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Preliminary communication

Alkene- and arene-π-complex formation with silver(I); a ^{13}C NMR study

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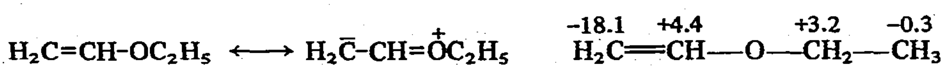
SUMMARY

^{13}C resonance shifts of alkenes and arenes occurring upon coordination with silver(I) are reported and discussed.

Organo-transition metal π-complexes are studied increasingly by ^{13}C NMR spectroscopy[1]. Recently we observed large alkyl-substituent effects on the silver(I)-induced shifts of unsaturated ^{13}C resonances in alkenes[2]. We now have looked more closely at the character of substituent effects using hetero-substituted alkenes (see Table 1).

Comparison of the shifts Δδ, observed upon alkene coordination, with the relative π-electron densities at the unsaturated carbon atoms, estimated from mesomeric structures, reveals a striking correlation. Thus, a high π-electron density is associated with an upfield resonance shift, and *vice versa e.g.*



$$H_2C{=}CH{-}OC_2H_5 \longleftrightarrow H_2\overset{-}{C}{-}CH{=}\overset{+}{O}C_2H_5 \qquad \overset{-18.1}{H_2C}{=\!=}\overset{+4.4}{CH}{-\!-}O{-\!-}\overset{+3.2}{CH_2}{-\!-}\overset{-0.3}{CH_3}$$

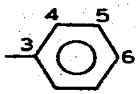
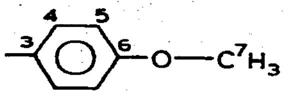
It would appear that π-complex formation with silver(I) enhances the differences in π-electron density present in the uncoordinated compounds.

Electron-withdrawing substituents (*e.g.* Br, Cl) tend to inhibit complex formation and *vice versa*. Thus, inductive effects are likely to be reflected in the strength of coordinative interaction with the C=C double bond.

The existence of a coordinative interaction between silver(I) and the alkene double bond as well as with the hetero-atom is clearly demonstrated by the observed shifts, Δδ, of allylic compounds. These shifts and those of the corresponding saturated compounds indicate that the presence of a C=C double bond reinforces the hetero-atom-silver(I) coordinative interaction.

TABLE 1

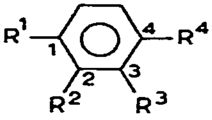
SHIFT OF ^{13}C NMR RESONANCES OF REPRESENTATIVE ALKENES (1.0 *M* in methanol) UPON COMPLEX FORMATION WITH SILVER NITRATE[a]

Alkene $H_2C^1=C^2H-R$	Δδ *(ppm)*[b]					
R	*C*¹	*C*²	*C*³	*C*⁴	*C*⁵	*C*⁶
$C^3H_2-C^4H_2-C^5H_2-C^6H_3$	−13.7	−3.2	+0.3	+0.6	0	0
	−10.8	−4.4	−1.9	+0.6	+0.3	+1.3
 [c]	−16.5	−5.1	−3.2	+0.6	+1.3	+1.6
$O-C^3H_2-C^4H_3$	−18.1	+4.4	+3.2	−0.3		
C^3N	+ 4.4	−1.6	+1.0			
Br[d]	− 0.6	0				
C^3H_2-OH	−12.1	−2.9	−1.3			
$C^3H_2-NH_2$[e]	+ 5.1	−2.2	+5.1			
$C^3H_2-C^4N$[f]	− 0.3	−1.9	+0.3	+3.8		

[a] All spectra were recorded at 25.2 MHz on a Varian XL-100/FT system, using cyclohexane as an internal standard. The values of Δδ are derived from measurements of solutions with a high ligand to silver salt molar ratio[2] and extrapolated to the molar ratio 1/1. [b] + = downfield shift; − = upfield shift. [c] Δδ (C^7) = +0.2 ppm. [d] Di-, tri- and tetra-halo-substituted ethylenes show no resonance shifts of C^1 and C^2. [e] $C^1H_3-C^2H_2-C^3H_2-NH_2$: Δδ ($C^1$) = −0.6; Δδ ($C^2$) = +1.5; Δδ ($C^3$) = +4.3 ppm. [f] $C^1H_3-C^2H_2-C^3H_2-C^4N$: Δδ ($C^1$) = −0.6; Δδ ($C^2$) = −0.6; Δδ ($C^3$) = −1.3; Δδ ($C^4$) = +0.6 ppm.

TABLE 2

SHIFT OF ^{13}C NMR RESONANCES OF REPRESENTATIVE ARENES (1.0 *M* in chloroform) UPON COMPLEX FORMATION WITH SILVER TETRAFLUOROBORATE[a]

Arene 				Δδ *(ppm)*[b]			
*R*¹	*R*²	*R*³	*R*⁴	*C*¹	*C*²	*C*³	*C*⁴
H	H	H	H	−0.3	−0.3	−0.3	− 0.3
CH_3	H	H	H	+6.0	−1.0	−5.7	− 7.6
CH_3	CH_3	H	H	+6.0	+6.0	−3.5	−10.2
CH_3	H	CH_3	H[c]	+5.7	+2.2	+5.7	− 7.0
CH_3	H	H	CH_3	+4.8	−5.4	−5.4	+ 4.8

[a,b] See footnotes *a* and *b*, Table 1. [c] Δδ (C^5) = −13.0 ppm.

We conclude that coordination of silver(I) with the C=C double bond and with a hetero-atom finds expression in the resonance shifts, $\Delta\delta$. However, these shifts are influenced strongly by mesomeric interactions of substituents.

Changes in the C—H coupling constants upon coordination are very small and point to a very small change in the degree of rehybridization of an alkenic system upon coordination, or to a rehybridization into a cyclopropane-like structure (the C—H coupling constants in cyclopropanes are nearly equal to those in alkenes[3,4]).

The ^{13}C resonances of alkyl-substituted benzenes exhibit relatively large shifts upon coordination, in contradistinction to the resonance of benzene itself (see Table 2). Comparing the values $\Delta\delta$ for alkyl-substituted benzenes with each other we conclude that the silver ion is situated above and between two adjacent ring carbons[5]. A resonance will then appear at a time-averaged position because of fast exchange of the silver ion between all possible coordination sites at the aromatic nucleus. The relative contribution of each coordination site will be dependent upon the substitution pattern of the aromatic nucleus.

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