] are 2.62 and 2.467(3) Å, respectively, the sum of the van der Waals radii for silver and fluorine is 3.15 ± 0.08 Å, and the sum of the van der Waals radii for carbon and fluorine is 3.05 ± 0.10 Å.[32]

In the structure of $[Ag(CO)_2][B(OTeF_5)_4]$, the $[Ag(CO)_2]^+$ complex cation at a general position has a five-atom O1–C1–Ag1–C2–O2 array that deviates slightly from linearity. The O1–C1–Ag1, C1–Ag1–C2, and Ag1–C2–O2 bond angles are 173(3)°, 169(1)°, and 178(3)°, respectively. The cations located at inversion centers have Ag–C–O bond angles of 174(4)° (Ag2–C3–O3) and 179(2)° (Ag3–C4–O4). Each of the $[Ag(CO)_2]^+$ cations is very weakly bonded to two or more $B(OTeF_5)_4^-$ anions. For example, Ag1 makes contact with seven fluorine atoms from several different anions, with Ag···F distances ranging from 2.75(1) to 3.19(1) Å. The other two silver ions have fewer Ag···F contacts: Ag2 has two at 3.02(1) Å and Ag3 has two at 2.96(1) Å (F9 and F9′) and two more at 3.09(2) Å (F35 and F35′). The closest C···F contacts in this compound are also greater than 3 Å.

Discussion

The Composition and Structure of Silver(I) Carbonyls. It is important from the outset to distinguish between the two possible reaction schemes shown below.

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

$$Ag^+ \underset{-2CO}{\overset{+2CO}{\rightleftharpoons}} [Ag(CO)_2]^+$$

Our data demonstrate conclusively that *both* $[Ag(CO)]^+$ and $[Ag(CO)_2]^+$ complex ions were formed, in the solid state or in solution, when silver(I) salts of weakly coordinating anions were placed under a CO atmosphere. Whether the monocarbonyl cation, the dicarbonyl cation, or a mixture of the two was formed depended on the counterion, the medium, and the CO pressure. For example, only the monocarbonyl complex $[Ag(CO)]^+$ (ν(CO) = 2189 cm^{-1}) was formed when a solid sample of $AgOTeF_5$ was treated with 1 atm of CO. In contrast, when the solid salts $AgB(OTeF_5)_4$, $Ag_2Zn(OTeF_5)_4$, $AgNb(OTeF_5)_6$, and $Ag_2Ti(OTeF_5)_6$ were treated with >350 Torr of CO, only the dicarbonyl

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(26) Others have observed single resonances at δ ~174 for solutions of silver salts and carbon monoxide: see refs 13b,f,g.

(27) $\gamma(^{107}Ag) = -1.0828 \times 10^7$ rad T^{-1} s^{-1}, $\gamma(^{109}Ag) = -1.2448 \times 10^7$ rad T^{-1} s^{-1}. Both nuclei have $I = {}^1/_2$.

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Table 3. Details of the X-ray Diffraction Study of $[Ag(CO)][B(OTeF_5)_4]$, $[Ag(CO)_2][B(OTeF_5)_4]$, and $[(CH_3)_2CHCO][SbCl_6]$[a]

compd	$[Ag(CO)][B(OTeF_5)_4]$	$[Ag(CO)_2][B(OTeF_5)_4]$	$[(CH_3)_2CHCO][SbCl_6]$
molecular formula	$CAgBF_{20}O_5Te_4$	$C_2AgBF_{20}O_6Te_4$	$C_4H_7Cl_6OSb$
formula wt, g mol^{-1}	1101.1	1129.1	405.6
space group unit cell dimensions:	$P2_1/n$	$P\bar{1}$	*Pnma*
a, Å	10.001(2)	10.367(5)	19.368(1) [19.847(20)]
b, Å	16.180(4)	13.146(7)	7.055(1) [7.121(6)]
c, Å	12.235(3)	16.560(10)	9.108(1) [9.144(10)]
α, deg	90	87.77(5)	90
β, deg	100.48(2)	76.38(4)	90
γ, deg	90	89.06(4)	90
unit cell volume, $Å^3$	1947(1)	2192(2)	1244.5(2) [1299]
Z	4	4	4
calcd density, g cm^{-3}	3.76	3.42	2.16 [2.07]
cryst dimens, mm	0.20 × 0.24 × 0.25	0.15 × 0.40 × 0.50	0.15 × 0.15 × 0.15
data collection temp, °C	−125(1)	−125(1)	−130(1) [25]
radiation (λ, Å)	Mo Kα (0.7107)	Mo Kα (0.7107)	Mo Kα (0.7107)
monochromator	graphite	graphite	graphite
abs coeff, cm^{-1}	72.84	63.25	3.462
scan type	θ–2θ	θ–2θ	θ–2θ
scan speed, deg min^{-1}	variable (4–30)	variable (4–30)	variable (2–60)
2θ range, deg	4–50	4–60	4–55
reflections	$h,-k,\pm l$	$\pm h,\pm k,l$	$h,\pm k,\pm l$
total no. of reflcns meas.	3774	12174	5842
no. of obsd reflcns, $\lvert F_o \rvert > n\sigma(F_o)$	2914 ($n = 2.5$)	7571 ($n = 2.5$)	1543 ($n = 2.5$)
data/param ratio	10.1	12.3	23.7
R	0.040	0.078	0.020
R_w	0.045	0.102	0.045
GOF	1.404	1.09	1.26
g (refined)	4.5×10^{-4}	5.2×10^{-4}	

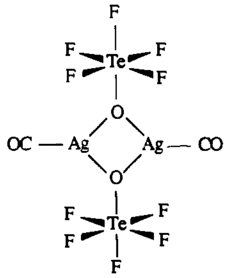
[a] Values in square brackets are taken from a previous structure determination (ref 28).

complex $[Ag(CO)_2]^+$ was present ($\nu_{asym}(CO)$ varied from 2196 to 2198 cm^{-1}). When a lower pressure was used, or when a sample of $[Ag(CO)_2][Y]$ was placed under vacuum for a few minutes, only the monocarbonyl complex was present ($\nu(CO)$ = 2204 to 2208 cm^{-1}; Y^- = $B(OTeF_5)_4^-$, $Nb(OTeF_5)_6^-$, $^1/_2Zn(OTeF_5)_4^{2-}$, or $^1/_2Ti(OTeF_5)_6^{2-}$). When a sample of $AgNb(OTeF_5)_6$ dissolved in the weakly coordinating solvent 1,1,2-$C_2Cl_3F_3$ was placed under ~1 atm of CO, bands attributable to both $[Ag(CO)]^+$ (~2209 cm^{-1}) and $[Ag(CO)_2]^+$ (2198 cm^{-1}) were observed.

It is striking that silver(I) teflate, $AgOTeF_5$, absorbs 1 equiv of CO at 1 atm but $AgSbF_6$ does not absorb any measurable amount of CO. The structure of the free teflate anion is a slightly distorted octahedron, with Te–O and average Te–F bond distances of 1.786(3) and 1.853(3) Å, respectively, and an average O–Te–F_{eq} bond angle of 95.2(2)°.[33] Therefore, teflate is nearly isostructural and isodimensional with octahedral SbF_6^- (Sb–F (av) = 1.844(8) Å in $KSbF_6$[34]). The difference in reactivity between the two silver(I) salts must be due to a subtle difference in cation–anion interactions in the solid state. We have reported that the solubilities of $AgOTeF_5$ and $AgSbF_6$ in dichloromethane at 25 °C are >2.5 M[35] and 0.16 M,[36] respectively, and that the pressures of dichloromethane vapor needed to bind one molecule of dichloromethane to half the Ag^+ ions present in solid samples of $AgOTeF_5$ and $AgSbF_6$ are 4 and 22 Torr, respectively.[35]

The weakly coordinating solvents nitromethane, toluene, diethyl ether, and dichloromethane could not be used to grow crystals of our silver(I) carbonyl complexes. These four solvents apparently coordinate more strongly to Ag^+ than does CO. For example, when a solution of $Ag_2Ti(OTeF_5)_6$ in dichloromethane under >300 Torr of CO was allowed to cool, crystals of $[Ag(CH_2Cl_2)_3]_2[Ti(OTeF_5)_6]$ were obtained.[37] Of all solvents tried, only 1,1,2-$C_2Cl_3F_3$ could be used for crystallizations (see Experimental Section). The structures of $[Ag(CO)][B(OTeF_5)_4]$ and the three unique cations in $[Ag(CO)_2][B(OTeF_5)_4]$ exhibit nearly linear Ag–C–O arrays which are characteristic of terminal metal carbonyls. The Ag–C–O angle in $[Ag(CO)][B(OTeF_5)_4]$ is 176(1)°. The Ag–C–O angles in $[Ag(CO)_2][B(OTeF_5)_4]$ are 173(3)° (C1), 178(3)° (C2), 174(4)° (C3), and 179(2)° (C4). The dicarbonyl cations have a two-coordinate linear structure (effective $D_{\infty h}$ symmetry): The C–Ag–C angles are 169(1)°, 180°, and 180° for Ag1, Ag2, and Ag3, respectively (Ag2 and Ag3 are located at inversion centers). These two crystalline compounds represent the only examples of structurally characterized silver(I) carbonyls to date.[23] In addition, the $[Ag(CO)_2]^+$ cation is the first example of a simple, structurally characterized $M(CO)_2$ complex of any metal[22a] (a second, recently determined example is the $[Hg(CO)_2]^{2+}$ cation[38]).

The chlorofluorocarbon solvent 1,1,2-$C_2Cl_3F_3$ could not be used to crystallize $[Ag(CO)][OTeF_5]$ because $AgOTeF_5$ is not soluble in it to any extent (the solubility of $AgB(OTeF_5)_4$ in 1,1,2-$C_2Cl_3F_3$ is ~4 mM at 25 °C[24]). We propose the following structure for $[Ag(CO)][OTeF_5]$, which is consistent with (i) the observed mutually exclusive IR and Raman bands for $\nu(CO)$, 2189 and 2193 cm^{-1}, respectively, and for $\nu(TeO)$, 787 and 812 cm^{-1}, respectively, and (ii) with the observed silver ion coordination sphere in the structure of $[Ag(CO)][B(OTeF_5)_4]$: The compound $[Ag(toluene)_2][OTeF_5]$, which has been shown to have a dimeric structure with a Ag–O–Ag–O core, also has mutually exclusive IR and Raman $\nu(TeO)$ bands, at 819 and 836 cm^{-1}, respectively.[25]



In 1924 Manchot and co-workers reported that a solution of Ag_2SO_4 in concentrated sulfuric acid reversibly absorbed carbon

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Table 4. Selected Interatomic Distances (Å) and Angles (deg) for $[Ag(CO)][B(OTeF_5)_4]$ and $[Ag(CO)_2][B(OTeF_5)_4]$

	$[Ag(CO)][B(OTeF_5)_4]$	$[Ag(CO)_2][B(OTeF_5)_4]$
C–O	1.077(16)[a]	1.07(5)[b]
C2–O2		1.09(5)
C3–O3		1.09(6)
C4–O4		1.08(4)
Ag–C	2.10(1)	2.20(4)[c]
Ag1–C2		2.16(4)
Ag2–C3		2.06(5)
Ag3–C4		2.14(5)
Ag–O1	2.324(6)	
Ag–O2	2.436(7)	
Ag–F4	3.076(8)	
Ag–F16	2.959(6)	
Ag–F8′	2.972(6)	
Ag–F19″	3.028(7)	
Ag1–F1		3.18(1)
Ag–F2		2.94(1)
Ag1–F18		2.87(1)
Ag1–F22		2.75(1)
Ag1–F12′		2.80(1)
Ag1–F39′		3.16(1)
Ag1–F40′		3.19(1)
Ag2–F20′, Ag2–F20″		3.02(1)
Ag3–F9′, Ag3–F9″		2.96(1)
Ag3–F35′, Ag3–F35″		3.09(1)
B–O	1.44(1)–1.50(1)	1.45(2)–1.48(2)
Te–O	1.833(7)–1.867(7)	1.81(1)–1.84(1)
Te–F	1.786(7)–1.838(6)	1.78(1)–1.87(1)
Ag–C–O5	175.7(1)	
Ag1–C1–O1		173(3)
Ag1–C2–O2		178(3)
Ag2–C3–O3		174(4)
Ag3–C4–O4		179(3)
C1–Ag1–C2		169(1)
C3–Ag2–C3′, C4–Ag3–C4′		180
O1–Ag–O2	56.1(2)	
O1–Ag–C	155.6(4)	
O2–Ag–C	148.3(4)	
B–O1–Ag	106.0(5)	
B–O2–Ag	100.8(6)	
B–O–Te	130.1(6)–138.2(6)	128.2(9)–133.2(10)
O1–B–O2	96.7(7)	
O–B–O	110.7(8)–114.0(7)[d]	106.1(1)–114.1(1)
O–Te–F_{eq}	88.4(3)–94.5(3)	89.5(6)–96.2(5)
O–Te–F_{ax}	175.5(3)–177.3(3)	175.9(6)–178.0(6)

[a] O = O5. [b] C = C1; O = O1. [c] Ag = Ag1; C = C1. [d] Not including O1–B–O2.

Table 5. Interatomic Distances (Å) and Angles (deg) for $[(CH_3)_2CHCO][SbCl_6]$

	this work (T = –130 °C)	Le Carpentier and Weiss (ref 28) (T = ~25 °C)
C1–O	1.101(4)	1.12(1)
C1–C2	1.458(4)	1.44(1)
C2–C3	1.538(3)	1.55(1)
C2–C1–O	177.4(3)	175.7(5)
C3–C2–C1	108.8(2)	108.3(5)
C3–C2–C3′	114.3(3)	116.9(7)
Sb–Cl1	2.3391(7)	2.347(1)
Sb–Cl2	2.3560(5)	2.364(1)
Sb–Cl3	2.3805(5)	2.383(1)
Sb–Cl4	2.3859(7)	2.389(1)
Cl–Sb–Cl	88.64(2)–91.81(2)	88.68(5)–92.12(5)

monoxide.[13j] A limiting Ag:CO stoichiometry of 2:1 was achieved when T = 0 °C and P_{CO} ~ 1 atm.[13i,j] Later, Souma and co-workers found that this phenomenon was general for a variety of Ag^+ salts in the neat protic acids H_2SO_4, HF, CF_3SO_3H, FSO_3H, and $BF_3{\cdot}H_2O$.[13f–h] This group was able to achieve an 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). Their IR spectrum of a mixture of Ag_2O and neat FSO_3H exhibited a band at 2190 cm^{-1}, which they assigned as ν_{asym}(CO) of the dicarbonyl cation $[Ag(CO)_2]^+$.[13f,g] This is probably not a correct assignment. Souma and co-workers assumed that the only silver species present in solution were Ag^+ and $[Ag(CO)_2]^+$: they did not consider the possible existence of the monocarbonyl cation $[Ag(CO)]^+$. However, according to their plot of Ag:CO ratio vs temperature, the species present in FSO_3H solution at 10 °C and 1 atm of CO (the conditions under which their IR spectrum was recorded) was probably $[Ag(CO)]^+$ since the Ag:CO ratio was 1:0.8.[13f,g]

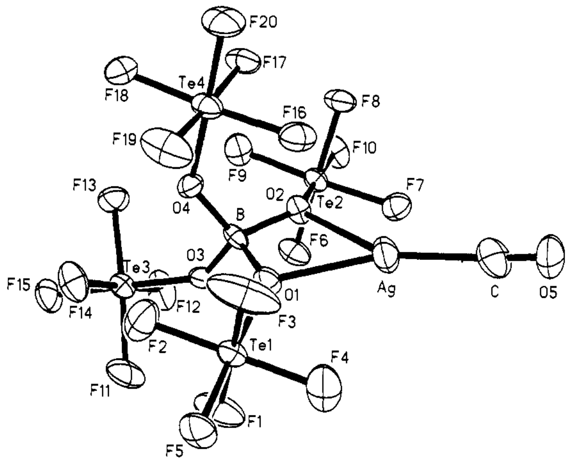

Figure 7. The overall structure of $[Ag(CO)][B(OTeF_5)_4]$ (50% probability ellipsoids). Selected distances (Å) and angles (deg): Ag–C, 2.10(1) Å; C–O, 1.077(16) Å; Ag–C–O, 176(1)°.

Souma and co-workers[13f,g] and Backèn and Ericsson[13b] reported ^{13}CO NMR spectra for mixtures of Ag^+, neat Brønsted acids, and CO. As in our study, they also observed only one resonance at δ ~170, which was attributed to rapid exchange of free and coordinated CO. One other report of a silver(I) carbonyl complex that is stable in solution is by Lenders and Kläui.[13a] They generated $[Ag(CO)][CpCo(P(O)R_2)_3]$ in hexane or in methanol and found a ν(CO) band at 2125 or 2147 cm^{-1}, respectively, in the two solvents. There are a number of reports of silver(I) carbonyl species generated in silver(I)-substituted zeolites,[14] in solid $Ag_3PW_{12}O_{40}$,[15a] and in low-temperature CO/O_2 matrices.[15b] In these materials, ν(CO) bands were observed in the 2165–2195 cm^{-1} range.

In an important sense, there is a parallel between our results and most of the earlier work on silver(I) carbonyls. In our work, silver(I) salts with extremely weakly coordinating, highly fluorinated anions formed silver(I) carbonyl complexes reversibly either in the solid state or in extremely weakly coordinating solvents such as chlorofluorocarbons. In the earlier work, silver(I) carbonyl complexes were reversibly formed from Ag^+ ions dissolved in neat Brønsted acids such as H_2SO_4 or FSO_3H, or from Ag^+ ions in a weakly interacting, hard oxide or oxide-like lattice. Except for the report by Lenders and Kläui,[13a] the labile, weakly bound $[Ag(CO)_n]^+$ complexes could only be generated *in the absence of competing ligands*, even ligands as weakly basic as perchlorate ion or dichloromethane.

The Nature of the Ag–CO Bond. The most striking feature of the cationic d^{10} carbonyls $[Ag(CO)]^+$ and $[Ag(CO)_2]^+$ is that they exhibit ν(CO) values far greater than that for the free CO molecule, 2143 cm^{-1}.[39] For example, infrared ν(CO) values for Nujol mull samples of $[Ag(CO)][Nb(OTeF_5)_6]$ and $[Ag(CO)_2][Nb(OTeF_5)_6]$ are 2208 and 2198 cm^{-1}, respectively, ~60 cm^{-1} higher than in free CO. The former value, 2208 cm^{-1}, is the

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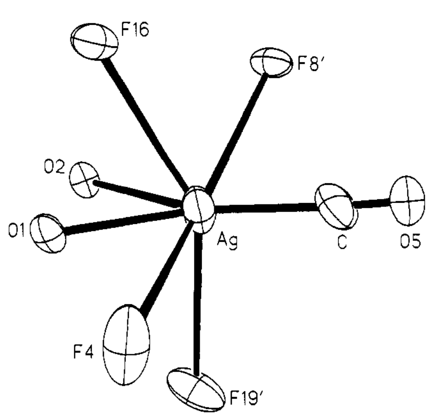

Figure 8. The Ag$^+$ coordination sphere in [Ag(CO)][B(OTeF$_5$)$_4$] (50% probability ellipsoids). Selected distances (Å) and angles (deg): Ag–C, 2.10(1) Å, Ag–O1, 2.324(6) Å, Ag–O2, 2.436(7) Å, Ag–F4, 3.076(8) Å, Ag–F16, 2.959(6) Å, Ag–F8', 2.972(6) Å, Ag–F19'', 3.028(7) Å, O1–Ag–C, 155.6(2)°, O2–Ag–C, 148.3(4)°, O1–Ag–O2, 56.1(2)°.

highest ever recorded for a metal monocarbonyl complex.[40] In contrast, classical metal carbonyl complexes exhibit CO stretching frequencies considerably lower than for free CO.[39a,b] A number of relevant comparisons can be made: Ni(CO)(PF$_3$)$_3$, which like our silver(I) carbonyls is a d^{10} complex, has a ν(CO) value of 2073 cm^{-1};[41] [Re(CO)$_6$]$^+$, which like our silver(I) carbonyls is cationic, has an average ν(CO) value of 2116 cm^{-1};[42] [RhCl(CO)]$_2$ and *trans*-RhCl(CO)(PPh$_3$)$_2$, which like our silver(I) carbonyls contain a monovalent 4d metal ion, have ν(CO) values of 2043 cm^{-1} (av)[43] and 1980 cm^{-1},[44] respectively; Fe(OEP)(CO)$_2$, which like [Ag(CO)$_2$]$^+$ has *trans* carbonyl ligands, has a ν_{asym}(CO) value of 2016 cm^{-1}.[45]

The classical picture of metal–carbonyl bonding is one in which CO acts as a σ-donor and a π-acceptor, as shown in Figure 11. The C–O bond is strengthened, and ν(CO) is raised, by σ-donation of the carbon atom "lone pair" (the HOMO of CO) to an empty orbital on another species, such as a metal ion. For example, ν(CO) is 2295, 2184, and 2165 cm^{-1} for CH$_3$CO$^+$,[18d] HCO$^+$,[46] and BH$_3$CO,[19b] respectively, three species in which E–C σ-bonding is the predominant, if not the only, type of bonding (E = C, H, or B). There are three possible explanations for this phenomenon. The simplest is that the carbon atom lone pair undergoes rehybridization when it becomes a bonding pair: the new bonding pair has less s character than the original lone pair, so the C–O σ-bond has increased s character and hence is stronger. A second explanation is that the carbon atom lone pair (the 5σ orbital) has some carbon–oxygen σ-antibonding character:[47] donation of this electron density to an empty orbital on another species will strengthen the C–O σ-bond. This is supported by the observation that ν(CO) for CO$^+$ is 2184 cm^{-1}, 41 cm^{-1} higher than in neutral CO.[39c] The third explanation is purely an electrostatic effect and is silent on the nature of E–C or C–O bonding orbitals: the carbon–oxygen bond in CO becomes stronger, and ν(CO) rises, if the molecule is placed in an electric field with the carbon atom facing the direction of increasing positive charge (e.g., toward an electrophilic center).[48] In contrast to M–C σ-bonding, metal→carbon d→π^* π-back-bonding lowers ν(CO) by populating one or both of the CO 2π (π^*) orbitals, decreasing the carbon–oxygen bond order.[5] For typical metal carbonyls, most theorists have concluded that π-back-bonding is more important to the overall metal–carbon bond strength than σ-bonding.[5] Whether or not this is true, the effect of π-back-bonding on ν(CO) is larger than the effect of σ-bonding since typical (classical) metal carbonyls exhibit CO stretching frequencies considerably lower than free CO.

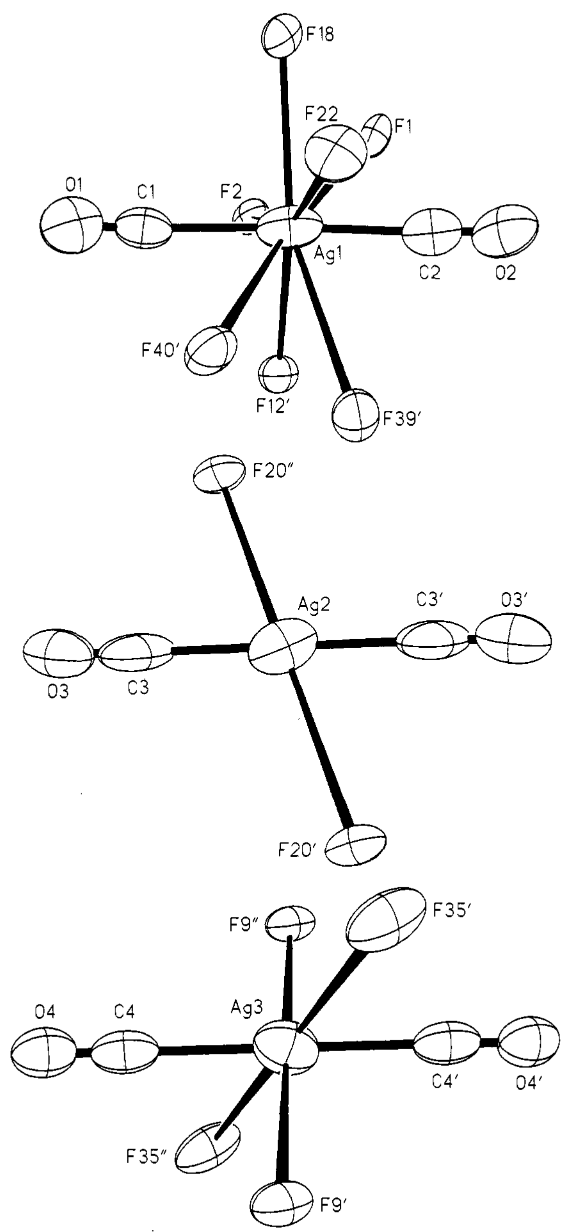

Figure 9. The three unique Ag$^+$ coordination spheres in [Ag(CO)$_2$][B(OTeF$_5$)$_4$] (30% probability ellipsoids). Selected distances (Å) and angles (deg): Ag1–C1, 2.20(4) Å, Ag1–C2, 2.16(4) Å, Ag2–C3, 2.06(5) Å, Ag3–C4, 2.14(5) Å, C1–O1, 1.07(5) Å, C2–O2, 1.09(5) Å, C3–O3, 1.09(6) Å, C4–O4, 1.08(4) Å, Ag1–C1–O1, 173(3)°, Ag1–C2–O2, 178(3)°, Ag2–C3–O3, 174(4)°, Ag3–C4–O4, 179(3)°, C1–Ag1–C2, 169(1)°, C3–Ag2–C3', 180°, C4–Ag3–C4', 180°.

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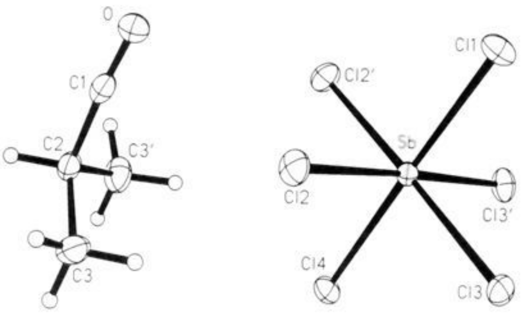

Figure 10. The overall structure of $[(CH_3)_2CHCO][SbCl_6]$ (50% probability ellipsoids). The separation of the anion and the cation is to scale. Selected distances (Å) and angles (deg): C1–O, 1.101(4) Å, C1–C2, 1.458(4) Å, C2–C3, 1.538(3) Å, C2–C1–O, 177.4(3)°.

An appealing explanation of our vibrational data is that the d^{10} Ag^+ ion does not measurably participate in π-back-bonding in $[Ag(CO)]^+$ and $[Ag(CO)_2]^+$, i.e., silver(I) is behaving predominantly or exclusively as a Lewis acid, albeit a soft one.[49] The Ag–C σ-bond raises $\nu(CO)$ from 2143 to ~2200 cm^{-1}, and there is no countervailing Ag–C π-bond to lower $\nu(CO)$. This conclusion is in harmony with the structural data. Let us consider the two monovalent, soft, period 5 cations Rh^+ and Ag^+. There is ample vibrational data proving that the former metal ion participates in π-back-bonding (see examples above). The Ag–C bond distances of ~2.1 Å in $[Ag(CO)]^+$ and $[Ag(CO)_2]^+$ are 0.3 Å longer than the ~1.8 Å Rh–C distances in $RhH(CO)(PPh_3)_3$[50] and $[RhCl(CO)_2]_2$[51] (the mean Rh–CO distance in 238 rhodium(0) and rhodium(I) carbonyls is 1.85(4) Å[52]). A lack of π-back-bonding would certainly be commensurate with an unusually long M–C distance: a theoretical study by Sherwood and Hall led to the prediction that if a Cr–C bond in $Cr(CO)_6$ was stretched 0.25 Å longer than its equilibrium distance, Cr–C π-back-bonding would be negligible and CO would act as a σ-only ligand.[53] Under these circumstances, Sherwood and Hall also found that the C–O distance would become shorter and $\nu(CO)$ would increase relative to free CO.

Due to uncorrected librational motion[54,55] and the large estimated standard deviations, it is not possible to say for certain whether the C–O bond distances in $[Ag(CO)][B(OTeF_5)_4]$ and $[Ag(CO)_2][B(OTeF_5)_4]$ are shorter than in free CO (1.12822(7) Å).[55] Shorter, stronger C–O bonds would certainly be consistent with the higher $\nu(CO)$ values and with theoretical predictions (see below). Nevertheless, since CO has a very steep potential energy surface, substantial changes in stretching frequency could be associated with only modest changes in bond distance. We have surveyed other structurally characterized species with unusually high $\nu(CO)$ values, including acylium ions (RCO^+) and nonclassical metal carbonyls, and in nearly all cases they also have high estimated standard deviations for the C–O bond distances, as shown in Table 6.[56–61] The only species with a C–O distance statistically shorter than in free CO (i.e., $R(CO) < 1.128$ Å–3σ) is $Pd(CO)_2(SO_3F)_2$, in which one of the two C–O distances is 1.102(6) Å.[61] To provide another example, we attempted to redetermine the structure of $[CH_3CO][SbCl_6]$[58] at a low temperature. During the refinement of the structure, it became clear that the $[CH_3CO]^+$ cation was disordered to some extent (see Experimental Section). No further refinement was attempted. The room temperature structures of $[CH_3CO][SbCl_6]$[58] and $[CH_3CO][SbF_6]$[56] may also exhibit disorder, but we have not tried to verify this. Instead, we redetermined the structure of $[(CH_3)_2CHCO][SbCl_6]$[28] at low temperature and found that the C–O bond distance, at 1.101(4) Å, is significantly shorter than the distance in free CO. Based on the vibrational spectra and structures of $Pd(CO)_2(SO_3F)_2$ and $[(CH_3)_2CHCO][SbCl_6]$, it is now sensible to conclude that nonclassical metal carbonyls in general have C–O bond distances slightly shorter than 1.128 Å.

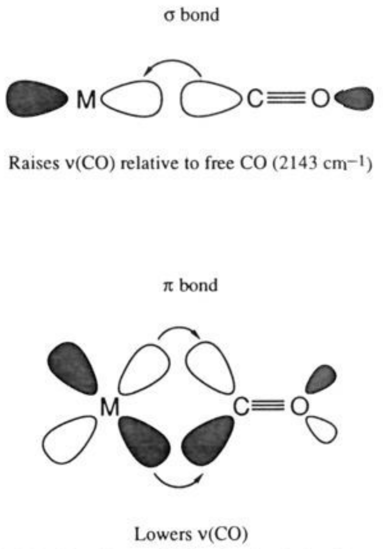

Figure 11. C→M σ-bonding and M→C π-back-bonding in an isolated M–C≡O fragment. In classical metal carbonyl complexes, π-bonding affects $\nu(CO)$ more than σ-bonding.

There are two ways to understand the apparent difference between silver(I) and rhodium(I) as far as π-back-bonding is concerned. First, since π-back-bonding involves a shift of electron density from metal orbitals to carbonyl ligand orbitals, it is related to removal of electron density from the metal and hence is related to ionization potentials. While the first ionization potentials of silver (7.58 eV) and rhodium (7.46 eV) are practically the same, the second ionization potential of silver (21.48 eV) is nearly 20% larger than that for rhodium (18.08 eV).[62] In fact, silver has the highest second ionization potential of all metallic elements except for the alkali metals.[62] Second, bond distances between p-block elements such as N, O, P, S, and Cl and silver(I) are invariably 0.1–0.4 Å longer than the corresponding distances involving rhodium(I).[52] Since π-bonding is a more sensitive function of distance than is σ-bonding, the naturally longer distances for silver(I) greatly diminish or preclude π-back-bonding in silver(I) carbonyls. It may not be possible to ever know whether there is no π-back-bonding in silver(I) carbonyls because the Ag–C bonds are too long or whether the Ag–C bonds are long because there is no π-back-bonding.

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Table 6. Carbon–Oxygen Bond Distances and Stretching Frequencies in Representative Acylium Ions and in Nonclassical Metal Carbonyls[a]

species	R(CO), Å	ν(CO), cm^{-1}	comments
CO	1.12822(7)[b]	2143[b]	refs 55 (R(CO)) and 39 (ν(CO))
$[CH_3CO]^+$	1.116(21)	2294	SbF_6^- salt; refs 56 (R(CO)) and 57 (ν(CO)); the structure of the cation may be disordered (see text)
$[CH_3CO]^+$	1.109(30)	2295	$SbCl_6^-$ salt; refs 58 (R(CO)) and 59 (ν(CO)); the structure of the cation may be disordered (see text)
$[(CH_3)_2CHCO]^+$	1.116(10)		$SbCl_6^-$ salt; ref 28; structure determined at ~25 °C
$[(CH_3)_2CHCO]^+$	1.101(4)	2257	$SbCl_6^-$ salt; this work; structure determined at −130 °C
$[1,2\text{-}C_6H_4(CH_3)CO]^+$	1.111(13)		$SbCl_6^-$ salt; ref 60a
$[1,4\text{-}C_6H_4(CH_3)CO]^+$	1.097(9)		$SbCl_6^-$ salt; ref 60b
$[Ag(CO)]^+$	1.077(16)	2204	$B(OTeF_5)_4^-$ salt; this work
$[Ag(CO)_2]^+$	1.07(5), 1.09(5), 1.09(6), 1.08(4)	2211	$B(OTeF_5)_4^-$ salt (R(CO)); $Nb(OTeF_5)_6^-$ salt (ν(CO)); this work
Au(CO)Cl	1.11(3)	2162[c]	refs 11a (R(CO)) and 11b (ν(CO))
$[Hg(CO)_2]^{2+}$	1.104(12)	2279	$Sb_2F_{11}^-$ salt; refs 38 (R(CO)) and 7 (ν(CO))
$Pd(CO)_2(SO_3F)_2$	1.102(6), 1.114(6)	2218	ref 61

[a] All data from solid-state samples unless otherwise indicated. [b] Gas phase samples. [c] Dichloromethane solution.

Table 7. One-Bond Silver–Carbon Coupling Constants[a]

compd	$^1J_{^{109}Ag^{13}C}$, Hz	ref
$[Ag(CO)][OTeF_5]$	265(12)	this work
$[Ag(CO)]_2[Zn(OTeF_5)_4]$	284(12)	this work
$[Ag(CO)]_2[Ti(OTeF_5)_6]$	263(12)	this work
$[Ag(CO)_2]_2[Zn(OTeF_5)_4]$	203(12)	this work
$[Ag(CO)_2]_2[Ti(OTeF_5)_6]$	190(12)	this work
$[Ag(CH_2PPh_3)_2]Cl$	104	64
$Ag[Ag(CF_3)_4]$	120	65
$Ag(CH_3)(P(n\text{-}Bu)_3)$	149.4	66
$[Li(OEt_2)_n][Ag(CH_3)_2]$	95.5	66
$[Li(OEt_2)_n][Ag(C_6H_5)_2]$	132	67
$Li[Ag(2\text{-}C_6H_4(CH_2NMe_2))_2]$	136	68

[a] From liquid or solid-state ^{13}C NMR spectra.

Table 8. Carbon-13 Isotropic Chemical Shifts, Principal Shielding Tensor Components, and Anisotropies for Representative Metal Carbonyls[a]

compd	δ_{iso}, ppm	$\sigma_\perp$, ppm	$\sigma_\parallel$, ppm	$\Delta\sigma$, ppm	ref
CO	181	−90(20)	316	406	71
$[Ag(CO)][OTeF_5]$	172.8(2)	−76(10)	295(10)	371	this work
$[Ag(CO)]_2[Zn(OTeF_5)_4]$	171.4(2)	−45(10)	280(10)	325	this work
$[Ag(CO)_2]_2[Zn(OTeF_5)_4]$	172.3(2)	−66(10)	291(10)	357	this work
$Cr(\eta^6\text{-}C_6H_6)(CO)_3$	234	−63(15)	382(15)	445	72
$Cr(CO)_6$	212	−70(15)	353	423	71
$Mo(CO)_6$	202	−75(15)	343	417	71
$Rh_2Cl_2(CO)_4$	180	−99	303	402	71
$Ru_3(CO)_{12}$					
axial	210	−54(10)	342	396	73
equatorial	189	−74(10)	321	395	
$Ir_4(CO)_{12}$	156	−81(10)	274	355	73

[a] Numers in parentheses are estimated errors.

Our NMR data can be used to further elucidate the nature of the Ag–C bonds in these new compounds (see Table 2). The $[Ag(CO)]^+$ and $[Ag(CO)_2]^+$ cations have very similar chemical shifts (~171–173 ppm), all of which are deshielded relative to free CO (δ 184 in dichloromethane; δ 185.8 in the gas phase[63]). For a given anion, there is a very slight shift to less deshielded values on going from the monocarbonyl complexes to the dicarbonyl complexes. For the monocarbonyl complexes, there is a very slight shift to more deshielded values as the coordinating ability of the anion decreases ($OTeF_5^-$ > $Zn(OTeF_5)_4^{2-}$ > $Ti(OTeF_5)_6^{2-}$). However, these changes are very small.

More significantly, however, the silver–carbon coupling constants, which range from 190 to 284 Hz, are the largest ever reported for any organometallic complex of silver. Other literature values of $^1J_{^{109}Ag^{13}C}$, which range from 96 to 149 Hz, are listed in Table 7.[64–68] Note that the literature values are for compounds with direct bonds between silver ions and sp^3 or sp^2 hybridized carbon atoms and therefore might be expected to be smaller than coupling constants between silver ions and an sp hybridized carbonyl carbon atom. Nevertheless, it is clear that there is significant s–s overlap, and hence significant covalency, in the Ag–C bonds in $[Ag(CO)]^+$ and $[Ag(CO)_2]^+$ despite the evidence that these bonds are labile and probably weak. For a given anion, the magnitude of the coupling constant decreases on going from the monocarbonyl complexes to the dicarbonyl complexes. This is a sensible result if one assumes that the bonds between the Ag^+ ions and the hard oxygen or fluorine atoms of the counterions are largely ionic in nature, since then the amount of silver 5s character in each Ag–C bond in the $[Ag(CO)_2]^+$ complex would be expected to be smaller than in the one Ag–C bond in the $[Ag(CO)]^+$ complex.

The reduced metal–carbon coupling constant, K_{MC}, is defined as follows:[69]

$$K_{MC} = J_{MC}[4\pi^2/h(\gamma_M\gamma_C)]$$

When the reduced coupling constants for our silver(I) carbonyl complexes and rhodium(I) carbonyl complexes are compared, $^1K_{^{109}Ag^{13}C}$ is found to be more than twice as large as $^1K_{^{103}Rh^{13}C}$, despite the fact that Rh–CO bonds are shorter, and presumably stronger, than the labile Ag–CO bonds in $[Ag(CO)]^+$ and $[Ag(CO)_2]^+$ (see above). For example, $^1K_{^{109}Ag^{13}C}$ for $[Ag(CO)][OTeF_5]$ is -18.8×10^{21} N A^{-2} m^{-3} ($^1J_{^{109}Ag^{13}C}$ = 265 Hz) while $^1K_{^{103}Rh^{13}C}$ for $Rh_2Cl_2(CO)_4$ is -7.2×10^{21} N A^{-2} m^{-3} ($^1J_{^{103}Rh^{13}C}$ = 69 Hz[70]). The difference in reduced coupling constants is no doubt due to the fact that the 5s orbital on the rhodium(I) ion must be covalently shared with four ligands in the square-planar complex whereas the 5s orbital on the silver(I) ion in $[Ag(CO)]^+$ is used largely, if not exclusively, for silver–carbon σ-bonding.

The two components of the ^{13}C chemical shift tensor, $\sigma_\perp$ and $\sigma_\parallel$, for three of the new compounds, $[Ag(CO)][OTeF_5]$, $[Ag(CO)]_2[Zn(OTeF_5)_4]$, and $[Ag(CO)_2]_2[Zn(OTeF_5)_4]$, were determined (an axially symmetric electron distribution for the carbonyl carbon atoms was assumed). These are listed in Table 8 along with values for a number of other metal carbonyls (all of which are classical metal carbonyls with significant π-back-

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bonding).[71-73] Interestingly, the shielding tensor components and the total chemical shift anisotropy do not change dramatically on going from free CO to σ-bonded CO to σ- and π-bonded CO. It appears that these solid-state ^{13}C NMR parameters will not be suitable as probes of the nature of a given metal–carbonyl bond.

Two independent groups have studied the cationic silver(I) carbonyl complexes $[Ag(CO)]^+$ and $[Ag(CO)_2]^+$ by *ab initio* theoretical methods.[74,75] The paper by Barnes, Rosi, and Bauschlicher (BRB)[74] compared these complexes with other 3d- and 4d-metal mono- and dicarbonyl monocations. The paper by Veldkamp and Frenking (VF)[75] compared silver(I) carbonyl cations to the corresponding gold(I) carbonyl cations. Both studies led to similar conclusions, one of which was that the metal–carbonyl interaction in $[Ag(CO)]^+$ is primarily electrostatic (this conclusion has been reached by others with respect to other transition metal monocarbonyl monocations[76]). The metal charge in $[Ag(CO)]^+$ was calculated by BRB and by VF to be 0.90+ and 0.97+, respectively. The dicarbonyl cation $[Ag(CO)_2]^+$ is predicted to contain considerably more covalent Ag–C bonds: here the metal charge was calculated by BRB and by VF to be 0.65+ and 0.82+, respectively. Both groups calculated Ag–CO dissociation energies for $[Ag(CO)]^+$ and $[Ag(CO)_2]^+$ to be ~20 kcal mol^{-1} (for comparison, the Rh–CO dissociation energies for $[Rh(CO)]^+$ and $[Rh(CO)_2]^+$ were calculated by BRB to be ~30 kcal mol^{-1}). Both BRB and VF calculate that the C–O distance should decrease by about 0.010 Å on going from free CO to either $[Ag(CO)]^+$ or $[Ag(CO)_2]^+$.

The relatively large $^1J_{^{109}Ag^{13}C}$ values observed for $[Ag(CO)][OTeF_5]$, $[Ag(CO)]_2[Zn(OTeF_5)_4]$, and $[Ag(CO)]_2[Ti(OTeF_5)_6]$ seem to be in conflict with the prediction that the Ag–C bond in $[Ag(CO)]^+$ is essentially ionic. Furthermore, the observed values of $^1J_{^{109}Ag^{13}C}$ decrease instead of increase on going from the $[Ag(CO)]^+$ salts to the $[Ag(CO)_2]^+$ salts. One possible explanation is the $[Ag(CO)]^+$ cations in the salts, with several weak (secondary) Ag···F and/or Ag···O bonding interactions, are poor models for an isolated $[Ag(CO)]^+$ cation. If that is true, however, the similarity in observed and calculated $\Delta\nu(CO)$ values remains to be explained ($\Delta\nu(CO)$ is the difference between $\nu(CO)$ for the $[Ag(CO)]^+$ cation and $\nu(CO)$ for free CO): Veldkamp and Frenking predicted $\Delta\nu(CO) = 59$ cm^{-1},[75] while we observed $\Delta\nu(CO) = 48$–65 cm^{-1} for the various $[Ag(CO)]^+$ salts (see Table 1).

Comparisons with Copper(I) and Gold(I) Carbonyls. Vibrational and structural data for representative carbonyl complexes of the group 11 M^+ ions are listed in Table 9.[77-82] There is no reported evidence that a compound of the formula Ag(CO)Cl can be prepared. In this work, we found no carbonyl stretching bands in the IR spectrum of a Nujol mull of AgCl in the presence of 1 atm of CO. In contrast, the compounds Cu(CO)Cl[83] and Au(CO)Cl[11c] are stable under a CO atmosphere and have been known for many years. An understanding of the failure of solid AgCl to undergo carbonylation starts with a comparison of the solid-state structures of CuCl, AgCl, and AuCl, which are all different. The copper(I) ions in CuCl (zinc-blende structure)[84] and in Cu(CO)Cl[9c] are both four-coordinate and tetrahedral. The gold(I) ions in AuCl[85] and in Au(CO)Cl[11a] are both two-coordinate and linear. The silver(I) ions in AgCl (rock salt structure)[86] are six-coordinate and octahedral. The structural reorganization necessary to form Ag(CO)Cl from AgCl may be too great to allow Ag–CO bonds to replace Ag–Cl bonds. This cannot be the only factor, however. Arlrichs, Schnöckel, and co-workers found that monomeric CuCl and CO in an argon matrix formed linear, two-coordinate Cu(CO)Cl.[9b] In contrast, monomeric AgCl did not form a carbonyl under the same conditions.[87] In addition, note that the lattice enthalpy of AgCl (219 kcal mol^{-1}) is smaller, not larger, than the lattice enthalpies of either CuCl (238 kcal mol^{-1}) or AuCl (255 kcal mol^{-1}).[88]

Table 9. Comparison of Vibrational and Structural Data for Copper(I), Silver(I), and Gold(I) Carbonyls

compd	$\nu(CO)$,[a] cm^{-1}	M–C, Å	C–O, Å	refs
CO	2143[b]		1.12822(7)[c]	39, 55
Cu(CO)(O-*t*-Bu)	2062			77
$Cu_2(CO)(dcmpz)_2(py)_2$[d]	2083	1.810(8)	1.126(8)	10
$Cu(CO)(C_2H_5SO_3)$	2117	1.784(8)	1.116(8)	78
Cu(CO)Cl	2127	1.86(2)	1.11(2)	9a,c
$[Cu(CO)][AsF_6]$	2180			79
$[Ag(CO)][OTeF_5]$	2189			this work
$[Ag(CO)][B(OTeF_5)_4]$	2204	2.10(1)	1.08(2)	this work
$[Ag(CO)][Nb(OTeF_5)_6]$	2204 IR			this work
	2206 Raman			this work
$[Ag(CO)_2][B(OTeF_5)_4]$	2198 IR	2.14(5)[e]	1.08(6)[e]	this work
$[Ag(CO)_2][Nb(OTeF_5)_6]$	2196 IR			this work
	2220 Raman			this work
Au(CO)Cl	2162[f]	1.93(2)[g]	1.11(3)[g]	11a,b
$[Au(CO)][OTeF_5]$	2179			80
$[Au(CO)][SO_3F]$	2195			81
$[Au(CO)_2][Sb_2F_{11}]$	2217 IR			12
	2254 Raman			12
$[Au(CO)_2][UF_6]$	2200 IR			82

[a] From IR spectra of solid-state samples, unless otherwise indicated. [b] Reference 39. [c] Reference 74. [d] Hdcmpz = 3,5-dicarbomethoxypyrazole. [e] Average of four values. [f] CH_2Cl_2 solution; ref 11b. [g] Reference 11a.

The other, perhaps more important, factor is the low intrinsic silver–carbon bond energy in an isolated $[Ag(CO)]^+$ cation. Barnes, Rosi, and Bauschlicher (BRB) calculated metal–carbonyl bond dissociation energies for $[Cu(CO)]^+$ and $[Ag(CO)]^+$ to be 33 and 19 kcal mol^{-1}, respectively[74] (cf. the experimental value of 37 kcal mol^{-1} for the $(CO)_5Cr$–CO bond in the gas phase[89]). The relative weakness of the silver–carbon bond was attributed to σ-repulsion. BRB noted that the $4d^95s^1$ (^1D) state of Ag^+ lies 131 kcal mol^{-1} above the ground state and so is less accessible energetically than the corresponding state of Cu^+, which only lies 75 kcal mol^{-1} above its ground state. This naturally leads to less sd_σ hybridization for Ag^+ than for Cu^+, and correspondingly more σ-repulsion for Ag^+ than for Cu^+.[74] BRB's calculations suggest some degree of π-back-bonding in $Cu(CO)^+$, but none for $Ag(CO)^+$ (the second ionization potentials for copper and silver are 20.29 and 21.48 eV, respectively[62]). The presence of π-back-bonding would strengthen the copper–carbon bond relative to the silver–carbon bond and is consistent with $\nu(CO)$ for Cu(CO)Cl, which, at 2127 cm^{-1}, is below that for free CO. Veldkamp and Frenking calculated metal–carbonyl bond dissociation energies for $[Ag(CO)]^+$ and $[Au(CO)]^+$ to be 21 and 45 kcal mol^{-1} (negligible π-back-bonding in both cases).[75] This difference is probably due to relativistic effects, which are larger for gold than

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for any other element.[90] This lowers the energies of s and p orbitals and raises the energies of d and f orbitals. The relativistic contraction of the 6s orbital of Au^+ results in shorter and stronger covalent bonds, in many cases, than for Ag^+.[90] In addition, the small 5d–6s gap results in considerably lower σ-repulsion for Au^+ than for Ag^+. Note that the Au–C distance of 1.93(2) Å in Au(CO)Cl is 0.17 Å shorter than the Ag–C distance of 2.10(1) Å in $[Ag(CO)][B(OTeF_5)_4]$.

There is little doubt that the $[Au(CO)_2]^+$ ions in $[Au(CO)_2][Sb_2F_{11}]$,[12] like the $[Ag(CO)_2]^+$ ions in $[Ag(CO)_2][B(OTeF_5)_4]$, are linear and have several weak Au···F contacts. The CO ligands in $[Au(CO)_2][Sb_2F_{11}]$ are not labile, and hence are probably *more* strongly bound than the CO ligands in $[Ag(CO)_2][B(OTeF_5)_4]$. This is consistent with the observation that the average value of ν(CO) is 2236 cm^{-1} for $[Au(CO)_2][Sb_2F_{11}]$ but only 2208 cm^{-1} for $[Ag(CO)_2][Nb(OTeF_5)_6]$: the higher value for the gold compound is the result of stronger Au–C σ-bonding, not weaker π-back-bonding. There is no compelling evidence for π-back-bonding in either ion. Furthermore, ν_{sym}(CO) − ν_{asym}(CO) is 37 cm^{-1} for $[Au(CO)_2][Sb_2F_{11}]$ but only 24 cm^{-1} for $[Ag(CO)_2][B(OTeF_5)_4]$. The higher value for the gold compound is also consistent with stronger Au–CO bonds (cf. ν_{sym}(CN) − ν_{asym}(CN) for the $[Au(CN)_2]^-$ and $[Ag(CN)_2]^-$ ions, 20 cm^{-1} [91] and 6 cm^{-1},[92] respectively).[39b]

A significant number of copper(I) carbonyls other than Cu(CO)Cl have been studied, in large measure because of their relevance to protein biochemistry[93] and to commercial Cu-promoted ZnO catalysts for methanol synthesis.[2a,c,94] Only representative data are listed in Table 9. The ν(CO) values are typically high relative to classical metal carbonyls, but in most cases they are below 2143 cm^{-1}. Two important exceptions are Cu(CO)(O-*t*-Bu), a sublimable compound which has a relatively low ν(CO) value of 2062 cm^{-1} indicative of significant π-back-bonding (cf. ν(CO) = 2073 cm^{-1} for $Ni(CO)(PF_3)_3$[41]), and $[Cu(CO)][AsF_6]$, which has a ν(CO) value of 2180 cm^{-1},[79] nearly as high as $[Ag(CO)][OTeF_5]$. The use of the weakly coordinating anion AsF_6^- leads to a high positive charge density on the copper(I) ion in $[Cu(CO)][AsF_6]$, which in turn leads to only small or negligible π-back-bonding.

There are a number of experimental and theoretical papers dealing with the interaction of CO and copper or silver atoms[95] or copper, silver, and gold surfaces.[96] In cases involving zerovalent silver, the ν(CO) values are well below 2143 cm^{-1}, indicating significant π-back-bonding. For example, McIntosh and Ozin reported a ν(CO) value of 1951 for neutral Ag(CO) in a krypton matrix[95g] (their interpretation has been challenged by Marian[95b]) and Wang and Greenler reported a value of 2060 cm^{-1} for CO adsorbed on a polycrystalline silver foil.[96d] On the other hand, when Ag, CO, and O_2 are co-condensed in an argon matrix at cryogenic temperatures, a band at 2165 cm^{-1} was observed and was attributed to the ion pair $[Ag(CO)]^+[O_2]^-$.[15b] Given the work reported in this paper, this is certainly a reasonable assignment.

Summary and Conclusions. The cations $[Ag(CO)]^+$ and $[Ag(CO)_2]^+$ have been isolated as salts of a number of anions containing the $OTeF_5$ moiety. These crystalline compounds, which are only stable under a partial pressure of CO (the exact pressure necessary depends on the anion), have been studied by manometry (CO uptake and loss), by IR, Raman, and liquid and solid NMR spectroscopy, and by X-ray crystallography. The spectroscopic and structural data strongly suggest that there is little or no Ag→C π-back-bonding, and so these compounds join the growing list of nonclassical (σ-only) metal carbonyls.

These compounds may become important as models for intermediates in silver(I) promoted or catalyzed carbonylation reactions[16] and in the silver promoted or catalyzed oxidation of carbon monoxide.[15b,96e,97] The study of silver(I) and other nonclassical carbonyls may also aid in our understanding of the copper(I) and zinc(II) carbonyl species that may be present in the catalytic synthesis of methanol.[2a,c] It is also possible that nonclassical carbonyls may provide new insight into reactions involving CO that are catalyzed by metals that form classical metal carbonyls. To our knowledge, no one has studied the reactivity consequences of slightly lengthening the M–CO distance, and consequently diminishing the amount of M→C π-back-bonding, in carbonyl species formed from metal clusters or on metal surfaces.

While there are a limited number of isolable isonitrile complexes of silver(I),[13a,98] there are no isolable PF_3 complexes of silver(I). Along with carbonyl complexes of group 3, 4, 11, and 12 metals and main-group elements, complexes such as $[Ag(PF_3)_n]^+$ remain as significant synthetic challenges.

Experimental Section

Inert Atmosphere. None of the new compounds appeared to be oxygen sensitive, but all were extremely moisture sensitive. Therefore, all preparations and physical measurements were carried out with rigorous exclusion of air and water. Schlenk, glovebox, and high-vacuum techniques were employed, with purified nitrogen or argon used when an inert atmosphere was required.[99]

Reagents and Solvents. These were reagent grade or better. The following compounds were used as received: AgCl (Alfa), $AgClO_4$ (Alfa), $AgSbF_6$ (Strem), CO (99.99%, Matheson). The following compounds were prepared following literature procedures: $AgOTeF_5$,[25] $AgB(OTeF_5)_4$,[24] $AgNb(OTeF_5)_6$,[37] $Ag_2Ti(OTeF_5)_6$,[37] $Ag_2Zn(OTeF_5)_4$,[100] $[CH_3CO][SbCl_6]$,[58] and $[(CH_3)_2CHCO][SbCl_6]$.[28] The following solvents were dried by distillation from sodium metal, P_2O_5, CaH_2, and/or activated 4 Å molecular sieves: dichloromethane, dichloromethane-d_2, toluene, nitromethane, diethyl ether, and 1,1,2-trichlorotrifluoroethane.

Physical Measurements. Tensimetric Measurements. A high-vacuum line equipped with a Rodder Toepler pump, mercury-in-glass manometers, and Baratron electronic manometers was used to measure amounts of carbon monoxide added to or evolved from solid samples of various silver-

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(I) compounds at various pressures. In a typical experiment 300 mg of $AgNb(OTeF_5)_6$ (0.183 mmol) was charged to a dry 75-mL stainless steel reaction vessel. Carbon monoxide (500 Torr) was added to the vessel and allowed to equilibrate with the silver salt for 3–5 h. After the reaction vessel was cooled to −78 °C for 15 min, the gaseous CO was removed under vacuum. After further cooling to −196 °C, 3 mL of toluene (28 mmol) were vacuum transferred into the vessel, which was closed and allowed to warm to room temperature. Since toluene rapidly replaces any bound CO (see above), this procedure allowed all of the bound CO to be liberated quickly. The volatiles from the reaction vessel were passed through three −196 °C U-traps, and the CO was collected and measured (2.0 equiv) with the Toepler pump.

Spectroscopic Methods. Samples for IR spectroscopy were typically mulls (Nujol or Fluorolube) between AgCl or AgBr windows. Spectra were recorded at room temperature on a Perkin-Elmer 983 or Nicolet 5PC spectrometer. A spectrum of $AgNb(OTeF_5)_6$ dissolved in 1,1,2-$C_2Cl_3F_3$ under ~1 atm of CO was recorded using a cylindrical internal reflectance cell.[101] Samples for Raman spectroscopy were crystalline solids sealed in 5-mm glass tubes under varying pressures of CO. Spectra were recorded at room temperature on a Nicolet System 800 FTIR spectrometer with a Nicolet FT-Raman accessory (1064 nm excitation). Total laser power incident on the samples was ca. 0.06 W. In all cases, peak positions are ± 1 cm^{-1} or better.

Samples for liquid ^{13}C and ^{19}F NMR spectroscopy were dichloromethane solutions in 5 mm glass tubes sealed under varying pressures of CO. The spectrometers, a Bruker SY-200 or WP-300, were tuned using separate samples of pure dichloromethane-d_2. Chemical shifts (δ scale) are relative to internal Me_4Si (^{13}C) or $CFCl_3$ (^{19}F). All ^{19}F NMR spectra were AB_4X patterns shielded relative to $CFCl_3$ ($X = {}^{125}Te$, $I = {}^1/_2$, 7% natural abundance).

Samples for solid ^{13}C NMR spectroscopy were crystalline solids loaded into 8 mm glass tubes sealed under varying pressures of CO. The sample size was typically 1.0 g. Spectra were recorded on modified Nicolet NT-150 and NT-200 spectrometers operating at ^{13}C frequencies of 37.70 or 50.31 MHz, respectively, using a home-built cross polarization/magic angle spinning (CP/MAS) unit which included the probe. The spinner system, a modified version of Gay's,[102] spun the sample tubes at 1.5–2.1 kHz. Single-pulse spectra were acquired with a 180–90–τ–90 pulse sequence to suppress baseline artifacts,[103] with $\tau = 5.8$ μs. Chemical shifts are relative to external Me_4Si, with adamantane as a secondary standard (δ 29.7, 38.7), and are accurate to ± 0.2 ppm.

Crystallographic Study. A Siemens *R*3*m* diffractometer equipped with a LT-2 variable temperature accessory was used. Crystals of $[Ag(CO)][B(OTeF_5)_4]$, $[Ag(CO)_2][B(OTeF_5)_4]$, and $[(CH_3)_2CHCO][SbCl_6]$ were examined at −20 °C or colder using an apparatus previously described.[35] When a suitable crystal was found, it was embedded in Halocarbon 25-5S grease at the end of a glass fiber and quickly placed in the cold nitrogen stream of the LT-2 unit.

Centering of 25 reflections allowed least-squares calculation[104] of the cell constants given in Table 3, which also lists other experimental parameters. The intensities of three control reflections monitored every 97 reflections showed no significant trend during the course of the data collections. Empirical absorption corrections, based on intensity profiles for 16 reflections over a range of setting angles (ψ) for the diffraction vector, were applied to the observed data for $[Ag(CO)][B(OTeF_5)_4]$ and $[Ag(CO)_2][B(OTeF_5)_4]$. The transmission factors ranged from 0.117 to 0.184 for $[Ag(CO)][B(OTeF_5)_4]$ and from 0.437 to 1.000 for $[Ag(CO)_2][B(OTeF_5)_4]$. Lorentz and polarization corrections were applied to the data.

The structures were solved by interpretation of Patterson maps ($[Ag(CO)][B(OTeF_5)_4]$ and $[Ag(CO)_2][B(OTeF_5)_4]$) or by direct methods ($[(CH_3)_2CHCO][SbCl_6]$).[105] The refinements involved anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms in the structure of $[(CH_3)_2CHCO][SbCl_6]$ were included in calculated positions (C–H = 0.96 Å, $U(H) = 1.2U_{iso}(C)$). Neutral-atom scattering factors (including anomalous scattering) were taken from ref 105. The weighted least-squares refinements converged (weights were calculated as $(\sigma^2(F) + |g|F_o^2)^{-1}$ for $[Ag(CO)][B(OTeF_5)_4]$ and $[Ag(CO)_2][B(OTeF_5)_4]$ and $(\sigma^2(F) + 0.0003F^2)^{-1}$ for $[(CH_3)_2CHCO][SbCl_6]$). In the final difference Fourier maps, the maximum and minimum electron densities were 1.13 and −1.33 e Å^{-3} for $[Ag(CO)][B(OTeF_5)_4]$, 2.59 and −2.11 e Å^{-3} for $[Ag(CO)_2][B(OTeF_5)_4]$, and 0.37 and −0.43 e Å^3 for $[(CH_3)_2CHCO][SbCl_6]$. Analysis of variance as a function of Bragg angle, magnitude of F_o, reflection indices, etc., showed no significant trends.

The structure of $[CH_3CO][SbCl_6]$ appeared to be disordered at −130 °C. Crystals of this compound were examined as described above. The orthorhombic unit cell edge lengths were found to be 7.089(1), 8.957(1), and 7.938(1) Å at −130(1) °C (cf. the literature values of 7.144(3), 9.091(5), and 7.974(4) Å at room temperature[58]). The structure was refined in both *Imm*2 (the space group used by the authors of the room temperature study[58]) and *I*222. In both cases, the thermal ellipsoid of the central carbon atom of the $[CH_3CO]^+$ cation was greatly elongated along the C–C–O direction, indicating that the methyl carbon atom and the oxygen atom are 2-fold disordered (drawings of the *Imm*2 and *I*222 asymmetric units at −130 °C are available as Supplementary Material). In fact, the space group *I*222, which was not considered by the authors of the room temperature study, requires this disorder.

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Supplementary Material Available: Drawings of the labeled asymmetric unit and packing diagrams and complete tables of atomic coordinates, bond distances and angles, and anisotropic thermal parameters for $[(CH_3)_2CHCO][SbCl_6]$ (5 pages); tables of observed and calculated structure factors for $[(CH_3)_2CHCO][SbCl_6]$ (4 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information. Similar information is available for $[Ag(CO)][B(OTeF_5)_4]$ and $[Ag(CO)_2][B(OTeF_5)_4]$: see the Supplementary Material paragraph at the end of refs 22b and 22a, respectively.

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