*Journal of Organometallic Chemistry*, 190 (1980) 403—416
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# TERMINAL ACETYLENE-SILVER TRIFLUOROMETHANESULFONATE π COMPLEXES. SYNTHESIS, STOICHIOMETRY, AND ACTIVATION OF THE TERMINAL CARBON—HYDROGEN BOND

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(Received October 4th, 1979)

## Summary

Terminal acetylene—silver(I) trifluoromethanesulfonate π complexes have been isolated. They are of 1 : 1 stoichiometry in the solid state and solution with all carbon—carbon triple bonds coordinated to silver ion. Their stability constants as measured by proton NMR are strongly solvent dependent and decrease in the order 1,5-hexadiyne > 1,7-octadiyne > 1-hexyne, 3-methyl-1-pentyne > 3,3-dimethyl-1-butyne. IR and NMR analysis indicates weakening and polarization of the terminal carbon—hydrogen bond upon silver ion coordination. In solution terminal acetylenes π coordinated to silver ion undergo deuterium exchange approximately $10^5$ times faster than uncoordinated acetylenes. The mechanism of deuterium exchange does not involve silver acetylides as intermediates.

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## Introduction

Olefin-silver(I) π complexes were among the earliest π complexes extensively studied. While numerous complexes of silver(I) have been isolated, they are in general among the least stable of the transition metal π complexes [1]. Evidence for the lability of the olefinic ligand is found in the rapid equilibrium between free and complexed olefin in solution. Several variables are important in affecting the relative stabilities of olefin-silver(I) complexes. Solvent effect is of major importance. The formation constants for cyclohexene-$AgBF_4$ complexes decrease in the solvent order of $CH_2Cl_2 > CH_3NO_2 > CH_3COCH_3$ [2]. Evidence has been presented that complex stability depends upon the identity of the silver salt anion [3]. In $CD_3COCD_3$ the complex stability decreases in the anion order $CF_3SO_3^- > SbF_6^- > BF_4^-$, and it appears that olefin π complexes of silver(I) trifluoromethanesulfonate (silver triflate) are the most stable silver π complexes yet studied [4].

The silver(I) π complexes of acetylenes have been only rarely studied. This is perhaps due to initial reports indicating their stability to be no greater than that of olefin complexes. The few measurements by VPC of stability constants for internal acetylene coordination to silver ion indicated that they are intermediate in stability between the corresponding *cis* and *trans* olefins [5]. Isolated complexes of 2-butyne, 2-pentyne, and 3-hexyne with silver perchlorate and nitrate were reported to evolve acetylene spontaneously such that variable elemental analyses were obtained [6]. Investigations of terminal acetylene π complexes of silver have not been popular due to their known propensity to form explosive silver acetylides.

In contrast to these earlier observations, we have found recently that internal acetylenes form isolable and characterizable π complexes of silver triflate [4]. Stability constants of these complexes are found to be comparable to those measured for the corresponding internal olefin-silver triflate complexes.

These observations led us to a systematic study of terminal acetylene-silver(I) π complexes. In this paper we report that by selection of proper media and silver salt anion those complexes can be prepared and isolated. In addition we have determined their favored stoichiometries and found a dramatic activation of the terminal C—H bond that does not involve the intermediacy of silver acetylides.

## Experimental

All proton NMR measurements were performed on a Varian T-60 spectrometer with a probe temperature of 35°C. Chemical shifts are accurate to ±1 Hz. All NMR samples contained TMS as internal standard. Infrared spectra were recorded on Perkin-Elmer Models 597 and 297 spectrometers. Isolated complexes were analyzed as KBr pellets with no observed KBr induced decomposition. Further analyses were performed by preparation of saturated solutions of silver triflate in the acetylene, followed by spectral measurement of the resulting solutions as thin films between salt plates. All spectra were calibrated against polystyrene. Melting points were taken in sealed, evacuated capillaries and are uncorrected. Elemental analyses for C and H were performed by Galbraith Laboratories, Knoxville, Tennessee and Chemalytics, Inc., Tempe, Arizona. Analyses for Ag were performed in our laboratories by Volhard titration.

Silver triflate (Aldrich or prepared by the method of Whitesides and Gutowski [7]) was recrystallized from ethyl ether/pentane mixtures and was dried under vacuum prior to use. It was stored in darkness. The acetylenes (Farchan) were distilled from $CaH_2$, degassed with nitrogen, and stored over 3A molecular sieves. Nitromethane-$d_3$ and acetone-$d_6$ (Aldrich) were not distilled but were dried and stored like the acetylenes. Transfers were carried out in a glove bag continually flushed with dried nitrogen.

### *Preparation of 1,7-octadiyne-silver triflate I*

Silver triflate (1.0 g) was dissolved in a stoichiometric excess of 1,7-octadiyne (25 ml) under dry nitrogen. The 1,7-octadiyne was slowly evaporated at room temperature under nitrogen flow until crystallization occurred. The crystals were filtered from solution, washed with pentane, and dried to give 1.18 g

(84%) of white crystals; m.p. 88—89°C. Anal. C, 29.70; H, 2.55; Ag, 29.31. $C_9H_{10}AgF_3O_3S$ calcd.: C, 29.77; H, 2.78; Ag, 29.71%.

The 1-hexyne complex of silver triflate can be prepared by the same procedure.

*Preparation of 1-hexyne-silver triflate, II*

Silver triflate (0.6 g) was dissolved in a mixture of $CH_2Cl_2$ (10 ml) and 1-hexyne (1 ml). As nitrogen was bubbled through the solution, hexane (40 ml total) was added slowly until crystallization occurred. The white crystals were filtered from solution, washed with pentane, and dried. The yield was 0.22 g (28%); m.p. 95—96°C. Anal. Found: C, 24.60; H, 2.84; Ag, 31.83. $C_7H_{10}AgF_3O_3S$ calcd.: C, 24.80; H, 2.97; Ag, 31.82%.

*Acetylene-silver triflate $\pi$ complex stability constants*

Values of $\Delta\delta_{max}$ were obtained by measuring the difference in chemical shift of acetylenic hydrogen between uncomplexed acetylene in $CD_3NO_2$ and that of a solution of acetylene in $CD_3NO_2$ containing enough silver triflate so that some silver salt remained undissolved in solution. Values of $\Delta\delta_{obs}$ were taken as the difference in chemical shift of the acetylenic hydrogen between uncomplexed acetylene in $CD_3NO_2$ and that of a 1 : 1 solution of acetylene and silver triflate in the same solvent. In both cases, concentration of acetylene was 0.4 *M*.

*Proton chemical shift with changing silver triflate concentration*

Solutions were prepared by transfer of a sample of silver triflate to a preweighed NMR tube. The mass of added silver salt was determined by difference, followed by addition of a small portion of solvent by syringe through a serum cap on the tube. The acetylene was added by syringe to obtain the desired silver : acetylene ratio. Finally solvent was added to make the solution 0.4 *M* in silver salt. All NMR tubes were precalibrated for volume to within ±1 μl. The proton NMR spectrum was recorded for each sample.

Alternatively, qualitatively identical plots could be obtained by the following method: A weighed sample of silver triflate was transferred to an NMR tube. Solvent was added through a serum cap by syringe to give a suspension of insoluble silver salt. Aliquots of acetylene were syringed into the tube such that the concentration of silver triflate and acetylene was 0.4 *M* when they were present in a 1 : 1 ratio. The proton NMR spectrum was recorded after each addition of acetylene.

*Relative rates of deuterium exchange by NMR*

Silver triflate was added to a serum capped NMR tube. The mass of silver triflate was determined by difference. Nitromethane-$d_3$ and acetylene were injected by syringe. The relative area of acetylene terminal hydrogen absorption was measured relative to the area of adjacent $CH_2$ group absorption. Enough acetic acid-$d_4$ was added to the NMR tube to give a 1 : 1 : 1 ratio of silver triflate: C≡C : acetic acid-$d_4$. Immediately after acid addition the spectrum was repeatedly integrated as rapidly as possible (average of once every 25 seconds) to record the changing area of terminal hydrogen absorption versus constant absorption area of adjacent $CH_2$ group. After the reaction reached equilibrium, the solution molarity was determined by measurement of final solution volume in the precalibrated NMR tube.

The reactions without silver salt were identical to the above except silver triflate was omitted.

*Relative rates of silver acetylide formation by NMR*

The above procedure for measuring relative rate of deuterium exchange was followed except: a) the addition of acetic acid-$d_4$ was omitted, b) final volume could be measured before analysis rather than after, and c) the change in area ratio of acetylenic terminal hydrogen absorption to adjacent $CH_2$ group absorption was measured over a period of days. The product silver acetylides were soluble although some darkening of the solutions occurred over a period of days even when the samples were stored in the dark.

## Results and discussion

*Synthesis*

The π complexes 1,7-octadiyne-silver triflate, I, and 1-hexyne-silver triflate II have been prepared and isolated. They can be prepared by either of two general methods: Either silver triflate is dissolved in a minimum amount of a 10% acetylene/$CH_2Cl_2$ solution, followed by addition of hexane to afford the white crystalline complexes, or the complexes can be prepared by dissolving silver triflate in an excess of the acetylene, followed by evaporation of the acetylene at room temperature in a stream of dry nitrogen until the complex precipitates. The π complexes are all of 1 : 1 stoichiometry in the solid state as determined by combustion analysis and Volhard titration. If cooled, the reaction mixtures form uncharacterized solids of greater than 1 : 1 acetylene to silver stoichiometry. Upon warming to room temperature these complexes slowly evolve some of their acetylene ligand. The 1 : 1 complexes are air and light stable over a period of days but eventually suffer partial loss of ligand upon standing. They melt sharply without detonation.

The thermodynamic stability to loss of ligand appears related to extent of alkyl substitution adjacent to the carbon—carbon triple bond. We have isolated the complex 3,3-dimethyl-1-butyne-silver triflate, III, but it loses ligand rapidly at room temperature such that reproducible analysis is impossible.

*Spectroscopic analysis*

Spectroscopic analysis establishes the π complex rather than silver acetylide nature of the complexes. Upon silver ion coordination the C≡C stretching frequency is reduced (Table 1) similarly to that reported for internal acetylene π complexes of silver triflate (29—53 $cm^{-1}$) [4]. The terminal C—H stretching absorption is not diminished in intensity but is reduced in frequency and exhibits significant broadening (Fig. 1). In the proton NMR all protons are deshielded upon silver ion coordination, with the extent of deshielding decreasing with distance (Table 2). The terminal hydrogen is most deshielded (Fig. 2), and the intensity of its absorption in the silver complex is not reduced compared to the uncoordinated acetylene.

TABLE 1

INFRARED STRETCHING FREQUENCIES (cm$^{-1}$) FOR UNCOORDINATED AND SILVER(I) TRIFLATE COORDINATED ACETYLENES

| Acetylene | $C_{sp}$—H Stretch | | C≡C Stretch | |
|---|---|---|---|---|
| | Uncoordinated Acetylene | Coordinated Acetylene | Uncoordinated Acetylene | Coordinated Acetylene |
| 1-Hexyne | 3307 | 3204 | 2118 | 2067 |
| 3-Methyl-1-pentyne | 3308 | 3218 | 2112 | 2052 |
| 3,3-Dimethyl-1-butyne | 3311 | 3222 | 2102 | 2049 |
| 1,5-Hexadiyne | 3295 | 3210 | 2120 | 2072 |
| 1,7-Octadiyne | 3291 | 3239 | 2118 | 2055 |

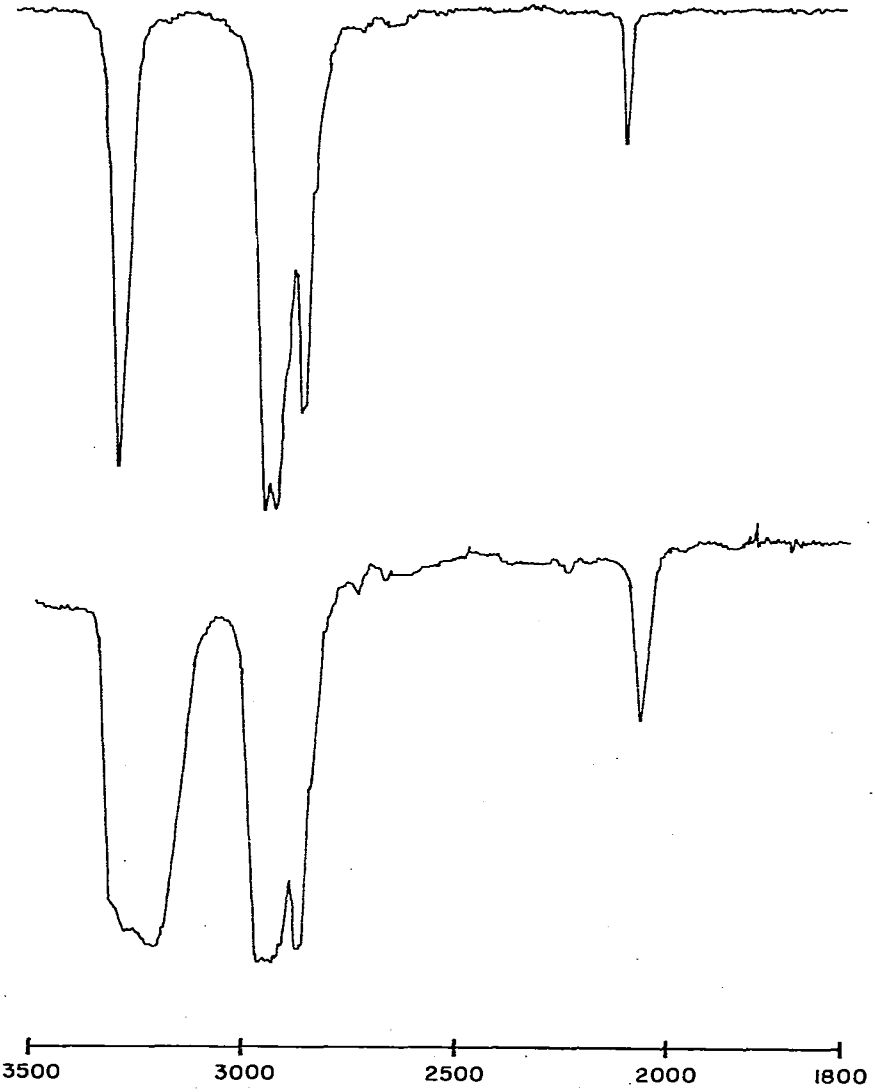


Fig. 1. Infrared spectrum of uncoordinated 1-hexyne (upper spectrum); 1-hexyne-silver triflate (lower spectrum).

TABLE 2

PROTON NMR CHEMICAL SHIFTS AND STABILITY CONSTANTS OF ACETYLENE $\pi$ COMPLEXES OF SILVER(I) TRIFLATE

| Compound | Chemical shift ($\delta$) of proton type | | | | | |
|---|---|---|---|---|---|---|
| | Terminal H | $\alpha$ $CH_2$ | $\alpha$ CH | $\beta$ $CH_3$ | $\beta$ $CH_2$ | Stability constants [a] |
| 1-Hexyne | 2.10 | 2.26 | | | 1.56 | |
| 1-Hexyne [b] | 3.53 | 2.67 | | | 1.67 | 1479 |
| 1-Hexyne [c] | 3.59 | 2.67 | | | 1.67 | |
| 3-Methyl-1-pentyne | 2.24 | | 2.49 | 1.18 | 1.46 | |
| 3-Methyl-1-pentyne [b] | 3.62 | | 2.83 | 1.33 | 1.62 | 1380 |
| 3-Methyl-1-pentyne [c] | 3.68 | | 2.87 | 1.35 | 1.63 | |
| 3,3-Dimethyl-1-butyne | 2.21 | | | 1.21 | | |
| 3,3-Dimethyl-1-butyne [b] | 3.57 | | | 1.38 | | 496 |
| 3,3-Dimethyl-1-butyne [c] | 3.67 | | | 1.40 | | |
| 1,5-Hexadiyne | 2.23 | 2.48 | | | | |
| 1,5-Hexadiyne [b] | 3.52 | 2.91 | | | | 2681 |
| 1,5-Hexadiyne [c] | 3.56 | 2.93 | | | | |
| 1,7-Octadiyne | 2.14 | 2.27 | | | 1.65 | |
| 1,7-Octadiyne [b] | 3.30 | 2.57 | | | 1.82 | 2176 |
| 1,7-Octadiyne [c] | 3.34 | 2.59 | | | 1.83 | |
| 1,7-Octadiyne [d] | 2.34 | 2.28 | | | 1.65 | |
| 1,7-Octadiyne [e] | 2.90 | 2.37 | | | 1.70 | 14.2 |
| 1,7-Octadiyne [f] | 3.19 | 2.44 | | | 1.75 | |

[a] Using chemical shift of the terminal proton. [b] Acetylene-silver triflate (1:1) in $CD_3NO_2$ (0.4 *M*). [c] Acetylene-silver triflate (1:1) in $CD_3NO_2$ (saturated solution). [d] Acetylene in $CD_3COCD_3$. [e] Acetylene-silver triflate (1:1) in $CD_3COCD_3$ (0.4 *M*). [f] Acetylene-silver triflate (1:1) in $CD_3COCD_3$ (saturated solution).

*Stability constants*

From measurement of chemical shift, stability constants can be determined using the method of Solodar and Petrovich [2]. For 1 : 1 complexes

$$K = \frac{\dfrac{\Delta\delta_{\text{obsd}}}{\Delta\delta_{\text{max}}}\,[\text{complex}]}{\left(\dfrac{\Delta\delta_{\text{max}} - \Delta\delta_{\text{obsd}}}{\Delta\delta_{\text{max}}}\,[\text{complex}]\right)^2} \qquad (1)$$

where $\Delta\delta_{\text{obsd}}$ is the downfield chemical shift at a given complex concentration, $\Delta\delta_{\text{max}}$ is the maximum downfield chemical shift in a solution saturated with complex, and [complex] is the total molarity of the acetylene-silver triflate $\pi$ complex. Using the data in Table 2 and the above equation, stability constants have been calculated and are presented in Table 2.

Chemical shifts of protons on carbons $\alpha$ and $\beta$ to the carbon—carbon triple bonds are not acceptable for stability constant calculations because the differences between $\Delta\delta_{\text{obsd}}$ and $\Delta\delta_{\text{max}}$ are approximately 0.02 ppm (1.2 Hz). Since the accuracy of chemical shift measurement with our spectrometer is ±1 Hz, the potential errors in using those chemical shifts are significant. It is thought that stability constant calculations are most accurate when based upon terminal acetylenic protons that exhibit greater differences in chemical shift.

Using the terminal proton chemical shifts, the complex stabilities are seen to depend upon the extent of substitution on the carbon $\alpha$ to the carbon—carbon

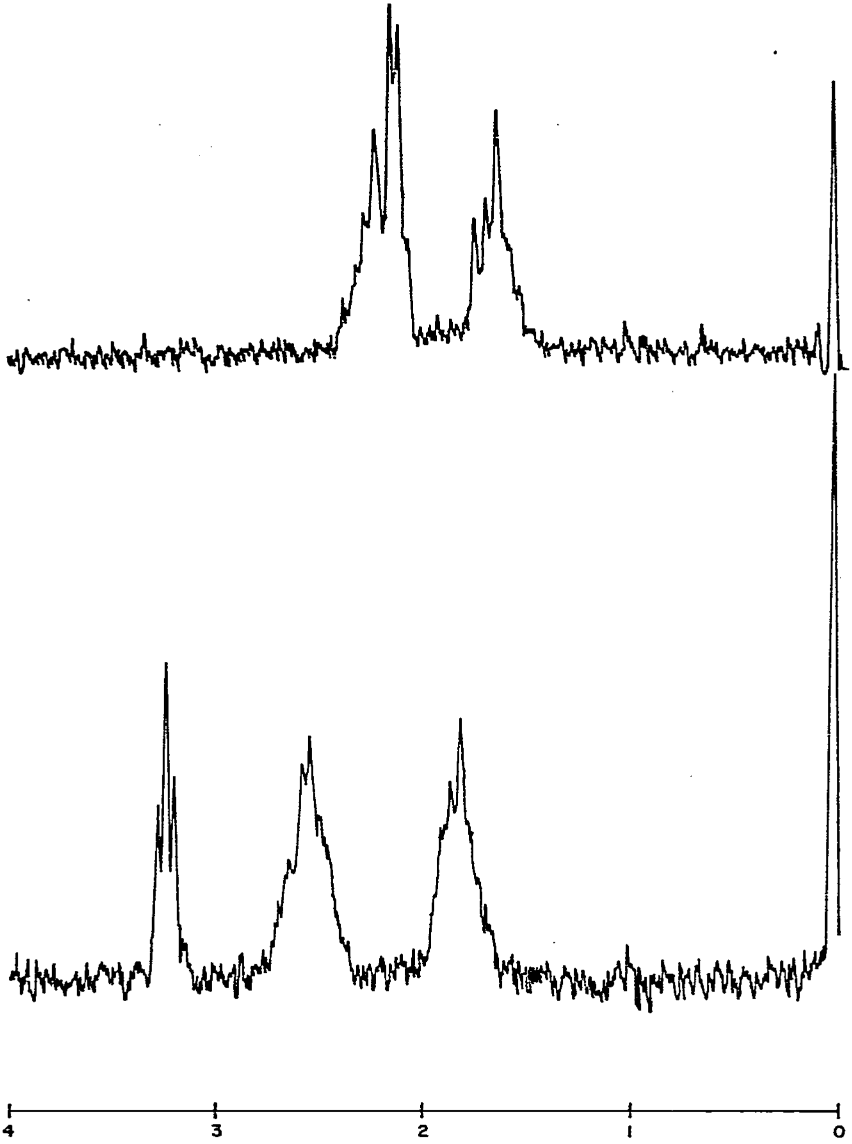


Fig. 2. Proton NMR spectrum of uncoordinated 1,7-octadiyne in $CD_3NO_2$ (upper spectrum); 1,7-octadiyne-silver triflate in $CD_3NO_2$ (lower spectrum).

triple bond. There is no difference in complex stability within experimental error between ligands with one alkyl group on the adjacent carbon (1-hexyne) and ligands with two alkyl groups adjacent (3-methyl-1-pentyne). However, with three alkyl groups on the adjacent carbon (3,3-dimethyl-1-butyne) there is a significant decrease. This is in contrast to previous measurements of olefin-silver nitrate complexes by VPC in which a more regular decrease in complex stability was found with increasing alkyl substitution on the carbon $\alpha$ to the double bond [5]. The discrepancy may be due to the difference in salts or solvents used in the two methods (silver triflate/$CD_3NO_2$ and silver nitrate/$HOCH_2CH_2OH$). More specifically, the steric effect of the third alkyl group may be more important if silver ion maintains some degree of contact ion pairing with anion during $\pi$ coordination. The extent of ion pairing between silver triflate and silver nitrate would be expected to differ. Also, the known tendency of terminal acetylenes to hydrogen bond [8] may affect the extent of asymmetry in silver ion coordination when the hydrogen bond donor changes from $CD_3NO_2$ to $HOCH_2CH_2OH$. Similarly to previously observed increasing stability of internal diyne compared to internal monoyne complexes of silver [4], 1,7-octadiyne and 1,5-hexadiyne-silver triflate complexes are more stable than those of 1-hexyne, 3-methyl-1-pentyne, and 3,3-dimethyl-1-butyne.

The stability constants are dependent upon solvents used for chemical shift measurement. Our earlier measurements with internal acetylenes were in $CD_3COCD_3$ [4]. The current measurements are in $CD_3NO_2$. This is because the rate of silver acetylide formation is solvent dependent. For 1,7-octadiyne-silver triflate complex solutions (0.4 *M*), the half-life of acetylide formation is 11 hours in $CD_3COCD_3$ and is 20 days in $CD_3NO_2$. Thus, $CD_3NO_2$ was chosen in order to minimize effect of acetylide formation upon measured chemical shift. However, in the case of 1,7-octadiyne-silver triflate the stability constants were measured in both $CD_3NO_2$ and $CD_3COCD_3$. The value of 14.2 in $CD_3COCD_3$ is significantly smaller than that of 2176 measured in $CD_3NO_2$. A decrease in stability constant with this solvent change at approximately the same concentration was reported previously for the cyclohexene-silver tetrafluoroborate system [2].

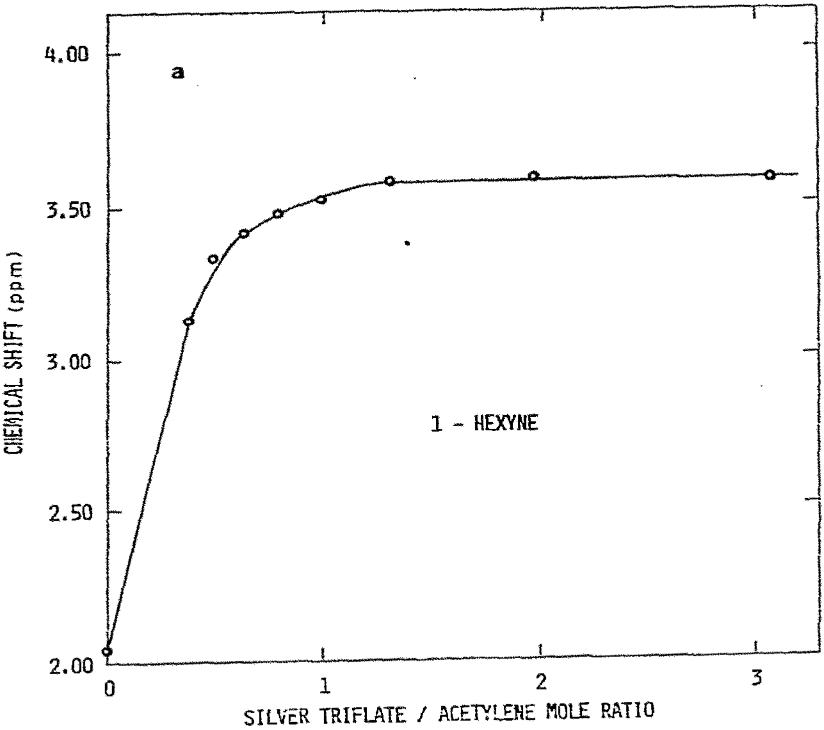
### *Solution stoichiometry*

The above analysis is valid only if the $\pi$ complexes are of 1 : 1 stoichiometry in solution. A 1 : 1 composition in the solid state does not necessarily demand the same in solution. The change in proton NMR chemical shift of terminal hydrogen with changing silver triflate : acetylene ratio has been measured for a series of terminal acetylenes. Plots of these data are shown in Fig. 3. With other silver salt complexes it has been shown that a breakpoint in the plot is indicative of the stoichiometry of the major species in solution [9]. It can be seen from the plots that in solution the favored ratio of terminal acetylene to silver triflate is 1 : 1. In fact, complete solution of silver triflate does not occur until the 1 : 1 ratio is reached.

The appearance of 1 : 1 complexes of both monoynes and diynes with all triple bonds coordinated implies variable coordination number of the silver ion. While the factors responsible for variable coordination are not clear, it appears to be common to Group IIB metals. For example, both cyclohexene-silver tetrafluoroborate [2] and (cyclohexene)$_2$-silver tetrafluoroborate [10] are known. Copper(I) may be monocoordinated [norbornylene-CuOTf], dicoordinated [1,5-cyclooctadiene-CuOTf], or tricoordinated [tris(*trans*-cyclooctene)-CuOTf] with all C=C coordinated to $Cu^+$ [11a,b]. Gold(I) also exhibits variable coordination number with *trans*-cyclooctene [11c].

### *C—H bond activation*

The reduction in terminal C—H bond stretching frequency upon $\pi$ coordina-


a
1 - HEXYNE
CHEMICAL SHIFT (ppm)
4.00
3.50
3.00
2.50
2.00
0
1
2
3
SILVER TRIFLATE / ACETYLENE MOLE RATIO

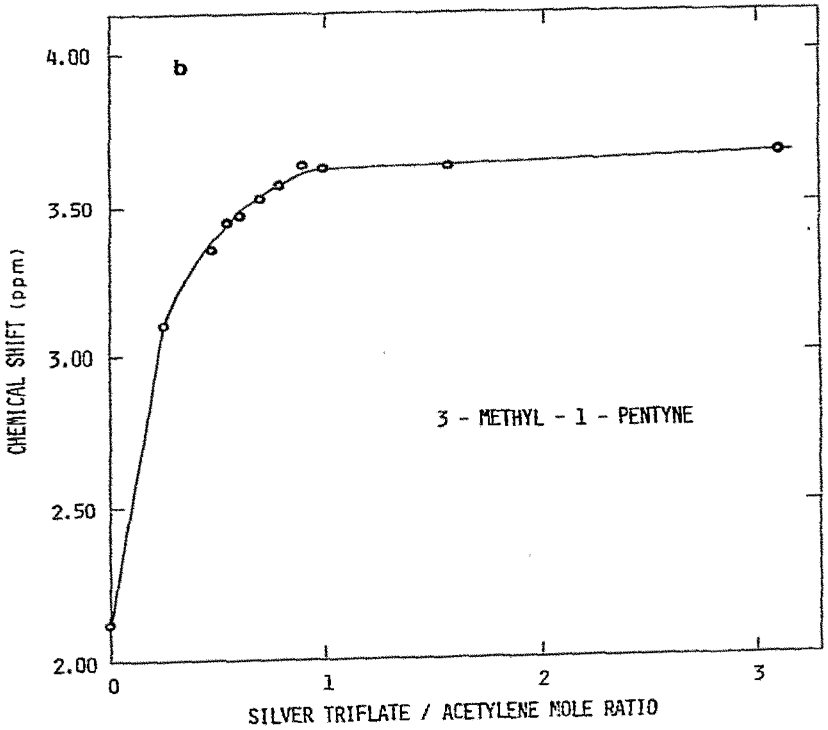

b
3 - METHYL - 1 - PENTYNE
CHEMICAL SHIFT (ppm)
4.00
3.50
3.00
2.50
2.00
0
1
2
3
SILVER TRIFLATE / ACETYLENE MOLE RATIO

Fig. 3. a and b.

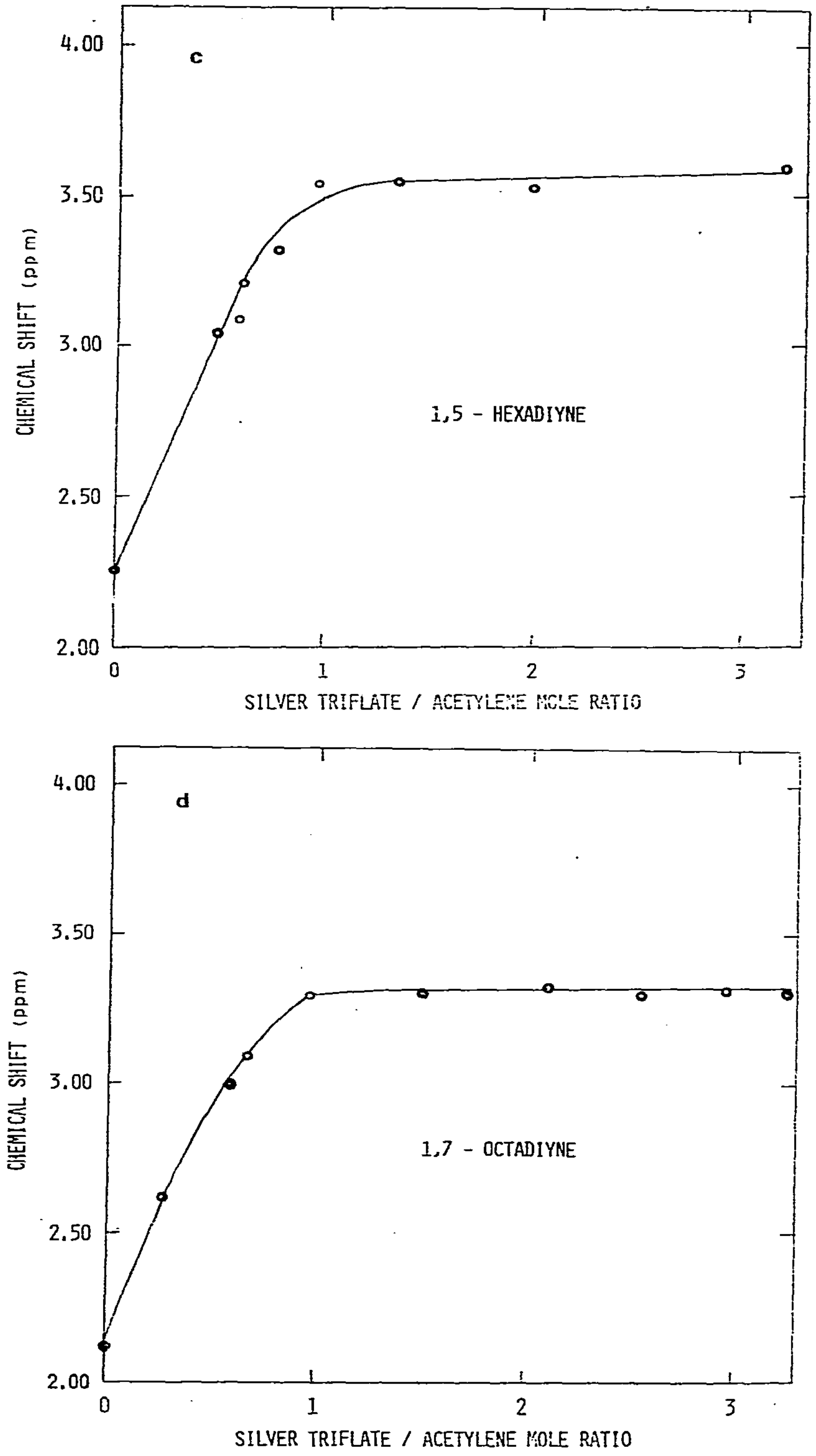

c
1,5 - HEXADIYNE
CHEMICAL SHIFT (ppm)
4.00
3.50
3.00
2.50
2.00
0
1
2
3
SILVER TRIFLATE / ACETYLENE MOLE RATIO
d
1,7 - OCTADIYNE
CHEMICAL SHIFT (ppm)
4.00
3.50
3.00
2.50
2.00
0
1
2
3
SILVER TRIFLATE / ACETYLENE MOLE RATIO

**Fig. 3.** c and d.

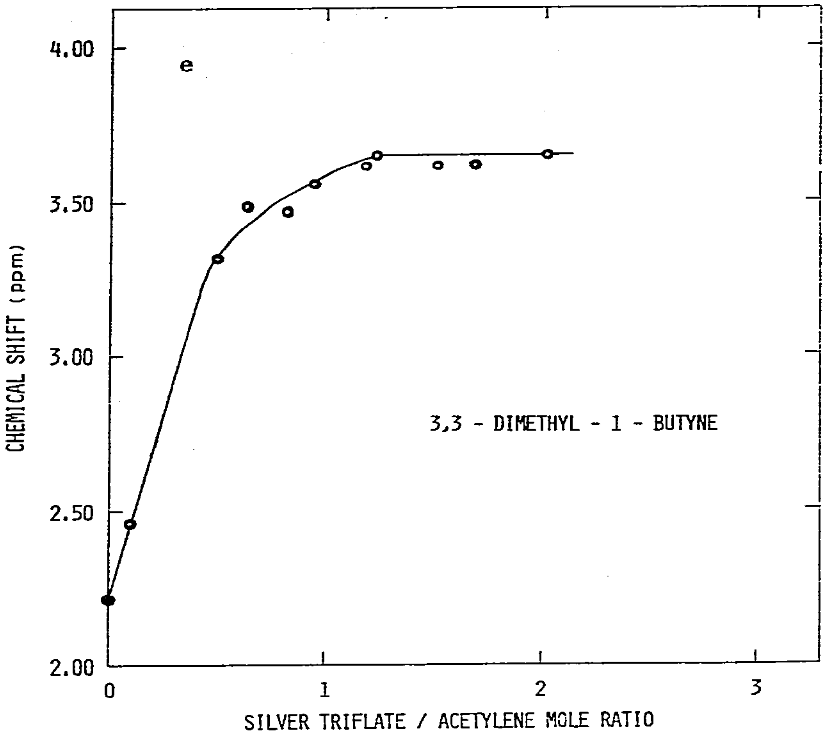
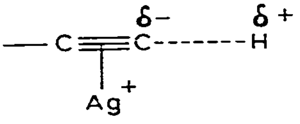


Fig. 3. Change in proton NMR chemical shift of acetylene terminal proton with varying amounts of silver triflate in $CD_3NO_2$. Chemical shift is downfield from TMS.

tion by silver ion indicates a concomitant weakening of that bond. The proton NMR spectrum shows a deshielding of the terminal hydrogen atom with π coordination. By themselves, these observations suggest electronic changes at the C—H bond caused by silver ion coordination similar to that expected in the activated complex for its heterolytic cleavage IV. Thus, silver ion coordination



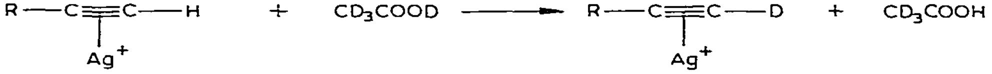
$$-C\equiv\overset{\delta-}{C}\cdots\cdots\overset{\delta+}{H}$$
$$\quad\;|\; Ag^{+}$$

(IV)

might be expected to increase the acidity of a terminal acetylene.

In order to complete the evidence for polarization of the terminal C—H bond, it would be desirable to demonstrate a silver ion induced increase in electron density at the terminal carbon. Previous carbon-13 NMR studies with terminal acetylenes have shown consistent upfield shifts of terminal carbon atoms caused by silver ion [12]. These upfield shifts range from 2.5 to 4.6 ppm. While it is tempting to interpret these carbon shift data as support for bond polarization, this is impossible at present due to our lack of knowledge regarding the relative importance of electron density in determining the total paramagnetic effect upon carbon screening [13]. Nonetheless, because of the partial evidence for bond weakening by polarization *, we have proceeded with experimental probes to determine possible silver ion induced bond activation.

The usual methods of measuring relative acetylene activation by ionization acidity involve reaction with cyclohexylamine/lithium cyclohexylamide [14] or $D_2O/Et_3N/DMF$ [15]. These methods are not applicable with the silver $\pi$ complexes due to the strong affinity of amine bases for silver ion. In our hands, all coordination of silver ion to the carbon—carbon triple bond is lost under these conditions. The method that we have developed is based upon the chance observation while obtaining NMR spectra in $CD_3COOD$ that the $\pi$ complex undergoes rapid deuterium exchange at the terminal carbon in the absence of added base. Precedent for the exchange is found in the passing observation by Vestin et al. that in $DCl/CuCl/D_2O$ solutions, acetylene undergoes deuterium exchange [16].

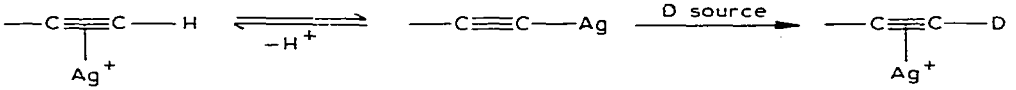


$$\underset{\mathrm{Ag^+}}{\mathrm{R{-}C{\equiv}C{-}H}} + \mathrm{CD_3COOD} \longrightarrow \underset{\mathrm{Ag^+}}{\mathrm{R{-}C{\equiv}C{-}D}} + \mathrm{CD_3COOH} \qquad (2)$$

Our method of analysis involves measurement of rates of exchange of D for H in the terminal acetylene-silver triflate $\pi$ complexes. The reactions are carried out in $CD_3NO_2$ in order to use the known solvent effect of $CD_3NO_2$ [2] to minimize $\pi$ complex dissociation. Enough $CD_3COOD$ is added to the solution to give a 1 : 1 ratio of $CD_3COOD$ to $\pi$ complex, and the rate of disappearance of the terminal hydrogen is monitored by proton NMR as a function of time. A typical plot of disappearance of terminal hydrogen versus time is shown in Fig. 4. The times required to reach equilibrium (eq. 2) are reported in Table 3 for a series of acetylene $\pi$ complexes. In all cases D exchange equilibrium is reached in 4.7 to 10.2 minutes. These reactions can be compared with that of 1,7-octadiyne under the same conditions without silver triflate. Uncoordinated 1,7-octadiyne undergoes only 17% D exchange in 764 days. This represents a D exchange rate enhancement for 1,7-octadiyne-silver triflate of $1.1 \times 10^5$. Because of the very long reaction times without silver ion, we have measured the extended time rate of D exchange without silver for 1,7-octadiyne only. However, short reaction times (approximately 1 week) for the other acetylenes without silver ion show negligible D exchange. Thus, the dramatic rate enhancement is common to all of the acetylenes.

It should be noted that the actual rate enhancement promoted by silver ion may be much larger than $10^5$. This is because the mechanism for the unpromoted process may be different from that with silver ion. For that reason $10^5$ should be considered only a minimum value.

A possible mechanism for D exchange could be postulated to involve prior formation of silver acetylide (eq. 3).



$$\underset{\mathrm{Ag^+}}{\mathrm{{-}C{\equiv}C{-}H}} \underset{-\mathrm{H^+}}{\rightleftharpoons} \mathrm{{-}C{\equiv}C{-}Ag} \xrightarrow{\text{D source}} \underset{\mathrm{Ag^+}}{\mathrm{{-}C{\equiv}C{-}D}} \qquad (3)$$

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* As further evidence of C—H polarization we have observed that phenylacetylene-silver triflate in $CD_3NO_2$ more strongly hydrogen bonds to donors like DMF than does uncoordinated phenylacetylene.

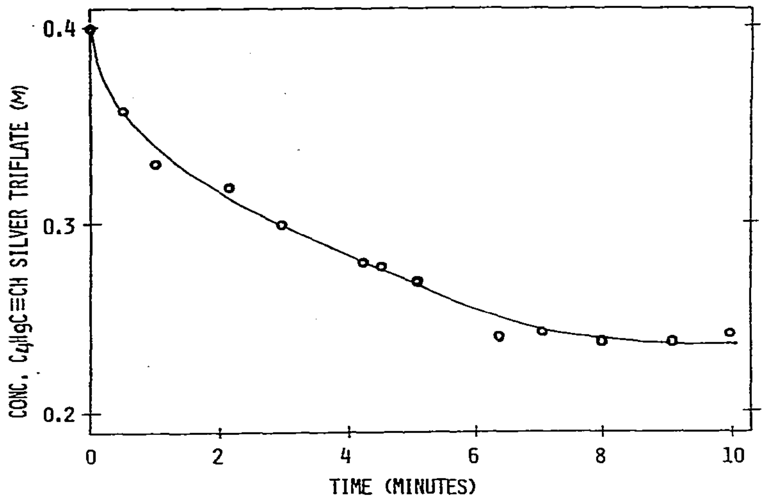

Fig. 4. Change in concentration of 1-hexyne-silver triflate versus time during deuterium exchange with $CD_3COOD$. The $CD_3NO_2$ solutions were initially 0.4 *M* in 1-hexyne-silver triflate and 0.4 *M* in $CD_3COOD$.

However, these intermediates can be eliminated as precursors to D exchange on the basis of the data in Table 3. Silver acetylide formation does occur in the absence of $CD_3COOD$, but it is a slow reaction compared to the rate of D exchange with $CD_3COOD$. This would eliminate step 1 of eq. 3 in which the equilibrium lies to the side of silver acetylide formation as the rate determining step. It could be argued that silver acetylide formation occurs rapidly, but the step 1 equilibrium lies far to the left. However, this argument is inconsistent with the observation that significant silver acetylide formation can occur over a comparatively long period of time.

While we have rationalized the rapid activation of the terminal C—H bond with spectral evidence predicting increased acidity, we do not wish to state that

TABLE 3

RELATIVE RATES OF DEUTERIUM EXCHANGE WITH $CD_3COOD$ AND ACETYLIDE FORMATION OF ACETYLENE-SILVER TRIFLATE π COMPLEXES [a]

| Compound | % D Exchange [b] | Time (min) | % Silver Acetylide Formation [c] | Time (min) |
|---|---|---|---|---|
| 1-Hexyne-AgOTf | 40 | 6.3 | 64 | 44,640 |
| 3-Methyl-1-pentyne-AgOTf | 39 | 4.7 | 21 | 9,000 |
| 3,3-Dimethyl-1-butyne-AgOTf | 43 | 7.9 | 20 | 4,500 |
| 1,5-Hexadiyne-AgOTf | 38 | 9.8 | 25 | 11,940 |
| 1,7-Octadiyne-AgOTf | 38 | 10.2 | 27 | 40,320 |
| 1,7-Octadiyne | 17 | $1.1 \times 10^6$ | — | — |

[a] All reactants were 0.4 *M* in $CD_3NO_2$. [c] For monoynes, the monoyne:$CD_3COOD$ ratio was 1:1. For diynes, the diyne:$CD_3COCD$ ratio was 1:2. In the absence of isotopic effects the maximum percent deuterium exchange is 50%. [c] The maximum amount of silver acetylide formation is 100% with monoynes and 50% with diynes.

the exchange of deuterium necessarily involves the simple, unimolecular ionization of the $\pi$ complex as the rate determining step shown in eq. 4.

$$\mathrm{R{-}\underset{Ag^+}{C{\equiv}C}{-}H} \longrightarrow \mathrm{R{-}\underset{Ag^+}{C{\equiv}C^-}} + \mathrm{H^+} \qquad (4)$$

In fact Kresge has shown that phenylacetylene undergoes base-catalyzed isotopic exchange in which a diffusion or rotation step following proton transfer is the rate determining step [17]. There are a number of alternative mechanisms that could incorporate deuterium, and only a detailed kinetic analysis will distinguish between them. The results of such an analysis will give hopefully an explanation of this enhanced hydrocarbon activation and will lead ultimately to its application in organic synthesis.

## Acknowledgement

Support of this work by the Research Corporation and Central Michigan University is gratefully acknowledged. We thank Robert D. Gilman for performing the hydrogen bonding experiment and Professor J.P. Lorand for helpful discussions.

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