

Synthesis and Characterization of the Gold(I) Tris(ethylene) Complex $[\text{Au}(\text{C}_2\text{H}_4)_3][\text{SbF}_6]^{**}$

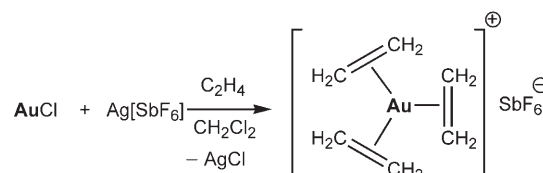
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Transition-metal ethylene complexes are historically and chemically among the most important classes of compounds in inorganic and organic chemistry. For example, Zeise's platinum–ethylene complex $\text{K}[\text{PtCl}_3(\text{C}_2\text{H}_4)] \cdot \text{H}_2\text{O}$, synthesized in 1827, was the first organometallic compound to be isolated in pure form.^[1,2] The seminal Dewar–Chatt–Duncanson model of olefin bonding was motivated in large part by a desire to understand the bonding of adducts, such as between silver and olefins.^[3–5] Coinage-metal (Cu, Ag, Au) ethylene complexes also figure prominently in a number of significant applications, in areas ranging from biochemistry to organic synthesis, and in several industrial processes.^[2]

Despite their significant fundamental and practical interest, the number of isolable and structurally authenticated Cu^I ,^[6–15] Ag^I ,^[16–21] and Au^I ethylene complexes are very limited,^[2] and are increasingly sparse moving down Group 11 towards gold, owing in large part to the poor thermal stability and the high lability of the olefin ligand, which create difficulties during their isolation.^[22] Indeed, the first structural data on a gold–ethylene complex appeared only very recently.^[23] Cinellu and co-workers have also reported a gold(I) complex of styrene and DFT calculations of its ethylene model complex;^[24] the latter species was also characterized by NMR spectroscopy.

Compounds that feature more than one ethylene moiety on Cu^I , Ag^I , and Au^I are exceedingly rare. To our knowledge, $[\text{Cu}(\text{C}_2\text{H}_4)_2\text{ClAlCl}_3]$ ^[14] and $[\text{Ag}(\text{C}_2\text{H}_4)_3][\text{Al}(\text{OC}(\text{CF}_3)_3)_4]$ ^[17] are the only well characterized molecules of this type in the literature. Herein we describe the first isolable tris(ethylene)

complex of gold(I). Remarkably, this cationic species was obtained by a facile process using the commercially available $[\text{SbF}_6]^-$ anion.



Our first encounter with the $[\text{Au}(\text{C}_2\text{H}_4)_3]^+$ complex was somewhat unexpected. During an attempted synthesis of $[\text{AuCl}(\text{C}_2\text{H}_4)]$ using a mixture of AuCl and ethylene in CH_2Cl_2 , colorless crystals were obtained among black decomposition products. Although the crystals were of poor quality, X-ray analysis yielded sufficient clues to indicate the formation of an unprecedented tris(ethylene)gold adduct $[\text{Au}(\text{C}_2\text{H}_4)_3][\text{AuCl}_4]$ (Supporting Information, Figure S1). Thus, we set out to synthesize $[\text{Au}(\text{C}_2\text{H}_4)_3]^+$ in a more systematic fashion using a more innocent and simple anion, namely the hexafluoroantimonate ion. Accordingly, the treatment of a dichloromethane solution of AuSbF_6 (prepared in situ from the metathesis reaction between AuCl and AgSbF_6) and excess ethylene afforded $[\text{Au}(\text{C}_2\text{H}_4)_3][\text{SbF}_6]$, which was obtained as a colorless crystalline product. This adduct is extremely air sensitive, and quickly decomposes to a black solid in air. NMR spectroscopy of $[\text{Au}(\text{C}_2\text{H}_4)_3][\text{SbF}_6]$ in CD_2Cl_2 gave resonances corresponding to the ethylene protons at $\delta(^1\text{H}) = 4.94$ ppm and carbons at $\delta(^{13}\text{C}) = 92.7$ ppm. These values agree very well with the calculated NMR spectroscopic shifts of $[\text{Au}(\text{C}_2\text{H}_4)_3]^+$ ($\delta(^1\text{H}) = 5.0$ ppm, $\delta(^{13}\text{C}) = 92.6$ ppm).^[25] The related NMR spectroscopy signals for free ethylene were observed significantly downfield relative to the gold tris(ethylene) complex, both experimentally ($\delta(^1\text{H}) = 5.40$ ppm and $\delta(^{13}\text{C}) = 123.4$ ppm) and computationally ($\delta(^1\text{H}) = 5.7$ ppm and $\delta(^{13}\text{C}) = 128.5$ ppm). The Raman spectrum of solid $[\text{Au}(\text{C}_2\text{H}_4)_3][\text{SbF}_6]$ was obtained with great difficulty, and has a $\text{C}=\text{C}$ stretching band at 1543 cm^{-1} , which is a decrease of 80 cm^{-1} with respect to free C_2H_4 ($\bar{\nu}_{\text{C}=\text{C}} = 1623\text{ cm}^{-1}$).

The X-ray crystal structure of $[\text{Au}(\text{C}_2\text{H}_4)_3][\text{SbF}_6]$ is shown in Figure 1. $[\text{Au}(\text{C}_2\text{H}_4)_3][\text{SbF}_6]$ crystallizes in the $P2_12_12_1$ space group with one molecule of dichloromethane. The gold atom coordinates to three ethylene molecules in a trigonal planar fashion forming a spoke-wheel arrangement. This planar arrangement of three ethylene molecules around the metal ion has been shown by several groups to be energetically more favored than the upright form.^[17,26,27] Our calculations

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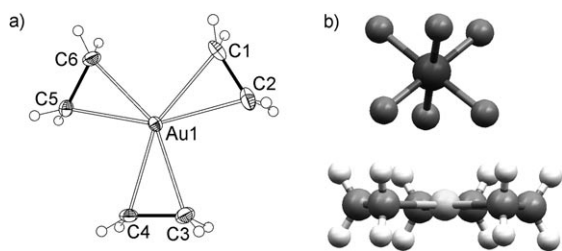


Figure 1. a) Molecular structure of $[\text{Au}(\text{C}_2\text{H}_4)_3]^+$. Thermal ellipsoids are set at 35% probability. b) View along the plane of the cation in $[\text{Au}(\text{C}_2\text{H}_4)_3][\text{SbF}_6]$. Selected bond lengths [Å] and angles [°] Au1–C1 2.271(5), Au1–C2 2.267(6), Au1–C3 2.267(4), Au1–C4 2.263(4), Au1–C5 2.269(4), Au1–C6 2.272(4), C1–C2 1.371(7), C3–C4 1.351(7), C5–C6 1.369(7); C4–Au1–C3 34.71(17); C2–Au1–C1 35.16(18), C5–Au1–C6 35.10(17).

show that the upright conformer is 19 kcal mol^{−1} higher in energy than planar for $[\text{Au}(\text{C}_2\text{H}_4)_3]^+$. The isolation of a three-coordinate gold(I) adduct rather than the more common two-coordinate species is surprising.^[28] The average ethylene C=C bond distance (1.364(7) Å, corrected for libration, 1.369 Å; calculated, 1.388 Å) in the gold complex is slightly longer than that of free ethylene (calculated, 1.338 Å). The average Au–C bond length is 2.268(5) Å. There are no close intermolecular Au⋯Au contacts in $[\text{Au}(\text{C}_2\text{H}_4)_3][\text{SbF}_6]$. There are two $[\text{SbF}_6]^-$ groups, one above and one below the AuC_6 plane, but the fluorine atoms are directed towards the ethylene groups rather than directly at the gold atom. The closest Au⋯F separation is 3.367 Å. The closest in-plane ethylene carbons are separated by an average distance of 3.065 Å, which is below the van der Waals contact separation of 3.40 Å.

Figure S2 of the Supporting Information shows important frontier orbital plots of $[\text{Au}(\text{C}_2\text{H}_4)_3]^+$. It has been reported that close, spoke-wheel arrangement of ethylenes (such as in the nickel adduct $[\text{Ni}(\text{C}_2\text{H}_4)_3]$) could lead to homoconjugation and to homoaromaticity.^[27,29]

The reaction of AgSbF_6 in dichloromethane saturated with ethylene under similar conditions has not yet produced any X-ray-quality crystals. However, the product obtained by evaporating the solvent from this solution under an ethylene stream and the previously reported $[\text{Ag}(\text{C}_2\text{H}_4)_3][\text{Al}\{\text{OC}(\text{CF}_3)_3\}_4]$ ^[17] show similar ¹H and ¹³C NMR spectroscopic data for the ethylene moiety ($\delta(^1\text{H}) = 5.83$ ppm and $\delta(^{13}\text{C}) = 116.9$ ppm for the former versus $\delta(^1\text{H}) = 5.77$ ppm and $\delta(^{13}\text{C}) = 116.4$ ppm for the latter). The Raman spectrum shows a sharp band at 1584 cm^{−1}. These data implicate the formation of $[\text{Ag}(\text{C}_2\text{H}_4)_3][\text{SbF}_6]$. Preliminary data show that it is also possible to obtain the corresponding Cu^I adduct, $[\text{Cu}(\text{C}_2\text{H}_4)_3][\text{SbF}_6]$. ¹H and ¹³C NMR spectroscopic data of the crystals obtained from a reaction between CuSbF_6 (prepared in situ from CuBr and AgSbF_6) and excess ethylene show signals corresponding to the ethylene protons and carbons at $\delta(^1\text{H}) = 5.44$ and $\delta(^{13}\text{C}) = 109.6$ ppm, respectively. A Raman spectrum of this very air-sensitive product shows a band at 1566 cm^{−1} attributable to the C=C stretching mode. Unfortunately, crystal quality was insufficient to obtain reliable metric parameters by X-ray analysis. Nevertheless, X-ray data of

this sample were collected and clearly show the presence of a trigonal planar $[\text{Cu}(\text{C}_2\text{H}_4)_3]^+$ moiety (Supporting Information, Figure S3), analogous to the gold complex. We are currently attempting to obtain higher quality crystals of $[\text{Cu}(\text{C}_2\text{H}_4)_3][\text{SbF}_6]$ for structural analysis.

We have performed a computational study of the $[\text{M}(\text{C}_2\text{H}_4)_3]^+$ (M = Cu, Ag, Au) series using the BP86 density functional and augmented basis sets (triple-zeta-plus-polarization and diffuse basis sets) for M, C, and H.^[25] The basic structural features of the coinage-metal complexes $[\text{M}(\text{C}_2\text{H}_4)_3]^+$ are very similar (Supporting Information, Table S1). The M–C bond lengths follow the expected trend both qualitatively and quantitatively based on the reported covalent radii^[30,31] of M^I (i.e., Cu–C < Au–C < Ag–C). For example, the average M–C bonds of $[\text{Au}(\text{C}_2\text{H}_4)_3][\text{SbF}_6]$ and $[\text{Ag}(\text{C}_2\text{H}_4)_3][\text{Al}\{\text{OC}(\text{CF}_3)_3\}_4]$ ^[17] from X-ray crystallographic data are 2.268(5) and 2.396(5) Å, respectively.

The $[\text{Au}(\text{C}_2\text{H}_4)_3]^+$ complex exhibits ¹H and ¹³C NMR resonances that are significantly upfield relative to the free ethylene. Such an upfield shift has been correlated to the degree of metal-to-ethylene π back-bonding.^[24] The experimental data for $[\text{Ag}(\text{C}_2\text{H}_4)_3][\text{Al}\{\text{OC}(\text{CF}_3)_3\}_4]$ ^[17] and $[\text{Au}(\text{C}_2\text{H}_4)_3][\text{SbF}_6]$ (e.g., $\Delta\delta(^{13}\text{C}) = (\delta(^{13}\text{C})_{\text{complex}} - \delta(^{13}\text{C})_{\text{ethylene}})$ for Ag, and Au = −7.0, −30.7 ppm, respectively) suggest that the silver(I) adduct shows much less M→ethylene back-bonding relative to that of the gold(I) analogue, which is consistent with the trend of promotion energies of M^I ions (Ag^I, 9.94 and Au^I, 7.83 eV).^[1] We have also observed similar trends in the $[\text{HB}(3,5\text{-(CF}_3)_2\text{Pz})_3]\text{M}(\text{C}_2\text{H}_4)$ family (M = Cu, Ag, Au).^[23] The C=C stretching frequency values of $[\text{M}(\text{C}_2\text{H}_4)_3]^+$ from Raman spectra also point to greater back-bonding in the gold analogue (e.g., $\Delta\tilde{\nu}_{\text{C=C}} = \tilde{\nu}_{\text{C=C}}(\text{complex}) - \tilde{\nu}_{\text{C=C}}(\text{ethylene})$ = for Cu, Ag, and Au are −57, −39, and −80 cm^{−1}, respectively).^[32]

A natural bond orbital (NBO) analysis of the three $[\text{M}(\text{C}_2\text{H}_4)_3]^+$ adducts supports the experimentally deduced trend as a function of metal in terms of the degree of π back-bonding. For example, the gold complex has the largest calculated population of the ethylene π^*_{CC} (0.20 e[−]) and the silver the lowest population (0.10 e[−]) with copper intermediate (0.16 e[−]).^[25] The NBO analysis further implies minimal direct covalent interaction between the ethylene ligands and the central metal ion. Thus, the NBO calculations implicate a bonding description for the cationic coinage metal tris(ethylene) complexes that is more befitting a π complex (electrostatic description) as opposed to a metallacyclopropane (covalent description), with the tris(ethylene) gold complex having the greatest metallacyclopropane (i.e., least π -complex) character.^[33]

A dominant electrostatic description for this novel series of ethylene complexes is consistent with their similar structural and spectroscopic properties, and helps address the issue of why the gold complex is three-coordinate rather than two-coordinate. Based on the careful analysis of coinage-metal bonding provided by Alvarez and co-workers,^[28] a more substantial structural difference among the coinage metals would be expected in a covalent bonding regime. Taken together, these pieces of evidence lead us to conclude that the bonding in this series of complexes is largely electrostatic in nature. In further support of a dominant electrostatic bonding

model for these complexes, the BP86-calculated binding enthalpies of a third ethylene to the bis(ethylene) complexes, $[\text{M}(\text{C}_2\text{H}_4)_2]^+$, were calculated, and found to be very similar ($\Delta H_{\text{bind}}(\text{C}_2\text{H}_4) = -17$ (Cu), -13 (Ag), -13 (Au) kcal mol^{-1}). Note that these binding enthalpies are sufficiently negative to overcome the unfavorable entropy contribution and yield $\Delta G_{\text{bind}}(\text{C}_2\text{H}_4) < 0$. Interestingly, binding a fourth ethylene is calculated to be endergonic at 298.15 K for all coinage-metal ions using the current level of theory.

In conclusion, we have described the synthesis of a novel tris(ethylene) adduct of Au^{I} , and spectroscopic data also point to the existence of silver and copper analogues. Analogous tris(ethylene) adducts of Group 10 metals (Ni, Pd, Pt) have been examined in some detail.^[29,34–38] The complex $[\text{Au}(\text{C}_2\text{H}_4)_3][\text{SbF}_6]$ is particularly remarkable as isolable gold complexes of even substituted alkenes are rare,^[24,39–43] and it also represents an unusual example of a three-coordinate Au^{I} complex.^[28] Group trends of coinage-metal adducts $[\text{M}(\text{C}_2\text{H}_4)_3]^+$ are also reported and point to a primarily electrostatic metal–ethylene bonding description for these novel complexes, although the gold complex is more disparate (i.e., has a greater covalent character) relative to its copper and silver congeners. Attempts to isolate similar adducts with other anions, as well as cationic species with different metal ion/olefin ratios are currently underway. It is noteworthy that, in these adducts, the metal atom holds three ethylenes in a favorable position for catalytic cycloaddition. Whether this potentially interesting catalysis can be achieved (e.g., as in nickel catalyzed processes) is an interesting question.^[2,44]

Experimental Section

$[\text{Au}(\text{C}_2\text{H}_4)_3][\text{SbF}_6]$: ^1H NMR (CD_2Cl_2 , 298 K): $\delta = 4.94$ ppm (s, $\text{CH}_2 = \text{CH}_2$). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 298 K): $\delta = 92.7$ (s, $\text{CH}_2 = \text{CH}_2$). Raman: $\tilde{\nu}_{\text{C}=\text{C}} = 1543 \text{ cm}^{-1}$. X-ray data: $[\text{Au}(\text{C}_2\text{H}_4)_3][\text{SbF}_6] \cdot \text{CH}_2\text{Cl}_2$, $\text{C}_7\text{H}_{14}\text{F}_6\text{Cl}_2\text{SbAu}$, Orthorhombic, $P2_12_12_1$, 100 K; $a = 8.4490(4) \text{ \AA}$, $b = 10.9541(5) \text{ \AA}$, $c = 16.0772(8) \text{ \AA}$, $V = 1487.96(12) \text{ \AA}^3$, $Z = 4$; $R1$ ($I > 2\sigma(I)$) = 0.0192, $wR2 = 0.0485$.

Further details of the synthesis, characterization, and additional data and figures including Raman spectra and X-ray crystallographic data tables are given in the Supporting Information. CCDC-656269 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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