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Cationic Gold Carbonyl Complex on a Phosphine Support

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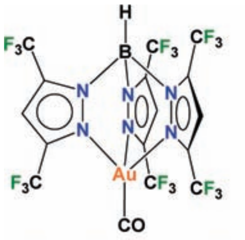
S *Supporting Information*

ABSTRACT: A cationic gold carbonyl complex has been synthesized and characterized using several techniques including X-ray crystallography. $[(Mes_3P)Au(CO)][SbF_6]$ (Mes = 2,4,6-$Me_3C_6H_2$) has a linear, two-coordinate gold atom. This compound displays the CO stretching frequency at 2185 cm^{-1}. The ^{13}C NMR signal of the gold-bound ^{13}CO appears as a doublet centered at δ 182.6 ($^2J_{C,P}$ = 115 Hz). A computational study shows that the Au—CO bond consists of electrostatic attraction, Au ← CO donation, and significant Au → CO π-back-bonding components. Polarization of the CO bond caused by the electrostatic effect of the cationic gold center is mainly responsible for the large blue shift in the CO stretching frequency.

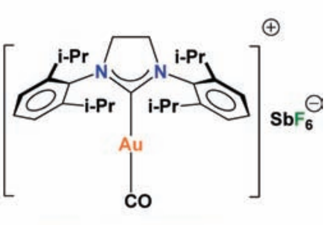
Gold is not a metal merely for coins, investing, and jewelry anymore. During the past few years, novel reactions involving unsaturated molecules like carbon monoxide (CO), alkenes, and alkynes mediated by gold have been reported in the literature on a regular basis and in ever-increasing numbers.[1−6] For example, gold catalyzes several reactions involving CO including oxidation to carbon dioxide under mild conditions, a water−gas shift reaction, and olefin carbonylation chemistry.[1,3,6−10] CO is also used as a reducing agent in the preparation of gold nanoparticles from gold salts.[11,12] Overall, there is significant interest in the isolable and well-characterized molecules featuring bonds between gold(I) and small unsaturated molecules like CO or various alkenes and alkynes.[13−15] Such species serve as useful models for likely intermediates in relevant gold-catalyzed processes and provide valuable spectroscopic and structural data.

In this paper, we describe the isolation of an interesting cationic gold(I) carbonyl complex $[(Mes_3P)Au(CO)][SbF_6]$ (where Mes = 2,4,6-$Me_3C_6H_2$) using a readily available phosphine as the supporting ligand. It is noteworthy that, despite the reported preparation of Au(CO)Cl in 1925 by Manchot and Gall[16] and the widespread interest in the chemistry between gold and CO, as is evident from the numerous spectroscopic and computational studies and various applications,[1−3,9−12,15,17−25] isolable gold carbonyl adducts are still rare, and structurally characterized species involving terminal Au−CO bonds are limited to Au(CO)Cl,[26] $[HB(3,5\text{-}(CF_3)_2Pz)_3]Au(CO)$,[27] $[Au(CO)_2]_2[SbF_6][Sb_2F_{11}]$,[28] and $[(SIDipp)Au(CO)][SbF_6]$.[29]

The gold(I) carbonyl complex $[(Mes_3P)Au(CO)][SbF_6]$ was synthesized by treatment with a dichloromethane solution of $(Mes_3P)AuCl$[30] (generated from AuCl and Mes_3P) with $AgSbF_6$ in the presence of CO (1 atm). $[(Mes_3P)Au(CO)][SbF_6]$ is a colorless, crystalline solid. The IR spectrum of $[(Mes_3P)Au(CO)][SbF_6]$ in KBr displays a strong absorption band at 2185 cm^{-1}, which can be assigned to the CO stretch. This value is significantly higher than that observed for the free CO ($\bar{\nu}_{CO}$ = 2143 cm^{-1})[20] and those observed for $[HB(3,5\text{-}(CF_3)_2Pz)_3]Au(CO)$ ($\bar{\nu}_{CO}$ = 2144 cm^{-1})[27] and Au(CO)Cl ($\bar{\nu}_{CO}$ = 2162 cm^{-1})[18] but lower than that of $[(SIDipp)Au(CO)][SbF_6]$ ($\bar{\nu}_{CO}$ = 2197 cm^{-1}).[29] $[Au(CO)]^+$ in a neon matrix that is perhaps the closest species to a "naked" gold carbonyl cation (i.e., without any or strongly bound supporting ligands), which displays a much higher ν_{CO} at 2237 cm^{-1}.[24] The high CO stretching frequency observed for $[(Mes_3P)Au(CO)][SbF_6]$ is usually considered to be the result of a primarily σ-type Au−CO interaction with negligible Au → CO π-back-donation augmented by the stiffening (reorganization) of the CO moiety caused by the electrostatic effect of the cationic gold center.[17−19,21] A more definite answer is given later in the manuscript.



$[HB(3,5\text{-}(CF_3)_2Pz)_3]Au(CO)$



$[(SIDipp)Au(CO)][SbF_6]$

The $^{13}C\{^1H\}$ NMR spectrum of $[(Mes_3P)Au(CO)][SbF_6]$ in CD_2Cl_2 collected at room temperature or at −10 °C showed a doublet centered at δ 182.6 ($^2J_{C,P}$ = 115 Hz), which can be assigned to the ^{31}P-coupled carbon resonance of the gold(I)-bound CO moiety.[31] For comparison, $[Au(CO)]^+$ in concentrated sulfuric acid and Au(CO)Cl in CD_2Cl_2 display their ^{13}CO chemical shifts at δ 164 and 172.3, respectively, while the free CO resonates at δ 184.[9,18] The ^1H NMR spectrum of $[(Mes_3P)Au(CO)][SbF_6]$ shows three separate signals for the three 2,4,6-methyl groups and a broad signal for the aryl ring 3- and 5-hydrogen atoms, indicating the restricted rotation of the mesityl groups about the P−C_{ipso} bonds at room temperature on the NMR time scale. The mesityl group resonances in the $^{13}C\{^1H\}$ NMR spectrum are also consistent with this observation. A similar situation has been reported for compounds such as $(Mes_3P)AuBr$ and (Mes_3P)-

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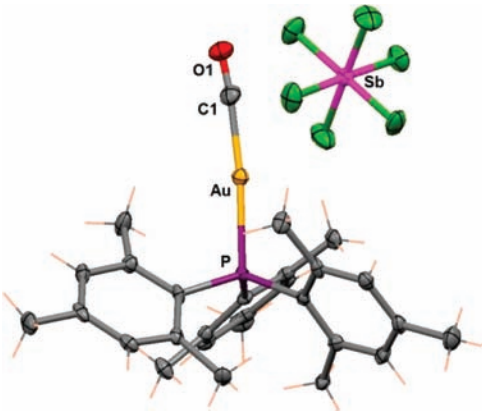

Figure 1. Molecular structure showing $[(Mes_3P)Au(CO)][SbF_6]$. Ellipsoids are shown at the 50% probability level. Selected bond distances (Å) and angles (deg): Au−C1 2.008(6), Au−P 2.3380(12), O1−C1 1.108(7); O1−C1−Au 174.2(5), C1−Au−P 173.31(17), C11−P−C20 111.2(2), C11−P−C2 111.0(2), C20−P−C2 113.4(2).

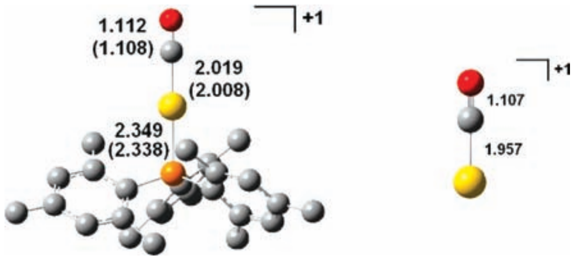

Figure 2. Calculated geometry of $[(Mes_3P)Au(CO)]^+$ and $[Au(CO)]^+$. The experimental bond lengths (Å) are in parentheses.

Table 1. NOCV-EDA Results for $[(Mes_3P)Au(CO)]^+$ and $[Au(CO)]^+$ (Energy Values in kcal/mol)

fragment	$(Mes_3P)Au^+ + CO$	$Au^+ + CO$
ΔE_{int}	−33.4	−58.9
ΔE_{Pauli}	168.3	201.1
ΔE_{elstat}[a]	−127.4 (63.1%)	−159.6 (61.4%)
ΔE_{orb}[a]	−74.3 (36.9%)	−100.4 (38.6%)
ΔE_{σ}[b]	−44.9 (61.4%)	−67.8 (67.5%)
ΔE_{π}[b]	−28.2 (38.0%)	−32.7 (32.5%)
ΔE_{rest}[b]	−1.2 (0.6%)	−0.05 (<0.1%)
E_{prep}	1.2	0.1
$-D_e$	−32.2	−58.8

[a] The values in parentheses give the percentage contribution to ΔE_{int}. [b] The values in parentheses give the percentage contribution to the orbital interactions ΔE_{orb}. The ΔE_{rest} term comes from orbitals that have higher symmetry than σ and π.

AuI.[32] Interestingly, the ^1H NMR spectrum of $[(Mes_3P)Au(CO)][SbF_6]$ in CD_2Cl_2 at −10 °C displayes two separate singlets for the aryl ring 3- and 5-hydrogen atoms. Two signals corresponding to *o*-methyl protons also get sharper at this temperature. The $^{31}P\{^1H\}$ NMR spectrum of $[(Mes_3P)Au(CO)][SbF_6]$ displays its ^{31}P resonance at δ −4.7, which is a downfield shift compared to that of the free Mes_3P signal (δ −35.9).

X-ray-quality crystals of $[(Mes_3P)Au(CO)][SbF_6]$ were obtained from a dichloromethane−hexane solution at 0 °C. It crystallizes in the $P2_12_12_1$ space group. As is evident from the ORTEP drawing of $[(Mes_3P)Au(CO)][SbF_6]$ (Figure 1), mesityl groups adopt a propeller arrangement around phosphorus. The gold center features an essentially linear geometry with a C1−Au−P angle of 173.31(17)°. The P−Au and Au−CO bond distances are 2.3380(12) and 2.008(6) Å, respectively. The Au−C bond distance is marginally longer than the corresponding bond distance in the two-coordinate, cationic $[Au(CO)_2]^+$ [1.971(8) Å][28] or $[(SIDipp)Au(CO)][SbF_6]$ [1.971(5) Å] but significantly longer than the Au−C distance of the neutral, four-coordinate gold(I) adduct $[HB(3,5-(CF_3)_2Pz)_3]Au(CO)$ [1.862(9) Å].[27] The P−Au bond distance in $[(Mes_3P)Au(CO)][SbF_6]$ is longer than that reported for $(Mes_3P)AuCl$ [2.2634(15) Å].[30] There are no close intermolecular Au···Au contacts in $[(Mes_3P)Au(CO)][SbF_6]$. However, there are two close (O)C···F-SbF_5 contacts at 2.758 and 2.844 Å between the carbon of the CO and fluorine atoms of two different $[SbF_6]^-$ counterions, which are within the sum of the van der Waals radii of the carbon and fluorine (3.17 Å). Such interactions have been considered as a sign of the electrophilic nature of the carbonyl carbon in cationic metal carbonyl adducts.[19]

We calculated the geometry and vibrational spectrum of the cations $[(Mes_3P)Au(CO)]^+$ and $[Au(CO)]^+$ at M05-2X/def2-TZVPP,[33] and we analyzed the $(Mes_3P)Au^+$−CO and Au^+−CO interactions with the NOCV-EDA[34] method in order to understand the blue shift of the CO stretching modes with regard to free CO. Details of the calculations are found in the Supporting Information section. The optimized geometry for $[(Mes_3P)Au(CO)]^+$ is in very good agreement with the experiment (Figure 2). The calculated harmonic frequencies for the CO stretching mode of $[(Mes_3P)Au(CO)]^+$ (2331 cm^{-1}) and free CO (2274 cm^{-1}) give a blue shift of 57 cm^{-1}, which is somewhat higher than the experimental value of 42 cm^{-1}. The calculated CO frequency of $[Au(CO)]^+$ (2396 cm^{-1}) gives a blue shift of 123 cm^{-1}, which is likewise a bit higher than the experimental value of 94 cm^{-1} using the above-mentioned frequency of 2237 cm^{-1} for $[Au(CO)]^+$ in a neon matrix as the reference.[24] Our theoretical value for the bond dissociation energy (BDE; D_e) of 32.2 kcal/mol (Table 1) indicates that the Au−CO bond in $[(Mes_3P)Au(CO)]^+$ is weaker than those in ClAuCO [D_e = 43.5 kcal/mol at CCSD(T)][22] and in $[Au(CO)]^+$ [D_e = 45.1 kcal/mol at QCISD(T)].[35] The latter ab initio value is lower than our density functional theory data (D_e = 58.8 kcal/mol; Table 1), which means that the calculated BDE for $[(Mes_3P)Au(CO)]^+$ is probably still too high.

Analysis of the $(Mes_3P)Au^+$−CO interactions with the NOCV-EDA method shows (Table 1) that roughly two-thirds comes from electrostatic attraction (ΔE_{elstat}), while only one-third comes from orbital interactions (ΔE_{orb}). The breakdown of the latter term into σ and π contributions indicates that ΔE_{π} provides 38.0% of ΔE_{orb}. A similar result is found for the Au^+−CO interactions, where the π-orbital interactions contribute 32.5% of ΔE_{orb}. This seems surprisingly high, considering the rather large calculated blue shifts of 57 and 123 cm^{-1}, respectively. It was shown in a detailed theoretical analysis of the interactions between positively charged atoms E^+ and CO in compounds $[E-CO]^+$ that the electrostatic effect of E^+ induces a change in the polarization of the C−O bonds, which strengthens the covalent interactions in the CO moiety.[36] We calculated the polarization of the σ and π orbitals in free CO and $[(Mes_3P)Au(CO)]^+$ as well as $[Au(CO)]^+$ with the natural

Table 2. Atomic Partial Charges and Polarization of the C−O *σ* and *π* Bonds in $[(Mes_3P)Au(CO)]^+$, $[Au(CO)]^+$, and Free CO Taken from NBO Calculations

compound	q(C)	q(O)	σ_{C-O}	$\pi(1)_{C-O}$	$\pi(2)_{C-O}$
$[(Mes_3P)Au(CO)]^+$	0.56	−0.33	C, 31.0%; O, 69.0%	C, 26.4%; O, 73.6%	C, 26.4%; O, 73.6%
$[Au(CO)]^+$	0.48	−0.27	C, 31.2%; O, 68.8%	C, 28.1%; O, 71.9%	C, 28.1%; O, 71.9%
CO	0.50	−0.50	C, 29.0%; O, 71.0%	C, 22.8%; O, 77.2%	C, 22.8%; O, 77.2%

bond order (NBO)[37] method. Table 2 shows that the contribution of the carbon atomic orbitals to the *σ* and *π* orbitals in the latter complexes is clearly larger than that in free CO. The calculated partial charges indicate that the oxygen atom in $[(Mes_3P)Au(CO)]^+$ and in $[Au(CO)]^+$ is much less negatively charged, while the carbonyl carbon atom becomes a bit more positive in the former complex but slightly less positive in the latter species. The calculated overall charge donations are 0.23e for $(Mes_3P)Au^+ \leftarrow CO$ and 0.21e for $Au^+ \leftarrow CO$. Analysis of the electronic structure of $[(Mes_3P)Au(CO)]^+$ and $[Au(CO)]^+$ suggests that the blue shift of the CO stretching mode is primarily due to the electrostatic effect of the metal fragment on the polarization of the C−O bond.

In summary, we describe the synthesis of an easily isolable gold carbonyl complex using readily available starting materials. We are currently exploring the catalytic properties of $[(Mes_3P)Au(CO)][SbF_6]$ as well as the utility of other widely available auxiliary ligands to stabilize gold carbonyl species.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. X-ray crystallographic data in CIF format, further details of the synthesis and characterization, computational methods, additional data, and figures. This material is available free of charge via the Internet at http://pubs.acs.org.

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