

## CARBON-13 AND SILICON-29 NMR SPECTRA OF SUBSTITUTED PHENYLSILANES\*

J. SCHRAML<sup>a</sup>, V. CHVALOVSKÝ<sup>a</sup>, M. MÄGI<sup>b</sup> and E. LIPPMÄA<sup>b</sup>

<sup>a</sup> Institute of Chemical Process Fundamentals,  
Czechoslovak Academy of Sciences, 165 02 Prague 6 - Suchbát, and

<sup>b</sup> Institute of Cybernetics, Estonian Academy of Sciences, Tallinn, U.S.S.R.

Received August 28th, 1974

<sup>13</sup>C and <sup>29</sup>Si NMR spectra are presented for various phenylsilanes (and a few benzylsilanes) substituted on the benzene ring. Spectra of ring carbon atoms agree with those predicted on the basis of the additivity rule and the assignment made previously for the spectra of phenyl-substituted silanes.

In the previous paper of this series<sup>1</sup>, in which NMR data for phenyl- and benzyl-substituted silanes were given, we were mainly concerned with the difference between the spectra of phenyl- and benzylsilanes and with the effects that interaction of the silicon atom and the benzene ring have on the NMR spectra of carbon and silicon. Since some conclusions drawn in that paper<sup>1</sup> were based on the assigned carbon-13 NMR lines, supporting evidence for those assignments has been sought and found in the spectra of related phenyl and benzylsilanes in which the benzene ring bears another substituent (besides the silyl group). Silicon-29 chemical shifts in this type of compounds are of current interest<sup>2</sup>.

### EXPERIMENTAL

NMR spectra were measured under the same conditions and on the same spectrometer as described earlier<sup>1</sup>. With the exceptions given below, the silanes studied here were prepared previously<sup>3-9</sup> and redistilled before measurements if necessary. Purity and identity of the compounds were checked by gas-liquid chromatography and <sup>1</sup>H-NMR spectroscopy.

*p*-Methoxyphenyltrichlorosilane was prepared in the usual way by the Grignard synthesis from *p*-bromoanisole and tetrachlorosilane. The fraction boiling at 130–132°C/15 Torr was obtained in 34% yield.

*p*-Tolyltrichlorosilane was prepared analogously in 38% yield (215–218°C fraction).

\* Part II in the series NMR Study of Organosilicon Compounds; Part I: This Journal 40, 875 (1975).

## RESULTS AND DISCUSSION

Carbon-13 and silicon-29 NMR data which could be obtained from the spectra are given in Table I; chemical shifts are given in p.p.m. with positive values indicating less shielding than in the reference compound. Tetramethylsilane was used as an (external) reference compound (for both nuclei) in accord with the published recommendations<sup>1,11-13</sup>, however, for the purpose of the application of additivity rules ring carbon chemical shifts are also given (Table II) relative to the benzene line. (For conversion, the value 128.1 p.p.m. was used as the chemical shift of the benzene line (proton decoupled) as determined in this laboratory, though other values can be found in the literature (e.g. 128.7 p.p.m.<sup>12</sup> or 128.5 p.p.m.<sup>13</sup>)).

Using the now well documented additivity rule for <sup>13</sup>C chemical shifts of ring carbon atoms<sup>13-15</sup>, these shifts were calculated from the shifts of monosubstituted benzenes. Unless otherwise noted, values given by Levy and Nelson<sup>13</sup> were used for the shifts of monosubstituted derivatives not containing a silicon atom. For the other substituents the values assembled in Table III were used. Taking into account the experimental errors involved, it was expected that the calculated shifts could differ from those observed by 0.7 p.p.m. (on the average).


The observed chemical shifts of aryl carbon atoms were ordered according to their magnitude and then assigned primarily on the basis of the order of the calculated shifts to individual carbon atoms. In all cases the shifts calculated for substituted carbon atoms corresponded to the lines of lower intensity, in accord with the symmetry of the molecules (exceptions to this rule were compounds in which the C-1 line accidentally coincided with that of the C-2 or C-3 carbon atom; in *p*-tolyl-dimethylfluorosilane and 4-chlorophenyltriethoxysilane the differences between the calculated shifts were less than meaningful (0.7 p.p.m.) so the assignments had to be corrected on the grounds of intensity). The difference between the shifts calculated for the C-1 and C-4 carbon atoms was always large enough to allow an unambiguous assignment of these two lines. Even larger were the differences between the calculated shifts of C-2 and C-3 and so the assignment was without problems.

In the case of fluorophenyl derivatives the assignment was verified by the relative magnitude of the <sup>19</sup>F-<sup>13</sup>C coupling constants. These constants have been found empirically to decrease in the order  $J_{CF}$  (~240 Hz) >  $J_{CCF}$  (~20 Hz) >  $J_{CCC}$  (~8 Hz) >  $J_{CCCC}$  (~3 Hz) in fluorobenzenes (the last relation might not hold in *ortho*-substituted compounds)<sup>17,18</sup>. In the compounds containing a Si-F bond the C-1 carbon atom bonded to the silicon atom could be also differentiated from the other (C-4) substituted carbon atom by the <sup>19</sup>F-<sup>13</sup>C coupling which for C-1 is close to 20 Hz and is about zero for the C-4 atom.

It is obvious from an inspection of Table II that the calculated shifts agree rather well with the experimental ones. The deviations show approximately normal distribution with standard deviations for C-1, C-2, C-3, and C-4 shifts of 1.096,

TABLE I  
Carbon-13 and Silicon-29 NMR Data for 1-X,4-Y-Substituted Benzenes<sup>a</sup>

Substituents		Chemical shifts						
1-X	4-Y	silicon $\delta_{Si}$	carbon $\delta_C$					
			C-1	C-2	C-3	C-4	SiCH <sub>3</sub>	other
Si(CH <sub>3</sub> ) <sub>3</sub>	F	-4.01 <sup>b</sup>	135.2	134.8 <sup>c</sup>	114.5 <sup>d</sup>	163.5 <sup>e</sup>	-1.5	-
	Cl	-3.78 <sup>f</sup>	137.9	134.3	127.7	134.8	-1.5	-
	Br	-4.1	139.0	135.1	131.2	123.9	-0.7	-
	CH <sub>3</sub>	-5.2	135.8	132.7	128.1	137.4	-1.1	21.2 (CH <sub>3</sub> )
	C <sub>2</sub> H <sub>5</sub>	-5.0	136.9	133.7	127.6	144.8	-0.7	29.3 (CH <sub>2</sub> ), 15.8 (CH <sub>3</sub> )
	Si(CH <sub>3</sub> ) <sub>3</sub>	-4.2	141.1	133.0	133.0	141.1	-0.7	-
Si(CH <sub>3</sub> ) <sub>2</sub> Cl	F	19.7	131.8	135.2 <sup>g</sup>	115.2 <sup>h</sup>	164.1 <sup>i</sup>	1.8	-
	Cl	19.8	134.7	134.7	128.6	136.9	2.3	-
	Br	19.7	134.6	134.6	131.2	125.2	2.4	-
	OCH <sub>3</sub>	19.6	126.6	134.3	113.6	161.1	2.1	54.6 (CH <sub>3</sub> )
Si(CH <sub>3</sub> )Cl <sub>2</sub>	Br	18.2	132.0	134.5	131.6	126.9	5.7	-
	CH <sub>3</sub>	19.3	130.4	133.6	129.7	142.3	6.0	22.1 (CH <sub>3</sub> )
SiCl <sub>3</sub>	Cl	-2.2	128.8	133.5	128.0	138.6	-	-
	CH <sub>3</sub>	-2.1	127.6	131.2	127.6	141.4	-	20.4 (CH <sub>3</sub> )
	OCH <sub>3</sub>	-2.2	121.0	133.8	113.1	162.1	-	54.1 (CH <sub>3</sub> )
Si(CH <sub>3</sub> ) <sub>2</sub> F	CH <sub>3</sub>	19.8 <sup>j</sup>	132.6 <sup>k</sup>	133.3	129.0	140.1	-1.3 <sup>l</sup>	21.3 (CH <sub>3</sub> )
Si(CH <sub>3</sub> )F <sub>2</sub>	CH <sub>3</sub>	-12.2 <sup>m</sup>	126.1 <sup>n</sup>	133.0	128.6	141.6	-6.1 <sup>o</sup>	20.6 (CH <sub>3</sub> )
CH <sub>2</sub> Si(CH <sub>3</sub> ) <sub>3</sub>	Cl	0.6	138.2	128.5	127.6	128.7	-2.2	26.2 (CH <sub>2</sub> )
CH <sub>2</sub> Si(OC <sub>2</sub> H <sub>5</sub> ) <sub>3</sub>	Cl	-53.4	153.8	129.4	127.2	129.2	-	17.7 (CH <sub>3</sub> ), 19.7 (CH <sub>2</sub> Si) <sup>p</sup>
CH <sub>2</sub> SiCl <sub>3</sub>	Cl	6.9	130.4	130.6	128.9	132.5	-	32.2 (CH <sub>2</sub> )
Si(CH <sub>3</sub> ) <sub>2</sub> R <sup>q</sup>	F	-8.3	133.7	136.2 <sup>r</sup>	115.2 <sup>s</sup>	164.3 <sup>t</sup>	-2.2	-

<sup>a</sup> Chemical shifts in  $\delta$  scale, *i.e.* in p.p.m. relative to the line of TMS (external), positive values indicate lower shielding, maximum error  $\pm 0.3$  p.p.m. Coupling constants in Hz. Ring carbon atoms C-1 do C-4 numbered according to the scheme ; <sup>b</sup> Value of ref.<sup>10</sup> after conversion into our scale; our value  $\delta = -4.4$ ; <sup>c</sup>  $J_{CCCF} = 6 \pm 1$ ; <sup>d</sup>  $J_{CCF} = 20 \pm 1$  Hz; <sup>e</sup>  $J_{CF} = 248 \pm 1$  Hz; <sup>f</sup> Value of ref.<sup>10</sup> after conversion into our scale; our value  $\delta = -4.2$ ; <sup>g</sup>  $J_{CCCF} = 7.5 \pm 1$  Hz; <sup>h</sup>  $J_{CCF} = 20.5 \pm 1$  Hz; <sup>i</sup>  $J_{CF} = 250 \pm 1$  Hz; <sup>j</sup>  $J_{SiF} = 279 \pm 1$  Hz; <sup>k</sup>  $J_{CF} = 16 \pm 1$  Hz; <sup>l</sup>  $J_{CF} = 14 \pm 1$  Hz; <sup>m</sup>  $J_{SiF} = 290 \pm 1$  Hz; <sup>n</sup>  $J_{CSiF} = 19 \pm 1$  Hz; <sup>o</sup>  $J_{CSiF} = 14 \pm 1$  Hz; <sup>p</sup> 57.8 (CH<sub>2</sub>O); <sup>q</sup> R = *p*-C<sub>6</sub>H<sub>4</sub>F; <sup>r</sup>  $J_{CP} = 6.5 \pm 1$  Hz; <sup>s</sup>  $J_{CF} = 19 \pm 1$  Hz; <sup>t</sup>  $J_{CF} = 249 \pm 1$  Hz.

0.692, 0.693, and 0.987 p.p.m., resp. (the standard deviation for the total of 80 chemical shifts is 0.882 p.p.m.). The slightly larger deviations for the substituted carbon atoms C-1 and C-4 are easy to understand, for these shifts are given by the balancing of two relatively large substituent effects. It is rather satisfying to see from Fig. 1 that the deviation from the ideal 45° line does not depend on the magnitude of the shift. The largest deviation is encountered in the compound with X = SiCl<sub>3</sub> and Y = OCH<sub>3</sub>. Any different assignment would, however, lead to even larger deviation.

Good numerical agreement between the calculated and observed chemical shifts gives sufficient reason to conclude that 1) the assignments made here and in the previous paper<sup>1</sup> are correct (and similarly it confirms the tentative assignments offered for ethylbenzene in ref.<sup>16</sup>), 2) the additivity relationship is applicable to the class of compounds studied (*i.e.* no specific interaction between the silicon atom and the substituent Y (in *para* position) could be noticed on the benzene ring), and 3) the shifts given in Table III can be used as the shielding contributions of the various silylated groups (X) to the shielding of the ring carbons in disubstituted benzenes. For the sake of completeness, the substituent effects not yet tested for disubstituted benzenes were also included in Table III. In the case of —CH<sub>2</sub>SiRR'R'', the substituent effects vary regularly and only slightly, so there is every reason to believe that the additivity and magnitude of these effects will be confirmed by future measurements (especially as the effects of the CH<sub>2</sub>SiR<sub>3</sub> groups were verified here).

In keeping with the general trends<sup>16</sup>, the additivity of the substituent effects is well applicable to *meta*-substituted silylbenzenes. In *ortho* derivatives, in which steric interference occurs between the neighbouring groups, considerable deviations from

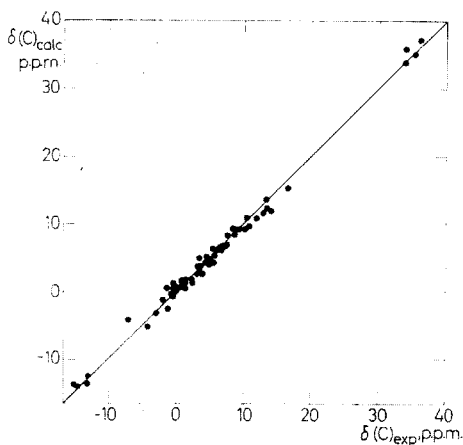


FIG. 1

<sup>13</sup>C Chemical Shifts Calculated According to Additivity Rule vs Experimental Shifts

additivity are apparent from the comparison of the following data.  $^{13}\text{C}$  Chemical shifts (exptl./calc.): 3-trimethylsilyltoluene C-1 (136.7/136.2), C-2 (134.1/133.5), C-3 (139.8/139.3), C-4 (130.7/129.9), C-5 (128.0/127.2), C-6 (129.9/129.0), 2-trimethylsilyltoluene C-1 (143.3/141.6), C-2 (138.0/140.1), C-3 (134.6/132.7), C-4 (125.5/124.4), C-5 (129.6/128.0), C-6 (130.1/128.2).

The  $^{13}\text{C}$  chemical shifts of  $\text{CH}_3\text{Si}$  carbon atoms deserve some comment. As the data of Table I indicate, these shifts vary only slightly but since in several classes

TABLE II  
Aryl Carbon-13 NMR Chemical Shifts in 1-X,4-Y-Substituted Benzenes<sup>a</sup>

Substituents		Carbon-13 chemical shifts							
1-X	4-Y	C-1		C-2		C-3		C-4	
		exptl. <sup>b</sup>	calc. <sup>c</sup>	exptl. <sup>b</sup>	calc. <sup>c</sup>	exptl. <sup>b</sup>	calc. <sup>c</sup>	exptl. <sup>b</sup>	calc. <sup>c</sup>
$\text{Si}(\text{CH}_3)_3$	F	7.1	6.8	6.7	6.1	-13.6	-13.7	35.4	35.0
	Cl	9.8	9.4	6.2	6.0	-0.4	-0.4	6.7	6.4
	Br	10.9	9.7	7.0	6.4	3.1	2.6	-4.2	-5.3
	$\text{CH}_3$	7.7	8.4	4.6	4.6	0.0	-0.1	9.3	9.1
	$\text{C}_2\text{H}_5$ <sup>d</sup>	8.8	9.1	5.6	5.1	-0.5	-0.9	16.7	16.2
	$\text{Si}(\text{CH}_3)_3$ <sup>e</sup>	13.0	11.5	4.9	3.9	4.9	3.9	13.0	11.5
$\text{Si}(\text{CH}_3)_2\text{Cl}$	F	3.7	3.6	7.1	6.5	-12.9	-12.7	36.0	37.0
	Cl	6.6	6.2	6.6	6.4	0.5	0.6	8.8	8.4
	Br	6.5	6.5	6.5	6.8	3.1	3.6	-2.9	-3.3
	$\text{OCH}_3$	-1.5	0.4	6.2	6.1	-14.5	-14.2	33.0	33.6
$\text{Si}(\text{CH}_3)\text{Cl}_2$	Br	3.9	2.5	6.4	6.0	3.5	3.0	-1.2	-2.6
	$\text{CH}_3$	2.3	1.2	5.5	4.2	1.6	0.3	14.2	11.8
$\text{SiCl}_3$	Cl	0.7	1.4	5.4	6.3	-0.1	0.9	10.5	10.9
	$\text{CH}_3$	-0.5	0.4	3.1	4.9	-0.5	1.2	13.3	13.6
	$\text{OCH}_3$	-7.1	-4.4	5.7	6.0	-15.0	-13.9	34.0	36.1
$\text{Si}(\text{CH}_3)\text{F}$	$\text{CH}_3$	4.5	5.0	5.2	4.7	0.9	0.5	12.0	10.9
$\text{Si}(\text{CH}_3)\text{F}_2$	$\text{CH}_3$	-2.0	-1.3	4.9	4.8	0.5	0.6	13.5	12.3
$\text{CH}_2\text{Si}(\text{CH}_3)_3$	Cl	10.1	9.1	0.4	0.4	-0.5	-0.5	0.6	1.2
$\text{CH}_2\text{Si}(\text{OC}_2\text{H}_5)_3$	Cl	7.7	6.9	1.3	1.2	-0.9	-0.5	1.1	1.7
$\text{CH}_2\text{SiCl}_3$	Cl	2.3	1.1	2.5	1.7	0.8	0.8	4.4	4.1

<sup>a</sup> Carbon-13 chemical shifts in p.p.m. relative to benzene line which is taken to be 128.1 p.p.m. in TMS scale; positive values indicate lower shielding; <sup>b</sup> converted from the experimental data of Table I; <sup>c</sup> calculated on the basis of additivity principle from the data of Table III and of ref.<sup>13</sup>; <sup>d</sup> data of ref.<sup>16</sup> were used in the calculation; <sup>e</sup> only data of Table I were used in the calculation.

of closely related compounds ( $\text{XC}_6\text{H}_4\text{SiMe}_3$  (ref.<sup>19-22</sup>,  $\text{XC}_6\text{H}_4\text{SiHMe}_2$  (ref.<sup>23,24</sup>,  $\text{XC}_6\text{H}_4\text{SiH}_2\text{Me}$  (ref.<sup>23,24</sup>,  $\text{XC}_6\text{SiM}_2\text{SiHMe}_2$  (ref.<sup>25</sup>) and  $\text{XC}_6\text{H}_4\text{SiH}_3$  (ref.<sup>23,24</sup>), linear Hammett-type correlations were found to hold for proton chemical shifts<sup>19-23</sup> and one bond coupling constants (proton-carbon<sup>19,22-25</sup> and proton-silicon<sup>23,24</sup>) such a relationship was also sought in the present data. Our failure to observe a relationship of this type is apparently due to relatively large experimental error (relative

TABLE III  
Substituent Effects on Aryl Carbon-13 Chemical Shift in 1-X-Substituted Benzenes<sup>a</sup>

Substituent X	Aryl carbon position			
	C-1	<i>ortho</i>	<i>meta</i>	<i>para</i>
$\text{Si}(\text{CH}_3)_3$	+11.3	+4.7	-0.8	+0.2
$\text{Si}(\text{CH}_3)_2\text{Cl}$	+ 8.1	+5.1	+0.2	+2.2
$\text{Si}(\text{CH}_3)\text{Cl}_2$	+ 4.1	+4.3	-0.4	+2.9
$\text{SiCl}_3$	+ 3.3	+5.0	+0.5	+4.7
$\text{Si}(\text{CH}_3)_2\text{F}$	+ 7.9	+4.8	-0.2	+2.0
$\text{Si}(\text{CH}_3)\text{F}_2$	+ 1.6	+4.9	-0.1	+3.4
$\text{CH}_2\text{Si}(\text{CH}_3)_3$	+11.0	-0.9	-0.9	-5.0
$\text{CH}_2\text{Si}(\text{OC}_2\text{H}_5)_3$	+ 8.8	-0.1	-0.9	-4.5
$\text{CH}_2\text{SiCl}_3$	+ 3.0	+0.4	+0.4	-2.1
$\text{SiF}_3$	(- 8.0)	(+5.8)	(0.0)	(+4.6)
$\text{SiH}_3$	(- 0.6)	(+7.4)	(-0.4)	(+1.3)
$\text{Si}(\text{CH}_3)_2(\text{OC}_2\text{H}_5)$	(+ 9.7)	(+4.9)	(-0.7)	(+0.9)
$\text{Si}(\text{CH}_3)(\text{OC}_2\text{H}_5)_2$	(+ 5.7)	(+4.8)	(-1.4)	(+0.7)
$\text{Si}(\text{OC}_2\text{H}_5)_3$	(+ 3.2)	(+6.1)	(-0.9)	(+1.4)
$\text{Si}(\text{C}_6\text{H}_5)_3$	(+ 6.4)	(+8.5)	(0.0)	(+1.8)
$\text{SiH}_2(\text{C}_6\text{H}_5)$	(+ 3.5)	(+7.9)	(+0.3)	(+2.1)
$\text{Si}(\text{CH}_3)(\text{C}_6\text{H}_5)_2$	(+ 8.3)	(+7.5)	(-0.1)	(+1.5)
$\text{CH}_2\text{Si}(\text{CH}_3)_2\text{Cl}$	(+ 7.8)	(-0.5)	(-0.5)	(-4.0)
$\text{CH}_2\text{SiCH}_3\text{Cl}_2$	(+ 5.5)	(+0.1)	(+0.1)	(-2.8)
$\text{CH}_2\text{Si}(\text{CH}_3)_2(\text{OC}_2\text{H}_5)$	(+10.3)	(-0.6)	(-0.6)	(-4.7)
$\text{CH}_2\text{Si}(\text{CH}_3)(\text{OC}_2\text{H}_5)_2$	(+ 9.5)	(-0.4)	(-0.4)	(-4.5)
$\text{CH}_2\text{Si}(\text{CH}_3)\text{F}_2$	(+ 8.8)	(-0.2)	(-0.2)	(-4.0)
$\text{CH}_2\text{SiCH}_3\text{F}_2$	(+ 5.5)	(-0.3)	(-0.3)	(-3.5)
$\text{CH}_2\text{SiF}_3$	(+ 2.9)	(+0.3)	(+0.3)	(-2.3)
$\text{CH}_2\text{CH}_2\text{Si}(\text{CH}_3)_3$	(+16.9)	(0.0)	(0.0)	(-2.4)
$\text{CH}_2\text{CH}_2\text{CH}_2\text{Si}(\text{CH}_3)_3$	(+14.3)	(+0.5)	(+0.5)	(-2.2)
$(\text{CH}_2)_4\text{Si}(\text{CH}_3)_3$	(+14.8)	(+0.7)	(+0.7)	(-1.9)

<sup>a</sup> Converted from the data of ref.<sup>1</sup> using chemical shift of benzene 128.1 p.p.m. In p.p.m. relative to external benzene, positive values indicate deshielding. Values derived for neat liquids, reliable to  $\pm 0.5$  p.p.m. Values in parentheses have not yet been verified by application of additivity rule.

to the overall variation) and by the necessity to measure the spectra in neat liquids. It is especially this latter factor that could account for masking the relationship, for it is known<sup>21</sup> that a solvent can alter the sign of the regression coefficient in a correlation of this type. It is very likely that the relationship in question could be found if Fourier transform NMR spectra were measured in diluted solutions. The relationship would be useful in comparison with a similar relationship for silicon-29 chemical shifts.

If the present data for silicon-29 chemical shifts (combined with the data taken from ref.<sup>1</sup> for the compounds with Y = H) are plotted against Hammett  $\sigma$  constants and compared with the data and similar plot of Maciel and coworkers<sup>10</sup>, then it is apparent that, after appropriate conversion, our data are generally shifted 0.5 p.p.m. to higher field than those of ref.<sup>10</sup>, but the slopes are of the same sign and of very similar magnitude in trimethylsilyl derivatives. The observed trend is in keeping with the naive expectation that the electron-withdrawing substituent should produce a shift of silicon resonance to a lower field in the same way that it shifts methyl proton resonance (in most solvents<sup>19-22</sup>) in this and in the related<sup>23,24</sup> classes of compounds. In a recent communication Spialter and coworkers<sup>2</sup>, however, reported that in substituted phenyltrifluorosilane the response of the silicon-29 magnetic shielding to substitution is opposite, *i.e.* that electron-withdrawing substituents produce unexpected shifts to higher field. Present limited data for the intermediate types of compounds (methyl difluoro- and dimethylfluorosilylbenzenes) do not guarantee reasonable estimation of the slopes for these intermediate cases.

*Clarifying discussions with Drs G. Engelhardt and H. Jancke, Central Institute of Physical Chemistry, Academy of Science of GDR, are gratefully acknowledged and critical comment of Prof. J. M. Bellama, University of Maryland, College Park, is appreciated.*

#### REFERENCES

1. Nguyen-Duc-Chuy, Chvalovský V., Schraml J., Mägi M., Lippmaa E.: *This Journal* 40, 875 (1975).
2. Ernst C. R., Spialter L., Buel G. R., Wilhite D. P.: *J. Organometal. Chem.* 59, C 13 (1973).
3. Včelák J., Bažant V., Chvalovský V.: *This Journal* 35, 136 (1970).
4. Chvalovský V., Bažant V.: *This Journal* 16, 580 (1951).
5. Hetflejš J., Mareš F., Chvalovský V.: *This Journal* 30, 1643 (1965).
6. Mareš F., Neudörfl P., Plizák Z., Chvalovský V.: *This Journal* 35, 2324 (1970).
7. Včelák J., Chvalovský V.: *This Journal* 38, 1055 (1973).
8. Mareš F., Plizák Z., Hetflejš J., Chvalovský V.: *This Journal* 36, 2957 (1971).
9. Vo-Kim-Yen, Papoušková Z., Schraml J., Chvalovský V.: *This Journal* 38, 3167 (1973).
10. Sholl R. L., Maciel G. E., Musker W. K.: *J. Am. Chem. Soc.* 94, 6376 (1972).
11. *IUPAC, Information Bulletin No 4, Recommendations for the Presentation of NMR Data*, IUPAC Secretariat 1970.
12. Stothers J. B.: *Carbon-13 NMR Spectroscopy*, p. 49. Academic Press, New York 1972.
13. Levy G. C., Nelson C. L.: *Carbon-13 Nuclear Magnetic Resonance for Organic Chemists*, Chap. 4. Wiley-Interscience, New York 1972.

14. Stothers J. B.: *Carbon-13 NMR Spectroscopy*, p. 196. Academic Press, New York 1972.
15. Tarpley A. R. jr, Goldstein J. H.: *J. Phys. Chem.* **76**, 515 (1972).
16. Lauer D., Motell E. L., Traficante D. D., Maciel G. E.: *J. Am. Chem. Soc.* **94**, 5335 (1972).
17. Weigert F. J., Roberts J. D.: *J. Am. Chem. Soc.* **93**, 2361 (1971).
18. Miyajima G., Akijama H., Nishimoto K.: *Org. Magn. Res.* **4**, 811 (1972).
19. Sakurai H., Ohtsuru M.: *J. Organometal. Chem.* **13**, 81 (1968).
20. Jaggard J. F. R., Pidcock A.: *J. Organometal. Chem.* **16**, 324 (1969).
21. Hess R. E., Haas C. K., Kaduk B. A., Schaeffer C. D. jr, Yoder C. H.: *Inorg. Chim. Acta* **5**, 161 (1971).
22. Freeburger M. E., Spialter L.: *J. Am. Chem. Soc.* **93**, 1894 (1971).
23. Nagai Y., Ohtsuki M., Nakano T., Watanabe H.: *J. Organometal. Chem.* **35**, 81 (1972).
24. Nagai Y., Matsumoto H., Nakano T., Watanabe H.: *Bull. Chem. Soc. Japan* **45**, 2560 (1972).
25. Cartledge F. K., Riedel K. H.: *J. Organometal. Chem.* **34**, 11 (1972).

Translated by the author (J. S.).