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CARBON-13 NUCLEAR MAGNETIC RESONANCE STUDIES OF ACETYLENE - SILVER PI COMPLEXES

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The carbon NMR spectra of acetylene-metal pi complexes have been measured for a few examples of Pt(II),[1] Pt(0),[2] and Co(0)[3] complexes. Carbon spectra of olefin-silver(I) complexes have been reported.[4-6] However, the factors affecting carbon chemical shifts are still the subject of debate.[7] In this communication we report the carbon spectra of acetylene pi complexes of silver(I) trifluoromethanesulfonate (triflate). The reported chemical shifts represent a time average of silver coordinated and uncoordinated acetylenes, for the equilibrium between them is rapid compared to the NMR time scale. The saturated and unsaturated carbons together exhibit unusual changes in chemical shifts as a result of silver ion coordination.

In general, the factors that should affect chemical shifts of different carbons within the same pi complex are a) hybridization of carbon, b) bond anisotropy, and c) relative electron density from metal - ligand bond formation or inductive effects.[8] For the acetylene - silver pi complexes in this study, the extent of sp carbon rehybridization is minimal compared to that of the acetylene - platinum complexes.[9] Upon silver ion coordination, the J (^{1}H - ^{13}C) remains unchanged at 250 ± 3 Hz. Analysis of the proton NMR after obtaining the carbon spectra indicates no isomerization or silver acetylide formation. The changes in acetylene carbon chemical shifts upon silver ion coordination are shown in Table I.

Internal acetylenes exhibit a net downfield shift of sp carbon resonances upon coordination of silver ion. This is distinctly different from internal olefin complexes of silver nitrate[5] and copper triflate[10] that exhibit upfield shifts. The effect upon chemical shift of the nonnucleophilic triflate ion is not clear although its effect upon olefinic proton chemical shifts is documented.[11] One would expect the deshielding effect of silver ion to decrease with distance from the triple bond, but the adjacent sp^3 carbons are even more deshielded! This phenomenon can be interpreted in terms of the Chatt theory[12] in which forward coordination from sp carbon to silver ion is partially offset by back donation (although weak) from silver ion. The back donation does not lessen as much the deshielding of the adjacent sp^3 carbons.

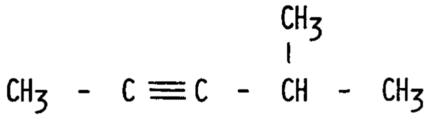
Table I. Change In Carbon Chemical Shift Upon Silver Triflate Coordination [a]

$CH_3-CH_2-C\equiv C-C_2H_5$

CH_3	CH_2	C	C	C_2H_5
+0.5	+1.6	+0.9		

$CH_3-C\equiv C-CH_2-CH_2-CH_3$

CH_3	C	C	CH_2	CH_2	CH_3
+1.6	+1.2	+0.5	+1.2	+0.5	0.0



$CH_3-C\equiv C-CH(CH_3)-CH_3$

CH_3	C	C	CH	CH_3
+1.6	+1.2	+0.8	+0.5	+1.7

$HC\equiv C-C(CH_3)_3$

HC	C	C	$(CH_3)_3$
-4.6	+5.6	+0.6	+1.9

$(HC\equiv C-CH_2)_2$

HC	C	CH_2
-2.2	+3.0	+1.7

$(HC\equiv C-CH_2-CH_2)_2$

HC	C	CH_2	CH_2
-3.1	+3.7	+0.7	+0.1

$HC\equiv C-CH_2-CH_2-CH_2-CH_2-CH_2-C\equiv CH$

HC	C	CH_2	CH_2	CH_2	CH_2	CH_2	C	CH
-2.5	+3.8	+0.7	+0.1	-0.2				

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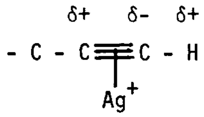
[a] All spectra were obtained on a Brucker WH-90 spectrometer at 22.615 MHz with proton decoupling. Spectra were recorded from 0.4M solutions of 1 : 1 acetylene : silver salt composition in CD_3NO_2 with TMS internal standard. Reproducibility was > ± 0.05 ppm. + = downfield, - = upfield.

In terminal acetylenes, the internal sp carbon is deshielded upon silver ion coordination, but the terminal sp carbon is shielded. The adjacent sp^3 carbon is still deshielded, but not to as great an extent as in the internal acetylenes. Proton NMR studies show that the hydrogen bonded to sp carbon is deshielded by 0.6 to 1.2 ppm in all of the silver complexes.

The lessened downfield shift of the adjacent sp^3 carbon in terminal acetylenes could be caused by a reduction in the equilibrium constant for complex formation. However, any reduction in extent of coordination would reduce the difference in chemical shift between silver ion and nonsilver ion coordinated sp carbons. Therefore, the change in chemical shift for the pure acetylene - silver pi complex would be larger than that indicated by our data.

In heteroatom substituted olefins, silver induced chemical shift differences between sp^2 carbons have been attributed to mesomeric effects.[6] Although mesomeric effects are not expected with our acetylenes, silver ion appears to enhance trends in chemical shifts present in the uncoordinated acetylenes. The shielding of one sp carbon and the deshielding of another adjacent may be attributed to unsymmetrical coordination of silver ion to the carbon - carbon triple bond, an imbalance in relative forward coordination and back donation at the two sp carbons, or poorly understood metal - ligand bond anisotropies. Evidence for unsymmetrical coordination is found in the x-ray structure determination of 1,7-octadiyne - silver triflate in which the silver ion is unsymmetrically coordinated to the triple bond with the silver ion lying closer to the terminal carbon. The apparent net effect is an increase in electron density on the terminal sp carbon at the expense of the internal sp carbon.



$$-C-\overset{\delta+}{C}\underset{Ag^{+}}{\equiv}\overset{\delta-}{C}-\overset{\delta+}{H}$$

The charge distribution on the terminal sp carbon - hydrogen bond appears similar to that expected in the transition state for its heterolytic cleavage. To test this hypothesis we are presently undertaking a study of the effect of silver salts upon the acidity of terminal acetylenes.

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