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STUDIES OF CATIONIC GOLD(I) COMPLEXES: PREPARATION OF TRIS(*trans*-CYCLOOCTENE)GOLD TRIFLUOROMETHANESULFONATE

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Summary

trans-Cyclooctene forms stable π-olefin complexes with aurous chloride and trifluoromethanesulfonate (triflate). The latter can be isolated as the tris *trans*-cyclooctene complex which shows no tendency for disproportionation of gold(I) to gold(III). It is compared to analogous cationic complexes from copper (I) and silver(I) triflates. Oxidative addition and electron transfer reactions of olefin—gold(I) complexes to afford gold(III) and gold(II) species, respectively, are examined. Attempts to prepare the simple and the coordinatively unsaturated phosphine complexes of gold(I) triflate are also described.

Introduction

Gold(I) compounds can serve effectively in catalytic reactions involving oxidative addition since gold(III) complexes are readily accessible [1]. We have sought the free uncoordinated cation, Au^+, since it should undergo such transformations with the greatest facility. Unfortunately, previous studies suggest that the cationic gold(I) ion is exceedingly unstable in aqueous solutions due to the large driving force for disproportionation ($K \approx 10^{10}$) [2] (eq. 1). Thus simple aurous salts

$$3\ Au^+_{aq} \overset{K}{\rightleftharpoons} Au^{3+}_{aq} + 2\ Au \qquad (1)$$

are unknown. The halides, pseudohalides and chalcogenides are the only binary compounds of gold(I) extant, but they exist with highly coordinated bridging ligands [3].

Coordination of gold(I) with neutral ligands such as phosphines also stabilizes it relative to disproportionation. Thus, a series of cationic gold(I) salts, AuL_n^+ ClO_4^- (where L = Ph_3P, n = 2—4) are known [4], but the phosphine ligands are rather tightly held in these complex ions and the salts are relatively unreactive. Alternatively, olefins as neutral ligands are generally more easily displaced than phosphines. Indeed, various olefin complexes of aurous chloride have been prepared and their stability is generally low, enabling the reversible addition and removal of the olefin ligands (Q) [5], e.g.:

$$[Q/AuCl]_n \rightleftharpoons [AuCl]_n + nQ \qquad (2)$$

The lability of olefins in these complexes provided the focal point for our attempts to prepare the gold(I) in cation in nonaqueous media as the salt of the poorly-coordinating trifluoromethanesulfonate (triflate, OTf) anion. In the course of this study we also examined the properties of these olefin—gold(I) complexes with regard to substitution and oxidation.

Results and discussion

Preparation of cationic phosphine—gold(I) complexes

The cationic bis(phosphine)gold(I) complex, $(Ph_3P)_2AuOTf$, can be readily prepared from chlorobis(triphenylphosphine)gold(I) by treatment with silver triflate in ethanol solution. The colorless solid after recrystallization from a mixture of acetone and pentane is similar to the related perchlorate and tetraphenylborate salts prepared previously [4]. The same mild metathesis of the monophosphine analog, chloro(triphenylphosphine)gold(I), and silver triflate in a mixture of methylene chloride and acetone again readily afforded a precipitate of silver chloride. However, attempts to isolate from solution the analogous monophosphinegold(I) salt $(Ph_3P)AuOTf$ under mild conditions only produced partially decomposed (purple) material. Similarly, the treatment of a suspension of aurous chloride in either acetone or benzene with silver triflate at room temperature only gave a mixture containing silver chloride and a black (reduced gold) solid. Attempts to prepare gold(I) triflate from the cyclohexene complex were also unsuccessful (see Experimental Section). This behavior of phosphinegold(I) complexes parallels that of the analogous copper(I) species. Thus molecular weight and conductivity studies have shown that the stable bis(phosphine) complex $(Ph_3P)_2CuOTf$ is monomeric in chloroform, whereas the 1/1 analog $Ph_3PCuOTf$ is dimeric and somewhat unstable [6]. Furthermore, copper(I) triflate can only be prepared as a hemibenzene adduct [8]. We conclude that gold(I) triflate, either as a simple salt or the monophosphine complex is unstable even in nonaqueous solutions.

$$(Ph_3P)_2AuCl + AgOTf \rightarrow (Ph_3P)_2AuOTf + AgCl \qquad (3)$$

Preparation of olefin gold(I) triflate

Treatment of an ethereal suspension of yellow aurous chloride with excess *cis*-cyclooctene (*cis*-C_8H_{14}) affords a colorless solution from which chloro(*cis*-cyclooctene)gold(I) [5b] can be isolated on cooling the reaction mixture to −78°C. The monoolefin complex is unstable, and produces a black (gold) precipitate on redissolution in either benzene or ether. Metathesis of the olefin complex with silver triflate in the presence of excess *cis*-cyclooctene leads to an immediate precipitate of silver chloride, and a solution from which *cis*-cyclooctenegold(I) tri-

$$AuCl + cis\text{-}C_8H_{14} \rightleftharpoons (cis\text{-}C_8H_{14})AuCl \qquad (4)$$

flate can be isolated as a colorless crystalline solid by chilling to —20° C. However, the complex decomposed within 30 min at room temperature to a purple amorphous solid even under a nitrogen atmosphere, and this prevented its thorough characterization. (See the experimental section for a similar description of the cyclohexene complex.)

In contrast, the treatment of aurous chloride with *trans*-cyclooctene leads irreversibly to a colorless precipitate of chloro(*trans*-cyclooctene)gold(I) which

$$\mathrm{AuCl} + trans\text{-}\mathrm{C_8H_{14}} \rightarrow (trans\text{-}\mathrm{C_8H_{14}})\mathrm{AuCl} \qquad (5)$$

can be recrystallized from a mixture of toluene and hexane. Thus, unlike the *cis* isomer and other monoolefin—chlorogold(I) complexes reported previously [5], the *trans*-cyclooctene adduct I is stable in solution. The olefinic ligand cannot be readily removed by solvent washing or vacuum pumping. The latter are in accord with the strong complexing power of *trans*-cyclooctene as a result of the torsional C=C strain which is partially relieved on coordination [7,8] (for example, the C=C stretching frequency decreases from 1650 $\mathrm{cm^{-1}}$ in the free olefin to 1535 $\mathrm{cm^{-1}}$ in I). We presume that chloro(*trans*-cyclooctene)gold exists as a chloro-bridged dimer similar to the structures of related copper(I) analogs [9].

The chloro ligands in this olefin complex can be readily replaced by triflate. Thus, when a toluene solution of chloro(*trans*-cyclooctene)gold(I) and excess *trans*-cyclooctene is treated with one equivalent silver triflate under an argon atmosphere at room temperature, an immediate precipitate of silver chloride is obtained. Separation followed by removal of the solvent in vacuo affords tris(*trans*-cyclooctene)gold(I) triflate (II) which can be recrystallized from acetone without decomposition.

$$(trans\text{-}\mathrm{C_8H_{14}})\mathrm{AuCl} + \mathrm{AgOTf} \xrightarrow{t\text{-}\mathrm{C_8H_{14}}} \underset{\mathrm{(II)}}{(trans\text{-}\mathrm{C_8H_{14}})_3\mathrm{AuOTf}} + \mathrm{AgCl} \qquad (6)$$

The proton NMR spectrum of II shows only a single resonance for the olefinic protons. II represents the first example of a monoolefingold(I) complex containing more than one coordinated olefin. Indeed, the presence of II of three magnetically equivalent (or time averaged) *trans*-cyclooctenes coordinated to gold(I) together with the weakly coordinating properties of triflate suggest that it be considered a cationic species.

Isolation of tris(*trans*-cyclooctene)gold(I) also allows for the first time a direct comparison of the properties of analogous π-olefin complexes of the other Group Ib metals, namely tris(*trans*-cyclooctene)copper(I) prepared previously [8], and tris(*trans*-cyclooctene)silver(I) prepared directly from silver triflate and excess *trans*-cyclooctene (see Experimental Section) [10]. Although these complexes all have the same molecular formulas, it cannot be taken for granted as yet that they have the same structures. Nonetheless, the infrared and proton NMR data in Table 1 show an interesting trend on proceeding from the copper(I), to silver(I) and gold(I) complexes. Further discussion [8] of these properties will be deferred until the X-ray crystallographic determination of their structures, presently in progress, is complete.

TABLE 1

INFRARED AND PROTON NMR SPECTRA OF *trans*-CYCLOOCTENE COMPLEXES OF COPPER(I), SILVER(I) and GOLD(I) TRIFLATES

L_nMOTf [a]	ν(C=C) [b] (cm^{-1})	δ(olefinic H) [c] (ppm)
L_3CuOTf	1570	5.26
L_3AgOTf	1590	5.93
L_3AuOTf	1540	5.15
LAuCl	1535	5.17 [d]
free L	1650	5.54

[a] L = *trans*-cyclooctene. [b] KBr disc. [c] in acetone-d_6 (TMS internal reference). [d] in $CDCl_3$ solution.

Reactions of olefin—gold(I) complexes

Substitution of the coordinated *trans*-cyclooctene in the chlorogold(I) complex is readily effected by triphenylphosphine in benzene solution at room temperature. The same chlorophosphinegold complex in eq. 7 is obtained either

$$(trans\text{-}C_8H_{14})AuCl + Ph_3P \rightarrow (Ph_3P)AuCl + trans\text{-}C_8H_{14} \qquad (7)$$

from the addition of triphenylphosphine to aurous chloride or displacement of the olefin from chloro(*cis*-cyclooctene)gold(I) by phosphine.

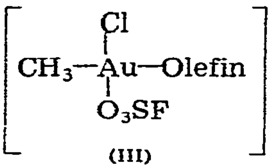
Coordinated *trans*-cyclooctene is also readily displaced from chloro(*trans*-cyclooctene)gold(I) by methyllithium. However, the expected lithium dimethylaurate was not stable [11] under these conditions, the reaction mixture depositing reduced gold species.

Methyl(triphenylphosphine)gold(I) is known to undergo oxidative addition of alkyl halides to afford gold(III) complexes [1]. In a similar vein, the reactions of chloro(*trans*-cyclooctene)gold with methyl triflate and fluorosulfate were examined for evidence of oxidative addition to either the gold(I) nucleus (vide supra) or to the coordinated olefin (the latter pertains to the observation of oxidative addition of bromine to olefinic phosphines coordinated to gold(I) [12]). However, exposure of chloro(*trans*-cyclooctene)gold to excess methyl fluorosulfate in the presence of free cyclooctene did not afford a methylated product or any evidence of a gold(III) product. Instead, methyl chloride was liberated and *trans*-cyclooctenegold(I) fluorosulfate obtained. The chloride-for-fluorosulfate exchange in eq. 8 is similar to other substitution reactions reported by

$$LAu^ICl + CH_3O_3SF \xrightarrow{L} L_3Au^IO_3SF + CH_3Cl \qquad (8)$$

L = *trans*-cyclooctene

Nichols [13]. It is not clear, however, whether such an exchange proceeds by prior oxidative addition via an intermediate such as III followed by reductive



$$\left[\begin{array}{c} Cl \\ | \\ CH_3\text{—}Au\text{—}Olefin \\ | \\ O_3SF \end{array}\right]$$

(III)

elimination. Indeed we have not observed as yet any evidence for ready oxidative addition to olefin—gold(I) complexes. Chloro(*trans*-cyclooctene)gold is even stable in benzene solution to a large excess of trifluoroacetic acid, and it can be recovered unchanged. However, protonation may obtain with the stronger triflic acid, since the reaction mixture turns black indicative of the reduction of gold.

Finally, it is noteworthy that the stabilizing effect of coordinated *trans*-cyclooctene on gold(I) is also evident in electron-transfer reactions. Thus, chloro(*trans*-cyclooctene)gold is essentially unreactive to the rather potent electron-transfer agent, hexachloroiridate(IV), under conditions in which both methyl(triphenylphosphine)gold(I) and trimethyl(triphenylphosphine)gold(III) are readily oxidized [14].

Experimental

Materials

The preparation of $AgO_3SCF_3(C_6H_6)_{0.5}$ [8], AuCl [15], $AuCl(PPh_3)$ [16], $AuCl(cis\text{-}C_8H_{14})$ [6b] and $AuCl(PPh_3)_2$ [4] were described previously. The solvents were commercial reagent grade chemicals and used without further purification. *trans*-Cyclooctene was prepared by the method described by Vedejs and Fuchs [17].

Analysis and spectroscopic measurements

Elemental analyses were performed by the Midwest Microlabs, Ltd. The proton NMR spectra were recorded on a Varian EM-360 spectrometer, and the infrared spectra were taken on a Perkin—Elmer 467 spectrometer using polystyrene film for calibration.

(trans-C_8H_{14})AuCl

To a suspension of aurous chloride (1.0 g) in anhydrous ether was added *trans*-cyclooctene (0.56 ml) at 0°C. After evaporation of the solvent, the residual solid was recrystallized from a mixture of toluene and n-hexane. Yield, 0.95 g. dec. p. 115°C. IR: ν(C=C), 1535m cm^{-1}; ν(Au—Cl), 330m cm^{-1}. Anal. Found: C, 28.17; H, 4.15. $C_8H_{14}ClAu$ calcd.: C, 28.05; H, 4.12%.

(trans-C_8H_{14})$_3$AuOTf

A solution of (*trans*-C_8H_{14})AuCl (121 mg) in toluene was treated with $AgOTf(C_6H_6)_{0.5}$ (105 mg) in toluene in the presence of excess free *trans*-cyclooctene under Ar. The reaction produced an immediate white precipitate at room temperature. After filtration, the solvent was removed under reduced pressure, and the residue extracted with acetone (20 ml). Evaporation of the acetone afforded a white solid, which was recrystallized from a small amount of acetone. M.p. 106—107°C (dec.). IR: ν(C=C), 1540 cm^{-1}; ν(OTf), 1030s, 1150s, 1270s cm^{-1} [18]. Anal. Found: C, 50.92; H, 7.06. $C_{25}H_{42}O_3SF_3Au$ calcd.: C, 51.11; H, 7.21%.

(trans-C_8H_{14})$_3$AgOTf

A benzene solution of $AgOTf(C_6H_6)_{0.5}$ (300 mg) was treated with *trans*-cyclooctene (0.40 ml) at room temperature. The white precipitate was filtered off, and the solution after concentration produced a colorless solid which was recrystallized from acetone (needles). Yield, 0.54 g. m.p. 126—128°C (dec.). IR: ν(C=C), 1590w cm^{-1}; ν(OTf), 1030s, 1130s, 1270s cm^{-1}. Anal. Found: C, 44.44; H, 6.33. $C_{25}H_{42}O_3SF_3Ag$ calcd.: C, 44.38; H, 6.26%.

Reaction of (trans-C_8H_{14})AuCl with methyl fluorosulfate

A solution of (*trans*-cyclooctene)AuCl (25 mg) in benzene (0.5 ml) was treated with excess MeO_3SF (ca. 0.5 ml) at room temperature in the presence of free *trans*-cyclooctene (0.1 ml). After standing one day, colorless crystals were deposited from the colorless solution. Filtration followed by washing with n-pentane several times and drying in vacuo afforded *trans*-cyclooctenegold fluorosulfate. NMR: δ 5.15 ppm (olefinic proton), IR: ν(C=C), 1540vw cm^{-1}; ν(SO_3F), 1280s, 1310sh cm^{-1}. No ν(Au—Cl) was observed. A significant amount of methyl chloride (which was not measured quantatively) was detected by gas chromatography. Further treatment of *trans*-cyclooctenegold fluorosulfate (obtained above) with excess methyl fluorosulfate at room temperature for two days in the absence of solvent led to a black precipitate and free *trans*-cyclooctene. Alternatively, *trans*-cyclooctenegold fluorosulfate was treated with methyl iodide at —20°C for one day. The starting material could be recovered and recrystallized.

Treatment of chloro(*trans*-cyclooctene)gold with methyl triflate under conditions similar to that described above led only to a black solution indicative of the decomposition of gold. The mixture was not analyzed further.

Reactions of (trans-C_8H_{14})AuCl, and (cis-C_8H_{14})AuCl with triphenylphosphine

(*cis*-C_8H_{14})AuCl (77.7 mg) dissolved in benzene (3 ml) in the presence of free *cis*-cyclooctene was treated with triphenylphosphine (64 mg). By adding n-pentane (3 ml) to the colorless solution, colorless crystals were formed. M.p. 243—244°C (lit. 242—243°C for (PPh_3)AuCl [10]). The same product was obtained by the reaction of (*trans*-C_8H_{14})AuCl or AuCl with triphenylphosphine.

Reaction of (trans-C_8H_{14})AuCl with trifluoroacetic acid

Excess trifluoroacetic acid did not react with (*trans*-C_8H_{14})AuCl in benzene at room temperature. Only the starting material was recovered, and stoichiometric amounts of triflic acid reacted with (*trans*-C_8H_{14})AuCl in benzene to give Au metal and a black material. Free *trans*-cyclooctene was detected by gas chromatography.

Attempted preparation of L_nAuOTf ($L = PPh_3$, $n = 0, 1, 2$)

A solution of $AgOTf(C_6H_6)_{0.5}$ (0.25 g) in ethanol (15 ml) was treated with $(PPh_3)_2AuCl$ (0.95 g) in ethanol (200 ml). The white precipitate (AgCl) was filtered and the solution concentrated under reduced pressure to give a white solid which was recrystallized from a mixture of acetone and n-pentane. M.p. 190—192°C. IR: ν(OTf), 1030s, 1280s, 1310s cm^{-1} [18]. Found: Au, 21.6. $C_{37}H_{15}AuP_2F_3SO_3$ calcd.: Au, 22.6%.

A solution of $AgOTf(C_6H_6)_{0.5}$ (0.30 g) in a mixture of dichloromethane and acetone was treated with a solution of (PPh_3)AuCl (0.50 g) in the same solvent to give a white precipitate (AgCl). After working up the mixture by the same procedure as described above, only a purple solid was obtained. A suspension of aurous chloride (232 mg) in either acetone or benzene was mixed with AgOTf-$(C_6H_6)_{0.5}$ (260 mg) at room temperature to give a white precipitate and black solid within 30 min.

Attempted preparation of gold(I) triflate from the cyclohexene complex

Cyclohexene (1 ml) was added to a suspension of aurous chloride (500 mg) in ether (20 ml) at 0°C under nitrogen to give a slightly yellow solution, together with a small amount of black precipitate. The mixture was filtered and the volume of the yellow solution was reduced in vacuo to give colorless crystals [5b] (the complex decomposed on drying even at -20°C). $(C_8H_{14})AuCl$ so obtained was treated with a slight excess of AgOTf in ether at 0°C to give a white precipitate and a slightly yellow solution. After filtration, the solution was pumped to dryness at 0°C but only produced a black semi-solid.

Alternatively, a heterogeneous mixture of AgOTf (700 mg) in ether was added to an ethereal solution of (cyclohexene)AuCl (which was prepared from AuCl (510 mg) and cyclohexene (1.0 ml) in ether (30 ml)). The reaction under a nitrogen atmosphere gave an immediate white precipitation at 0°C. After filtration, the solvent was carefully removed in vacuo at 0°C from the solution. However, only a black solid was obtained.

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