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Copper(I), silver(I), and gold(I) complexes of *all-Z*-tribenzo[12]annulene

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Abstract—The copper(I) and silver(I) complexes of *all-Z*-tribenzo[12]annulene were synthesized and the structures were determined by X-ray analysis. The trigonal olefinic cavity of the [12]annulene incorporates copper and silver cations to produce stable complexes, whereas the gold(I) complex was unstable, yielding a cyclization product via isomerization of the *Z*-double bonds. © 2000 Elsevier Science Ltd. All rights reserved.

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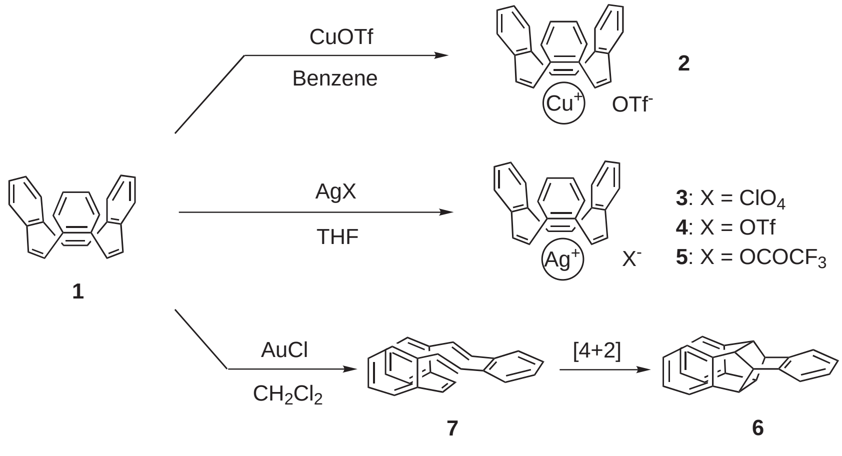
all-Z-Tribenzo[12]annulene **1** is a cylindrical π-conjugated molecule with a medium-size concavity.[1] Cylindrical molecules have received considerable interest because of their unique structures[2] and host/guest interactions,[3] and [2.2.2]cyclophanes include a silver cation through cation–π interactions to produce 'π-prismands'.[4] In addition, silver(I) and copper(I) complexes based on cyclophanes have recently been reported as polymeric metal complexes, which can be regarded as new solids with interesting physical and chemical properties in crystal engineering.[5] Thus, silver(I) and copper(I) ions play an important part in the construction of multidimensional coordination polymers.[6] We now report here the syntheses of copper(I) and silver(I) complexes **2**–**5**, together with the formation of **6** by the reaction of **1** with gold(I) chloride.

Our preliminary observation indicated that **1** forms a 1:1 complex **4** with AgOTf.[7] Complex **4** was stable in air, moisture, and light. Because only a limited number of the copper(I)–olefin complexes have been reported and analyzed by the X-ray diffraction method up until now,[8] and in order to clarify the structures and properties of metal complexes from **1**, we planned to synthesize the corresponding copper(I), silver(I), and gold(I) complexes of **1** (Scheme 1). The copper(I) complex **2** was first



Scheme 1. Reactions of **1** with Cu(I)OTf, Ag(I)X, and Au(I)Cl.

Keywords: annulenes; cage compounds; complexation; copper and compounds; silver and compounds.

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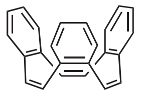

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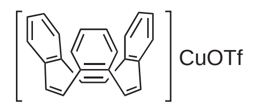

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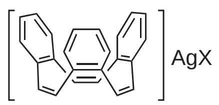
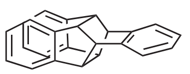


3: X = ClO_4; **4**: X = OTf
5: X = $OCOCF_3$



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prepared; the reaction of **1** with CuOTf (1.2 equiv.) in benzene produced the corresponding 1:1 complex **2** in 63% yield. The copper complex **2** was fairly stable in air, moisture, and light but gradually decomposed at room temperature. Single crystals of **2** were obtained by recrystallization from benzene. In a similar manner, the 1:1 silver(I) complexes **3**–**5** were prepared in 83, 82, and 80% yields by the reaction of **1** with $AgClO_4$ (1.2 equiv.), AgOTf (1.5 equiv.), and $AgOCOCF_3$ (1.5 equiv.) in THF, respectively. Single crystals were obtained by recrystallization of **4** and **5** from hexane–dichloromethane. In the case of gold(I) complexes, AuCl–olefin complexes were prepared and reported to be very unstable.[9] In accord with these observations, the gold(I) complex of **1** was unstable, and the reaction of **1** with AuCl[10] (1.5 equiv.) in CH_2Cl_2 at room temperature for 2 h resulted in the formation of **6**[11] in 88% yield. The formation of **6** can be explained by considering the AuCl-catalyzed isomerization of the *Z*-double bonds to give **7**, followed by the intramolecular [2+2+2]cyclization of **7** (Scheme 1).

The crystal structures of **2** and **4** were determined by X-ray analysis (Figs. 1 and 2).[12] As shown in Fig. 1(a) and (b), the copper atom in **2** is located in the center of the cavity of the [12]annulene to form a C_3-symmetric structure. However, there is no interaction between the copper ion and the benzene rings in the crystal. The Cu–O distance (2.088(6) Å) of **2** is longer than that (2.05 Å) of [1,5-COD]·CuOTf.[8] The Cu–C(olefin) distances of the complex **2** vary only in the range from 2.225(8) to 2.263(8) Å (average 2.24 Å), indicating almost equal coordination with the three ethylene units (Fig. 1(b)). The average Cu–C distance (2.24 Å) is slightly longer than those (1.88–2.2 Å) of the reported copper(I) complexes with alkenes,[8] reflecting coordination properties of the trigonally-coordinated olefin–copper(I) complex. The annulene ring shows only little distortion, and the C=C distances (average 1.35 Å) are 0.01 Å longer than those of **1** (the calculated distances: 1.341 Å by B3LYP).[13] To our knowledge, **2** is the first example of a tris(olefin)–copper(I) complex determined by X-ray analysis.

In a similar manner to **2**, the silver atom in **4** is located in the center of the cavity of the [12]annulene (Fig. 2(a)). The Ag–C(olefin) distances of the complex **4** vary only in the range from 2.530(9) to 2.687(9) Å (average 2.61 Å), indicating almost equal coordination with the three ethylene units. The average Ag–C distance (2.61 Å) is longer than those (2.36–2.53 Å) of most of the reported silver complexes with alkenes,[14,15] and is comparable to that (2.65 Å) of the $AgNO_3$ 1:1 adduct with cyclooctatetraene.[16] The annulene ring shows little or no distortion, and the distances (average C=C(alkene) 1.33 Å) and angles of the alkene parts are similar values to those of **1**. Interestingly, the plane Ag1–C1–C2 is not perpendicular to the C1–C2–C3–C12 plane but rather forms an angle of 76° with it, although that angle observed in the copper complex **2** is 86°. Thus, the silver ion is distorted by an average 14° in the direction of the *cis* hydrogens, i.e. Ag^+ is located slightly below the coordination site of the three alkene ligands (Fig. 2(a)). A similar observation was made for the $AgNO_3$ 3:1 complex with *Z*,*Z*,*Z*-1,4,7-cyclononatriene.[16] As shown in Fig. 2(b), the silver ion is bonded to two oxygen atoms of the different counter anions at Ag–O distances of 2.404(6) and 2.506(9) Å to form a one-dimensional polymer. No interaction between the silver ion and the benzene rings is observed.

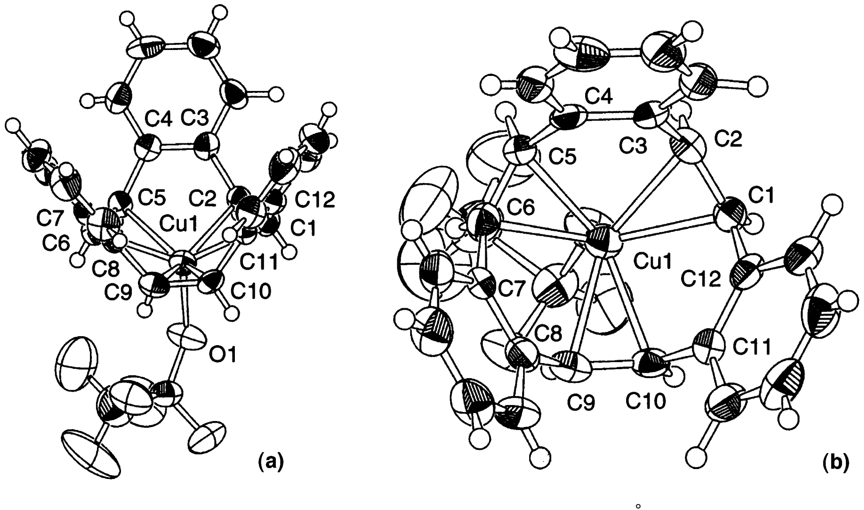

Figure 1. ORTEP diagram of **2**. (a) Side view; (b) top view. Selected bond lengths (Å) and angles (°): Cu1–O1 2.088(6), Cu1–C1 2.229(8), Cu1–C2 2.226(8), Cu1–C5 2.263(8), Cu1–C6 2.230(9), Cu1–C9 2.247(9), Cu1–C10 2.225(8), C1–C2 1.36(1), C2–C3 1.49(1), C3–C4 1.39(1), C4–C5 1.49(1), C1–C12 1.47(1), C1–C2–C3 125.1(8), C2–C3–C4 119.7(8), C2–C1–C12 126.8(8).

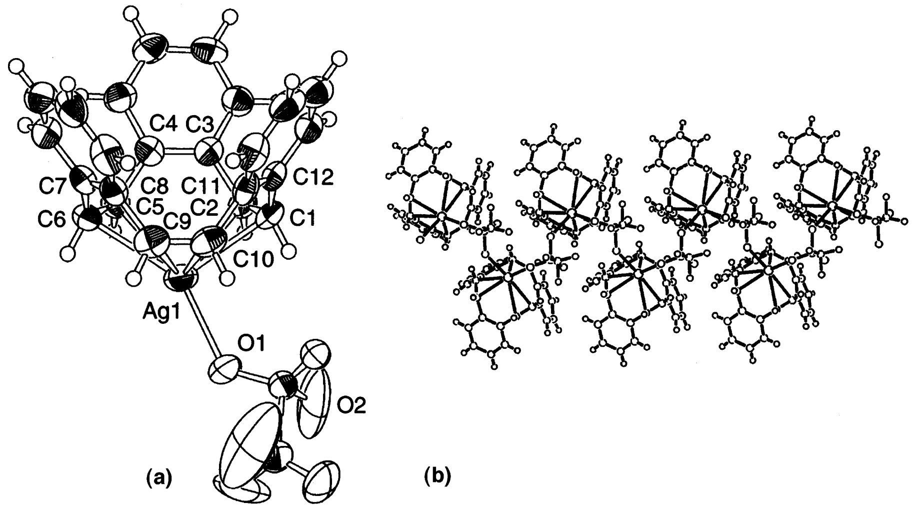

Figure 2. ORTEP diagram of **4**. (a) Side view; (b) crystallographic packing. Selected bond lengths (Å) and angles (°): Ag1–O1 2.404(6), Ag1–O2 2.506(9), Ag1–C1 2.530(9), Ag1–C2 2.532(8), Ag1–C5 2.573(8), Ag1–C6 2.611(9), Ag1–C9 2.687(9), Ag1–C10 2.624(9), C1–C2 1.31(1), C2–C3 1.490 (10), C3–C4 1.39(1), C4–C5 1.47(1), C1–C12 1.51(1), C1–C2–C3 124.5(7), C2–C3–C4 122.4(7), C2–C1–C12 126.6(7).

In order to investigate the structures of complexes **2**–**5** in solution, the ^{1}H NMR spectra of **2**–**5** were measured in $CDCl_3$ or in CD_2Cl_2. As shown in Table 1, the ^{1}H NMR parameters of **2**–**5** clearly indicate the formation of copper and silver complexes in solution. Since the olefinic protons at δ 6.76 in **1** shift downfield to δ 7.27–7.58, the structure of the complexes can be assigned to the olefinic complex **8** similarly as determined by the X-ray structures. However, the aromatic protons at δ 6.95 and 7.07 in **1** also shift downfield to δ 7.04–7.10 in **2**–**5**, and the formation of the benzenoid complex **9** might take place in solution, although the contribution of **9** would be very small. B3LYP density functional calculations for **8** and **9** suggest that **9** is less stable than **8**, but the energy difference in the heat of formation between **8** and **9** ($M^+ = Cu^+$ and Ag^+) is small ($\Delta E_{Cu} = 13.5$ kcal mol^{-1} and $\Delta E_{Ag} = 2.4$ kcal mol^{-1}).[13] For gold complexes, the calculations also predicted formation of complexes **8** and **9** ($M^+ = Au^+$). The space-filling diagrams of **8** and **9** ($M^+ = Cu^+$) show that the copper ion can be accommodated closely in the olefinic and aromatic cavities in **10** (olefinic complex) and **11** (benzenoid complex).

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Table 1. ^{1}H NMR data of **1**–**5**[a]

Compound	Olefinic H (δ)	Aromatic H (δ)
1	6.76	6.95, 7.07
2	7.49	7.09
3	7.58	7.10
4	7.48	7.09
5	7.27	7.04, 7.10

[a] 500 MHz in $CDCl_3$ at room temperature.

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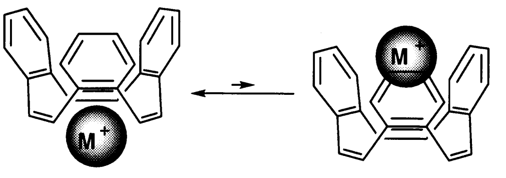
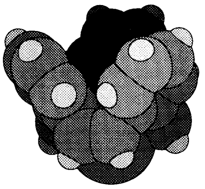


8 **9**



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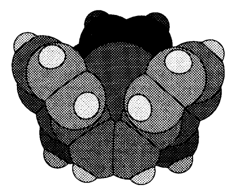

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12. Crystal data for **2** and **4**. Compound **2**: $C_{25}H_{18}O_3F_3SCu$, $M_w = 519.02$, triclinic, space group P-1 (No. 2), $a = 12.755(4)$, $b = 20.375(6)$, $c = 8.648(3)$ Å, $\alpha = 91.11(3)^\circ$, $\beta = 119.63(2)^\circ$, $\gamma = 90.69(2)^\circ$, $V = 2242(1)$ Å^3, $Z = 4$, $D_c = 1.537$ g cm^{-3}, $R = 0.052$, $R_w = 0.051$, GOF = 1.58 for 3398 reflections with $I > 3.00\sigma(I)$. Compound **4**: $C_{25}H_{18}O_3F_3SAg$, $M_w = 563.34$, monoclinic, space group Cc (No. 9), $a = 13.240(4)$, $b = 21.687(6)$, $c = 8.825(4)$ Å, $\beta = 119.63(2)^\circ$, $V = 2202(1)$ Å^3, $Z = 4$, $D_c = 1.699$ g cm^{-3}, $R = 0.055$, $R_w = 0.054$, GOF = 3.33 for 2089 reflections with $I > 3.00\sigma(I)$.
13. The nonlocal hybrid density functional calculations at the B3LYP level were carried out with the effective core potential and basis sets on Cu, Ag, and Au developed by Hay and Wadt.[17] The contraction schemes used were (5s5p5d)/[3s3p2d] for Cu, (5s5p4d)/[3s3p2d] for Ag, and (5s5p3d)/[3s3p2d] for Au in standard notation. The split-valence 6-31G(d) basis set was used for C and H. All calculations were carried out using the Gaussian 98 program.
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