

Unusual ^{77}Se NMR behaviour of Lewis acid - Selenide Complexes.

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Introduction

Our interest in the generation and reactivity of carbon-electrophiles containing selenium moieties ¹ led us to investigate the interaction of bis(phenylseleno)-1,3 propenes 1 with silver

perchlorate by ^{77}Se NMR spectroscopy. To our astonishment, the selenium nuclei were increasingly shielded upon addition of silver perchlorate to the selenide solution (Figure 1).

While the observed chemical shifts are incompatible with a cationic species ^{2,3} they can be explained by subsequent formation of two labile complexes (Scheme 1) of different stoichiometries.

In order to gain some insight into the structural factors causing the unexpected shielding ⁴ we extended our investigation on selenide structure, Lewis acid and the solvent.

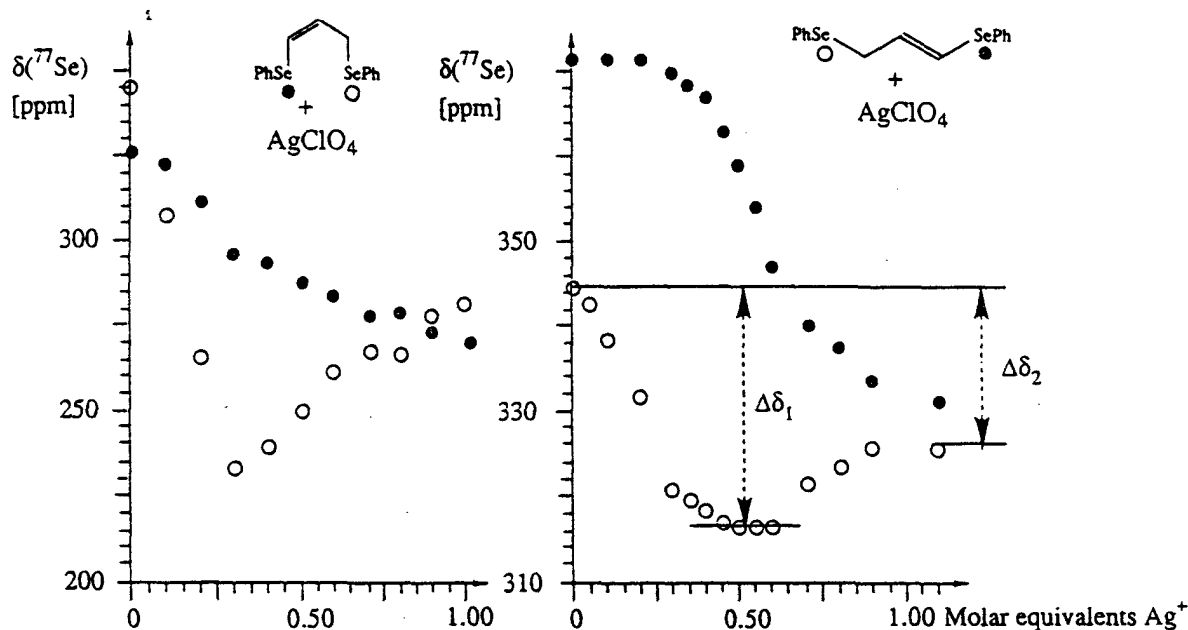
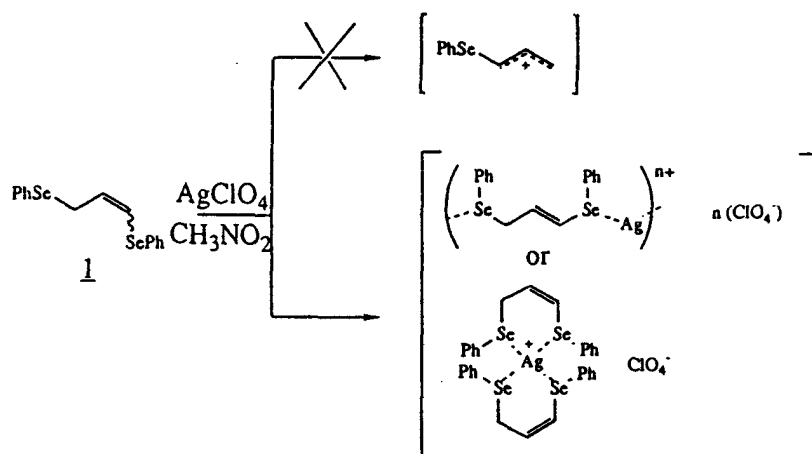


Figure 1: ^{77}Se NMR 'titration curves' of E- and Z-Bis (phenylseleno)-1,3-propenes.



Scheme 1: proposed complexes formed by interaction of E- and Z-Bis (phenylseleno)-1,3-propenes with silver perchlorate.

1. Influence of selenide structure.

A series of 25 structurally different selenides were examined (Table), all exhibiting analogous 'titration curves' (characterized by $\Delta\delta_1$ and $\Delta\delta_2$) with the only

exceptions being dimethylselenide (entry 18) and bis(methylseleno)-1,1 methyl-3 butene-2 (entry 21) which are both deshielded.

The values for benzyl- and phenyl methylselenides (entries 1-12) exhibit good

correlation with Hammett-type σ^- substituent parameters (Figure 2), the negative slopes indicating increased shielding by increasingly electron-accepting substituents. This is the opposite of what is normally observed for selenides ^{5,6}.

Equally noteworthy is that $\Delta\delta_1$ vs. $\Delta\delta_2$ points corresponding to compounds of these two families fall on a single straight line (Figure 3).

entry	Selenide	δ	$\Delta\delta_1$	$\Delta\delta_2$
1	p-NO ₂ C ₆ H ₅ SeCH ₃	238.1	-60.8	-63.8
2	p-CH ₃ COC ₆ H ₅ SeCH ₃	219.9	-54.0	-54.0
3	p-CH ₃ OCOC ₆ H ₅ SeCH ₃	220.1	-52.8	-52.8
4	C ₆ H ₅ SeCH ₃	198.5	-41.1	-33.1
5	p-CH ₃ OC ₅ H ₅ SeCH ₃	190.2	-38.8	-30.8
6	o,p-(CH ₃ O) ₂ C ₆ H ₄ SeCH ₃	139.3	-66.5	-69.5
7	o,p-(NO ₂) ₂ C ₆ H ₄ SeCH ₃	346.0	-34.3	-

8	p-CNC ₆ H ₂ CH ₂ SeCH ₃	191.9	-43.7>	-42
9	p-FC ₆ H ₅ CH ₂ SeCH ₃	177.9	-32.8>	-27.4
10	C ₆ H ₅ CH ₂ SeCH ₃	175.0	-28.0>	-15.4
11	m-CH ₃ OC ₆ H ₅ CH ₂ SeCH ₃	172.8	-22.5>	-14.2
12	p-CH ₃ OC ₆ H ₅ CH ₂ SeCH ₃	172.6	-26.6>	-15.4

13	E PhSeCH=CHCH ₂ SePh	{ a.344.4	-27.7	-18.6
		{ v.372.2	-12.3	-40.0
14	Z PhSeCH=CHCH ₂ SePh	{ a.344.6	-112.5	-57.5
		{ v.326.3	-29.7	-58.3
15	PhSeCH ₂ CH ₃	322.3	-45.7	-20.9
16	PhSeCH=CH ₂	393.6	-59.6	-54.0
17	PhSeCH ₂ CH=CH ₂	328.6	-38.9	-15.4

18	CH ₃ SeCH ₃	0	+20.0	+30.3
19	CH ₃ SeCH=CH ₂	191.7	-59.4	-49.7
20	CH ₃ SeCH ₂ CH=CH ₂	99.7	-27.4	-21.2
21	(CH ₃ Se) ₂ CHCH=C(CH ₃) ₂	216.3	+2.0	+5.5
22	CH ₃ SeCH ₂ C(SeCH ₃)=CH ₂	{ a.125.3	-49.4	-49.4
		{ v.211.9	-104.9	-102.3

23	PhSePh	416.6	-47.7	-41.1
24	(PhSeCH ₂) ₂	338.9	-108.8	>102.8
25	(PhSeCH ₂) ₂ CH ₂	290.1	-37.7	-28.9

Table 1: ⁷⁷Se NMR parameters of selenide-Ag⁺ interaction.

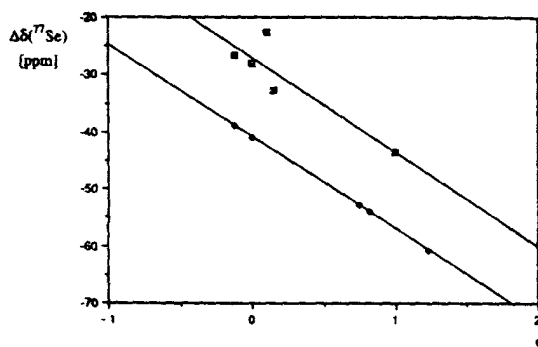


Figure 2: correlation between $\Delta\delta_1$ and σ^- for substituted phenyl- and benzyl methylselenide-Ag⁺ complexes.

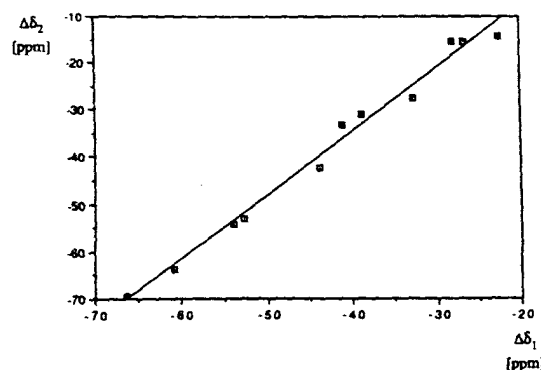


Figure 3: correlation of $\Delta\delta_1$ and $\Delta\delta_2$ complexation shifts of phenyl- and benzyl methylselenides.

2. Influence of Lewis acid.

A series of six Lewis acids exhibit quite different behaviour: while AgClO₄, [Cu(CH₃CN)₄]ClO₄⁷, and ZnCl₂·OEt₂⁸ brings about shielding of the ⁷⁷Se nuclei, deshielding is observed with SnCl₄, TiCl₄ and Pd(CH₃CO₂)₂ (Figure 4). Thus, it appears that selenium shielding occurs only in complexes with d-electron rich metals (capable of d- π -d π back-donation).

3. Influence of solvent.

Strongly n-donating solvents (DMF, CH₃CN) suppress the formation of the ML₄-type complexes and simultaneously increase the ⁷⁷Se-shielding for the ML complexes (at higher M:L ratio) (Figure 5).

4. Interpretation.

The chemical shielding⁹

$$\sigma = \sigma_d + \sigma_p$$

of a heavy nucleus as ⁷⁷Se should be dominated by the paramagnetic term¹⁰

$$\sigma_p = -(2e^2 \hbar^2 / 3m^2 c^2) (\Delta E)^{-1} (\langle r^{-3} \rangle_p P_u + \langle r^{-3} \rangle_d D_u)$$

which is governed by the mean electronic excitation energy (ΔE), the mean electron-nucleus distance $\langle r^{-3} \rangle$ and the electron unbalance in p (P_u) and d (D_u) valence orbitals.

It is generally admitted that the lowest frequency UV-Vis absorption of the compound can be considered as an approximate value for ΔE . For shielding to occur one should observe a hypsochromic shift upon complexation. Since however we observe for 1-Z a bathochromic shift (Figure 6) we conclude that ΔE doesn't play a major role here.

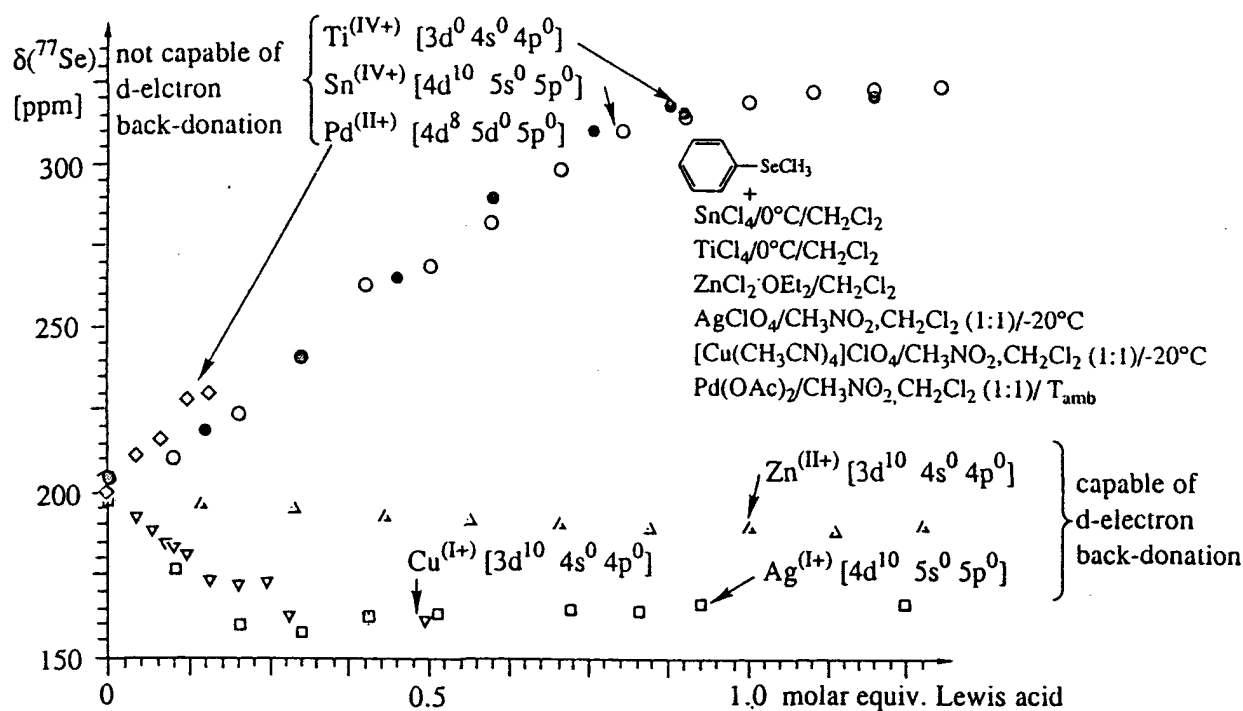


Figure 4: ^{77}Se NMR 'titration curves' of selenoanisole with different Lewis-acids.

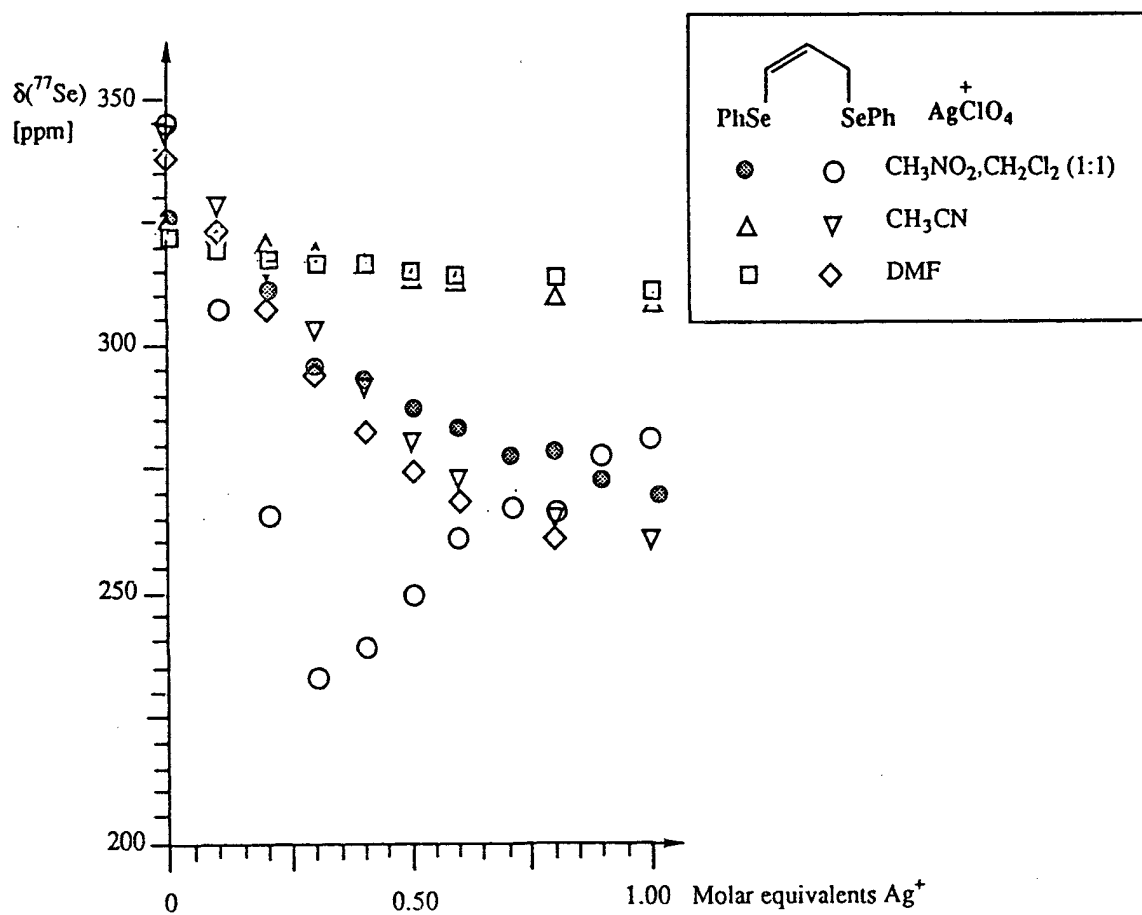


Figure 5: ^{77}Se NMR 'titration curves' of Z-Bis (phenylseleno)-1,3-propenes 1 in different solvents.

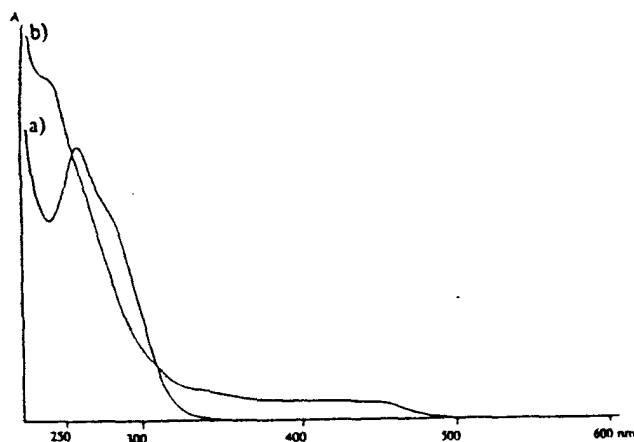


Figure 6: UV-Vis absorption spectrum of **1** (a) and the **1**-AgBF₄ complex (b) in CH₂Cl₂.

Therefore electron-density and/or unbalance changes around the selenium atoms should be the determining contribution ¹¹.

Together with our other results we suggest d_π-d_π back donation ¹² from Ag⁺ to Se.

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