

¹³C NMR STUDY OF Π -COMPLEX FORMATION
I. CHARACTERISTIC SHIFTS OF THE CARBON RESONANCES
OF ALKENES INDUCED BY SILVER (I)

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Several authors have utilized ¹³C NMR spectroscopy (CMR) for the investigation of organo-transition metal π -complexes ¹. In the field of organosilver complex chemistry [†] some CMR measurements have been reported recently by Parker and Roberts ². Comparing the CMR spectra of cyclopentene and cyclohexene in aqueous silver nitrate solution with those of the free compounds, they found the unsaturated carbon resonances to be shifted upfield by 4.4 ppm upon complex formation. However, this feature has not been studied in any detail so far.

We have examined the interaction of alkenes with silver nitrate and tetrafluoroborate in methanol and with silver tetrafluoroborate in chloroform. The observed shifts ($\Delta\delta$) of the carbon resonances upon complex formation are dependent on both alkene and silver concentrations as a consequence of the rapid exchange in solution between free and complexed alkene. Hence, the position of the time-averaged resonances is influenced directly by the extent of dissociation of the complex under consideration, as pointed out by Solodar ³. In order to exclude the effect of differences in dissociation as much as possible we recorded spectra of solutions with a high alkene to silver salt molar ratio. Consequently, the observed $\Delta\delta$ -values are a measure for the real alkene-silver ion interaction. Some of our results in methanol are summarized in Table I.

Coordination of ethylene with silver (I) results in an upfield shift $\Delta\delta$ of the unsaturated carbon resonance, in accordance with the hitherto reported CMR data of transition metal complexes. This upfield shift has been explained by an increase in the σ character of the bonds at the carbon atoms upon coordination ². However, this does not fit in with our measurements of coupling constants J_{C-H} , which upon coordination show either no change or even a very small increase (for instance 1-pentene: J_{C^1-H} changes from 154 to 155 Hz and J_{C^2-H} from 146 to 148 Hz upon addition of half an equivalent of silver nitrate). A more reasonable explanation of the observed shift seems to be the occurrence of small changes in the excitation energy as a consequence of a decreasing π -orbital energy upon coordination ².

[†] for a review on organosilver chemistry see ref. 4.

Table I. Shift of CMR resonances^a of alkenes (1.0 M in methanol) upon complex formation with silver nitrate in the molar ratio alkene/AgNO₃ = 8/1

alkene R ¹ R ² C ¹ =C ² R ³ R ⁴				Δδ(Hz) ^{b,c}		
R ¹	R ²	R ³	R ⁴	C ¹	C ²	
H	H	H	H	d	d	
H	H	H	n-C ₄ H ₉	-43	-10	-18
H	H	H	n-C ₅ H ₁₁	-43	-10	-15
H	H	H	n-C ₆ H ₁₃	-43	-10	+9
H	H	H	i-C ₄ H ₉	-44	-12	-47
H	H	H	t-C ₄ H ₉	-46	-7	+13
H	H	H	C ₆ H ₅	-34	-14	
H	H	H	CH ₂ C ₆ H ₅	-40	-9	+32
H	H	C ₂ H ₅	C ₂ H ₅	-49	+29	
H	H	CH ₃	n-C ₃ H ₇	-46	+26	-38
C ₂ H ₅	H	C ₂ H ₅	H cis	-15	-15	
C ₂ H ₅	H	C ₂ H ₅	H trans	-15	-15	-28
CH ₃	H	i-C ₃ H ₇	H cis	-20	-20	-7
CH ₃	H	i-C ₃ H ₇	H trans	-14	-12	
CH ₃	H	CH ₃	CH ₃	-16	+7	-10
CH ₃	CH ₃	CH ₃	CH ₃	0	0	
H	H	CH ₃	C(CH ₃)=CH ₂	-18	+4	-3
CH ₃	CH ₃	H	CH=C(CH ₃) ₂	+8	-18	

cycloalkene	Δδ(Hz) ^{b,c}	
	C ¹	C ²
	-18	-18
	-15	+9
	-47	+26
	-17	+13
	-48	+32
	-38	-38
	-28	-28
	-16	-7
	-10	-10
	-3	-3


^a All spectra were measured at 25.2 MHz on a Varian XL-100/15 FT system, using cyclohexane as an internal standard.

^b + = downfield shift ; - = upfield shift.

^c The saturated carbon atoms are generally shifted downfield upon coordination in the range 0-5 Hz in methanol and 0-20 Hz in chloroform.

^d Complex formation of ethylene with silver nitrate and tetrafluoroborate in methanol and with silver tetrafluoroborate in chloroform (saturated solutions) resulted in an upfield shift.

Table II. Shift of CMR resonances^a of alkenes (1.0 M in methanol and chloroform) upon complex formation with silver tetrafluoroborate in the molar ratio alkene/AgBF₄ = 8/1

alkene	R ¹ R ² C ¹ =C ² R ³ R ⁴				solvent	Δδ (Hz) ^{b,c}	
	R ¹	R ²	R ³	R ⁴		C ¹	C ²
	H	H	H	H	CH ₃ OH	d	d
					CHCl ₃	d	d
	H	H	H	n-C ₅ H ₁₁	CH ₃ OH	-48	-12
					CHCl ₃	-60	+13
	H	H			CH ₃ OH	-50	+29
					CHCl ₃	-78	+94
	n-C ₄ H ₉	H	n-C ₄ H ₉	H trans	CH ₃ OH	-24	-24
					CHCl ₃	-26	-26
	CH ₃	H	CH ₃	CH ₃	CH ₃ OH	-20	+9
					CHCl ₃	-56	+74
	CH ₃	CH ₃	CH ₃	CH ₃	CH ₃ OH	0	0
					CHCl ₃	+23	+23

a,b,c,d: see corresponding footnotes Table I.

For substituted ethylenes the extent and direction of the shifts Δδ, observed for the unsaturated carbon resonances upon coordination, strongly depends on the substitution pattern at the C=C double bond. The diamagnetic (upfield) shift, found upon coordination of ethylene, is counteracted by a strong paramagnetic (downfield) effect from an alkyl substituent at the unsaturated carbon atom under consideration and slightly enhanced by a diamagnetic (upfield) effect of an alkyl substituent at the neighbouring unsaturated carbon atom. This picture is generally consistent for the alkenes studied. For instance, going from 1-heptene to 2-ethyl-1-butene (Table 1) a strong paramagnetic effect on the C²- and a weaker diamagnetic effect on the C¹-resonance shift emerge. The strong paramagnetic contributions even cause in general an unexpected downfield shift (positive Δδ) of a disubstituted carbon resonance upon coordination.

As shown in Table 2 the effects mentioned above are much more pronounced in chloroform than in methanol, probably because of different solvating capacities of these solvents.

The occurrence of an upfield as well as a downfield resonance shift within one alkene with asymmetric substitution could indicate a nonsymmetric orientation of the silver ion relative to the C=C double bond system, similar to that suggested by Quinn and coworkers⁵. However, a potential nonsymmetric orientation of the silver ion is not the governing factor for the direction and magnitude of the observed shifts Δδ, because the effects are roughly the same for both symmetrically and asymmetrically substituted alkenes.

Obviously, the shifts $\Delta\delta$ are determined mainly by electronic interactions of the substituents with the unsaturated system. Steric effects clearly play an important role in the complex formation of tetramethylethylene. Whereas a moderate downfield shift is observed in chloroform, no shift is found in methanol, probably because of preferential coordination of the silver ion by the latter solvent.

CMR spectroscopy thus seems to be an attractive technique for a systematic study of π -complex formation of several unsaturated systems with transition metals. We have observed that the determination of complex dissociation constants from CMR shifts, which are much larger than PMR shifts³, is another promising application.

It also has been found that silver salts can be employed with success in CMR spectroscopy as specific, inexpensive shift reagents for distinguishing several unsaturated systems in one molecule.

Further results based on these observations will be published shortly.

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