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ON THE STRUCTURE OF α-METALLO BENZYLSELENIDES

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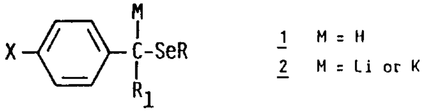
Decreasing electron attracting ability of the para substituent X leads to an upfield shift of the ^{77}Se signal of para substituted benzylselenides. Reverse results are however observed when the measurements are performed on the corresponding para substituted metallo benzylselenides.

It is well established that the elements of the third and higher periods stabilize better a negative charge on an adjacent carbon atom than do those of the second period [1-4] however, the exact nature of this effect has not yet been clearly elucidated [1,3,4].

In this paper we wish to report results of ^{77}Se NMR measurements on a series of para-substituted benzylmetals 2 stabilized by selenenyl moieties (Table) which we believe may contribute to the understanding of the above phenomena.

TABLE



	X	a	b	c	d	e	f	g	h	i	j	k	l
		R=Me, R_1=H			R=R_1=Me			R=Ph, R_1=H			R=Ph, R_1=SePh		
		M=H*	M=Li*	Δδ	M=H*	M=Li*	Δδ	M=H*	M=Li*	Δδ	M=H*	M=K*	Δδ
1	CN	204	32	172	283	138	145	394	237	157	450	431	19
2	Cl	193	53	140	272	159	113	374	249	125	443	441	2
3	H	182	54	128	264	168	96	357	254	103	440	446	-6
4	Me	--	--	--	262	180	82	--	--	--	--	--	--
5	MeO	182	69	113	264	193	71	357	264	93	437	453	-16

* The values presented below refer to ^{77}Se NMR shifts. The measurements have been performed in THF-Hexane at -78°C on a JEOL FX 90Q spectrometer. Dimethylselenide was used as an external standard.

These organometallics have been quantitatively prepared in THF from the corresponding selenoacetals (i) by cleavage of the C-Se bond by n-butyllithium for the synthesis of α-metalloselenides [5] or (ii) by metallation with potassium diisopropylamide (KDA) for the generation of α-metalloselenoacetals [6]. The benzylselenides used for comparison purposes have been obtained by protonation of α-metalloselenides prepared from the corresponding selenoacetal according to (i).

We found that decreasing the electron attracting ability of the para-substituent X, leads to an upfield shift of the δ^{77}Se signal of the selenides 1 (Table, compare entries 1 to 5 in columns a,d,g,j). This effect can reasonably be attributed to the change in electron density around the selenium atom.

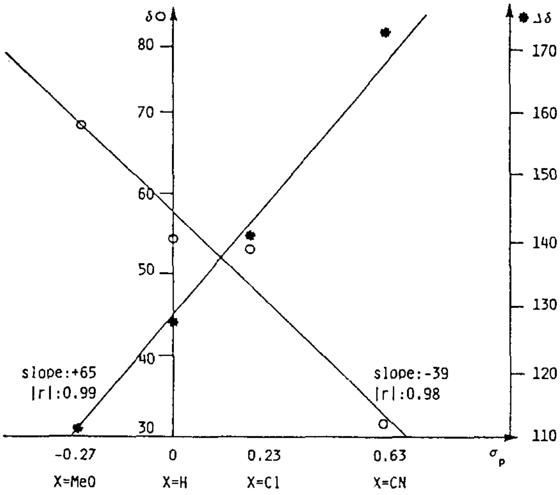
The situation changes however dramatically when the measurements are performed on the corresponding α-selenobenzyl metals 2 (Table, columns b,e,h,k) where unexpectedly downfield shifts of the ^{77}Se NMR signals are observed under similar circumstances (compare in each column entries 1 to 5). This effect is even more pronounced when $\Delta\delta$ values (difference between the shifts of the selenobenzyl metals 2 and of the corresponding selenides 1) are instead compared (Table, compare entries 1 to 5 in columns c,f,i,l).

These results are presented in figures 1,2,3 and 4. These show excellent linear correlation (r) between the δ^{77}Se of the organometallics or the corresponding $\Delta\delta^{77}$Se and the Hammet σ_p values [7] for the ring substituents in para position.

The negative slope of the δ vs. σ_p lines for the lithium derivatives indicates that these unexpected chemical shifts must arise from two or more factors operating in opposed directions. Undoubtedly one of these factors is charge density which should generate a positive slope. Clearly another, more important phenomenon having an inverse effect is superimposed, leading thereby to the observed overall negative slope. We feel that this phenomenon may be identified as a change in hybridization [×] of the selenium atom from sp^3 to something in between sp^3 and sp^2 reflecting delocalization of the negative charge towards this atom on going from an electron attracting to an electron donating para substituant (X).

[×] The δ^{77}Se NMR data for selenone $R_2C = Se$ range [8] from 1600 to 2100 ppm.

Figure 1

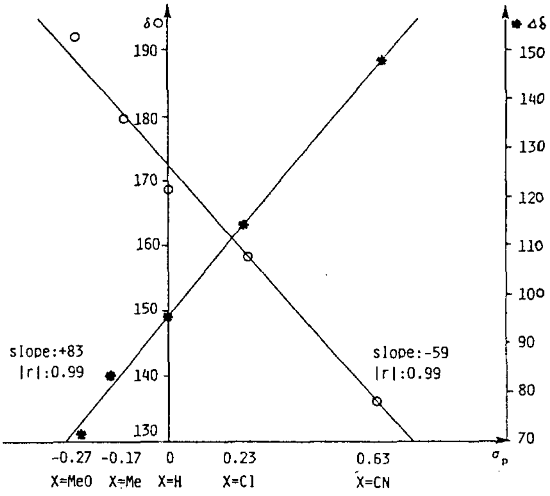


refers to δ^{77}Se NMR for compound 2b

refers to $\Delta\delta^{77}$Se NMR between compounds 1a and 2b

1a R = Me, R_1 = H, M = H ;
2b R = Me, R_1 = H, M = Li

Figure 2

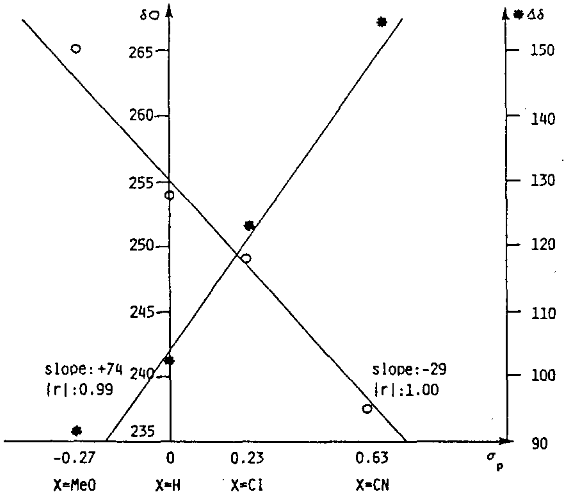


refers to δ^{77}Se NMR for compound 2e

refers to $\Delta\delta^{77}$Se NMR between compounds 1d and 2e

1d R = R_1 = Me, M = H ;
2e R = R_1 = Me, M = Li

Figure 3

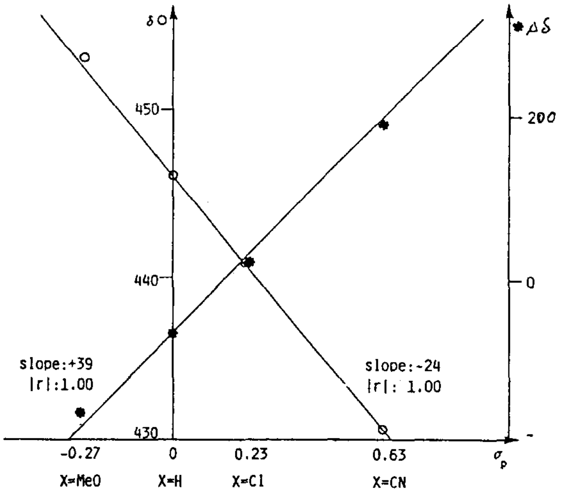


refers to δ^{77}Se NMR for compound 2b

refers to $\Delta\delta^{77}$Se NMR between compounds 1g and 2h

1g R = Ph, R_1 = H, M = H ;
2h R = Ph, R_1 = H, M = Li

Figure 4



refers to δ^{77}Se NMR for compound 2k

refers to $\Delta\delta^{77}$Se NMR between compounds 1j and 2k

1j R = Ph, Ph = SePh, M = H ;
2k R = Ph, R_1 = SePh, M = K

Indeed in the former case one would expect the carbanionic negative charge to be delocalized towards the substituted phenyl ring, whereas delocalization would be more efficient towards the selenium atom with electron donating substituants (X), leading to increased sp^2 character and therefore to a downfield shift of the ^{77}Se NMR signal. Such a delocalization has been recently proposed [9] to explain ^{13}C and ^{6}Li NMR spectra of α-selenoalkyllithiums possessing a labelled ^{6}Li and ^{13}C carbanionic center.

Furthermore, the tightness of the carbon-lithium bond is altered by the substituents rendering the carbanionic negative charge more available for delocalization in the case of electron withdrawing X groups. Most certainly this effect also contributes to the observed chemical shifts.

Much work is required to further support or refute the proposed explanation.

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Reprints are not available from the authors.

REFERENCES

1. "Synthetic methods using α-heterosubstituted organometallics", A. Krief, Tetrahedron, 36, 2531 (1980).
2. "Organic chemistry of selenium and tellurium containing functional groups", A. Krief, volume 2, to be published, S. Patai, Z. Rappoport, John Wiley Ed.
3. F.G. Bordwell, J.E. Barres, J.E. Bortmess, G.E. Drucker, J. Gerhold, G.J. Mc. Callum, M. Van Der Pu, M.R. Vanier and W.S. Matthews, J. Org. Chem., 42, 326 (1977).
4. J.M. Lehn, G. Wipff and J. Demuynck, Helv. Chim. Acta, 60, 1239 (1977).
5. M. Clarembeau and A. Krief, Tetrahedron Lett., 27, 1719 (1986).
6. M. Clarembeau and A. Krief, Tetrahedron Lett., 27, 1723 (1986).
7. H.J. Jaffé, Chem. Reviews, 191 (1953).
8. E.R. Cullen, F.S. Guziec, C.J. Murphy, T.C. Wong and K.K. Andersen, J. Am. Chem. Soc. , 103, 7055 (1981).
9. D. Seebach, J. Gabriel and R. Hässig, Helv. Chim. Acta, 67, 1083 (1984).

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