Use of [SbF$_6$]$^-$ to Isolate Cationic Copper and Silver Adducts with More than One Ethylene on the Metal Center

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Supporting Information

ABSTRACT: A cationic tris(ethylene)copper(I) and tris(ethylene)silver(I) adduct has been isolated using hexafluoroantimonite counterion. X-ray crystallographic analysis shows that the metal atom in these adducts coordinates to three ethylene molecules in a trigonal planar fashion, forming a spoke-wheel arrangement. In [M(C$_2$H$_4$)$_3$][SbF$_6$] adducts (M = Cu, Ag, Au), the average M–C distances of 2.189 Å for Cu and 2.410 Å for Ag can be compared with the corresponding distance of 2.268 Å for Au and show that the copper(I) complex has the shortest while the silver adduct displays the longest M–C distances. These agree well with the computed values (2.172, 2.408, and 2.308 Å for Cu, Ag, and Au analogues, respectively) and follow the same trend as the covalent radii of M(II). Structural data on [μ$_3$-Cl(Cu(C$_2$H$_4$)$_3$)][SbF$_6$], which features bis(ethylene)copper(I) moieties, are also presented. It has a trigonal planar CuCl$_3$ core with a triply bridging chloride ion bonded to three trigonal planar copper centers. Ethylene molecules are bonded in an η$^2$-fashion. The data indicate that while these [M(C$_2$H$_4$)$_3$]$^+$ complexes may be primarily electrostatic in their metal–ethylene binding, there remains an important covalent contribution, particularly for the copper and gold congeners.

INTRODUCTION

Coinage metals (Cu, Ag, Au) figure prominently in a number of applications and reactions involving ethylene.$^{1-4}$ For example, copper mediates oxchlorination of ethylene, which is an important industrial process.$^{5-6}$ Copper(I) is believed to be the ethylene receptor in metalloenzymes, where ethylene serves as a plant hormone that regulates several aspects of the plant life cycle.$^{7-8}$ Copper and silver salts are also important in olefin paraffin separation and in the chromatography of alkenes.$^9$ Silver is the metal of choice in the direct oxidation of ethylene to ethylene oxide, a major industrial process.$^{6,10-12}$ Small gold clusters or gold salts also catalyze the oxidation and hydrogenation of olefins including ethylene.$^{13-20}$ There are reports of gold mediating the conversion of methane to ethylene.$^{21,22}$ Coinage metal–ethylene adducts are likely intermediates in many of these processes. Therefore, structures, bonding, properties, and spectroscopic data on coinage metal ethylene adducts are of significant interest.

Isolable and structurally authenticated Cu, Ag, and Au ethylene complexes however are rather limited, especially as one moves down group 11 toward gold.$^{1,23-26}$ Furthermore, compounds that feature more than one ethylene moiety on Cu, Ag, and Au are exceedingly rare. In 2008, we communicated the synthesis and crystal structure of a novel tris(ethylene) adduct involving gold(I), [Au(C$_2$H$_4$)$_3$][SbF$_6$] (1), and spectroscopic data on its silver and copper analogues (Figure 1). In 2003, Martin et al. and Krossing et al. reported [Cu(C$_2$H$_4$)$_3$ClI$_3$]$_2$ (2) and [Ag(C$_2$H$_4$)$_3$][Al(OC-}

Figure 1. First structurally authenticated coinage metal adducts involving more than one ethylene on the metal center.

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(CF₃)₃Al₂[(OC(CF₃)₃)₄]₄ (3), respectively, which represent the first structurally characterized molecules involving more than one ethylene on copper or silver. Since then, [Cu(C₂H₄)₃][Al(OC(CF₃)₃)₄]₃₀, [Ag(C₂H₄)₂][((CF₃)₂CO)₃Al[(μ-F)-Al]{OC(CF₃)₃)₄]₃¹, [Ag(C₂H₄)₂][(μ-(CF₃)₂CO)(HCO)Al(OC(CF₃)₃)₄]₃¹ and [Au(C₂H₄)₃][Al(OC(CF₃)₄)₄]₃² which belong to this category of compounds, have also been reported. These complexes have all been stabilized using large fluorinated counterions.

In this work, we describe the first crystal structures of cationic tris(ethylene) copper(1) and silver(1) complexes 4 and 5 involving the simple, commercially available [SbF₆]⁻ anion (Figure 2). In addition, we also describe the structure of a novel bis(ethylene)copper adduct, [μ-Cl(Cu(C₂H₄)₃)][SbF₆] (6).

Figure 2. Cationic species involving more than one ethylene on copper and silver that have been isolated using [SbF₆]⁻ counterions.

RESULTS AND DISCUSSION

Synthetic details of [Cu(C₂H₄)₃][SbF₆] were reported earlier in a communication.²⁷ It was obtained from a reaction of CuBr and AgSbF₆ in the presence of ethylene in dichloromethane as a colorless crystalline product. It is a very air sensitive compound. Upon exposure to air, crystals of this material rapidly lose ethylene and form a metallic copper-colored film, followed by blue-green and then black species (this process can be observed under a microscope).¹⁹ H and C¹³ NMR spectra in CD₂Cl₂ at room temperature show peaks corresponding to the ethylene protons and carbons at δ 5.44 and 109.6 ppm, respectively. [Cu(C₂H₄)₃][Al(OC(CF₃)₄)₄] is also known, and it shows copper-bound ethylene proton and carbon resonances at δ 5.47 and 110.0 ppm, respectively.³⁰ For comparison, the corresponding signals of free ethylene appear at δ 5.40 and 123.3 ppm, respectively. A Raman spectrum of solid [Cu(C₂H₄)₃][SbF₆] shows a band at 1566 cm⁻¹, attributable to the C=C stretching mode, which is a ca. 57 cm⁻¹ decrease with respect to free C₂H₄ (ν_C=C = 1623 cm⁻¹).

Although we first synthesized [Cu(C₂H₄)₃][SbF₆] in 2007,²⁷ all the crystals obtained under a variety of conditions show complicated twinning. After much difficulty, a complete analysis of one of these data sets was achieved to yield a satisfactory X-ray crystal structure. The diffraction pattern from this compound exhibited satellite reflections, and the analysis of the structure required the use of a four-dimensional superspace approach to refine the incommensurately modulated structure.³³ The average structure consists of seven [Cu(C₂H₄)₃][SbF₆] moieties in the asymmetric unit (Figure 3). Each copper ion is coordinated to three ethylene molecules and adopts a trigonal planar geometry. Ethylene molecules are bonded in the expected n²-fashion. Ethylene carbon atoms and copper adopt a planar, spoke-wheel structure (rather than the upright conformation which is also commonly referred to as barrel or trigonal prismatic conformation), which is the lowest energy conformation predicted via DFT simulations. The cationic moiety in [Cu(C₂H₄)₃][Al(OC(CF₃)₄)₄] shows a similar structure. Considering the complicated twinning exhibited by [Cu(C₂H₄)₃][SbF₆] crystals, it is less than ideal for detailed bond distance and angle comparison. Nevertheless, the observed Cu–C distances of [Cu(C₂H₄)₃][SbF₆] can be analyzed, and they range from 2.176 to 2.218 Å with an average Cu–C distance of 2.193 Å. Each copper center shows
two axial Cu–F contacts at a distance near or less than the sum of van der Waals radii of copper and fluorine atoms (2.87 Å).\textsuperscript{34} The shortest Cu–F distance to each copper site ranges from 2.50 to 3.05 Å.

The attempted synthesis of [Cu(C\textsubscript{2}H\textsubscript{4})\textsubscript{3}][Sbf\textsubscript{6}] using CuCl (instead of CuBr) and AgSbf\textsubscript{6} under similar conditions produced an interesting crystalline solid (albeit in low yield). This product is a mixture of [Cu(C\textsubscript{2}H\textsubscript{4})\textsubscript{3}][Sbf\textsubscript{6}] (4) and [μ\textsubscript{1}-Cl][Cu(C\textsubscript{2}H\textsubscript{4})\textsubscript{3}][Sbf\textsubscript{6}] (6), which results from an incomplete metathesis. The latter species may be viewed as a result of a reaction between ClCu(C\textsubscript{2}H\textsubscript{4})\textsubscript{3} and two molecules of [Cu(C\textsubscript{2}H\textsubscript{4})\textsubscript{3}][Sbf\textsubscript{6}] (The X-ray crystal structure revealed that these molecules co-crystallize, resulting in crystals containing two molecules of [μ\textsubscript{1}-Cl][Cu(C\textsubscript{2}H\textsubscript{4})\textsubscript{3}][Sbf\textsubscript{6}] and one molecule of [Cu(C\textsubscript{2}H\textsubscript{4})\textsubscript{3}][Sbf\textsubscript{6}] in the asymmetric unit (Figure 4) and thus producing useful information on two interesting copper–ethylene adducts. Note that these crystals also show twinning, but fortunately it was relatively less complicated and could be resolved satisfactorily using the Cell_NOW and SHELEX tools of software.

Not surprisingly, structural features of [Cu(C\textsubscript{2}H\textsubscript{4})\textsubscript{3}][Sbf\textsubscript{6}] found in the mixed crystal are similar to those observed for pure [Cu(C\textsubscript{2}H\textsubscript{4})\textsubscript{3}][Sbf\textsubscript{6}] (Table 1). The Cu–C distances of this [Cu(C\textsubscript{2}H\textsubscript{4})\textsubscript{3}][Sbf\textsubscript{6}] unit range from 2.154 to 2.183 Å with an average Cu–C distance of 2.164 Å. The copper center shows two axial Cu–F contacts (2.62 and 2.82 Å with fluorine atoms of adjacent [Sbf\textsubscript{6}]\textsuperscript{−} counterions) at a distance near the sum of van der Waals radii of copper and fluorine, forming what is essentially an axially distorted trigonal bipyramidal copper center (Figure 5).

The complex [μ\textsubscript{1}-Cl][Cu(C\textsubscript{2}H\textsubscript{4})\textsubscript{2}\textsubscript{3}][Sbf\textsubscript{6}]\textsubscript{2} is unique, featuring three bis(ethylene) copper(I) moieties held together by a chloride ion (Figures 2 and 4). [Cu(C\textsubscript{2}H\textsubscript{4})\textsubscript{3}ClAlCl\textsubscript{3}] (2) is the closest and only analogue with a similar motif in the literature.\textsuperscript{28} There are two chemically similar but crystallographically different [μ\textsubscript{1}-Cl][Cu(C\textsubscript{2}H\textsubscript{4})\textsubscript{3}][Sbf\textsubscript{6}] molecules in the asymmetric unit. The two chloride atoms and each of the six copper sites adopt a trigonal planar geometry. All the ethylene molecules are bonded in n\textsuperscript{2}-fashion with Cu–C distances ranging from 2.095 to 2.153 Å (average 2.123 Å). These Cu–C distances are shorter than the corresponding distances observed for [Cu(C\textsubscript{2}H\textsubscript{4})\textsubscript{3}][Sbf\textsubscript{6}], which is perhaps a reflection of reduced steric crowding at copper centers. They are also slightly shorter than the corresponding bond lengths of [Cu(C\textsubscript{2}H\textsubscript{4})\textsubscript{3}ClAlCl\textsubscript{3}], which range from 2.115 to 2.172 Å (with an average distance of 2.145 Å). As with [Cu(C\textsubscript{2}H\textsubscript{4})\textsubscript{3}][Sbf\textsubscript{6}], the copper atoms of [μ\textsubscript{1}-Cl][Cu(C\textsubscript{2}H\textsubscript{4})\textsubscript{3}][Sbf\textsubscript{6}] (6) also show Cu–F contacts through open axial sites, as illustrated in Figure 6. [Cu(C\textsubscript{2}H\textsubscript{4})\textsubscript{3}ClAlCl\textsubscript{3}] also has a trigonal planar Cu(C\textsubscript{2}H\textsubscript{4})\textsubscript{2}Cl moiety but with long axial Cu–Cl contacts. The Cu–Cl (equatorial) distance of 2.348(3) Å in [Cu(C\textsubscript{2}H\textsubscript{4})\textsubscript{3}ClAlCl\textsubscript{3}] is slightly longer than the Cu–Cl separation (av = 2.302 Å) found in Cl[Cu(C\textsubscript{2}H\textsubscript{4})\textsubscript{3}][Sbf\textsubscript{6}]. Note that the latter species is dicationic and has a triply bridging Cl bonded to Cu and AlCl\textsubscript{3} moieties.

We have also succeeded in obtaining structural data on a tris(ethylene)silver(I) aduct. The reaction of AgSbf\textsubscript{6} with excess ethylene in dichloromethane at ~20 °C produced [Ag(C\textsubscript{2}H\textsubscript{4})\textsubscript{3}][Sbf\textsubscript{6}] (5), which is an air-sensitive, colorless crystalline solid. NMR spectroscopic details were reported earlier.\textsuperscript{27} The Raman spectrum of this solid shows a sharp band at 1584 cm\textsuperscript{-1}. The X-ray crystal structure of [Ag(C\textsubscript{2}H\textsubscript{4})\textsubscript{3}][Sbf\textsubscript{6}] is given in Figure 7. The silver atom coordinates to three ethylene molecules in a trigonal planar fashion, forming a spike-wheel arrangement. [Ag(C\textsubscript{2}H\textsubscript{4})\textsubscript{3}][Sbf\textsubscript{6}] also displays two axial Ag–F contacts (2.80, 2.87 Å) between the silver center and fluorine atoms of the adjacent [Sbf\textsubscript{6}]\textsuperscript{−} counterions.
Table 1. Selected Bond Distances (average in italics and range) from X-ray Crystal Structural, Raman, and DFT-Calculated (in blue) Data for Molecules Featuring $[\text{M(C}_2\text{H}_4\text{)}_3]^+$ (M = Cu, Ag, Au). The adducts of $[\text{M(C}_2\text{H}_4\text{)}_3]^+$ involving $[\text{SbF}_6]^{-}$ are in red.

<table>
<thead>
<tr>
<th>Compound</th>
<th>M-C (Å)</th>
<th>C=C (Å)</th>
<th>$\bar{\nu}_{C=C}$ (cm$^{-1}$)</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>free $\text{C}_2\text{H}_4$</td>
<td>-</td>
<td>1.313(1)</td>
<td>1623</td>
<td>4</td>
</tr>
<tr>
<td>free $\text{C}_2\text{H}_4$</td>
<td>-</td>
<td>1.3369(16)</td>
<td></td>
<td></td>
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<tr>
<td>$[\text{Cu(C}_2\text{H}_4\text{)}_3][\text{SbF}_6]$ seven independent molecules</td>
<td>2.193</td>
<td>1.359</td>
<td>1656</td>
<td>This work</td>
</tr>
<tr>
<td>$[\text{Cu(C}_2\text{H}_4\text{)}_3][\text{SbF}_6]$ part of a mixed crystal involving compound 6</td>
<td>2.164</td>
<td>1.387</td>
<td></td>
<td>This work</td>
</tr>
<tr>
<td>$[\text{Cu(C}_2\text{H}_4\text{)}_3][\text{Al(OC)}(\text{CF}_3)_3]_4$</td>
<td>2.147</td>
<td>1.331</td>
<td>1577</td>
<td>30</td>
</tr>
<tr>
<td>$[\text{Cu(C}_2\text{H}_4\text{)}_3]^+$</td>
<td>2.172</td>
<td>1.374</td>
<td>1543</td>
<td>27</td>
</tr>
<tr>
<td>$[\text{Ag(C}_2\text{H}_4\text{)}_3][\text{SbF}_6]$</td>
<td>2.410</td>
<td>1.323</td>
<td>1584</td>
<td>This work</td>
</tr>
<tr>
<td>$[\text{Ag(C}_2\text{H}_4\text{)}_3][\text{Al(OC)}(\text{CF}_3)_3]_4$ (recollected later)</td>
<td>2.396</td>
<td>1.307</td>
<td>1585</td>
<td>29</td>
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<tr>
<td>$[\text{Ag(C}_2\text{H}_4\text{)}_3]^+$</td>
<td>2.406</td>
<td>1.333</td>
<td></td>
<td>31</td>
</tr>
<tr>
<td>$[\text{Ag(C}_2\text{H}_4\text{)}_3][\text{Al(OC)}(\text{CF}_3)_3]_4$</td>
<td>2.396</td>
<td>1.329(2)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$[\text{Ag(C}_2\text{H}_4\text{)}_3]^+$</td>
<td>2.306</td>
<td>1.345</td>
<td>1545</td>
<td>32</td>
</tr>
<tr>
<td>$[\text{Au(C}_2\text{H}_4\text{)}_3][\text{SbF}_6]$</td>
<td>2.308</td>
<td>1.388</td>
<td>1523</td>
<td>27</td>
</tr>
</tbody>
</table>

These contacts are within the van der Waals separation of Ag and F (3.19 Å). The Ag–C distance ranges from 2.398 to 2.417 Å (with an average distance of 2.410 Å). The average ethylene C=C distance (1.323 Å) is short and essentially identical to that of free ethylene within experimental error. However, keep in mind that the C=C bond distance change as a result of coordination to silver(I) in these (and many of other reported) adducts is small and often overshadowed by experimental errors associated with routine X-ray crystallography, high esd values, librational effects, and the anisotropy of the electron density.

We have reported the structural data on the gold analogue $[\text{Au(C}_2\text{H}_4\text{)}_3][\text{SbF}_6]$ in 2007. Thus, with the availability of structural data on $[\text{Cu(C}_2\text{H}_4\text{)}_3][\text{SbF}_6]$ and $[\text{Ag(C}_2\text{H}_4\text{)}_3][\text{SbF}_6]$ we now have a complete series of coination metal tri(ethylene) adducts for comparison. Notably, these adducts can be obtained using the simple, commercially available [SbF6]$^{-}$ counterion. All three $[\text{M(C}_2\text{H}_4\text{)}_3]^+$ adducts (M = Cu, Ag, Au) adopt planar,
spoke-wheel structures, rather than the upright conformation (Figure 8). This planar arrangement of three ethylenes around the metal ion has been computed to be energetically more favored than the upright form by several groups. Calculations and spectroscopic and structural data indicate that the isoelectronic, neutral \([\text{M}(\text{C}_2\text{H}_4)_3]\) (\(\text{M} = \text{Ni}, \text{Pd}, \text{Pt}\)) systems also adopt similar structures.

The average \(\text{M}–\text{C}\) distances listed in the Table 1 (2.193 or 2.164 (with an overall weighted average of 2.189 Å), 2.410, and 2.268 Å for \(\text{Cu}, \text{Ag}, \text{and Au}\), respectively) show that the copper(1) adduct has the shortest distances, while the silver adduct displays the longest \(\text{M}–\text{C}\) distances. They agree well with the computed values (2.172, 2.408, and 2.308 Å for \(\text{Cu}, \text{Ag}, \text{and Au}\) analogues). Interestingly, these distances follow the same trend as the covalent radii of \(\text{M}\). Structural data on \([\text{M}([\text{C}_2\text{H}_4]_3)]^+\) involving the large fluorinated counterion \([\text{Al}([\text{OC}(_3\text{F}_5)_3]_2\text{]}^-\) are available, and their basic structural features are similar. The average \(\text{Ag}–\text{C}\) distances are also nearly identical between the hexafluoroantimonate and \([\text{Al}([\text{OC}(_3\text{F}_5)_3]_2\text{]}^-\) systems. The average \(\text{Cu}–\text{C}\) distance however is slightly longer in the adducts involving the \([\text{SbF}_6]^-\) counterion (i.e., 2.193 vs. 2.147 Å for \([\text{Cu}([\text{C}_2\text{H}_4]_3)]^+\) vs. \([\text{Al}([\text{OC}(_3\text{F}_5)_3]_2\text{]}^-\) ). It is possible that \(\text{Cu}–\text{F}\) contacts in \([\text{Cu}([\text{C}_2\text{H}_4]_3)]^+\) have some effect on these distances. The average \(\text{Au}–\text{C}\) distance in contrast is slightly shorter in the \([\text{Al}([\text{OC}(_3\text{F}_5)_3]_2\text{]}^-\) system (Table 1) relative to the corresponding value in \([\text{Au}([\text{C}_2\text{H}_4]_3)]^+\).

Coinage metal adducts of the type \([\text{M}([\text{norbornene}]_3)]^+\) of \([\text{SbF}_6]^-\) are known and offer a useful comparison. They also display spoke-wheel structures. The average \(\text{M}–\text{C}\) distances of 2.198, 2.409, and 2.292 Å for \(\text{M} = \text{Cu}, \text{Ag}, \text{and Au}\), respectively, are larger than those observed in systems in Table 1. However, the average \(\text{Au}–\text{C}\) distance is smaller in these systems. The corresponding \(\text{SbF}_6^-\) adducts generally no show a large difference compared to the corresponding separations of the tri(ethylene) adducts listed in Table 1.

As noted earlier, experimental \(\text{C}–\text{C}\) distances may be less than ideal for a detailed comparison due to systematic errors. However, we note that DFT-computed values for the isolated cations \([\text{M}([\text{C}_2\text{H}_4]_3)]^+\) predict the longest \(\text{C}–\text{C}\) distances in the gold adduct and the shortest for the silver congeners. Moreover, the values assigned to the \(\text{C}–\text{C}\) stretching band from experimental Raman data on crystalline \([\text{M}([\text{C}_2\text{H}_4]_3)]^+\)
[SnF₆] (Table 1) are in good agreement with the predicted structural trend. There is also a method reported in the literature to estimate the C=C distance of these coinage metal ethylene adducts using their Raman-active C=C stretch.⁴¹,³²⁴,⁴⁷ Accordingly, it is possible to obtain calculated C=C distances of 1.350, 1.343, and 1.361 Å for [Cu₂(C₂H₄)₃][SnF₆], [Au(C₂H₄)₃][SnF₆], and [Au(C₂H₄)₃][BF₄] respectively, using experimentally observed ν(C=C) values of 1566, 1584, and 1543 cm⁻¹ (Table 1). These distances can be compared to the X-ray crystallographically obtained average C=C bond lengths of 1.359, 1.323, and 1.364 Å (Table 1).

These trends as a function of coinage metal ion are also reflected in the calculated ν₁(C=C) and ¹H and ¹²C NMR chemical shifts for [M(C₂H₄)₃]⁺.²⁷ Additionally, DFT-calculated binding energies suggest that the binding of a fourth ethylene is endergonic, while the first three ethylenes bind exergonically. Combined with natural bond orbital (NBO) analyses of the electronic structures, these data were interpreted as indicating a predominantly electrostatic description of the M(I)–ethylene interaction, with Ag(I) and Au(I) being the most and least ionic, respectively, among the group 11 triad. In a subsequent analysis,⁴⁸ these proposals were generalized for other coinage metal–ethylene complexes and the structural implications discussed.

Another interesting observation is that of the preferred wheel-spoke arrangement in this family of complexes (Figure 8) as opposed to an upright or trigonal prismatic conformation (Figure 9). The former arrangement is ideal, for example, for a potential olefin cyclotrimerization catalyst. As stated above, DFT calculations corroborate the crystal data in that the spoke-wheel arrangement is energetically preferred. For example, DFT calculations on C₂₅[M(C₂H₄)₃]⁺ transition states with a single upright ethylene (imaginary frequencies, ≤600 cm⁻¹) correspond to ethylene rotation back to a spoke-wheel conformation) yield free energy barriers of 3.1 (Cu), 1.5 (Ag), and 3.2 (Au) kcal/mol. As with many of the other experimental and computed properties, one sees a greater congruity between the gold and copper congeners, with silver being more dissimilar.

While the various pieces of experimental and computational data paint a picture of a predominantly ionic coinage metal–ethylene interaction, one might propose that in the limit of a completely ionic interaction the nondirectionality of ionic bonding would lead to realization of the sterically preferred upright arrangement (Figure 9). An NBO analysis of πCC and πCCₐ occupation per ethylene, which should best reflect the degree of σ-donation and π-back-donation, respectively, embodied in the classical Dewar–Chatt–Duncanson model⁴⁹,⁵⁰ shows that rotation of the ethylene moieties from the spoke-wheel to an all-upright conformation results in a diminution of both π-donation and π-back-donation. This decrease is ~0.05 e⁻⁻ per ethylene (πCCₐ, πCCₐ⁻⁻⁻ in spoke-wheel to πCCₐ, πCCₐ⁻⁻⁻ in upright) for the more ionic [Ag(C₂H₄)₃]⁺ and a somewhat smaller ~0.1 e⁻⁻ per ethylene (πCCₐ, πCCₐ⁻⁻⁻ in spoke-wheel to πCCₐ, πCCₐ⁻⁻⁻ in upright) for the more covalent [Au(C₂H₄)₃]⁺ (the Cu congener was not a stable stationary point in the all-upright configuration, and thus an NBO analysis could not be performed) for comparison spoke-wheel conformation of Cu congener has πCCₐ, πCCₐ⁻⁻⁻ occupation per ethylene). The dichotomy in πCC and πCCₐ occupations is especially obvious in the one-up C₅₀ transition states for [M(C₂H₄)₃]⁺, for which all pertinent stationary points could be isolated for all three coinage metals. While the πCC occupations are nearly identical for the upright and spoke-wheel ethylenes (δ ≤ 0.02 e⁻⁻) in the one-up configurations, the πCCₐ occupation is nearly double for the latter as compared to the upright ethylene (0.16 versus 0.07 e⁻⁻ for Cu₅₀,[Cu(C₂H₄)₃]⁺; 0.10 versus 0.05 e⁻⁻ for Au₅₀,[Ag(C₂H₄)₃]⁺; 0.20 versus 0.11 e⁻⁻ for Au₅₀,[Au(C₂H₄)₃]⁺). Two points are of interest in the context of coinage metal–olefin binding. First, the changes in πCC and πCCₐ occupation support the notion that this structural preference is orbital driven and hence has a covalent origin. Second, closer inspection of πCC and πCCₐ occupations shows that the latter is reduced a bit more than the former upon the spoke-wheel to upright perturbation. Taken together, the calculations suggest that the preference for a spoke-wheel arrangement in [M(C₂H₄)₃]⁺ arises primarily from less effective π-back-bonding in the upright form.

Overall, this paper reports structural data for a series of tris(ethylene)copper(I) and tris(ethylene)silver(I) adducts involving the hexafluororoantimonate counterion, which are the missing members of the isomorphous [M(C₂H₄)₃][BF₄] family. The results reveal several interesting facets of coinage metal–olefin binding. X-ray analysis shows that the metal atom in these adducts coordinates to three ethylene molecules in a trigonal planar fashion, forming a spoke-wheel arrangement. The average M–C distance in these materials follows the same trend as the covalent radii of M(I): Cu–C < Ag–C >> Au–C.²⁴,⁴⁵ The complex [μ₃-C(Cu(C₂H₄)₃)₂][SnF₆]₂, which features bis(ethylene)coppper(I) moieties, has also been isolated and characterized structurally. They also have trigonal planar copper sites. Analysis of the bonding suggested that the preference for the spoke-wheel arrangement was dominated by orbital considerations, leading to a coconformation decrease in both π-bonding and π-back-bonding, with the latter being more significant. Taken together, the various pieces of data indicate that while these [M(C₂H₄)₃]⁺ complexes may be defined as primarily electrostatic in their binding, there remains an important covalent contribution to the metal–ligand bonding, particularly for the copper and gold congeners.

**EXPERIMENTAL SECTION**

All manipulations were carried out under an atmosphere of pure ed nitrogen using standard Schlenk techniques and/or a glovebox. CuH;
CuCl, Ag[SF₅], and ethylene were purchased from commercial sources and used as received.

\[ [Cu(C₂H₅)₂][SF₅] \] was synthesized as reported earlier using CuBr, Ag[SF₅], and excess ethylene in dichloromethane.²⁷ This compound is quite sensitive to moisture and air.

\[ [Cu(C₂H₅)₂][SF₅] \] was obtained by reacting a dichloromethane solution using a procedure similar to that described above for \[ [Cu(C₂H₅)₂][SF₅] \]. but using CuCl as the copper(I) precursor instead of CuBr. The yield was very low, and only a few crystals were obtained. This is also a very air and moisture sensitive compound.

\[ [Ag(C₂H₅)₂][SF₅] \] was synthesized as reported earlier using excess ethylene and Ag[SF₅] in dichloromethane.²⁷ This compound is quite sensitive to air and moisture and tends to decompose, leaving a silver mirror on the walls of the vial.

X-ray Crystallographic Data. A suitable crystal covered with a layer of cold hydrocarbon oil was selected and mounted with paratone-N oil in a cryoloop and immediately placed in a low-temperature nitrogen stream. The X-ray intensity data were measured at 100(2) K on a Bruker SMART APEX CCD area detector system equipped with an Oxford Cryosystems 700 Series cooler, a graphite monochromator, and a Mo Kα fine-focus sealed tube (λ = 0.71073 Å). The data frames were integrated with the Bruker SAINT-Plus software package. Data were corrected for absorption e effects using the multiscan technique (SADABS or TWINABS). Structures were solved and re ned using Bruker SHELXL software package.²⁴ X-ray structural graphs were generated using Olex2.²² Further details are given in the CIFs (Supporting Information).

[Cu(C₂H₅)₂][SF₅]. The X-ray quality crystals of \[ [Cu(C₂H₅)₂][SF₅] \] were obtained from a supersaturated dichloromethane solution under an ethylene atmosphere at ~20 °C. This is a very air sensitive compound. Despite numerous attempts, all the crystals obtained showed twinning. However, a data set was collected on a twinned crystal, and the structure was solved. This structure is a commensurate modulated structure that was re ned with the JANA2000 program using the super-space group P2₁/mn (no.60).²⁸ Cerial functions were used for the [SF₅]⁻ groups and Legendre polynomials, which ensure orthogonality of modulation functions. Crystal data for \[ Cu₂(C₂H₅)₂Cl₂[F₅] \] (X = 283.45): orthorhombic, space group P2₁/mn (no. 31), a = 7.1915(6) Å, b = 10.4076(9) Å, c = 54.0773(5) Å, V = 4006.6(6) Å³, Z = 14, T = 100(2) K.

[Ag(C₂H₅)₂][SF₅]. Crystalline \( [Ag(C₂H₅)₂][SF₅] \) material was obtained from a dichloromethane solution using a procedure similar to that described above for \[ [Cu(C₂H₅)₂][SF₅] \]. The crystal structure shows that two molecules of \( [Cu(C₂H₅)₂][SF₅] \) cocystalize with a molecule of \[ [Cu(C₂H₅)₂][SF₅] \]. This structure was determined to be a four-component nonohedral twin with the CELL_NOW program. The rections from all four twin domains were simultaneously integrated with the SAINT program. The TWINABS program was used to carry out absorption corrections and to produce the hkl VAL format for reference data. Crystal data for \[ Cu₂(C₂H₅)₂Cl₂[F₅] \] (M = 2115.31): triclinic, space group P1 (no. 2), a = 8.8814(4) Å, b = 18.1377(9) Å, c = 20.3187(10) Å, α = 101.544(4)°, β = 96.973(2)°, γ = 93.263(2)°, V = 3064.8(3) Å³, Z = 2, T = 100(2) K.

X-ray quality, colorless crystals were obtained from a CH₂Cl₂/hexane xylene (1:1) solution at ~20 °C. This compound is quite sensitive to moisture and tends to decompose, leaving a silver mirror on the walls of the vial. Structure solution and refinement proceeded smoothly. All the non-hydrogen atoms were re ned anisotropically. Crystal data for \[ Cu₂(C₂H₅)₂[AgF₅] \] (M = 427.78): monoclinic, space group P2₁/c (no. 14), a = 8.2940(7) Å, b = 11.9751(5) Å, c = 11.9959(1)Å, β = 95.204(1)°, V = 11864.4(17) Å³, Z = 4, T = 100(2) K.

Computational Methods. All quantum calculations employed the Gaussian03 package.²⁵ The BP86 functional was employed in conjunction with the Stevens (SBRK)⁶¹ valence basis sets and e active core potentials for the cation. Valence basis sets of the transition metals were augmented with the Croy–Hall⁶¹ p functions (fully uncontracted) and the f polarization functions of Frenking and co-workers.²⁶ The 6-311++G(d,p) basis set was utilized to model C and H atoms. All complexes modeled were closed-shell species and modeled within the restricted Kohn–Sham formalism. All systems were fully optimized, and calculations of the energy vs. species as minima.

ASSOCIATED CONTENT

S Supporting Information
CIF and X-ray crystallographic data tables and additional computational data are given. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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(47) Note that there are two different equations reported for C=H distance calculation using Raman data in refs 31 and 32. We used the equations given in ref 31 in this article. Overall, this method could be re-tuned further, as even free ethylene is predicted to show a C=H distance change, albeit minor.