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Stability of Organogold(III) Complexes. Isolation and Crystal Structure of Dimethylgold Trifluoromethanesulfonate

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A variety of interesting σ-bonded organogold complexes have been prepared and characterized.[1] Donor ligands (L, such as phosphines) are commonly required for stabilization of these organometals. For example, trimethylgold is itself unstable[2] and has never been isolated, whereas the phosphine complexes such as $(CH_3)_3AuPPh_3$ have been thoroughly characterized.[3] Similarly, an extensive series of mononuclear *cis*-dimethylgold(III) derivatives, $(CH_3)_2XAuL$ where X = anion, have been prepared and characterized in an elegant series of Raman, infrared, and nuclear magnetic resonance studies principally by Tobias and co-workers.[4] An interesting feature of the $(CH_3)_2Au^{III}$ moiety, however, is that solutions of even the simple aquo cation $(CH_3)_2Au(aq)^+$ are quite stable in water.[5] We wished to examine the chemistry of this interesting organometallic ion in nonaqueous media, and in this report we present the isolation and crystal structure of dimethylgold trifluoromethanesulfonate (triflate) together with a limited study of its thermal stability. [The triflate salt was chosen because of its general properties as a stable and weakly coordinating anion.[6]]

Experimental Section

Materials. The gold and silver complexes $[(CH_3)_2IAu]_2$,[7] (*trans*-cyclooctene)$_3$AuOTf,[8] and $AgOTf(C_6H_6)_{0.5}$[9] were prepared by using the published procedures. *trans*-Cyclooctene was synthesized by the method described by Vedejs and Fuchs.[10] The solvents were reagent grade commercial products and were distilled over benzophenone dianion under argon before use. Olefins were also reagent grade commercial products and distilled over CaH_2 before use. The proton NMR spectra were recorded either on a Varian EM-360, T-60 or XL-100FT spectrometer. Infrared spectra were taken on a Perkin-Elmer 467 spectrometer using a polystyrene film for calibration.

Dimethyliodogold (223 mg) was dissolved in benzene and a solution of $AgOTf(C_6H_6)_{0.5}$ (187 mg) in benzene was added, resulting in an immediate precipitation of a yellowish powder consisting of AgI (153 mg, 103%). The clear colorless solution obtained after filtration was concentrated in vacuo at 0 °C by the freeze-dry method to afford a white solid consisting of $(CH_3)_2AuOTf$, I; yield 90%. The compound is soluble in benzene, toluene, ether, tetrahydrofuran, acetone, and water. The molecular weight in benzene determined by the cryoscopic method was 738. After recrystallization from the mixture of toluene and *n*-pentane, I yielded I′ with mol wt 581 and the following ^1H NMR data: δ 1.00 ppm (singlet) in benzene for Me_2Au; in acetone-d_6, 0.70 ppm (s) for $(CH_3)_2Au$, 4.97 ppm (s) for water at room temperature, and 0.88 (s), 8.10 (s) ppm at −98 °C; in water, 1.22 ppm (s). Chemical shifts are referred to external TMS in $CHCl_3$. IR (KBr disk): 2950 cm^{-1} (ν_{CH}); 1150 and 1270 cm^{-1} (ν_{OTf}).

Crystallography. Since crystals of I′ decomposed slowly under ambient conditions, a well-formed crystal of dimensions 0.78 mm × 0.086 mm × 0.072 mm (001, 110, 1–10 forms) was transferred from the crystallization liquid to a goniostat equipped with a gaseous nitrogen cooling system for characterization. The sample was maintained at −160 °C throughout the characterization and data collection. Reflections located in a limited region of reciprocal space could be indexed as orthorhombic, space group *Abam* (nonstandard setting of *Cmca*, No. 64), with cell dimensions of $a = 17.301$ (4), $b = 14.417$ (4), and $c = 7.076$ (2) Å based on a refinement of angular data from 17 reflections. A calculated density of 2.97 g/cm^3 for $Z = 8$ indicated that the molecule must possess molecular symmetry, and this fact was confirmed by the subsequent solution and refinement.

The diffractometer system used was locally constructed using a Picker goniostat and TI980 minicomputer[11] and was equipped with a highly oriented graphite monochromator (002 reflection). Redundant data were collected between 4 and 100° 2θ using standard θ–2θ scan techniques with a scan speed of 2.0° min^{-1}. The redundant data were then corrected for Lorentz and polarization terms as well as absorption (μ(Mo Kα) = 168.73 cm^{-1}; maximum and minimum transmission coefficients are 0.090 and 0.020) and standard errors were calculated assuming an ignorance factor of 0.05. Of the 2078 unique intensities, 2019 were nonzero, 1812 had values greater than the calculated σ based on counting statistics, and 1541 had values greater than 2.33 times their σ's.

The structure was solved using direct methods and refined by full-matrix least squares using anisotropic thermal parameters for all atoms.[12] A refinement minimizing $\sum w(|F_o| - |F_c|)^2$, where $w = 1/\sigma(F)$, converged to $R(F) = 0.056$ and $R_w(F) = 0.036$, where $R(F) = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_w(F) = \sum w||F_o| - |F_c||/\sum w|F_o|$. The goodness of fit for the last cycle was 1.23. Final values of the fractional coordinates and thermal parameters are given in Table I, and observed and calculated structure amplitudes are available as supplementary material. A difference Fourier synthesis at this point revealed a residual of nearly 3.0 e/Å^3 at the gold site as well as numerous other peaks of electron density 0.5–1.3 e/Å^3, some of which could be questionably assigned to hydrogen positions. In an attempt to define the hydrogen positions unambiguously, various other Fourier maps with selected (sin θ)/λ cutoffs were computed, and refinements minimizing $\sum w(|F_o|^2 - |F_c|^2)^2$ were utilized. In all cases the residuals were essentially identical, with a large peak at the gold site and numerous other smaller peaks randomly distributed within the asymmetric cell.

An interesting feature of the structure is the short O(2)···O(3) distances of 2.699 (12) Å. This distance is shorter than the 2.8 Å expected for a van der Waals contact.[13] It is typical of that found for hydrogen-bonded O···H–O distances.[14] Hydrogen bonding of the triflate O(2) and O(2)′ atoms to the hydrogens of O(3) offers a convenient explanation for the rather large (compared to the expected tetrahedral) Au(1)–O(1)–S(1) angle of 128.7 (2)° and the fact that the triflate ligand lies in the plane of the molecule.

Results and Discussion

Isolation and Molecular Structure of Dimethylgold Triflate. Treatment of the dimeric dimethyliodogold with a stoichiometric amount of silver triflate–hemibenzene in dry benzene under an argon atmosphere afforded an immediate precipitate of silver iodide (eq 1). Filtration of the mixture followed by

$$[(CH_3)_2AuI]_2 + 2AgOTf(C_6H_6)_{1/2} \rightarrow [(CH_3)_2AuOTf]_2 + 2AgI \quad (1)$$

freeze-drying of the solution at 0 °C afforded a colorless crystalline material I. Complex I was identified as dimethylgold triflate by its proton NMR and IR spectra [^1H NMR (benzene) δ 1.00 ppm (s) for Au–CH_3 (external TMS); IR (KBr disk) ν_{CH} 2950 cm^{-1}, ν_{OTf} 1150 (s), 1270 (s) cm^{-1} [15]]. The molecular weight of 738 determined cryoscopically in benzene suggests a dimeric structure of I [calculated mol wt 376 for the monomer] in solution, in common with some other dimethyl(aniono)gold(III) complexes.[1,7,16]

Complex I can be readily recrystallized from a mixture of *n*-pentane and toluene to afford colorless needles of I′, which differs from I by the presence of a molecule of water (eq 2).

$$[(CH_3)_2AuOTf]_2 \xrightarrow[\text{(recryst)}]{H_2O} 2(CH_3)_2Au(H_2O)OTf \quad (2)$$

Moreover, the apparent molecular weight decreased to 581 after recrystallization. Despite repeated and careful attempts to rigorously exclude water during the recrystallization of I, only I′ was always obtained. We attribute this observation to the extremely hygroscopic nature of I. [Indeed, I′ is also very hygroscopic.]

The x-ray crystal structure of I′ shown in Figure 1 indicates that dimethylgold triflate hydrate is a monomeric species with the expected square-planar configuration about the gold atom. The cis methyl groups are bonded normally to gold.[16-18] The

Table I. Atomic and Thermal Parameters for Dimethylgold Triflate Monohydrate[a]

Atom	10^5x	10^5y	10^5z	10^5b_{11}	10^5b_{22}	10^5b_{33}	10^5b_{12}	10^5b_{13}	10^5b_{23}
Au(1)	73 672 (2)	−2 346 (2)	0	138 (1)	156 (1)	768 (5)	15 (1)	0	0
S(1)	11 830 (11)	17 353 (13)	0	141 (6)	190 (7)	930 (33)	29 (5)	0	0
F(1)	97 943 (32)	23 910 (43)	0	216 (21)	472 (33)	2432 (172)	162 (22)	0	0
F(2)	815 (22)	88 822 (33)	84 720 (82)	220 (14)	646 (27)	2769 (131)	−17 (16)	232 (35)	480 (54)
O(2)	13 420 (26)	22 376 (28)	17 144 (63)	264 (16)	319 (20)	791 (77)	−11 (13)	−17 (29)	−55 (33)
O(1)	14 427 (35)	7 747 (41)	0	190 (20)	164 (23)	2269 (169)	38 (18)	0	0
O(3)	30 351 (34)	16 509 (36)	0	179 (20)	183 (22)	1241 (116)	−31 (16)	0	0
C(3)	62 831 (54)	2 830 (70)	0	171 (26)	375 (45)	2104 (232)	98 (29)	0	0
C(2)	01 410 (50)	15 831 (67)	0	162 (29)	374 (45)	1845 (218)	50 (30)	0	0
C(1)	21 998 (53)	89 354 (52)	0	266 (32)	146 (28)	1481 (178)	1 (23)	0	0

[a] The form of the exponential for the anisotropic thermal parameters is $\exp[-(h^2b_{11} + k^2b_{22} + l^2b_{33} + 2hkb_{12} + 2hlb_{13} + 2klb_{23})]$.

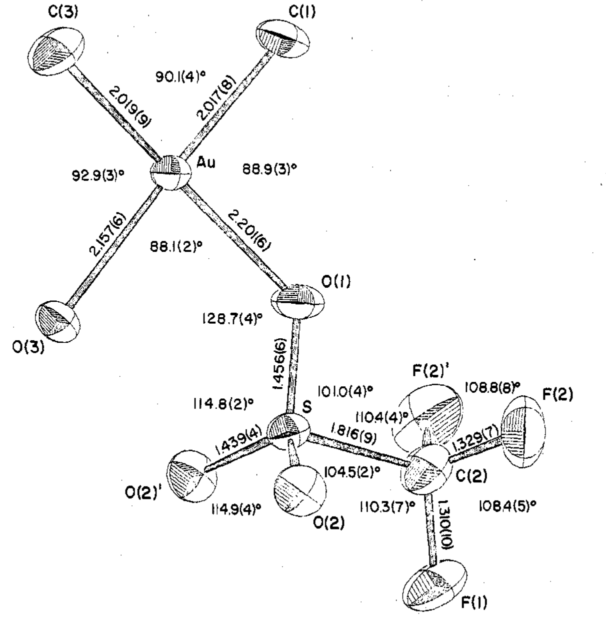

Figure 1. ORTEP drawing of the molecule showing important distances and angles. F(2)′ and O(2)′ are related to F(2) and O(2) by a crystallographic mirror plane which passes through all remaining atoms in the molecule. All thermal ellipsoids are drawn at the 50% confidence level.

gold–oxygen bonds to triflate and water are more or less similar to those found in the tetrameric dimethylgold(III) hydroxide,[17] but the oxygen angle of 129° is larger than the tetrahedral angle (compare Experimental Section).

The crystal structure of I′ in Figure 1 belies its dynamic properties in solution. Thus, the proton NMR spectrum of I′ in acetone-d_6 consists of two sharp singlets, one at δ 0.70 ppm for *cis*-$(CH_3)_2Au$. The other singlet at 4.97 ppm, assigned to coordinated water, is shifted to higher fields as successive amounts of water are added to the solution. The shift in the water resonance is attributed to a fast exchange with gold, since the resonance at 2.3 ppm due to traces of water in the solvent (acetone-d_6) is shifted to lower fields by adding excess water. The methyl resonance in I′ is unaffected by water at these concentrations and remains an unresolved singlet down to −90 °C. If the structure of dimethylgold triflate in Figure 1 remained intact and static in solution, two singlets, one for each CH_3 group, would be expected in the proton NMR spectrum of I′.[4,19] However, the equivalence of the two methyl groups on the NMR time scale coupled with the shift in the water resonance indicates the presence of one or more dynamic processes leading to a facile site interchange on gold. Moreover, the nonintegral molecular weight observed for I′ in benzene solution suggests that (partial) dimerization of dimethylgold species may also be associated with this exchange. Unfortunately, the results on hand do not allow a rigorous distinction between water and triflate (or both) as the exchanging ligands during the dynamic changes of I′ in solution.

Reductive Elimination of Dimethylgold Triflate. 1. Thermal. Dimethylgold triflate (either as I or I′) is extremely soluble in water and affords a solution whose properties have been described previously by Tobias and co-workers.[5] No reductive elimination was observed within a 24-h period at room temperature even in air. On the other hand, dimethylgold triflate in benzene solution undergoes a smooth reductive elimination of ethane according to the stoichiometry in eq 3.

$$(CH_3)_2AuOTf \rightarrow CH_3CH_3 + AuOTf \qquad (3)$$

No methane was observed, and the gold appeared as a black precipitate, presumably due to the rapid disproportionation of gold(I) triflate noted previously[8,20] [$3AuOTf \rightarrow 2Au + Au(OTf)_3$]. The rate of reductive elimination at 45 °C follows a half-order dependence on the concentration of dimethylgold triflate but only for the initial period (<10% decomposition). At higher conversions, the apparent half-order rate constant increases significantly, suggestive of an autocatalytic decomposition.[21]

2. Phosphine Induced. Addition of slightly less than 1 equiv of triphenylphosphine to a solution of dimethylgold triflate in benzene affords *cis*-dimethyl(triflato)triphenylphosphinegold,[19a] II, which is the phosphine analogue of I′, the hydrate. The phosphine complex II, however, is much less stable than the hydrate I′, undergoing ready reductive elimination of ethane even at −50 °C.[19a] Addition of 2 equiv of triphenylphosphine to dimethylgold triflate affords the significantly more stable cationic complex $(CH_3)_2Au(PPh_3)_2{}^+OTf^-$ previously examined by Tobias et al.[22,23]

3. Olefin Induced. Addition of *trans*-cyclooctene to a toluene or benzene solution of I′ at room temperature caused the complete reductive elimination of ethane within 1 h (eq 4).

$$(CH_3)_2Au(H_2O)OTf + 3\,trans\text{-}C_8H_{14} \xrightarrow{-H_2O} CH_3CH_3 + (trans\text{-}C_8H_{14})_3AuOTf \qquad (4)$$

Colorless crystals of tris(*trans*-cyclooctene)gold(I) triflate were collected in high yields and identified by comparison of its IR spectrum and melting point with those of an authentic sample.[8]

Reactions of dimethylgold triflate with various types of other olefins were also examined by following the changes in the proton NMR spectra. Neither styrene, vinyl acetate, nor methyl methacrylate induced any spectral changes in I, and reductive elimination was not observed. A slight downfield shift of the olefinic protons but no other change was observed for 1,5-ocyclooctadiene and cyclohexene. When acrylonitrile was added to a pentane or toluene solution of I, a yellow oil separated whose IR spectrum showed the nitrile band absorbing at 2280 cm^{-1}, representing a shift by 55 cm^{-1} to a higher frequency from that of free acrylonitrile. Coordination of acrylonitrile to the gold complex through the cyano function is suggested.[24] The complex, however, is weakly bound since I can be recovered from the yellow oil simply by removal of the acrylonitrile in vacuo.

The difference in behavior of dimethylgold triflate toward *trans*-cyclooctene and the other olefins examined in this study is striking. The driving force for reductive elimination of ethane is no doubt the greatest with *trans*-cyclooctene since its olefin–gold(I) complex is the most stable. However, it is difficult to completely rationalize the mechanism by which *trans*-cyclooctene alone so readily induces reductive elimination of dimethylgold triflate.[25] A similar question arises as to why the phosphine complex II is much less stable than the aquo complex I′, when the reverse is generally true of other transition metal–organic species. The problem may be related to the ease with which ligands, both L and X, are lost from the square-planar gold species, *cis*-$(CH_3)_2Au(X)L$, since reductive elimination from all of those organogold(III) complexes studied heretofore in detail[19a,23,26,27] involve unstable three-coordinate gold intermediates formed via a dissociative process.[28]

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Registry No. I, 63105-42-0; I′, 63105-43-1; $[(CH_3)_2IAu]_2$, 14951-47-4; AgOH, 2923-28-6.

Supplementary Material Available: Tables of observed and calculated structure amplitudes for compound I′ (20 pages). Ordering information is given on any current masthead page.

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