

## 2D $^{13}\text{C}$ , $^{77}\text{Se}$ Correlation, a New NMR Method for Organoselenium Compounds Leading to Correction of Structural Assignments

Thomas Fäcke, Ronald Wagner, and Stefan Berger\*

Department of Chemistry, Philipps University Marburg, Hans Meerwein Strasse,  
D-35032 Marburg, Germany

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Two dimensional  $^{13}\text{C}$ ,  $^{77}\text{Se}$  correlation spectroscopy is used for the first time to assign the selenium and carbon NMR signals in 2,2-bis(phenylseleno)styrene and related compounds. Two different methods, which correlate carbon and selenium atoms over one, as well over two to four bonds, are reported.  $^1\text{H}$ ,  $^{77}\text{Se}$  HOESY spectra show close steric contact between hydrogen and selenium. The structures of two compounds reported in the literature are corrected.

In compounds bearing more than one selenium atom in similar environments it is often difficult to assign the  $^{77}\text{Se}$  NMR spectra<sup>1</sup> unambiguously. Due to the relatively high natural abundance of  $^{77}\text{Se}$ , the  $^{13}\text{C}$  NMR spectra show satellites from which  $^1J$ ,  $^2J$ , and  $^3J$   $^{13}\text{C}$ ,  $^{77}\text{Se}$  coupling constants can be measured; in favorable cases these can be used for assignment purposes of both the carbon and the selenium NMR spectra. However, due to the relatively large  $^1J$   $^{13}\text{C}$ ,  $^{77}\text{Se}$  spin coupling constants, these satellites can be hidden by other signals; for quaternary carbon atoms it is often difficult to observe these satellites at all. On modern NMR spectrometers, equipped with an independent third radiofrequency channel, these spin couplings could be used to establish a 2D correlation between  $^{13}\text{C}$  and  $^{77}\text{Se}$  under complete proton decoupling, which to the best of our knowledge has not yet been reported.

Up to now only a limited number of 2D correlations between carbon and other heteronuclei have been reported in the literature including  $^{13}\text{C}$ ,  $^2\text{H}$ ,<sup>2</sup>  $^{13}\text{C}$ ,  $^6\text{Li}$ ,<sup>3</sup>  $^{13}\text{C}$ ,  $^{15}\text{N}$ ,<sup>4</sup> and  $^{13}\text{C}$ ,  $^{31}\text{P}$ .<sup>5-7</sup> Recently, we have systematically compared three different pulse sequences for  $^{13}\text{C}$ ,  $^{31}\text{P}$  correlation,<sup>8</sup> extended the use of the HMQC method<sup>9</sup> for  $^{13}\text{C}$ ,  $^{29}\text{Si}$ ,<sup>10,11</sup> and reported the first  $^{13}\text{C}$ ,  $^{119}\text{Sn}$  correlation.<sup>12</sup> Here we show the utility of these methods for a difficult assignment problem in the case of an organodiselenium compound. In addition, this led to a correction of reported literature structures.

### Results and Discussion

To demonstrate the power of our method we chose 2,2-bis(phenylseleno)styrene (1)<sup>13</sup> as an example, since this

(1) For a review on  $^{77}\text{Se}$  NMR see McFarlane, H. C. E.; McFarlane, W. In *Multinuclear NMR*; Mason, J., Ed.; Plenum Press: New York, London, 1987; p 417.

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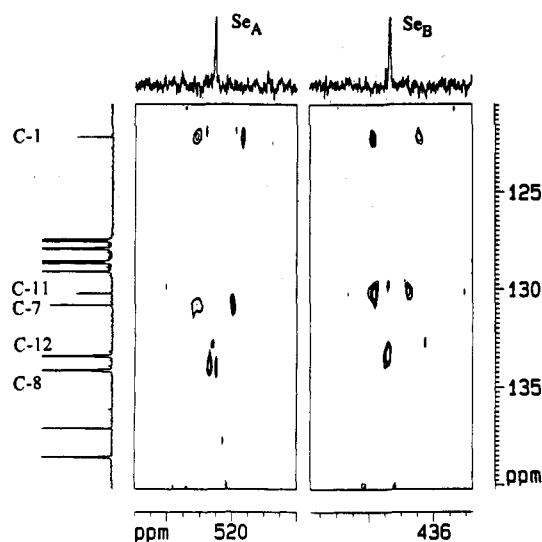


Figure 1. Extension of a  $^{77}\text{Se}$ -detected  $^{13}\text{C}$ ,  $^{77}\text{Se}$  2D spectrum of 1 obtained by the polarization transfer method<sup>8</sup> with a refocusing delay corresponding to  $^1J(^{13}\text{C}, ^{77}\text{Se})$  of 110 Hz.

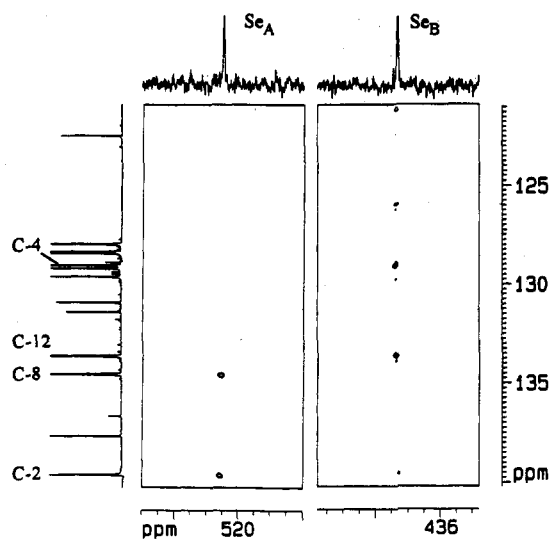


Figure 2. Extension of a  $^{77}\text{Se}$ -detected  $^{13}\text{C}$ ,  $^{77}\text{Se}$  2D spectrum of 1 obtained by the INEPT-HMQC method<sup>11</sup> with a refocusing delay corresponding to  $^2J(^{13}\text{C}, ^{77}\text{Se})$  of 10 Hz.

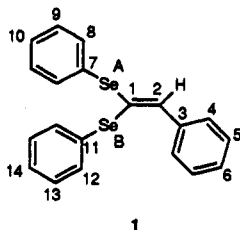
synthetically important compound provides a rather difficult assignment problem and is, to our knowledge, spectroscopically not yet fully characterized. The  $^1\text{H}$  NMR signals form, even at 500 MHz, only a rather narrow band

Table I.  $^{77}\text{Se}$ ,  $^{13}\text{C}$ , and  $^1\text{H}$  NMR data for Styrene 1<sup>a</sup>

atom	$\delta$	$^1J(\text{Se,C})$	$^2J(\text{Se,C})$	atom	$\delta$
Se <sub>A</sub>	520.5				
Se <sub>B</sub>	437.3				
C-1	122.54	142.2 (A) 134.1 (B)			
C-2	139.58		8 (A,B)	H-2	7.387
C-3	137.64				
C-4	129.09		7 (B)	H-4	7.516
C-5	129.66			H-5	7.378
C-6	128.02			H-6	7.310
C-7	131.43	104.9 (A)			
C-8	134.56		11 (A)	H-8	7.596
C-9	128.40			H-9	7.385
C-10	128.48			H-10	7.439
C-11	130.95	104.0 (B)			
C-12	133.65		12 (B)	H-12	7.510
C-13	129.24			H-13	7.304
C-14	128.01			H-14	7.344

<sup>a</sup>  $^{77}\text{Se}$   $\delta$  values are in ppm with respect to external  $\text{Me}_2\text{Se}$  and  $^{13}\text{C}$   $\delta$  values with respect to TMS. Spin coupling constants are in hertz; only the absolute values are given. The signs of the spin coupling constants were not determined. Characters in brackets indicate the coupling selenium atom.

of overlapping aromatic multiplets including surprisingly the olefinic proton at C-2. The signal of H-2 is found in the middle of the other aromatic signals, probably due to the vicinity of two aromatic ring systems.



The  $^{13}\text{C}$  NMR spectrum reveals, as expected, a set of 14 closely resonating signals; of the four quaternary signals three have  $^{77}\text{Se}$  satellites. The resonances of the hydrogen-bearing carbon atoms can be grouped into ortho, meta, and para carbon atoms by observing the fine structure within the  $^1\text{H}$ -coupled  $^{13}\text{C}$  NMR spectrum;<sup>14</sup> further assignments, however, are at this stage rather tentative. All three ortho carbon atoms show long-range  $^{77}\text{Se}$  satellites.

In Figure 1 we show the  $^{13}\text{C}$ ,  $^{77}\text{Se}$  correlation performed by the polarization transfer method,<sup>9</sup> where the refocusing delay was adjusted corresponding to a  $^1J(^{13}\text{C}, ^{77}\text{Se})$  spin coupling constant of 110 Hz. Due to the fact that quaternary carbon atoms had to be correlated with selenium atoms which were not protonated, a relatively long relaxation delay of 20 s was necessary. In our earlier work comparing different correlation methods for 2D  $^{13}\text{C}$ ,  $^{31}\text{P}$  spectroscopy, it was shown that this method has the best performance with respect to long relaxation times.<sup>8</sup> Inspection of Figure 1 immediately reveals the assignment of C-1, with both selenium atoms connected and, furthermore, relates the upfield selenium resonance at  $\delta = 437.3$  to the carbon signal at  $\delta = 130.95$  and, in addition, the downfield selenium resonance at  $\delta = 520.5$  to the carbon signal at  $\delta = 131.43$ . However, a relative assignment of the two selenium signals or the carbon signals is not yet possible with this information. Since correlations over

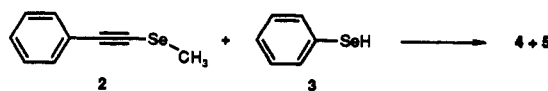
two bonds are less sensitive due to the relatively long refocusing delay, we chose our INEPT-HMQC sequence<sup>11</sup> introduced for  $^{13}\text{C}$ ,  $^{29}\text{Si}$  correlations, as the best method to perform a  $^{13}\text{C}$ ,  $^{77}\text{Se}$  correlation over more than one bond. Prior to the experiment, it was shown that a 1D refocused  $^{77}\text{Se}$  INEPT spectrum increased the S/N ratio by about 3 using a refocusing delay corresponding to a Se,H spin coupling constant of 8 Hz. Using 10 Hz as the active coupling between selenium and carbon the correlation shown in Figure 2 was performed; here only a 3-s relaxation delay was necessary, since the relaxation of the hydrogen atoms dominate the repetition time of this experiment.<sup>11</sup>

Inspection of Figure 2 again immediately secures the assignment of one carbon, C-2, since it displays cross peaks to both selenium atoms. Furthermore the corresponding connections to the ortho carbon atoms within the selenylated phenyl rings can be clearly seen. In addition, besides some unavoidable  $t_1$  noise, one observes a coupling constant between the high field Se<sub>B</sub> signal and the ortho carbon atoms of the remaining phenyl ring. Nevertheless, the question of which selenium or carbon signal belongs to the *E* or *Z* side of the styrene molecule has yet to be answered.

However, since the assignment of C-2 is secure owing to the correlation with both selenium atoms, the corresponding hydrogen could be identified by an inverse H,C correlation; similarly the position of the ortho hydrogens at C-4, C-8, and C-12 was revealed by this experiment. C-4 could be secured by observing an inverse long-range correlation signal to H-2.

A Se,H correlation revealed three cross peaks. Both selenium atoms are coupled to H-2 with different coupling constants of 13.1 and 6.8 Hz. We have to assume that the larger Se,H coupling constant connects H-2 with the trans selenium atom Se<sub>B</sub>, since only this is in accordance with the observation that selenium atom Se<sub>B</sub> couples with both H-4 and C-4 (*vide infra*). Our assignments are corroborated by finding a NOESY cross peak between H-2 and H-8. The remaining signals could be assigned by the standard combination of COSY, NOESY, and H,C correlation, leading to the values given in Table I.

However, the assignment of the larger Se,H spin coupling to the *trans* olefinic moiety is in clear contradiction to literature reports. Johannsen, Henriksen, and Eggert<sup>15</sup> have investigated the  $^{77}\text{Se}$  NMR spectra of several diseleno-substituted alkenes with a low-field instrument. Their analyses was done only in mixtures without chemical separation and purification of the various compounds. Since, in the light of our example, their results were questionable, we decided to reinvestigate two of their reported compounds, which are closely related to 1. Thus, we reacted 1-phenyl-2-(methylseleno)acetylene (2) with benzeneselenol (3) in refluxing THF and obtained two compounds, which were purified by MPLC chromatography and identified by high-resolution mass spectroscopy, as two isomers containing a methylseleno and a phenylseleno group.



From compound 4 we obtained the  $^{77}\text{Se}$  chemical shifts at  $\delta = 319.5$  and  $422.8$  and from the isomer 5 the  $^{77}\text{Se}$

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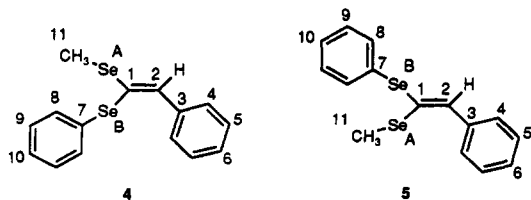
(15) Johannsen, I.; Henriksen, L.; Eggert, H. *J. Org. Chem.* 1986, 51, 1657.

Table II.  $^{77}\text{Se}$ ,  $^{13}\text{C}$ , and  $^1\text{H}$  NMR data for Styrenes 4 and 5<sup>a</sup>

4				5				
atom	$\delta$	$^1J(\text{Se,C})$	$^2J(\text{Se,C})$	other $J$	$\delta$	$^1J(\text{Se,C})$	$^2J(\text{Se,C})$	other $J$
Se <sub>A</sub>	319.5				257.2			
Se <sub>B</sub>	422.8				489.6			
C-1	121.28	139.6 (A) 133.1 (B)			121.97	139.9 (A) 134.0 (B)		
C-2	135.00		6 (A) 7.4 (B)		139.59		8.7 (A) 13.8 (B)	
C-3	137.05				137.01			
C-4	128.37			5.6 (B) <sup>e</sup>	128.56			8.5 (A) <sup>e</sup>
C-5	127.77				127.83			
C-6	127.07 <sup>b</sup>				127.08 <sup>b</sup>			
C-7	130.79	102.7 (B)			131.34	108.4 (B)		
C-8	132.42		12.3 (B)		131.80		12.8 (B)	
C-9	128.67				129.04			
C-10	127.15 <sup>b</sup>				127.23 <sup>b</sup>			
C-11	9.58	67.9 (A)	12.2 (B)		10.53	65.5 (A)	10.5 (B)	
H-2	6.92			5.3 (A) <sup>c</sup> 11.6 (B) <sup>c</sup>	7.165			11.0 (A) <sup>e</sup> 8.9 (B) <sup>e</sup>
H-4	7.18				7.17-20			
H-5	6.98				7.01			
H-6	6.88 <sup>b</sup>				6.92			
H-8	7.20				7.24-9			5 (B) <sup>e</sup>
H-9	6.89				6.97			
H-10	6.96 <sup>b</sup>				6.92			
H-11	1.85			11.0 (A) <sup>d</sup>	1.82			12.1 (A) <sup>d</sup>

<sup>a</sup>  $^{77}\text{Se}$   $\delta$  values are in ppm with respect to external  $\text{Me}_2\text{Se}$  and  $^{13}\text{C}$   $\delta$  values with respect to TMS. Spin coupling constants are in hertz; only the absolute values are given. The signs of the spin coupling constants were not determined. Characters in brackets indicate the coupling selenium atom. <sup>b</sup> Relative assignment tentative. <sup>c</sup>  $^3J(\text{Se,H})$ . <sup>d</sup>  $^2J(\text{Se,H})$ . <sup>e</sup>  $^4J(\text{Se,C})$ .

chemical shifts at  $\delta = 257.2$  and  $489.6$ . From these values the compounds can be identified as **3b** and **3c** in the work of Eggert.<sup>15</sup> On standing in  $\text{CDCl}_3$  in sealed NMR tubes, the compounds interconvert slowly into each other, approaching a 1:1 mixture after weeks. Performing  $^{13}\text{C}$ ,  $^{77}\text{Se}$  correlations, however, reveals that in **4** and **5** both seleno groups are bound to the same olefinic carbon, thus the structures reported by Eggert with the seleno groups at opposite ends of the double bond must be wrong as well as their conclusions on the stereochemical relationship of  $^3J(\text{Se,H})$  deduced from these wrong structures. Using all the assignment methods reported for compound **1**, we assign the structures of **4** to the compound **3b**<sup>15</sup> and **5** to **3c**.<sup>15</sup> Our stereochemical differentiation between **4** and **5** relies on NOE contacts between the olefinic proton in **5** and the ortho hydrogens of the selenylated phenyl ring, whereas in **4** a NOE contact between the methyl group and the olefinic proton is revealed. Using a Se,H correlation it could then be shown, that, in both compounds, the *trans*  $^3J(\text{Se,H})$  spin coupling constants with 11.6 and 11.0 Hz are larger than the corresponding *cis*  $^3J(\text{Se,H})$  spin coupling constants with 5.3 and 8.9 Hz in full accord with our results obtained from **1**. We feel that this result may well be general. The full NMR data for **4** and **5** are given in Table II.



In all three compounds reported in this paper we observe a spin coupling constant over four formal bonds between one selenium atom and the ortho carbon of the cisoid phenyl ring. Although a spin coupling over four bonds is not unusual for heteroatoms within a skeleton of  $\text{sp}^2$

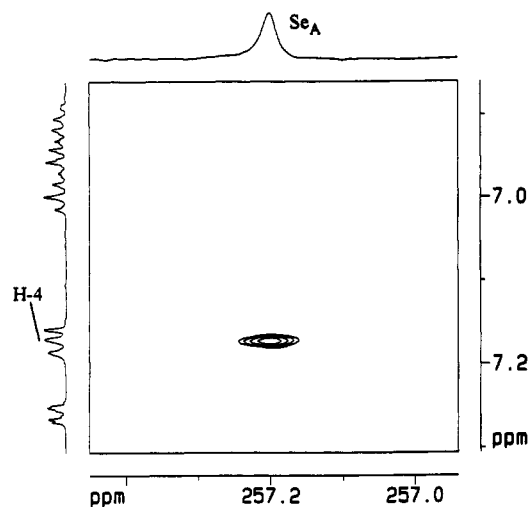


Figure 3. Extension of a  $^{77}\text{Se}$ -detected  $^1\text{H}$ ,  $^{77}\text{Se}$  2D HOESY spectrum of **5** obtained with a relaxation delay of 3 s and a mixing time of 100 ms.

hybridized carbon atoms, the stereochemical dependence is remarkable, since in all three compounds the corresponding *trans*-selenium atom does not show a spin coupling constant for the same number of intervening bonds. This could be a case of through-space spin coupling<sup>16</sup> as molecular models show rather close contacts of the selenium to the cisoid phenyl ring. This steric contact should be revealed by observing a HOESY<sup>17</sup> signal connecting the hydrogen atoms H-4 with the cisoid selenium. Indeed, such a  $^1\text{H}$ ,  $^{77}\text{Se}$  HOESY contact was measured in compound **5** and thus independently corroborates our stereochemical assignments. This can be seen from Figure 3, which displays a HOESY contact of

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(17) Rinaldi, P. L. *J. Am. Chem. Soc.* 1983, 105, 5167. Yu, C.; Levy, G. C. *J. Am. Chem. Soc.* 1984, 106, 6533.

selenium atom  $\text{Se}_A$  with H-4. To the best of our knowledge, this is the first example of an  $^1\text{H}$ ,  $^{77}\text{Se}$  HOESY spectrum, whereas this technique is widely used for  $^1\text{H}$ ,  $^6\text{Li}$ .<sup>18</sup>

### Conclusion

In this work we have shown the feasibility of 2D  $^{13}\text{C}$ ,  $^{77}\text{Se}$  correlation spectroscopy; with a three-channel spectrometer and a corresponding multinuclear triple resonance probe head these experiments are not very difficult to perform. The figures presented in this work demonstrate how difficult assignments may be easily made by simple inspection of these 2D matrices. Furthermore, this method has led to reassignments of structures reported in the literature.

### Experimental Section

All spectra were recorded on a Bruker AMX-500 spectrometer at 300 K using a saturated sample of 1 in  $\text{CD}_2\text{Cl}_2$ ; 4 and 5 were 30% solutions in  $\text{CDCl}_3$ . A triple resonance probe head with a

(18) Bauer, W.; Ragué-Schleyer, P. v. *Adv. Carbanion Chem.* 1992, 1, 89.

$^1\text{H}$  coil in inverse geometry was used; this coil was double tuned to  $^{13}\text{C}$  at 125.76 MHz. A second multinuclear tunable coil was adjusted to  $^{77}\text{Se}$  at 95.36 MHz. The 2D spectra were taken for 2048 data points in  $F_2$  and with 64 time increments in  $F_1$  using relaxation delays of 20 s and 140 scans for each FID in the case of the correlation over one bond and 3 s when using the INEPT-HMQC method. An exponential window in  $F_2$  and a  $\pi/2$  shifted squared sinebell window in  $F_1$  was applied.  $\delta_{\text{Se}}$  values are referenced to external  $\text{Me}_2\text{Se}$ ;  $\delta_{\text{C}}$  values were measured vs  $\text{CD}_2\text{Cl}_2$  or  $\text{CDCl}_3$  and calculated with  $\delta(\text{TMS}) - \delta(\text{CD}_2\text{Cl}_2) = 53.73$  and  $\delta(\text{TMS}) - \delta(\text{CDCl}_3) = 77.0$ .

Compound 1 was prepared according to literature procedures<sup>13</sup> and compounds 4 and 5 according to reference 15 with the exception that selenophenol was used directly. Reaction of 2.5 g of 2 and 2.0 g of 3 gave 3.7 g of an orange mixture after high vacuum condensation. MPLC-chromatography on Lichroprep Si60 (63–125  $\mu\text{m}$ ) (Merck) with PE (40–60 °C) gave clean separation of 4 and 5.

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