Geminal Tetraauration of Acetonitrile: Hemilabile-Phosphine-Stabilized Au$_8$Ag$_4$ Cluster Compounds

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S Supporting Information

ABSTRACT: Unprecedented geminal tetraauration of acetonitrile has been realized through C−H activation by Au(I)−Ag(I) clusters under mild conditions. The reaction of [OAu$_3$Ag(dppy)$_3$](BF$_4$)$_2$ (dppy = diphenylphosphino-2-pyridine) (**1**), AgBF$_4$, and acetonitrile in the presence of methanol at room temperature resulted in the isolation of the novel cluster [(CCN)$_2$Au$_8$Ag$_4$(dppy)$_8$(CH$_3$CN)$_2$]-(BF$_4$)$_6$ (**2**). The centrosymmetric structure consists of two Au$_4$Ag$_2$ motifs stabilized by hemilabile phosphines. Triply deprotonated acetonitrile (CCN^{3-}) is found in a Au$_4$Ag environment with the terminal carbon bridging four Au(I) centers and the nitrogen donor linking a Ag(I) ion, which is the first example of a μ_5-CCN^{3-} coordination mode. A concerted metalation/deprotonation process for the C−H activation of acetonitrile that indicates the importance of the oxo ion of the oxonium Au(I) cluster is proposed. Cluster **2** emits bright green light in the solid state at room temperature upon UV irradiation.

Gold-mediated C−H activation is of great recent interest.[1] The isolation of aurated hydrocarbons can provide very useful information for understanding the mechanism of C−H activation and the nature of gold catalysis.[2] The auration of organic species has been studied extensively in terms of organometallic reactivity.[3] However, examples of tetraauration of terminal methyl carbons are still rare because C(sp^3)−H bonds are extremely inactive.[4]

Acetonitrile is a commonly used solvent, and its C−H bonds have weak acidity because of the cyano substituent.[5] Examples of metalation of acetonitrile to give M−CH$_2$CN complexes are known,[6] and there have been a few reports on triply deprotonated acetonitrile.[7] Surprisingly, rare examples of auration of acetonitrile have been reported. It was found that acetonitrile could be only monoaurated even when both a gold reagent and a strong base were used.[8] To date, no precedential report on auration of acetonitrile to generate fully deprotonated acetonitrile (CCN^{3-}) has appeared. Herein we report a novel heteronuclear cluster containing tetraaurated acetonitrile moieties, namely, [(CCN)$_2$Au$_8$Ag$_4$(dppy)$_8$(CH$_3$CN)$_2$](BF$_4$)$_6$ (**2**) (dppy = diphenylphosphino-2-pyridine). This complex displays an unprecedented coordination mode of fully deprotonated acetonitrile, and the geminal tetraauration of acetonitrile is observed for the first time. NMR studies suggested that the C−H activation of acetonitrile goes through

a synergistic pathway, and the oxo ion of the oxonium cluster was proved to be critical.

The C−H activation of acetonitrile was serendipitously found in our attempt to construct heterometallic clusters with hemilabile phosphines.[9] The addition of AgBF$_4$ to an acetonitrile/methanol solution of [OAu$_3$Ag(dppy)$_3$](BF$_4$)$_2$ (**1**)[10] at room temperature resulted in a slow color change from pale yellow to brown-yellow. After the mixture was stirred overnight, the solution was evaporated to dryness to give a crude solid. The solid was recrystallized by diffusion of diethyl ether into its solution in 1:3 (v/v) MeCN/CH$_2$Cl$_2$, affording yellow crystals of **2** in 78.5% yield. An IR band at 2153 cm^{-1} indicated that the deprotonation of acetonitrile occurred. The ^{31}P NMR spectrum in CD$_3$CN showed one slightly broad singlet at 37.9 ppm, indicating the phosphines to be in identical environments (a dynamic process might take place in solution). The ^{1}H, ^{13}C, and HSQC NMR spectra were consistent with the formula (see the Supporting Information).

Because the crystals of **2** easily lose cocrystallized solvent molecules, the structural determination was carried out at low temperature.[11] As shown in Figure 1, cluster **2** has a centrosymmetric structure containing eight Au(I) and four Ag(I) ions. The basic unit is a Au$_4$Ag$_2$ motif in which four
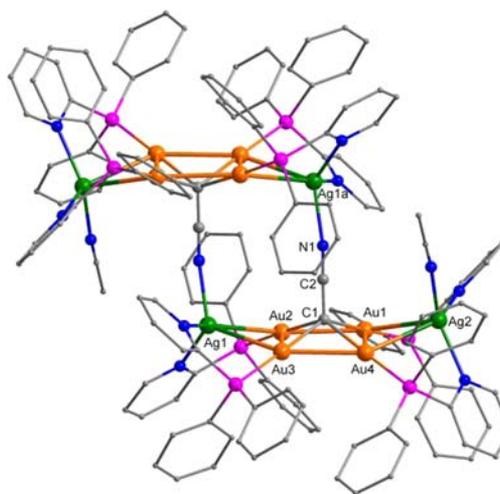
Figure 1. Centrosymmetric structure of [(CCN)$_2$Au$_8$Ag$_4$(dppy)$_8$(CH$_3$CN)$_2$]$^{6+}$ in **2**.

Au(I) ions form a square and two Ag(I) ions are linked to two opposite $Au^I \cdots Au^I$ edges through the binding of pyridyl groups of dppy ligands. The P and N donors of the dppy ligands are bound to Au(I) and Ag(I), respectively. The $Au^I \cdots Au^I$ distances are in the range 2.7918(5)−2.8683(5) Å within the gold square. The $Au^I \cdots Ag^I$ distances range from 2.8592(8) to 2.9512(8) Å. The C−C and C−N bond lengths of the triply deprotonated acetonitrile (CCN^{3-}) moiety are 1.162(13) and 1.410(14) Å, respectively, indicating that the triple-bond character of CN is retained. The CCN^{3-} ligand bridges the Au(I) square with its terminal carbon in a square-pyramidal fashion, and the Au−C bond lengths are in the range 2.116(9)−2.170(9) Å. The N donor of the CCN^{3-} ligand is linked to one Ag(I) ion of the other Au_4Ag_2 moiety with a Ag−N bond length of 2.228(8) Å, and thus, two moieties dimerize to form the cyclic structure illustrated in Chart 1. The coordination configurations of the

Chart 1. Schematic Illustration of Cluster 2
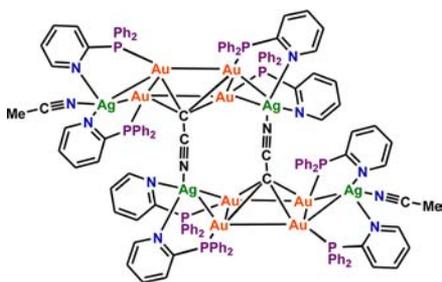
two types of Ag(I) ions are similar but not equivalent. Ag1 is coordinated by two pyridyl N donors and a third N donor from the CCN^{3-} ligand, while Ag2 is ligated by two pyridyl N donors and a third N donor from an acetonitrile solvent molecule.

There are several bridging modes of triply deprotonated acetonitrile that connect up to three metal centers.[12] The triply deprotonated acetonitrile in **1** functions as a μ_5-bridging ligand connecting four metal centers at the carbon end and one metal center at the nitrogen end. The present work represents the first observation of this coordination mode of CCN^{3-}.

It is noteworthy that C−H activation of acetonitrile by a gold complex is not very common, as gold complexes normally activate nitriles, leading to the formation of amides through hydration.[13] It was reported that [PPh$_3$AuCl] can monoaurate acetonitrile in the presence of a guanidine N-superbase.[8] In the present work, **1** led to the geminal tetraauration of acetonitrile in the presence of methanol. The reaction also took place when methanol was replaced by ethanol or phenol. However, no reaction was observed in the absence of a protic solvent, and the addition of an aprotic solvent such as tetrahydrofuran did not cause any reaction either. This observation suggests that the C−H activation of acetonitrile involves the participation of protons. The role of protons was confirmed by the fact that when acetic acid was added to an acetonitrile solution of **1**, C−H activation of acetonitrile took place.

On the basis of these observations, we propose that the reaction undergoes a concerted metalation/deprotonation process[14] involving the transition state illustrated in Scheme 1. The auration gives out water molecules as a result of the interaction between O^{2-} of **1** and hydrogen atoms. The formation of water was verified by ^1H NMR studies (Figure 2). **1** was dissolved in CD_3OD/CH_3CN, and the solution was monitored by ^1H NMR spectroscopy. A broad signal of H_2O at 4.4 ppm was observed, indicating the continuous generation of

Scheme 1. Possible Transition State of the Auration of Acetonitrile
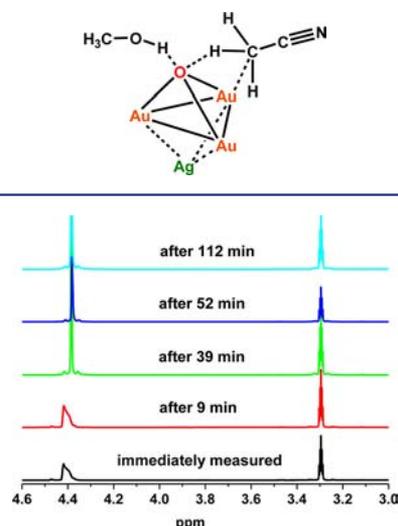
Figure 2. ^1H NMR spectra of **1** as a function of time at room temperature in 2:1 (v/v) CD_3OD/CH_3CN.

H_2O from the reaction. Once the reaction was complete, the profile of H_2O peak became narrow and stayed narrow in the remaining time. When the same procedure was performed in CD_3OD/CD_3CN, no broad signal of water was observed because the dynamic generation of D_2O was not observable in the ^1H NMR spectrum.

The oxo ion was proved to be very important. Mixing dppyAuCl/AgBF$_4$ in MeCN/MeOH did not activate the C−H bond of acetonitrile. However, the C−H activation of acetonitrile occurred as a result of the in situ generation of oxonium cluster **1** in MeCN/MeOH, as the one-pot reaction of dppyAuCl, Ag$_2$O, and NaBF$_4$ in MeCN/MeOH afforded the tetraauration cluster **2**.[15] It is noteworthy that Ag$_2$O is commonly used as an additive in Au(I)-catalyzed reactions.[16]

In addition, the importance of AgBF$_4$ was also verified. NMR spectra of the reaction mixture were measured with and without the addition of AgBF$_4$ (Figure S18 in the Supporting Information). The results clearly showed that several dynamic species were present before AgBF$_4$ was added, and the NMR signal of the title product became predominant after the addition of AgBF$_4$.

One of the driving forces for auration is the strong carbophilicity of LAu$^+$ ions, which is related to relativistic effects.[17] The bridging of hemilabile phosphines and the metallophilic interactions (including both $Au^I \cdots Au^I$ and $Au^I \cdots Ag^I$ contacts) favor the formation of the title cluster.

Cluster **2** exhibits intense green emission (λ_{max}^{em} = 509 nm) in the solid state at room temperature (Figure 3). Its orange luminescence (λ_{max}^{em} = 565 nm) is weak in dichloromethane solution. The room-temperature emission shows single-exponential behavior with lifetimes of 17.9 and 8.5 μs in solution and the solid state, respectively. The lifetime on the microsecond scale and the large Stokes shift suggest that the emission is phosphorescence. Interestingly, **2** also displays thermochromic luminescence behavior. In 9:1 MeOH/EtOH, it emits orange light at room temperature and bright green light at 77 K.

Similar tetraauration of acetonitrile was also successful with another gold−silver oxonium cluster containing the dppy
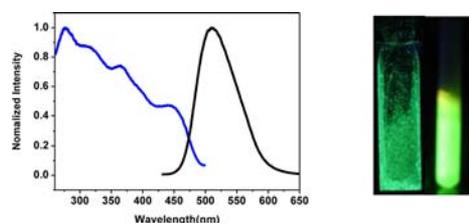
Figure 3. (left) Excitation (blue) and emission (black) spectra of **2** in the solid state. (right) Photograph showing the luminescence from **2** in the solid state and frozen glass.

derivative 2-diphenylphosphino-4-methylpyridine (PPh$_2$-4-Mepy). The reaction of $[OAu_3Ag(PPh_2\text{-}4\text{-Mepy})_3](BF_4)_2$ and AgBF$_4$ in acetonitrile/methanol at room temperature led to the isolation of the cluster $[(CCN)_2Au_8Ag_4(PPh_2\text{-}4\text{-Mepy})_8(CH_3CN)_2](BF_4)_6$ (**3**), which is isostructural to **2** (Figure S19).

This work demonstrates that oxonium Au(I)−Ag(I) clusters can fully deprotonate acetonitrile, leading to unprecedented tetraauration of acetonitrile with the assistance of a protic solvent. The oxo ion plays a key role in the C−H activation of acetonitrile, and this provides new insight in terms of the involvement of Ag$_2$O in gold-catalyzed processes. Further investigation using hemilabile-phosphine-stabilized heterometallic oxonium complexes for Au(I)-mediated C(sp^3)−H activation under mild conditions is in progress.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Synthesis and characterization details. 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.

■ ACKNOWLEDGMENTS

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(11) Crystal data for **2**·2MeCN·2CH$_2$Cl$_2$: C$_{144}$H$_{118}$B$_6$N$_{12}$F$_{24}$P$_8$Au$_8$Ag$_4$·2MeCN·2CH$_2$Cl$_2$, a = 16.4701(8) Å, b = 26.2361(11) Å, c = 20.4873(8) Å, β = 113.624(5)°, V = 8110.9(6) Å^3, space group $P2_1/n$, Z = 2, T = 100 K, 43126 reflections measured, 18826 unique (R_{int} = 0.0466), final R_1 = 0.0501, wR_2 = 0.1074 for 13220 observed reflections $[I > 2\sigma(I)]$. Crystal data for **3**·2MeCN·4-H$_2$O: C$_{152}$H$_{134}$B$_6$N$_{12}$F$_{24}$P$_8$Au$_8$Ag$_4$·2MeCN·4H$_2$O, a = 15.7499(5)Å, b = 17.0792(4) Å, c = 31.1378(11) Å, β = 90.373(3)°, V = 8375.7(4) Å^3, space group $P2_1/n$, Z = 2, T = 173 K, 32575 reflections measured, 17702 unique (R_{int} = 0.0626), final R_1 = 0.0893, wR_2 = 0.1495 for 12154 observed reflections $[I > 2\sigma(I)]$.

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