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Silver π-Complexes in Chloroform. Stoichiometry, Stabilities and Proton NMR Bound Shifts

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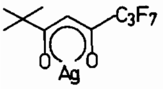
Silver alkene complexes in chloroform are 1:1 rather than 1:2. Stabilities were determined by a solubility method from ^1H NMR integrals. The stability constants decrease in the order $RR'C{=}CH_2$ > $RHC{=}CR'H$ > $RR'C{=}CR''H$ > $RR'C{=}CR''R'''$ > arene. The NMR bound shifts include the first silver-induced ^1H upfield shift reported so far. They seem to be a composite of electronic and geometric influences from Ag^+ and its anion.

Introduction

The well-known lanthanide shift technique in NMR spectroscopy was recently extended to unsaturated hydrocarbons by the addition of a silver compound [1–4]. With an optically active shift reagent, the enantiomers of chiral substrates like terpenes or helicenes can be resolved in the spectrum [3c, 5, 6]. Depending on the substrate, the effects (induced shifts, chiral splittings, line broadenings) vary over more than a power of ten. In order to understand the reasons, we studied the interaction of silver and a π-bond alone. Such data are only sparingly available from the literature [7] for the NMR solvent chloroform, although the characterization of silver π-complexes has been a matter of interest [8].

Polar silver compounds such as $AgBF_4$, $AgCF_3SO_3$, and Agfod (*1*) dissolve only very poorly in solvents like tetrachloromethane, chloroform, or nitromethane. Alkene solutions do much better, because silver π-complexes [9] are formed. The poor solubility is a benefit for complex stability determinations and an obstacle to stoichiometric studies.



Agfod (1)

Experimental

Materials

(6,6,7,7,8,8,8-Heptafluoro-2,2-dimethyl-3,5-octanedionato)silver(I), Agfod (*1*), was prepared from Nafod [6]. As gifts we received Nafod from Merck, Darmstadt, 4-*tert*-butylcyclohexane from Professors F. C. Alderweireldt and J. A. Lepoivre, Antwerpen, Belgium, 1,2-cyclononadiene from W. Munninger, Regensburg, Germany, and (*E*)-1-methyl-2-(1-methyl-2-adamantylidene)adamantane from Dr. D. Lenoir, Munich, F.R.G. All other compounds were commercially supplied.

Instruments

The following experiments were performed by PFT NMR on a D-locked Bruker WH 90 at 33 °C,

– varying benzene concentration at silver saturation,

– varying *2* concentration at low constant silver concentration,

– Agfod solubility in chloroform.

All other spectra were recorded on a Varian T 60 at 33 °C with internal lock (mostly TMS, occasionally $CHCl_3$). The shifts are accurate to ±0.04 ppm.

Procedures

Agfod, substrate, and $CDCl_3$ were equilibrated at 33 °C for at least ten minutes. The mixtures were filtered through a thermostatted device into the NMR tube. Integrations were repeated two to six times. Either the methyne (in $CDCl_3$ $\delta = 6.08$ ppm) or the *tert*-butyl (in $CDCl_3$ $\delta = 1.24$ ppm) resonance of Agfod, or both, were used.

Agfod solubility in chloroform (A_m). $CDCl_3$ was saturated with Agfod as described above. By ^1H NMR integration, A_m was related to the residual $CHCl_3$ concentration, which in turn was determined from $CDCl_3$ samples loaded with weighed amounts of $CHCl_2CCl_3$ or $CHBr_2CHBr_2$. From six experiments: $[CHCl_3] = 0.025$ mol l^{-1} (standard deviation 0.003), corresponding to 99.80% isotopic

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TABLE I. 1:2 *vs.* 1:1 Constants for Agfod–Cyclohexene Complexes.[a]

B_0	v_m	$K_{1:2}$	$K_{1:1}$
1.60	0.53	102	77.8
1.51	0.54	114	80.8
1.44	0.53	112	77.5
1.44	0.56	135	87.4
1.01	0.58	213	93.2
0.93	0.57	215	89.1
0.68	0.58	303	90.7
0.52	0.59	405	92.1
0.35	0.53	385	68.6
0.25	0.61	796	88.7

[a] B_0, Total cyclohexene concentration, in mol l^{-1}. v_m, $[\text{Agfod}]_0/[\text{cyclohexene}]_0$ at maximum silver concentration. $K_{1:2}$, defined by eqn. (1), in l^2 mol^{-2}. $K_{1:1}$, defined by eqn. (5), in l mol^{-1}.

purity. From three experiments: A_m = 0.014 mol l^{-1} (standard deviation 0.001). From regressions to equation (9) (*vide infra*): A_m = 0.012 and 0.016 mol l^{-1}, respectively.

Results and Discussion

Stoichiometry

The maximum concentration of Agfod in chloroform at 33 °C is only 0.014 mol l^{-1}. Most of the monoenes in our study co-solved only 0.5 to 0.7 equivalents of Agfod. Therefore, neither accurate Job's plots [10] nor molar ratio plots [11] with a sufficient v range (v is the molar ratio of Agfod to alkene), say up to v = 3, could be constructed.

1:2 complexes

The fact that his chloroform solutions of alkenes co-solved approximately 0.5 equivalents $AgBF_4$ misled Quinn to assume 1:2 complexation (1 silver, 2 alkenes) [12]. However, under the prevailing conditions of fast exchange [13], the maximum silver to alkene ratios only contain information about complex stability, but not about stoichiometry.

We can definitely exclude a relevant amount of 1:2 complexes for

– cyclohexene, as 1:2 'constants' defined by eqn. (1)* increase inversely with cyclohexene concentration, whereas the 1:1 constants from eqn. (5) show only experimental scatter (Table I),

TABLE II. Evidence against 1:2 Complexation of 2-Methyl-2-butene and α-Pinene: Constant Induced Shift δ_f at Different Substrate Concentrations in Silver Saturated Solutions (*cf.* eqn. (10)).[a]

Substrate	B_0	v_m	δ of[b]	
			^xH	^oH
2-methyl-2-butene	1.9	0.17	5.25	
	1.6	0.20	5.27	
	1.6	0.20	5.25	
	0.9	0.17	5.25	
	0.9	0.24	5.25	
α-pinene	1.6	0.19	5.31	1.71
	1.5	0.19	5.30	1.71
	1.4	0.18	5.28	1.72
	0.21	0.20	5.30	1.72
	0.15	0.21	5.29	1.73
	0.15	0.18	5.30	1.71
	0.15	0.18	5.28	1.70
	0.13	0.17	5.29	1.72

[a] B_0, Total substrate concentration in mol l^{-1}, ±20%. v, Silver to substrate ratio (A_0/B_0). δ, Agfod induced shift, in ppm. [b] The protons are designated as in Table V; shifts in ppm relative to TMS.

$$K_{1:2} = \frac{v_m - A_m/B_0}{B_0A_m(1 - v + A_m/B_0)^2} \qquad (1)$$

– compound *2* because of the linearity of the Armitage plot [14] discussed in the section 'Alternative Methods' (for the formula, see Table V),

– 1-octene, β-pinene, camphene, 2-methyl-1-butene, 2,3-dimethyl-1-butene, cyclooctene, cyclohexene, 3-methylcyclohexene, and 4-*tert*-butylcyclohexene by molar ratio plots, where the observed shifts of 28 signals increased linearly with the added silver amount even beyond v = 0.5 (*e.g.* Fig. 1). Such a behaviour is compatible with 1:2 complexation only if 1:1 complexes coexist and if the 1:1 bound shifts are exactly twice the respective 1:2 bound shifts, which would be an odd coincidence for all 28 signals considered.

– 2-Methyl-2-butene, 2,3-dimethyl-2-butene, 1-methyl-cyclohexene, and α-pinene, because the observed substrate shifts at Agfod saturation were independent of the substrate concentration as illustrated in Table II, in keeping with eqn. (10). With 1:2 complexes, the substrate concentration should influence the observed shift.

1:1 complexes

All the afore-mentioned results are compatible with 1:1 complexation. We cannot conclusively

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*The symbols are defined next to eqn. (4).

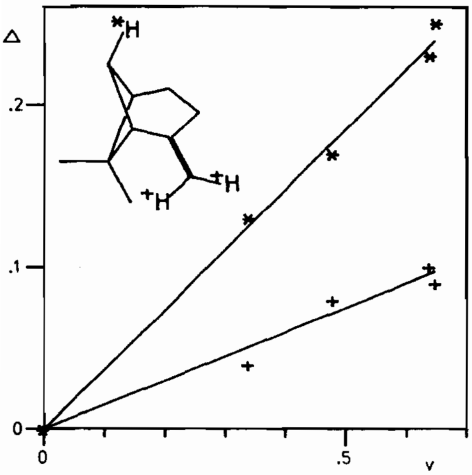


Fig. 1. Evidence against 1:2 complexation of Agfod to β-pinene: linear molar ratio plot beyond v = 0.5. Δ, Agfod induced shift ($\delta - \delta_f$, in ppm). v = $[\text{Agfod}]_0/[\beta\text{-pinene}]_0$.

rule out the association of two silver ions to one double bond, but such 2:1 complexes seem to be somewhat unlikely,

– If ever, they should be formed especially at v > 1, but molar ratios above unity could not be achieved experimentally.

– The addition of a second silver cation to the positively charged 1:1 complex seems to be energetically unfavorable.

Therefore, we conclude that the regular stoichiometry in silver π-complexation is one Ag^+ per isolated double bond. Speculatively, we will also treat a phenyl ring and the two cumulated double bonds in 1,2-cyclononadiene as a single binding site.

Complex Stabilities

Formalism of the solubility method

The maximum amount of silver which is cosolved by an alkene is a measure of the silver π-complex stability. Consider a test tube, wherein a chloroform alkene solution equilibrates with excess solid Agfod. Agfod is co-solved, until equilibrium and the maximum concentration of free Agfod in chloroform is reached.

$$K = \frac{C}{A_m B}, \tag{2}$$

$$A_0 = A + C, \tag{3}$$

$$B_0 = B + C, \tag{4}$$

where K: stability constant of the 1:1 complex, C: concentration of silver π-complex, A: concentration of Agfod, B: concentration of alkene, and subscripts 'm' and 'o' refer to a maximum free and to a total concentration.

B and C in eqn. (2) are substituted by (3) and (4) to give (5), which reduces to (6), when the conditions (7) and (8) are satisfied,

$$K = \frac{v_m - A_m/B_0}{A_m(1 - v_m + A_m/B_0)} =$$

$$= \frac{v_m}{1 - v_m} \frac{1}{A_m} \frac{1 - A_m/A_0}{1 + A_m/(B_0 - A_0)}, \tag{5}$$

where $v = A_0/B_0$ and $v_m = A_0/B_0$ for $A = A_m$.

$$K \simeq K_a = \frac{v_m}{1 - v_m} \frac{1}{A_m}, \tag{6}$$

$$A_m/A_0 \ll 1, \tag{7}$$

$$A_m/(A_0 - B_0) \ll 1. \tag{8}$$

As the ^{1}H NMR spectra of silver π-complexes are in the fast exchange limit at 60 MHz [13], the free and bound species of the alkene give only a single averaged spectrum. v is measured as the ratio of the signal integrals of Agfod and alkene. Once the maximum concentration of Agfod in chloroform is determined, eqn. (6) provides a simple and fast method to measure silver π-complex stabilities, which circumvents the lengthy and error-bound determination of absolute concentrations.

Alternative methods reported in the literature or developed in our laboratory are discussed in the following section. They give at best similar accuracy, but consume much time and material.

Alternative methods

A. Varying substrate concentration at silver saturation. Chloroform alkene solutions, which are saturated with silver, are described by eqns. (9) and (10), where δ_f and δ_b are the shifts of free and bound alkene, and δ_m is the observed averaged shift at silver saturation,

$$v_m = A_m \frac{1}{B_0} + \frac{KA_m}{1 + KA_m}, \tag{9}$$

$$\delta_m = \delta_f + \frac{KA_m}{1 + KA_m}(\delta_b - \delta_f). \tag{10}$$

Equation (10) predicts that, regardless of the actual alkene concentration, the signal positions are constant for 1:1 complexes. Indeed, when $CDCl_3$ cyclohexene solutions (0.25 to 1.6 *M*, 17 experiments) were saturated with Agfod, the shifts of the vinylic and the allylic proton signals of cyclohexene were constantly 5.97 ppm (standard deviation 0.01)

TABLE III. Stabilities of 1:1 Agfod π-Complexes, Determined by the Solubility Method.

Substrate	a	v_m	K_a	K_c
1-octene	2	0.73 ± 0.03	193 ± 31	183 ± 28
2-methyl-1-butene	2	0.74 ± 0.01	198 ± 7	188 ± 7
2,3-dimethyl-1-butene	3	0.80 ± 0.04	286 ± 75	268 ± 61
β-pinene	3	0.64 ± 0.01	127 ± 6	121 ± 5
camphene	2	0.81 ± 0.04	305 ± 106	285 ± 99
cyclooctene	2	0.85 ± 0.02	389 ± 73	360 ± 67
cyclohexene	17	0.57 ± 0.04	94 ± 14	90 ± 14
3-methylcyclohexene	2	0.62 ± 0.03	117 ± 14	111 ± 15
4-*tert*-butylcyclohexene	2	0.54 ± 0	84	80
1,2-cyclononadiene	2	0.64 ± 0.01	127 ± 6	121 ± 6
2-methyl-2-butene	5	0.20 ± 0.03	17 ± 4	16 ± 3
1-methylcyclohexene	3	0.24 ± 0.01	23 ± 2	21 ± 1
α-pinene	8	0.19 ± 0.01	17 ± 1	15 ± 1
2,3-dimethyl-2-butene	4	0.095 ± 0.02	7.5 ± 1.8	6.6 ± 1.5
2			23 ± 14[b]	
benzene	2	0.045 ± 0.005	3.4 ± 0.4	2.7 ± 0.4
hexadeuterobenzene			2.4[c]	
1,5-cyclooctadiene	2	1.20 ± 0.02	106 ± 3[d]	101 ± 4
norbornadiene	3	1.01 ± 0.02	72 ± 4[d]	69 ± 4

[a] Number of v_m determinations. v_m, Average silver to substrate ratio at silver saturation, ± standard deviation s. K_a, Approximate stability from eqn. (6), in l mol^{-1}. K_c, Corrected stability, according to eqns. (12) and (13), using B_0 = 1.3. The K ranges are defined by v_m ± s. [b] From the average intercepts of three regressions (for three different signals) to eqn. (11). [c] From a regression to eqn. (9), using A_m = 0.014. [d] From $v_m/2$.

and 2.13 ppm (standard deviation 0.01). These induced shifts are the most reliable and the only simple indicators for the activity of a given sample of Agfod when used for silver/lanthanide induced shifting [6].

In nine experiments with the substrate cyclohexene and eight experiments with the substrate hexadeuterobenzene, the total substrate concentrations B_0 were determined by weighing. From regressions to eqn. (9), A_m was computed as 0.012 and 0.016 mol l^{-1}, respectively, and the stability constants were 100 (cyclohexene) and 2.1 l mol^{-1} (benzene). These values agree with those from other experiments (*cf.* Experimental and Table III), but the correlations are very poor as the experimental error in v_m is much larger than the variation induced by a change in B_0. All in all, varying substrate concentration at silver saturation seems to yield correct results, but with large uncertainty when the solvent is chloroform, and it requires time and material.

B. Varying substrate concentration at low constant silver concentration (Armitage's method). When varying the substrate concentration with constant silver concentration the latter is so low that $(\delta - \delta_f)/(\delta_b - \delta_f) \ll 1$, the binding constant and the bound shifts of a 1:1 complex can be deduced from a linear regression of B_0 against $1/(\delta - \delta_f)$, as expressed in eqn. (11). Competing 1:2 complexes are excluded by the linearity of the plot [14],

$$B_0 \cong A_0(\delta_b - \delta_f)\frac{1}{\delta - \delta_f} - (1/K + A_0) \qquad (11)$$

2 (see formula in Table V) was available in mg amounts only and studied by this approach. At A_0 = 0.024 mol l^{-1}, the positions of four signals (–H, –Me, two unassigned) increased linearly with $[2]_0$ up to v = 0.32. 'K' values of –181, 20, 48, and 18 are computed from the intercepts. Although stoichiometric evidence and reasonable bound shifts may be gained, the silver-induced shifts are too small to allow K determinations by Armitage plots.

C. Molar ratio method. At constant substrate concentration, δ is monitored as function of v. Then, K and sometimes δ_b for the 1:1 complex are fitted iteratively to the data [15]. An alternative way to treat the data requires prior knowledge of δ_b, and was already used to calculate silver π complex stabilities [8]. The observed shift, δ, at sufficiently large v, say v = 3, may be used as close approximation to the bound shift δ_b. If we employed δ at the largest achieved v values, which were below unity (see Table III), as δ_b, we would overestimate the complex stabilities by several orders of magnitude. The

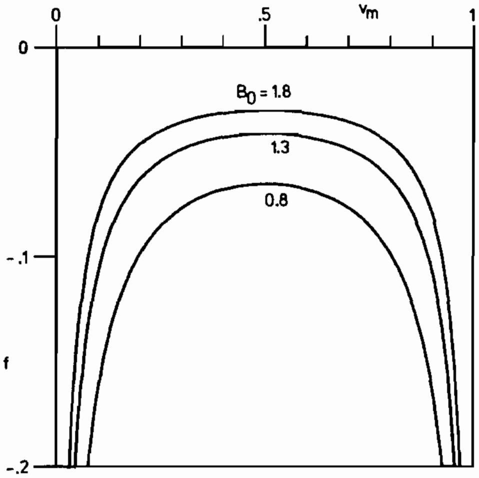


Fig. 2. Relative error f of complex constants determined by the solubility method (*cf.* eqns. (12) and (13)). v_m, Agfod to substrate ratio in silver saturated solutions. B_0, Total substrate concentration.

limited accessible v range also prevents the iterative regression [15].

Limits and error of the solubility method

The accuracy of the complex constants approximated by eqn. (6) depends upon the extent to which the conditions (7) and (8) are satisfied, *i.e.* upon the total alkene concentration B_0. In our experiments, B_0 fell into the range 0.8 to 1.8 *M*.

In Fig. 2, the relative error f as defined by eqn. (12), where K_a is the approximate constant from (6) and K is the real constant from (5), is depicted for the limiting and the median B_0 values. In the range $0.15 < v < 0.85$, K_a is 3 to 12% larger than K. To account for this systematic error, we define a corrected K_c, using f for $B_0 = 1.3$ mol l^{-1},

$$f = \frac{K - K_a}{K_a} = \frac{A_m}{v_m\{B_0(v_m - 1) - A_m\}}, \tag{12}$$

$$K_c = K_a(1 + f). \tag{13}$$

Hence, the saturation method implies an inaccuracy of 2 to 7% for the complex constants, which is less than the experimental error. There seems to be no point in the laborious measurement of the absolute concentrations required by the exact eqn. (5).

TABLE IV. Maximum Molar Amount of Agfod, v_m, Co-solved by Polyfunctional Substrates (Footnotes, see Table III).

Substrate	a	v_m
4-vinylcyclohexene	2	0.94 ± 0.02
limonene	5	0.71 ± 0.02
styrene	2	0.34 ± 0.02
2,4,6-trimethylstyrene	2	0.24 ± 0
4-nitrostyrene	2	0.036 ± 0.009
indene	3	0.10 ± 0.01
3-methylindene	2	0.038 ± 0.003
acenaphthene	4	0.13 ± 0.03
trans-stilbene	2	0.045 ± 0.006
trans, trans, cis-1,5,9-cyclododecatriene	3	1.36 ± 0.03

Substrate structure and complex stability

The 1:1 complex constants for 16 monodentate hydrocarbons are compiled in Table III. Approximate stability ranges of various structural elements can be extracted as follows:

– 180 to 290 for terminal double bonds,
– 80 to 110 for 1,2-disubstituted double bonds,
– 15 to 20 for trisubstituted double bonds,
– less than 10 for tetrasubstituted double bonds,
– less than 5 for arenes.

Complexation is reduced by

– conjugation of the double bond (*cf.* 1-octene and styrene in Table IV),

– electron withdrawal from the double bond (*cf.* 4-nitrostyrene in Table IV; tetrachloroethene and hexachlorobutadiene did not show any effect at all),

– steric hindrance above and below the double bond (*cf.* β-pinene and 2,4,6-trimethylstyrene in Table IV).

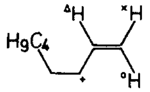
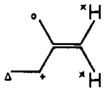
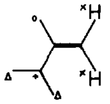
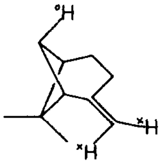
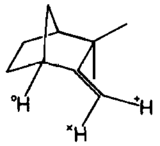
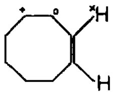
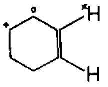
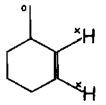
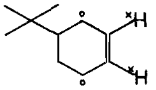
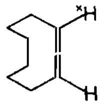
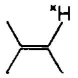
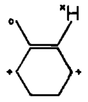
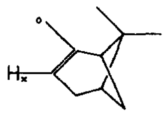
The relatively high stabilities of cyclooctene and compound *2* might be due to a release of steric strain in the complex. The shifts which a mixed silver/lanthanide reagent induces on unsaturated substrates [1–3, 6] can be ordered parallelly to the silver π-complex stabilities we found. Following the trends described above one can assess which shift effects are to be expected for a given substrate molecule.

Polyfunctional substrates

We also investigated twelve compounds with two or three binding sites. For these, the experimental v_m is composed from two or three complexation equilibria, and the individual constants cannot be computed from v_m. Therefore, we report only the v_m values in Table IV. For the symmetric compounds 1,5-cyclooctadiene and norbornadiene, v_m was simply divided by the number of binding sites (two) and processed by eqn. (6) to yield an average constant for one double bond. These values can immediately be compared to the constants of monodentate substrates and are therefore appended to Table III.

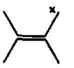
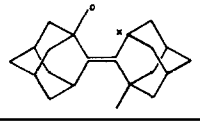
Nonadditivity. If, in a bifuncational substrate, the two double bonds complexed independently of each

TABLE V. Free and Bound Shifts for Monofunctional Substrates in Agfod π-Complexes.

Substrate	Formula	a	δ of			
			^{x}H	^{o}H	^{+}H	$^{\Delta}H$
1-octene		10	4.92 0.21	4.97 0.06	2.03 0.22	5.86 0.45
2-methyl-1-butene		11	4.70 0.06	1.73 0.28	2.03 0.24	1.02 0.12
2,3-dimethyl-1-butene		6	4.68 0.11	1.70 0.30	2.25 0.21	1.02 0.14
β-pinene		6	4.58 0.16	1.40 0.38		
camphene		6	4.72 0.27	2.66 0.23	4.49 0.11	1.01 0.25
cyclooctene		9	5.59 0.38	2.12 0.32	1.49 0.05	
cyclohexene		31	5.69 0.51	2.01 0.23	1.66 0.07	
3-methylcyclohexene		6	5.54 0.70	0.97 0.19		
4-*tert*-butylcyclohexene		5	5.66 0.63	1.93 0.33		
1,2-cyclononadiene		3	5.26 0.59			
2-methyl-2-butene		6	5.23 0.11 0.05			
1-methylcyclohexene		5	5.36 0.45 0.02	1.57 0.37 0.05	1.86 0.25 0.03	
α-pinene		10	5.21 0.38 0.06	1.66 0.35 0.10		

(continued on facing page)

TABLE V. *(continued)*

Substrate	Formula	a	δ of ^{x}H	^{o}H	$^{+}$H	$^{\Delta}$H
2,3-dimethyl-1-butene		5	1.65 -0.42 0.09			
2			3.18[b] 0.31	1.16[b] 0.39		

[a] Number of experiments used for regression to eqn. (14). For each substrate, the free shift δ_f is given in the first line, the induced bound shift $\delta_b - \delta_f$ in the second one, and the standard deviation of $\delta_b - \delta_f$ in the third one. Standard deviations smaller than 0.02 ppm have not been entered. [b] From an Armitage plot.

other, the observed v_m should be the sum of the v_m of appropriate structure elements. Limonene, for example, might be regarded as a composite of 2,3-dimethyl-1-butene and 1-methylcyclohexene. However, no molecule in Table IV conforms to this idea. All experimental v_m are lower than the sums of appropriate single v_m values. Obviously, the presence of the first silver particle in the complex hinders the association of a second one, even to a double bond remote from the first binding site. This supports one of the arguments against 2:1 complexation at a single double bond (*vide supra*).

Bound Shifts

Evaluation

Bound shifts belong to the complexed substrate. They contain information about the geometry and the electronic situation in the complex, and they are the largest shifts which can be obtained with a given substrate. Observed shifts, on the other hand, are a weighted average of free and bound shifts, where the weights are given by the thermodynamics of the contributing equilibria [15]. Therefore, observed shifts are a composite of structural and thermodynamic effects and are an unsound basis for structural discussions [12, 16] which should instead consider bound shifts.

From molar ratio plots [11], bound shifts can be read off as the limiting shift value at high v, *i.e.* at high reagent concentrations. As our molar ratio plots cease at $v < 1$, the experimental shifts had to be extrapolated. As the shift curves were linear up to v_m, the bound shifts δ_b were computed from eqn. (14), where δ_b and δ_f are the coefficients of a linear regression of the observed shift δ *vs.* v.

$$\delta = (\delta_b - \delta_f)v + \delta_f \qquad (14)$$

Anion induced shifts

The resulting bound shifts are found in Table V. The methyl signals of 2,3-dimethyl-2-butene are shifted to higher field. This is the first upfield shift induced by silver complexation to be reported. $AgBF_4$ causes the familiar downfield shift: together with the irregular pattern of the δ_b values this indicates that Ag^+ is not the only origin of δ_b, but that the anion contributes considerably. Two mechanisms can be envisaged. The basicity of the anion might alter the electronic demand of Ag^+, and the anisotropy of the anion bounds might directly influence certain substrate nuclei, depending on the geometric matching of anion and substrate molecule. Anionic influence upon δ_b is documented by

– a change in the vinylic δ_b, when cyclohexene in acetone is complexed by $AgBF_4$, $AgSbF_6$, or $AgCF_3SO_3$, respectively [17],

– different observed relative shifts, when cyclohexene in chloroform is complexed by $AgBF_4$ or by $Ag(CF_3CO)_2CH$ [18] and Agfod (Table V),

– the upfield δ_b of the methyl signals of 2,3-dimethyl-2-butene, when complexed with Agfod, and the downfield δ_b, when complexed with $AgBF_4$,

– the large δ_b for nuclei remote from the double bond, as found for β-pinene, camphene, and *2*,

– the chiral recognition brought about by the optically active anion of a mixed silver/lanthanide reagent [5,6].

Whereas both the electronic and the geometric factor might be responsible for the first three items, only geometry can bring about the latter two phenomena. This effect of the silver ion upon the substrate is similar in its nature to the well-known aromatic solvent induced shift, ASIS [19], and we term it therefore *A*nion a*N*isotropy *I*nduced *S*hift, *ANIS*.

Conclusions

In chloroform 1:2 Agfod π-complexes are irrelevant, and 1:1 complexation is probable. The stability constants range from 2 to 300 l mol^{-1}. Terminal double bonds are the strongest, π-bonds in an aromatic ring or with more than two substituents the weakest ligands. The solubility determination by NMR which we used is both fast and reliable and can be employed for similar systems, provided both the reagent and the substrate contain the same magnetic nucleus.

On 2,3-dimethyl-2-butene, Agfod induces the first ^{1}H NMR upfield shift of an alkene reported so far. The bound shifts are, as a rule, smaller than 0.7 ppm and show an irregular pattern when compared to the substrate structures. We suppose a considerable contribution from the anion, containing geometric information about the complex and the substrate.

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References

1 D. Evans, J. N. Tucker and G. C. de Villardi, *J. Chem. Soc., Chem. Commun.*, 205 (1975).
2 A. Dambska and A. Janowski, *Org. Magn. Reson.*, *13*, 122 (1980);
A. Dambska and A. Janowski, *Chemia Analityczna*, *25*, 77 (1980).
3 (a) T. J. Wenzel, T. C. Bettes, J. E. Sadlowski, R. E. Sievers, *J. Am. Chem. Soc.*, *102*, 5903 (1980);
(b) T. J. Wenzel and R. E. Sievers, *Anal. Chem.*, *53*, 393 (1981);
(c) T. J. Wenzel and R. E. Sievers, *J. Am. Chem. Soc.*, *104*, 382 (1982).
4 W. B. Smith, *Org. Magn. Reson.*, *17*, 124 (1981).
5 A. I. Meyers and M. E. Ford, *J. Org. Chem.*, *41*, 1735 (1976).
6 W. Offermann and A. Mannschreck, *Tetrahedron Lett.*, *22*, 3327 (1981);
W. Offermann and A. Mannschreck, in preparation.
7 F. R. Hartley, *Chem. Rev.*, *73*, 163 (1973).
8 J. P. Ginnebaugh, J. W. Maki and G. S. Lewandos, *J. Organomet. Chem.*, *190*, 403 (1980).
9 M. J. S. Dewar, *Bull. Soc. Chim. Fr.*, *18*, C79 (1951).
10 K. Roth, M. Grosse and D. Rewicki, *Tetrahedron Lett.*, 135 (1972);
P. MacCarthy, *Anal. Chem.*, *50*, 2165 (1978).
11 F. R. Hartley, C. Burgess and R. M. Alcock, 'Solution Equilibria', Ellis Horwood, Chichester, 1980. 1st edition.
12 H. W. Quinn and R. L. Van Gilder, *Canad. J. Chem.*, *47*, 4691 (1969).
13 J. Solodar and J. P. Petrovich, *Inorg. Chem.*, *10*, 395 (1971).
14 I. Armitage, G. Dunsmore, L. D. Hall and A. G. Marshall, *Canad. J. Chem.*, *50*, 2119 (1972).
15 *Cf.* J. Grandjean, P. Laszlo, W. Offermann and P. Rinaldi, *J. Am. Chem. Soc.*, *103*, 1380 (1981);
J. Feeney, J. G. Batchelor, J. P. Albrand and G. C. K. Roberts, *J. Magn. Reson.*, *33*, 519 (1979).
16 H. W. Quinn, J.S. McIntyre and D. J. Peterson, *Canad. J. Chem.*, *43*, 2896 (1965).
17 G. S. Lewandos, D. K. Gregston and F. R. Nelson, *J. Organomet. Chem.*, *118*, 363 (1976).
18 W. Partenheimer and E. H. Johnson, *Inorg. Chem.*, *11*, 2840 (1972).
19 E. M.Engler and P. Laszlo, *J. Am. Chem. Soc.*, *93*, 1317 (1971).