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SILVER(I) TRIFLUOROMETHANESULFONATE π-COMPLEXES OF OLEFINS AND ALKYNES. STABILITY AND STRUCTURE

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Summary

The decrease in chemical shift of the vinylic protons of cyclohexene with increasing silver(I) salt concentration indicates that extent of olefin π-complexation to silver salt decreases in the order silver trifluoromethanesulfonate > silver hexafluoroantimonate > silver tetrafluoroborate. Proton NMR analysis shows that alkynes π-complex nearly as well as olefins to silver trifluoromethanesulfonate. Silver trifluoromethanesulfonate π-complexes of monoenes, dienes, trienes, monoynes, and diynes have been prepared and isolated. All complexes are 1 : 1 in the solid state and solution, and all carbon—carbon multiple bonds are coordinated to silver ion. Stability constants measured by proton NMR for the alkyne—silver trifluoromethanesulfonate complexes decrease in the order 1,8-cyclotetradecadiyne > 3-hexyne > 2-hexyne > 4-methyl-2-pentyne.

Introduction

The interaction of silver(I) salts with unsaturated hydrocarbons has been widely studied and has been the subject of extensive review [1—3]. The stabilities of the olefin—silver(I) π-complexes are affected by olefin basicity, steric effect of substituents on the olefin, solvation effects, and degree of association between Ag^+ and its anion. Stability studies in the solid state [4] and in concentrated aqueous solution [5] indicate that complex stability decreases in the anion order $SbF_6^- > BF_4^- > ClO_4^- > NO_3^-$. This order parallels the decreasing strengths of the corresponding conjugate acids: the stronger the acid, the more stable the complex containing the conjugate base of the acid as the anion.

Trifluoromethanesulfonic acid (CF_3SO_3H) is the strongest monobasic acid known [6]. Thus, the silver(I) trifluoromethanesulfonate (silver triflate) salt may exhibit even greater olefin—silver complex stability due to the diminished basicity of the triflate anion. To date the only reported π-complexes of silver triflate contain aromatic ligands [7].

While examples of olefin—silver π-complexes are legion, there is a paucity of information regarding the interaction of silver(I) ion with the carbon—carbon triple bond. It has been suggested that the silver of a silver acetylide can intermolecularly bond to a carbon—carbon triple bond [8,9], and unstable, crystalline complexes of silver nitrate and perchlorate with 2-butyne, 2-pentyne, and 3-hexyne have been reported [10].

Stability constants have been reported for alkyne—silver nitrate complexes. These stability constants have been determined by solubility methods for six alkynes [11] and by GLC methods for six alkynes [12].

In the present work we have undertaken an analysis by ^{1}H NMR to test the prediction of greater olefin—silver triflate π-complex stability. The results of our analysis have led us to examine the stability of alkyne—silver triflate π-complexes relative to olefin—silver triflate π-complexes. We have also prepared and isolated silver triflate complexes of monoenes, dienes, trienes, alkynes, and alkadiynes for comparison purposes. The stability constants of the alkyne and alkadiyne complexes are reported.

Results and discussion

NMR analysis of olefin—silver(I) complexation

The ^{1}H NMR spectra of olefins exhibit downfield shifts upon coordination of olefin to silver ion. We have found that extent of downfield shift is dependent upon the identity of the anion of the silver salt. The chemical shift of vinylic protons of cyclohexene (1.19 mmol) relative to the concentration of silver salt in CD_3COCD_3 (0.40 ml total volume) is shown in Fig. 1. The ability of the silver

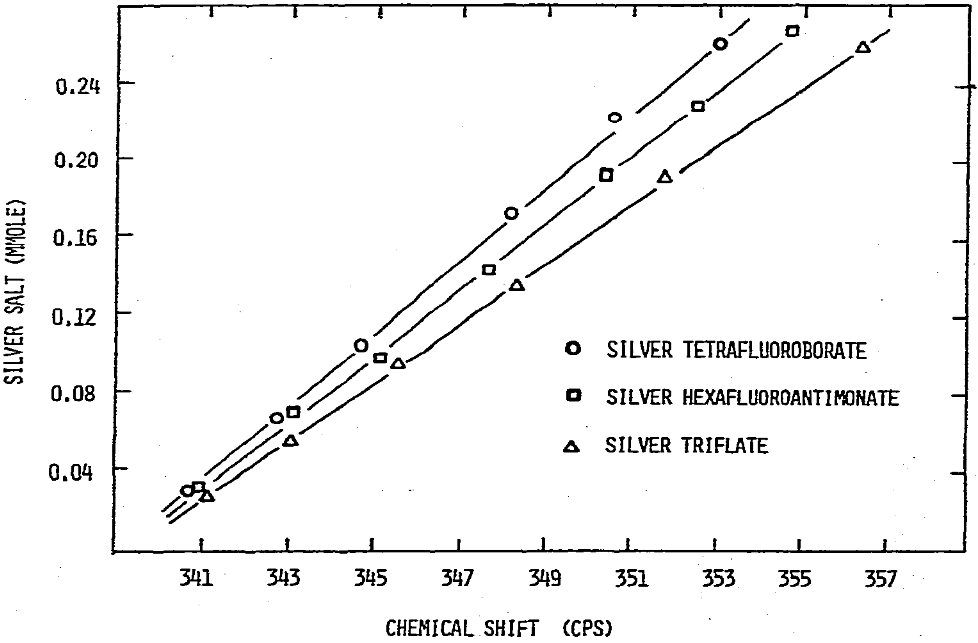


Fig. 1. Chemical shift change of cyclohexene vinylic protons with silver salt concentration in CD_3COCD_3.

salt to deshield vinylic protons (and hence complex olefin) decreases in the order silver triflate > silver hexafluoroantimonate > silver tetrafluoroborate.

The stoichiometry of the olefin—silver complex in CD_3COCD_3 is unknown; however, the linear plot of observed chemical shift versus silver ion concentration is consistent with formation of a single olefin—silver complex in much greater concentration than that of any other olefin—silver complex present. Since the measurements were made with a large excess of cyclohexene, we assume that the complex stoichiometry is one in which the maximum number of olefin molecules that silver ion can accommodate are associated with it. We find that the chemical shifts of all three complexes become constant at a 1 : 1 olefin/silver salt stoichiometry. This indicates a 1 : 1 olefin/silver salt complex formation in solution, and is consistent with the 1 : 1 complex in the solid state and the 1 : 1 complex favored in solution and in the solid state between alkyne and silver triflate (vide infra). Quinn and Van Gilder have evidence for a 2 : 1 cyclohexene/silver tetrafluoroborate complex in $CDCl_3$ [13], but results in $CDCl_3$ do not appear applicable to those in CD_3COCD_3.

Recent work by Crist et al. has shown that silver(I) ion can bond to ketones [14]. Silver tetrafluoroborate lowers the carbonyl stretching frequency and deshields the α-CH_3 protons of aliphatic and aromatic ketones. This ketone—silver ion interaction in our system with CD_3COCD_3 is markedly reduced. When silver salt in the maximum amount used for any analysis is added to acetone to make 0.40 ml of solution, the carbonyl stretching frequency is reduced, and the protons are deshielded. However, when cyclohexene (1.19 mmol) is present in the acetone—silver salt solution (0.40 ml total volume), the carbonyl stretching frequency and proton chemical shift of acetone return to normal, indicating that at the concentration of our NMR analysis cyclohexene effectively competes with acetone for coordination site(s) on silver, Also, the chemical shift and absorption intensity in the NMR of $CHCl_3$, the internal standard, are unaltered by changing silver concentration over the range of silver salt concentrations employed.

NMR analysis of silver(I) complexation to olefin and alkyne

In addition to the ^1H NMR analysis indicating that silver triflate complexes effectively to the carbon—carbon double bond of cyclohexene, we find that it shows similar ability to form a π-complex with the internal alkyne 3-hexyne. Cyclohexene and 3-hexyne (0.395 mmol each) were placed with CD_3COCD_3 (0.250 ml) and TMS in an NMR tube, and the chemical shifts of their protons were measured. Silver triflate (0.142 mmol) was added to the NMR tube, and proton chemical shifts were again measured. Finally, an excess of silver triflate was added (1.10 mmol total), and the proton chemical shifts were again measured. The NMR data are shown in Table 1. With 0.142 mmol of silver triflate the chemical shift of cyclohexene vinylic protons is 28.9% of their maximum chemical shift with excess silver triflate. However, the chemical shift of 3-hexyne CH_2 protons is 27.3% of their maximum chemical shift. Thus, in competition between 3-hexyne and cyclohexene, 3-hexyne complexes silver ion nearly as well as does cyclohexene. This conclusion is based upon the assumption that 1 : 1 organo/silver complexes are formed and that addition of an excess (1.10 mmol) of silver triflate gives the maximum chemical shift. Formation of 1 : 1

TABLE 1

^{1}H NMR CHEMICAL SHIFT DATA OF CYCLOHEXENE AND 3-HEXYNE COMPETING FOR SILVER(I) TRIFLATE [a]

Protons	Chemical shift (δ)		
	No added AgOTf	0.142 mmol added AgOTf	1.10 mmol added AgOTf
Cyclohexene vinylic	5.65	5.87	6.41
Cyclohexene allylic	1.97	2.05	2.24
3-Hexyne CH_2	2.14	2.23	2.47
3-Hexyne CH_3	1.04	1.08	1.19

[a] Silver salt added to cyclohexene and 3-hexyne (3.95×10^{-4} mol each) in CD_3COCD_3 (0.250 ml) with TMS internal standard.

complexes is supported by no observed increase in proton chemical shift at silver ion to ligand ratio greater than 1 for cyclohexene and 3-hexyne. Addition of 1.10 mmol of silver triflate does provide the maximum chemical shift, for when the chemical shift is measured with 0.790 mmol of silver triflate (one silver ion for each cyclohexene and 3-hexyne molecule) the same chemical shift is observed as with 1.10 mmol. Under the analysis conditions no isomerization or other reaction is observed. These results are in agreement with those from the GLC analysis [12] in which the stability constant of 3.6 for cyclohexene—silver nitrate is reasonably close to that of 2.6 for 3-hexyne—silver nitrate.

With observation that the ability of silver triflate to bond to alkynes is similar to its ability to bond to olefins, we undertook the study of the interaction of silver triflate with norbornene, norbornadiene, 4-vinylcyclohexene, (*E,E,Z*)-1,5,9-cyclododecatriene, 2-hexyne, 4-methyl-2-pentyne, and 1,8-cyclotetradecadiyne. A plot of chemical shift of the CH_2 protons α to the carbon—carbon triple bond vs. the silver triflate to alkyne ratio for 1,8-cyclotetradecadiyne in CD_3COCD_3 is shown in Fig. 2. The chemical shift increases up to a 1 : 1 silver triflate/alkyne ratio and then becomes constant at higher ratios. A breakpoint at the 1 : 1 silver triflate/ligand stoichiometry is also found in similar plots for the other olefins and alkynes indicating the generality of that stoichiometry.

Synthesis and properties of silver triflate π-complexes of olefins and alkynes

Since NMR analysis indicates that olefin and alkyne complexes of silver triflate are comparatively stable, we undertook the synthesis of monoene, diene, triene, monoyne, and diyne complexes. The complexes cyclohexene—silver triflate (I), norbornene—silver triflate (II), norbornadiene—silver triflate (III), 4-vinylcyclohexene—silver triflate (IV), (*E,E,Z*)-1,5,9-cyclododecatriene—silver triflate (V), 3-hexyne—silver triflate (VI), 2-hexyne—silver triflate (VII), 4-methyl-2-pentyne—silver triflate (VIII), and 1,8-cyclotetradecadiyne—silver triflate (IX) (Table 2) are easily prepared in high yield by heating silver triflate with an excess of the hydrocarbon. This method is in contrast to the preparation of olefin—copper(I) triflate complexes in which an intermediate benzene—copper(I) triflate complex must be used [15].

All of the complexes can be washed repeatedly with hydrocarbon solvent and can be subjected to vacuum without loss of the organic ligand. They may be

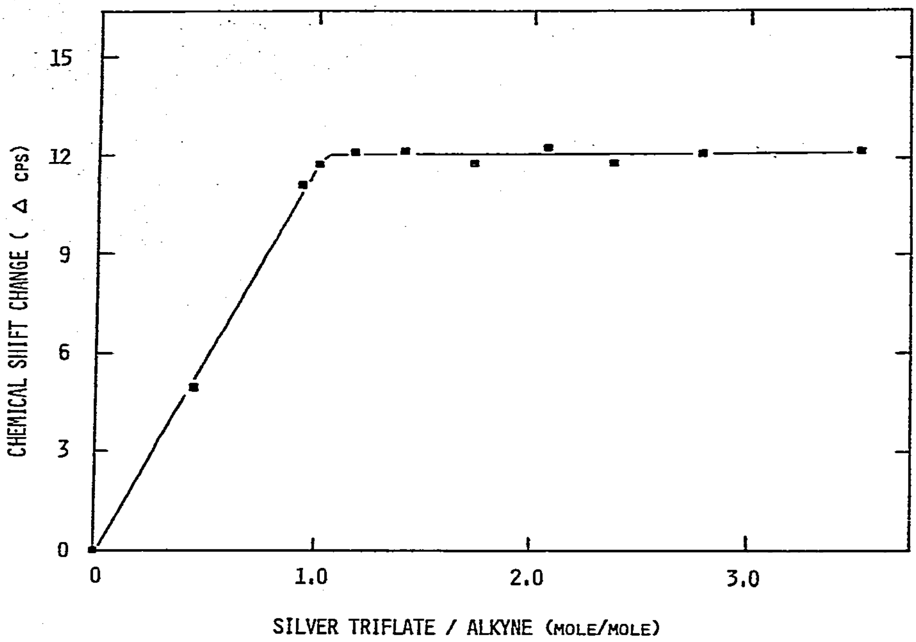
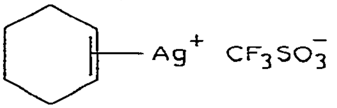
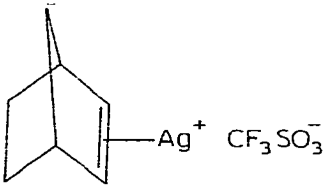


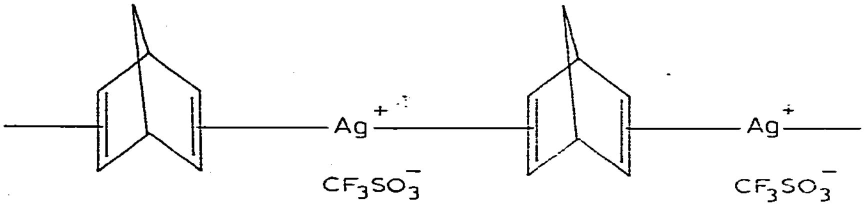
Fig. 2. Change in proton NMR chemical shift of CH_2 protons α to the carbon—carbon triple bond in 1,8-cyclotetradecadiyne with silver triflate in CD_3COCD_3 (0.300 ml). Change in chemical shift is downfield from uncomplexed 1,8-cyclotetradecadiyne absorption.



(I)



(II)



(III)

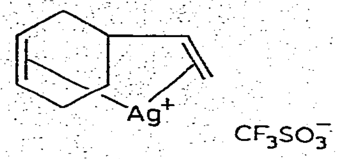
stored for months if kept in darkness and under nitrogen. All complexes slowly decompose in contact with air with the exception of IX, which is remarkably stable.

The cyclohexene—silver triflate complex (I) is the second reported example of a 1 : 1 cyclohexene complex of silver. A 1 : 1 cyclohexene—silver tetrafluoro-

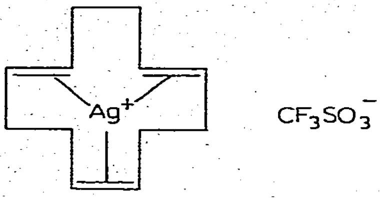
TABLE 2

OLEFIN AND ALKYNE COMPLEXES OF SILVER(I) TRIFLUOROMETHANESULFONATE

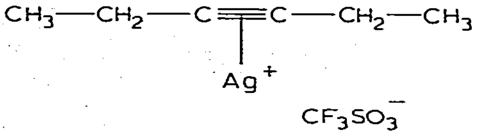
Complex	Ligand	Ligand/ silver ratio	Yield (%)	M.p. (°C)	Elemental analysis Found (calcd.) (%)		
					C	H	Ag
I	Cyclohexene	1 : 1	89	170—171	24.70 (24.80)	2.94 (2.97)	31.68 (31.81)
II	Norbornene	1 : 1	93	161—163	27.34 (27.37)	2.71 (2.87)	31.09 (30.72)
III	Norbornadiene	1 : 1	91	111 dec.	27.07 (27.53)	2.25 (2.29)	31.25 (30.90)
IV	4-Vinylcyclohexene	1 : 1	82	123—126	28.63 (29.61)	3.07 (3.31)	29.56 (29.54)
V	*E,E,Z*-1,5,9-Cyclododecatriene	1 : 1	97	113—115	36.80 (37.25)	4.25 (4.33)	25.91 (25.73)
VI	3-Hexyne	1 : 1	67	103—105	25.11 (24.80)	2.99 (2.97)	32.19 (31.81)
VII	2-Hexyne	1 : 1	38	97—98	25.21 (24.80)	2.72 (2.97)	32.49 (31.81)
VIII	4-Methyl-2-pentyne	1 : 1	67	117—118	24.87 (24.80)	2.75 (2.97)	31.53 (31.81)
IX	1,8-Cyclotetradecadiyne	1 : 1	58	155—159 dec.	40.26 (40.46)	4.50 (4.53)	24.23 (24.23)



(IV)

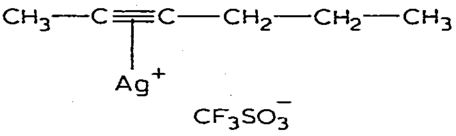


(V)



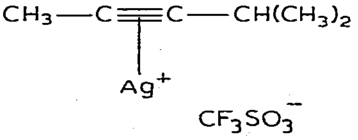
$CH_3-CH_2-C\equiv C-CH_2-CH_3$ Ag^+ $CF_3SO_3^-$

(VI)



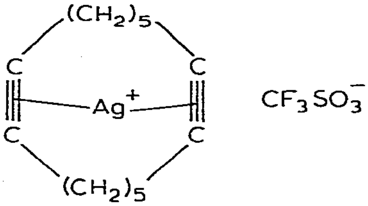
$CH_3-C\equiv C-CH_2-CH_2-CH_3$ Ag^+ $CF_3SO_3^-$

(VII)



$CH_3-C\equiv C-CH(CH_3)_2$ Ag^+ $CF_3SO_3^-$

(VIII)



(IX)

borate complex that is hygroscopic and efflorescent has been reported [16], however complete NMR and IR data were not reported. The 74 cm^{-1} reduction in C=C stretching frequency of I relative to free cyclohexene (Table 3) is larger than that for dicyclohexene—silver(I) tetrafluoroborate (68 cm^{-1}) [13] and dicyclohexene—silver(I) perchlorate (71 cm^{-1}) [17].

The norbornene—silver triflate complex (II) is also a 1 : 1 complex. It is of note that the deshielding of vinylic protons in complex I is greater than in II,

TABLE 3

INFRARED C=C AND C≡C STRETCHING FREQUENCIES (cm^{-1}) FOR FREE AND SILVER(I) TRIFLATE COORDINATED OLEFINS AND ALKYNES [a]

Complex	Complexed olefin [b]	Free olefin [c]	Δ
I	1577	1651	74
II	1498	1566	68
III	1476, 1459	1541	65, 82
IV	1592, 1579	1645, 1635	53, 56
V	1593, 1580	1670, 1650	77, 70
Complex	**Complexed alkyne [b]**	**Free alkyne [c]**	**Δ**
VII	2181	2210	29
VIII	2178	2231	53

[a] Complexes VI and IX exhibited no absorption in this region. [b] Obtained in KBr pellets. No KBr induced dissociation of complex was observed. [c] Obtained in neat solution for liquids and KBr pellets for solids.

but the deshielding of allylic protons in II is greater than in I (Table 4). Similarly, Salomon and Kochi [18] have reported a deshielding of allylic protons simultaneous with a shielding of vinylic protons in norbornene—copper triflate, indicating that unusually high withdrawal of electron density from the allylic protons in cationic complexes of norbornene may be a general phenomenon. One rationale is that *exo* complexation of silver ion in II may position it closer to the allylic protons in II than in I. The work by Brown and Kawakami indicates that in solution silver ion prefers the *exo* face of norbornene for steric reasons [19], but we have no data to demand *exo* complexation and X-ray analysis would not be conclusive for structure in the solid state does not correspond perforce to that in solution. Another rationale is that back donation from *d* orbitals of silver ion into the π^* orbital of the ligand may be lesser in II than in I. This would lead to a relative decrease of the electron density in the region of the allylic protons of II.

In the 1 : 1 complex of norbornadiene—silver triflate (III), *exo* complexation of silver is suggested by the 0.28 δ deshielding of the C-7 bridge protons. This, together with a decrease in the stretching frequency of both carbon—carbon double bonds and its insolubility in ether, implies a polymeric structure with alternating silver triflate and norbornadiene units as suggested for the analogous nitrate [20] and tetrafluoroborate [21] complexes. Like norbornadiene—silver tetrafluoroborate [21], III shows two complexed C=C stretching absorptions at 1476 and 1459 cm^{-1}. The reason for the unequal coordination of both double bonds is not readily apparent.

To date no silver complexes of 4-vinylcyclohexene have been reported. The terpenoid 3-isopropenyl-4-methyl-4-vinylcyclohexene does form a 2 : 1 adduct with silver nitrate in which one silver ion is associated with the cyclohexene π-bond and the other is bonded to the vinyl and isopropenyl π-bonds [22]. In contrast the 4-vinylcyclohexene—silver triflate (IV) appears to have both π-bonds coordinated to one silver ion, for unlike polymeric complexes it is soluble in ether. Molecular models indicate a conformation of 4-vinylcyclohexene in which

TABLE 4

^{1}H NMR CHEMICAL SHIFT DATA FOR FREE AND SILVER(I) TRIFLATE COORDINATED OLEFINS [a]

Complex	Proton Type	Chemical shift (δ)		
		Complexed olefin	Free olefin	$\Delta\delta$
I	Vinylic	6.42	5.65	0.77
	Allylic	2.24	1.98	0.26
	Secondary	1.71	1.60	0.11
II	Vinylic	6.59	6.00	0.59
	Allylic	3.19	2.82	0.37
III	Vinylic	7.51	6.72	0.79
	Allylic	4.10	3.53	0.57
	C-7	2.15	1.87	0.28
IV	Vinylic (2H)	6.10	5.72	0.38
	Vinylic (3H)	5.92	5.58	0.34
V	Vinylic (2H)	5.97	5.31	0.66
	Vinylic (4H)	5.71	5.18	0.53
	Allylic	2.30	2.05	0.25

[a] Olefin—silver triflate salts (0.177 mmol) in acetone-d_6 (0.5 ml) with TMS.

the silver ion can coordinate simultaneously to both π-bonds. Further evidence for the proposed structure of IV comes from the 1 : 1 stoichiometry, the deshielding of all vinylic protons, and the reduction in stretching frequency of both carbon—carbon π-bonds.

We have isolated the 1 : 1 adduct of (*E,E,Z*)-1,5,9-cyclododecatriene with silver triflate (V). Evidence for the *hexahapto* nature of V is found in the significant reduction of stretching frequency of all three carbon—carbon π-bonds in the solid state coupled with deshielding of all vinylic protons. Both 1 : 1 and 2 : 1 complexes of (*E,E,Z*)-1,5,9-cyclododecatriene with silver nitrate have been reported [23]. The 1 : 1 complex has the two *trans* π-bonds coordinated to silver ion, but the 2 : 1 complex has only one *trans* π-bond coordinated. In both cases the *cis* π-bond is uncoordinated. Thus V more resembles the reported 1 : 1 complex with copper triflate in which the copper ion appears associated with all three π-bonds [24].

Both carbon—carbon triple bonds of 1,8-cyclotetradecadiyne—silver triflate (IX) are coordinated to silver ion. Elemental analysis eliminates any but a 1 : 1 complex, and the absence of any C≡C stretching vibration in the IR (KBr pellet) does not support an unsymmetrical structure with only one carbon—carbon triple bond coordinated to silver. King et al. have reported reaction of 1,8-cyclotetradecadiyne with pentacarbonyliron to form the tricyclic cyclopentadienyl complex $[C_{14}H_{19}Fe(CO)_2]_2$ [25], with cyclopentadienyldicarbonylcobalt to form the tricyclic cyclobutadiene complex $C_5H_5CoC_{14}H_{20}$ [26], and with cyclopentadienyldicarbonylrhodium to form the tricyclic cyclobutadiene complex $C_5H_5RhC_{14}H_{20}$ [27]. Silver triflate does not promote transannular reaction of 1,8-cyclotetradecadiyne, for upon treatment of IX with aqueous sodium chloride, 1,8-cyclotetradecadiyne is liberated in near quantitative yield. Proton NMR analysis of the preparative reaction mixture indicates no absorption due to cyclopentadienyl or cyclobutadiene compounds or their expected reaction products. The proposed structure of IX is reasonable in light of the ability of chelating ligands (1,7-octadiene and 1,9-decadiene) to form 1 : 1 complexes with silver perchlorate in which both carbon—carbon double bonds are complexed to silver [28]. Dale et al. have shown the favored conformation of 1,8-cyclotetradecadiyne to have the two carbon—carbon triple bonds spatially proximate [29], so that simultaneous coordination of both to silver ion is possible.

Stability constants of alkyne—silver triflate π-complexes

Proton chemical shifts of all alkyne—silver triflate complexes are concentration dependent (Table 5) indicating a rapid (on the NMR time scale) equilibrium 1 between free and complexed alkyne. Solodar and Petrovich [16] have deter-

$$\text{alkyne} + \text{Ag}^+\text{OTf}^- \rightleftharpoons [\text{alkyne—Ag}]^+\,\text{OTf}^- \qquad (1)$$

mined equilibrium constants by proton NMR for the equilibria between olefins and silver tetrafluoroborate and silver perchlorate using the relationship:

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

TABLE 5

^{1}H NMR DATA FOR ALKYNES AND ALKYNE—SILVER(I) TRIFLATE π-COMPLEXES

Compound	Chemical shift (δ) for proton type				
	α-CH	α-CH$_2$	α-CH$_3$	β-CH$_2$	β-CH$_3$
3-Hexyne		2.14			1.04
VI [a]		2.36			1.15
VI [b]		2.47			1.20
2-Hexyne		2.07	1.72		
VII [a]		2.28	1.92		
VII [b]		2.39	2.03		
4-Methyl-2-pentyne	2.49		1.71		1.09
VIII [a]	2.69		1.93		1.17
VIII [b]	2.89		2.11		1.23
1,8-Cyclotetradecadiyne		2.19		1.58	
IX [a]		2.36		1.67	
IX [b]		2.39		1.69	

[a] Alkyne—silver triflate (0.177 mmol) in CD_3COCD_3 (0.5 ml). [b] Alkyne—silver triflate in CD_3COCD_3 (saturated solution).

where $\Delta\delta_{obs}$ is the downfield chemical shift at a given complex concentration, $\Delta\delta_{max}$ is the maximum downfield chemical shift in a solution saturated with complex, and [complex] is the total molarity of the organo—silver salt complex. The equation is valid for equal total molar content of silver salt and organic ligand. Using the data in Table 5 and the method of Solodar and Petrovich, we have calculated K for equilibrium 1. The K values are 16.95 for the 3-hexyne—silver triflate system, 15.70 for the 2-hexyne—silver triflate system, 5.65 for the 4-methyl-2-pentyne—silver triflate system, and 106.70 for the 1,8-cyclotetradecadiyne—silver triflate system in CD_3COCD_3. The very high value for 1,8-cyclotetradecadiyne—silver triflate is consistent with its observed stability in the solid state (vide supra) and is consistent with the observation of Muhs and Weiss [12] that chelating dienes (e.g. 1,5-cyclooctadiene, $K = 75$) form more stable complexes than nonchelating monoenes (e.g. *cis*-cyclooctene, $K = 14.4$). Also, the symmetrically substituted 3-hexyne complexes stronger to silver triflate than the unsymmetrically substituted 2-hexyne. Branching on the carbon α to the carbon—carbon triple bond further reduces complexation to silver triflate.

In the technique of Solodar and Petrovich [16] the maximum chemical shift, $\Delta\delta_{max}$, was determined by adding increasingly larger excesses of silver salt to olefin until the downfield chemical shift increased no further. In our analysis, the maximum chemical shift was taken as the chemical shift of a saturated solution of the 1 : 1 alkyne—silver triflate π-complex. We think that our method for determining the maximum chemical shift is valid due to the previously mentioned observation that a 1 : 1 ratio of alkyne/silver triflate at these concentrations gives the maximum increase in chemical shift and that addition of more silver triflate results in no further change in chemical shift.

Experimental

Microanalyses for carbon and hydrogen were performed by Chemalytics, Inc., Tempe, Arizona. Analyses for silver were performed in our laboratories by thiocyanate titration. Melting points were obtained in sealed, evacuated capillaries with a Thomas—Hoover Unimelt (oilbath) apparatus and are uncorrected. Infrared spectra of solids were taken as potassium bromide pellets, and spectra of liquids were taken as thin films on a Perkin—Elmer Model 237B spectrometer. Each spectrum was calibrated with polystyrene film. No potassium bromide induced decomposition of silver triflate complexes occurred, for the infrared spectra showed no absorption due to free carbon—carbon multiple bonds. Proton NMR spectra were recorded on Varian A-60 and EM-360 spectrometers in CD_3COCD_3 solution with TMS or $CHCl_3$ internal standard.

Silver triflate (Aldrich Chemical Company), silver tetrafluoroborate (PCR, Inc.), and silver hexafluoroantimonate (Alfa Inorganics) were recrystallized from boiling ethyl ether/pentane, dried under vacuum, and stored in a dark desiccator under nitrogen. The olefins (Aldrich Chemical Company), 3-hexyne, 1,8-cyclotetradecadiyne (Farchan Research Laboratories), 2-hexyne, and 4-methyl-2-pentyne (Chemical Samples Company) were purified by distillation from calcium hydride (liquids) or by sublimation (solids).

Effect of anion upon stability of olefin—silver salt π-complex

The ^1H NMR spectra were recorded on a Varian EM-360 spectrometer with a probe temperature of 24 degrees and at a sweep width of 300 cps. Samples of the silver salt were transferred under an atmosphere of dry nitrogen in a glove bag to previously weighed and degassed NMR tubes. The tubes were reweighed to determine the amount of silver salt in each tube. Cyclohexene (0.120 ml, 1.19 mmol), chloroform (1 drop), and enough CD_3COCD_3 to give a total volume of 0.400 ml were then added to each tube by syringe through a rubber cap. The position of vinylic proton absorption of cyclohexene in the NMR relative to chloroform (internal standard) was determined at varying concentration of silver salt for silver triflate, silver tetrafluoroborate, and silver hexafluoroantimonate. Throughout all analyses the solutions remained clear and homogeneous.

Competition between cyclohexene and 3-hexyne for silver triflate

The ^1H NMR spectra were recorded on a Varian EM-360 NMR spectrometer with a probe temperature of 24 degrees and at a sweep width of 300 cps. All transfers were carried out under an atmosphere of dry nitrogen. Cyclohexene (0.395 mmol), 3-hexyne (0.395 mmol), and CD_3COCD_3 with 1% TMS (0.250 ml) were added by syringe to an NMR tube, and their proton chemical shifts were measured. Silver triflate (0.142 mmol) was added to the solution, and the proton chemical shifts were measured. Second (0.790 mmol total added) and third (1.10 mmol total added) portions of silver triflate were added to the contents of the NMR tube, and the chemical shifts were measured after each addition. Throughout the analysis the solution remained clear and homogeneous.

Effect of silver concentration upon olefin and alkyne proton chemical shifts

Silver triflate (0.142 mmol) was added to an NMR tube. The tube was capped with a rubber septum and degassed with nitrogen. CD_3COCD_3 with 1% TMS (0.300 ml) was added to the tube by syringe. Various samples of an olefin or alkyne were syringed into the NMR tube, and the proton NMR spectrum was recorded after each addition. The chemical shift change was plotted as a function of silver to olefin or alkyne ratio. In the analyses with norbornene and 1,8-cyclotetradecadiyne, preweighed samples of each were added to the NMR tube under an atmosphere of dry nitrogen in a glove bag.

Preparation of silver triflate π-complexes of olefins and alkynes

In general, the complexes were prepared by dissolving silver triflate in a minimum amount of the boiling olefin or alkyne. The precipitates that formed upon cooling of the solutions were filtered from solution, washed with pentane, and dried under vacuum to give white, crystalline complexes in 37 to 98% yield (Table 2). Filtrations of alkyne—silver triflate complexes were carried out under argon.

For the preparation of 1,8-cyclotetradecadiyne—silver triflate (IX), the 1,8-cyclotetradecadiyne and silver triflate were dissolved in a minimum amount of anhydrous ethanol prior to cooling.

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