Previously, we have measured the orientation of the CO bound to Fe_{a3}^{2+} as 21° from the heme normal compared to an angle of 51° when it is bound to Cu_B^+.[7] Molecular modeling suggests that the CO vector of Cu_B^+–CO points away from the heme plane. The CO must therefore move approximately 4 Å and rotate 30° to bind to Cu_B^+. We estimate an initial recoil velocity of ~14 Å/ps for the CO on the basis of the energetics proposed for HbCO photodissociation.[13] Accordingly, in free flight, the ejected CO could move 4 Å within 300 fs. It is highly improbable, however, that the CO is able to move this far without colliding with other atoms in the heme pocket. In the case of Hb, the crystal structure indicates that the CO can move no more than 1 Å in free flight[14] and it has been concluded that collisions rapidly (~300 fs) render the motion of the CO diffusive (~1 Å/ps).[13] The unusually narrow infrared line width for CO bound to Fe_{a3}^{2+} in CcO (half that in HbCO[15]) suggests a rigid, confined heme pocket[15,16] which would likely restrict the motion of "free" CO. Clearly the picture of a "free" CO diffusing through the heme pocket to Cu_B^+ is not consistent with the observed rise time of the Cu_B^+–CO transient, which requires motion of the CO from Fe_{a3}^{2+} to Cu_B^+ closer to free flight at supersonic velocity than purely diffusive at a thermalized velocity. A concerted mechanism in which the Cu_B^+–CO bond begins to form as the Fe_{a3}^{2+}–CO bond breaks appears a more accurate description of the CO transfer. The close proximity of the Cu_B^+, which is potentially in van der Waals contact with CO bound to Fe_{a3}^{2+}, makes a concerted transfer possible. When CO is bound to Fe_{a3}^{2+}, the CO absorption frequency, bandwidth, and insensitivity to changes at Cu_B^+ suggest that the Cu_B^+–O interaction is weak.[15,16] As the CO dissociates, however, it can begin to interact with Cu_B^+ via the carbon and form a new bond.

Whether the reaction is concerted or stepwise, the CO likely arrives at Cu_B^+ with considerable excess energy which must be dissipated along with the energy of the Cu_B^+–CO bond formation. It is difficult to estimate the rates of the intramolecular vibrational energy transfer processes which dissipate this excess energy, since the magnitude of the excess energy and the structure and vibrational coupling of the Cu_B^+–CO center are not known. The observed rise time of the Cu_B^+–CO absorption, however, requires that these processes be very rapid, at most hundreds of femtoseconds.

The remarkable rate of CO transfer from Fe_{a3}^{2+} to Cu_B^+ provides new insight into the structure of CcO. The heme pocket must be elegantly designed to restrict the motion of bound CO but to facilitate rapid transfer between metal centers of photodissociated CO. The rapidity of this transfer does not allow for any barriers to CO translation and rotation nor for any ligand reorganization at Cu_B^+. These features of the protein are significant to the role of Cu_B as a ligand shuttle to Fe_{a3} in the functional dynamics of the protein.[1] This reaction is also of interest from a fundamental standpoint in understanding the elementary steps involved in coordination and atom-transfer dynamics, in the same sense that chlorophyll reaction centers have become a paradigm for understanding ultrafast electron transfer.

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$Ag(CO)B(OTeF_5)_4$: The First Isolable Silver Carbonyl

Paul K. Hurlburt, Oren P. Anderson, and Steven H. Strauss*

Department of Chemistry, Colorado State University
Fort Collins, Colorado 80523

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From an academic or an industrial point of view, carbon monoxide is one of the most important ligands in transition-metal chemistry. Only a handful of metals in the d block have failed to yield an isolable carbonyl complex, and silver is one of them.[1-3] Despite this, there has been interest in $Ag(CO)_n^+$ species as catalysts for the carbonylation of alkanes, arenes, alkenes, aldehydes, alcohols, and amines.[4] Until now, $Ag(CO)_n^+$ species have only been detected in zeolite hosts[5] or in strongly acidic media such as concentrated H_2SO_4 or $BF_3{\cdot}H_2O$ (generally at low temperatures and high pressures).[6] In this communication we report the synthesis, structure, and IR spectrum of $Ag(CO)B(OTeF_5)_4$. Not only is this the first isolable silver carbonyl, it also exhibits one of the highest CO stretching frequencies of *any* metal carbonyl species (2204 cm^{-1}).

When $AgOTeF_5$,[7] $B(OTeF_5)_3$ (which is volatile),[8] and excess CO (final pressure = 200 Torr) were mixed in a glass vessel at 25 °C, 2 equiv of CO was taken up (all CO uptake and evolution experiments were carried out quantitatively (±0.05 equiv) by using high vacuum line manometry):

$$AgOTeF_5 + B(OTeF_5)_3 \xrightarrow[25\ ^\circ C,\ 36\ h]{excess\ CO} Ag(CO)_2B(OTeF_5)_4$$

When this compound was placed under vacuum, 1 equiv of CO was evolved within minutes, leaving $Ag(CO)B(OTeF_5)_4$, which slowly (hours) lost the remaining equivalent of CO and re-formed $AgOTeF_5$ and $B(OTeF_5)_3$. Both carbonyl complexes are extremely hygroscopic: water vapor displaced the CO ligands and reacted with the $B(OTeF_5)_4^-$ counterions, liberating $HOTeF_5$. When $AgOTeF_5$ alone was treated with CO (P_{CO} = 320 Torr), only 1 equiv of CO was taken up (this process was also reversible).

The solid-state IR spectrum of $Ag(CO)B(OTeF_5)_4$ exhibited ν(CO) at 2204 cm^{-1} ($\nu(^{13}CO)$ = 2154 cm^{-1}). The carbon–oxygen stretching frequency is significantly higher than in free CO (2143 cm^{-1}),[9] a clear indication that CO is acting merely as a Lewis base

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(1) 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 $Pt(CO)(AuPPh_3)_8Ag(NO_3)_3$[2a] and $Cp(CO)_2Mo(\mu\text{-}Ag(PPh_3))(\mu\text{-}PPh_2)Mn(CO)_4$,[2b] with all Ag—C(O) distances ≥2.7 Å, are not silver carbonyls.

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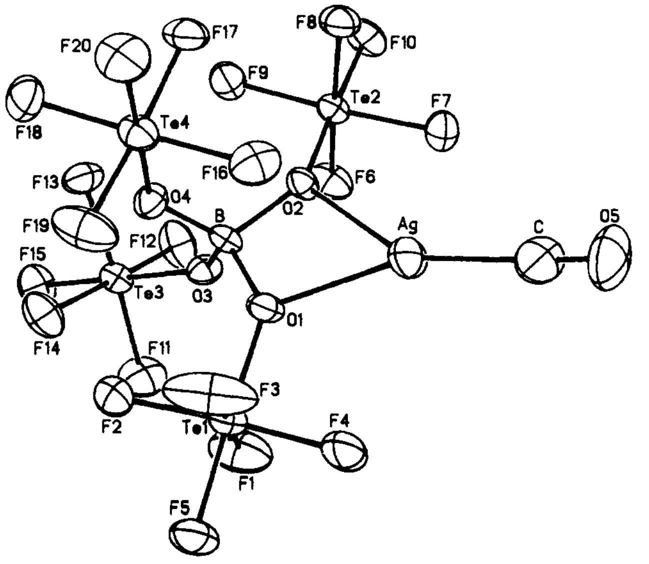

Figure 1. Drawing of the $Ag(CO)B(OTeF_5)_4$ molecule (50% probability ellipsoids). Selected distances and angles: Ag–C, 2.10 (1) Å; C–O, 1.077 (16) Å; Ag–C–O, 176 (1)°; Ag–O1, 2.324 (6) Å; Ag–O2, 2.436 (7) Å; Ag–F4, 3.076 (8) Å; Ag–F16, 2.959 (6) Å; Ag–F8′, 2.972 (6) Å; Ag–F19″, 3.028 (7) Å.

in this compound and is exhibiting no π-acidity (i.e., since the carbon atom "lone pair" in CO is slightly antibonding,[10] donation of it to a metal ion strengthens the bond and raises ν(CO)). The value 2204 cm^{-1} is apparently the highest ever reported for *any* molecular metal monocarbonyl[9b,12,13] and underscores the extreme degree of coordinative unsaturation of the Ag^+ ion in $AgB(OTeF_5)_4$ (see below). Compare, for example, ν(CO) for BH_3·CO, which is 2165 cm^{-1},[11] a full 39 cm^{-1} *lower* than in $Ag(CO)B(OTeF_5)_4$.

When a Nujol mull of $Ag(CO)B(OTeF_5)_4$ was coated onto the inside surfaces of AgCl windows of a gas-phase IR cell filled with CO, a band at 2207 cm^{-1} was observed ($\Delta\nu_{1/2}$ = 15 cm^{-1}; cf. $\Delta\nu_{1/2}$ = 15 cm^{-1} for the 2204-cm^{-1} band of $Ag(CO)B(OTeF_5)_4$). The new band is tentatively assigned as ν_{asym}(CO) for the complex $Ag(CO)_2B(OTeF_5)_4$. This process is reversible: the 2204-cm^{-1} band reappeared when P_{CO} was reduced to ~0 Torr for 15 min. When the same procedure was used, a band at 2189 cm^{-1} was observed for the compound with the stoichiometry $Ag(CO)OTeF_5$. For comparison, IR[6d] and Raman[6b] spectra of the putative $D_{\infty h}$ $Ag(CO)_2^+$ ion in neat HSO_3F at -50 °C exhibited ν(CO) bands at 2190 and 2179 cm^{-1}, respectively.[14]

When $Ag(CO)B(OTeF_5)_4$ was dissolved in 1,1,2-$C_2Cl_3F_3$, some CO was released, suggesting that even this weakly basic solvent competes with CO for coordination to Ag^+ ions. Coordination of this Freon solvent has not yet been proven, however, since crystallization of a mixture of $AgOTeF_5$ and $B(OTeF_5)_3$ from 1,1,2-$C_2Cl_3F_3$ in the absence of CO yielded crystals of the unsolvated salt $AgB(OTeF_5)_4$.[15] Each Ag^+ ion is bound to three $B(OTeF_5)_4^-$ anions by means of three Ag–O(Te,B) contacts at 2.500 (5), 2.601 (5), and 2.755 (5) Å and six Ag–F(Te) contacts which range from 2.644 (5) to 3.017 (5) Å (see supplementary material for drawings of this structure).

When CO is present, crystals of $Ag(CO)B(OTeF_5)_4$ are obtained from 1,1,2-$C_2Cl_3F_3$ solution.[16] The structure, shown in Figure 1, has a nearly linear Ag—C≡O linkage (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). Considering structural results for carbonyl complexes of Rh^+, another monovalent period 5 metal ion, the Ag–C distance of 2.10 (1) Å is quite long (cf. Rh–C bond distances of 1.77–1.85 Å in $RhH(CO)(PPh_3)_3$[17a] and $Rh_2Cl_2(CO)_4$[17b]). In harmony with the unusually high CO stretching frequency, the C–O distance of 1.077 (16) Å in $Ag(CO)B(OTeF_5)_4$ is unusually short (cf. C–O distances in CO, BH_3·CO, and $Cr(CO)_6$, which are 1.128 22 (7),[18] 1.131,[19] and 1.141 (2) Å,[20] respectively). Relative to $AgB(OTeF_5)_4$, carbon monoxide binding has weakened the interaction of each Ag^+ ion with two neighboring borate anions while strengthening it to the third: each metal ion is now bound to only two oxygen atoms from the same borate anion, with shorter Ag–O(Te,B) distances (2.324 (6) and 2.436 (7) Å) and fewer (four vs six) Ag–F(Te) contacts (2.959 (6)–3.076 (8) Å).[21]

The borate anions in both $AgB(OTeF_5)_4$ and $Ag(CO)B(OTeF_5)_4$ contain nearly tetrahedral BO_4 cores and exhibit the same overall structure observed in Tl(mesitylene)$_2B(OTeF_5)_4$[22] and Tl(1,2-$C_2H_4Cl_2$)$B(OTeF_5)_4$.[23] The virtue of this large, polyfluorinated counterion is that its metal salts are soluble in solvents such as aromatic hydrocarbons,[22] chlorocarbons,[23,24] and chlorofluorocarbons that are, at best, extremely weakly coordinating. It also allows complexes such as $Ag(CO)B(OTeF_5)_4$, with its very weak Ag–C bond, to be isolated and fully characterized. The coordination chemistry of salts of $B(OTeF_5)_4^-$ and other, larger fluoro anions and the catalytic properties of these new Ag^+ carbonyls will be the subjects of forthcoming papers from this laboratory.

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Supplementary Material Available: Drawings of $Ag(CO)B(OTeF_5)_4$ (inner coordination sphere, Figure S-1) and $AgB(OTeF_5)_4$ (Figures S-2 and S-3) and tables of atomic coordinates, bond distances, bond angles, and anisotropic thermal parameters for $Ag(CO)B(OTeF_5)_4$ (9 pages); listing of observed and calculated structure factors for $Ag(CO)B(OTeF_5)_4$ (21 pages). Ordering information is given on any current masthead page.

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