73GE, 17O, 13C NMR SPECTRA OF ALKOXYGERMANES

E. LIEPIŅŠ, I. ZICMANE and E. LUKEVICS*

Institute of Organic Synthesis, Latvian S.S.R., Academy of Sciences, Riga (U.S.S.R.)

(Received November 22nd, 1985)

Summary

^{13}C, ^{17}O and ^{73}Ge NMR spectra of seven tetraalkoxygermanes have been investigated. ^{73}Ge resonance signals in these compounds are more sensitive to structure variations than those of ^{29}Si in isostructural alkoxysilanes. ^{17}O and ^{13}C NMR spectra of alkoxygermanes $Me_{4-n} Ge(OR)_n$ (R = Et, Pr, Bu, i-Bu, s-Bu, $CH_2CH=CH_2$, CH_2CH_2OMe, CH_2CF_3; $n = 1-3$) have been studied.

It has been shown that the magnitude of $(p-d)_\pi$-bonding in the Ge–O bond is smaller than in the Si–O bond, but variation in the extent of $(p-d)_\pi$-overlapping in alkoxygermanes with different substituents is similar to that in the isostructural alkoxysilanes.

Introduction

Alkoxygermanes and germoxanes, unlike alkoxysilanes, have not been thoroughly studied by NMR spectroscopy. The data obtained are generally confined to ^1H [1–10] and ^{13}C NMR [7,11,12] spectra. The above-mentioned germanium compounds possess the Ge–O bond which implies $(p-d)_\pi$-interaction between the lone pair of the oxygen atom and the vacant d-orbitals of the germanium atom. It is assumed that the extent of this interaction in alkoxygermanes is less apparent than in alkoxysilanes [13,14]. Therefore one of the stages of our systematic investigation of alkoxy derivatives of the Group IVB elements by multinuclear NMR spectroscopy is the study of electronic effects in alkoxygermanes using ^{73}Ge, ^{17}O, ^{13}C nuclear resonance signals.

Results and discussion

^{73}Ge NMR spectroscopy

There are practically no data on the ^{73}Ge NMR of alkoxygermanes in the literature. So far ^{73}Ge NMR spectra have been obtained only for $Ge(OMe)_4$ [15]. The quadrupole properties of ^{73}Ge nuclei ($I = 9/2$; quadrupole moment $Q = -0.22$

TABLE 1

^{73}Ge, ^{17}O, ^{13}C NMR PARAMETERS FOR ALKOXYGERMANES $R^1_{4-n}Ge(OR)_n$

No.	R¹	R	n	δ(⁷³Ge) (ppm)	Δν₁/₂ (Hz)	δ(¹⁷O) (ppm)	Δν₁/₂ (Hz)	δ(¹³C)(ppm) R¹	OR	
1	Me	Pr	1	–	–	13.4	260	0	66.69	26.78	10.33
2	Me	GeMe₃	1	–	–	14.6	160	3.51	3.51	–	–
3	Me	CH₂CH=CH₂	1	–	–	14.2	200	0.32	65.71	139.27	114.45
4	Bu	Pr	1	–	–	-7.2	420	a	66.61	27.07	10.45
5	Bu	CH₂CH=CH₂	1	–	–	-12.6	550	b	65.97	139.60	113.86
6	Me	CH₂CF₃	1	–	–	-17.7	180	0.19	64.32	125.48	–
7	Me	Pr	2	–	–	18.2	360	-1.62	65.97	26.56	10.39
8	Me	i-Pr	2	–	–	54.3	200	-0.33	65.70	26.49	–
9	Me	CH₂CH=CH₂	2	–	–	17.4	500	-1.17	65.19	138.43	114.58
10	Me	CH₂CF₃	2	–	–	-6.0	400	-1.50	62.88	125.50	–
11	Me	Pr	3	–	–	18.0	370	-4.48	66.29	26.45	10.27
12	Me	CH₂CH=CH₂	3	–	–	16.8	440	-3.44	65.32	137.78	114.97
13	Ph	Et	3	–	–	17.0	380	c	60.38	18.89	–
14	–	Me	4	-37.8	10	-26.2	160	–	53.73	–	–
15	–	Et	4	-43.9	30	15.0	330	–	61.29	18.70	–
16	–	Pr	4	-45.6	40	9.4	460	–	67.26	26.36	10.19
17	–	i-Pr	4	-49.7	25	51.0	350	–	67.52	26.00	–
18	–	Bu	4	-45.6	40	8.0	700	–	65.23	35.35	19.04 d
19	–	i-Bu	4	-45.5	30	7.6	460	–	72.06	31.38	18.84
20	–	s-Bu	4	-47.5	45	42.8	460	–	72.38	32.55	9.94
										23.26	
21	–	CH₂CH=CH₂	4	-43.8	32	8.8	440	–	66.35	136.93	115.75
22	–	CH₂CF₃	4	-48.1	70	-12.3	310	–	64.28	124.51	–

^{a} δ(^{13}C$_{Bu}$): 14.93 (C_α), 26.49 ($C_{\beta,\gamma}$), 13.76 (C_δ). ^{b} δ(^{13}C$_{Bu}$): 15.14 (C_α), 26.45 ($C_{\beta,\gamma}$), 13.71 (C_δ). ^{c} δ(^{13}C$_{Ph}$): 129.27 (C_i), 133.54 (C_o), 128.88 (C_m), 131.14 (C_p). ^{d} δ(^{13}C$_{C(4)}$) 13.91.

barn [16]) impose strong restrictions on the compounds under investigation: high symmetry of valency electrons is required (or low symmetry in combination with rapid chemical exchange that smoothens symmetry). Therefore, in order to obtain [73]Ge NMR spectra, it is necessary for the electric field gradient at the germanium atom to be close to zero. This is illustrated by the fact that the signals of tetraalkoxygermanes are relatively narrow, but we failed to register [73]Ge NMR spectra for other alkoxygermanes.

The [73]Ge NMR spectral parameters of the studied compounds are summarized in Table 1. The halfwidth of [73]Ge resonances ($\Delta \nu_{1/2}$) varies over the 30–65 Hz range. The [73]Ge resonance signal tends to broaden with the increasing molecular mass of the tetraalkoxygermane.

The [73]Ge resonance signals of alkoxygermanes are shifted to higher fields, as compared to alkylgermanes, and vary over a 15 ppm range [15,17–19]. No satisfactory relationship between [73]Ge CS (chemical shifts) and the inductive and steric constants of substituents in the alkoxy radical ($r = 0.68$) was observed. That may be due, in part, to difficulties in chemical shift measurements because of the relatively large linewidth of the signals. Therefore, we have to limit ourselves to some empirical observations. Thus the position of [73]Ge resonance shifts irregularly to higher fields with the increasing alkyl chain length in the alkoxy radical, the values of individual upfield shifts being larger than those for the [29]Si resonance in the corresponding silicon analogues [20]. A linear relationship was noted between the [29]Si and [73]Ge chemical shifts in the tetraalkoxy derivatives of germanium and silicon (Fig. 1), showing that the [73]Ge resonance signal is more sensitive to structural alterations than the [29]Si resonance:

$$\delta(^{73}\text{Ge}) = 88.7(\pm 13.3) + 1.6(\pm 0.2)\delta(^{29}\text{Si}) \ (r = 0.97; \ n = 10) \tag{1}$$

The points borrowed from the literature [21] for the alkoxy derivatives of pentavalent germanium and silicon also provide a good fit with this plot. A relationship [19] relating the [73]Ge CS with the CS of other Group IVB elements (Si, Sn) has been recently found for isostructural analogues:

$$\delta(^{73}\text{Ge}) = 39.9 + 3.32\delta(^{29}\text{Si}) \ (r = 0.967; \ n = 29) \tag{2}$$

However, by supplying our values of [73]Ge and [29]Si shifts for tetraalkoxygermanes and -silanes [20] it could be concluded that this equation is hardly applicable to the alkoxy derivatives of germanium and silicon.

It must be pointed out that the authors themselves [19] have noted that $E(OMe)_4$, $E(OMe)(OCH_2CH_2)_3N$ and $E(OPr)(OCH_2CH_2)_3N$ (E = Ge, Si) deviate from eq. 2 and the exclusion of these points from the plot improves the obtained correlation:

$$\delta(^{73}\text{Ge}) = 13.1 + 3.29\delta(^{29}\text{Si}) \ (r = 0.995; \ n = 26) \tag{3}$$

If the [73]Ge and [29]Si chemical shifts are dominated only by variations in the paramagnetic component of screening (σ^{para}), the slope of the $\delta(^{73}\text{Ge})/\delta(^{29}\text{Si})$ plot should match the ratios of p-orbital radii $\langle r^{-3} \rangle_{np}$ [22], which for Ge/Si is calculated to be 3.3 (± 0.5) [19]. However, the slopes of $\delta(^{73}\text{Ge})/\delta(^{29}\text{Si})$ differ from the ratio of p-orbital radii in an even more limited series of compounds, such as alkylgermanes and tetraalkyl-, tetraarylgermanes (2.01) [18]. Consequently, the chemical shift of the central atom in alkyl- and tetraalkoxygermanes and -silanes are determined not only by $\langle r^{-3} \rangle_{np}$, but also by differences in other factors of the
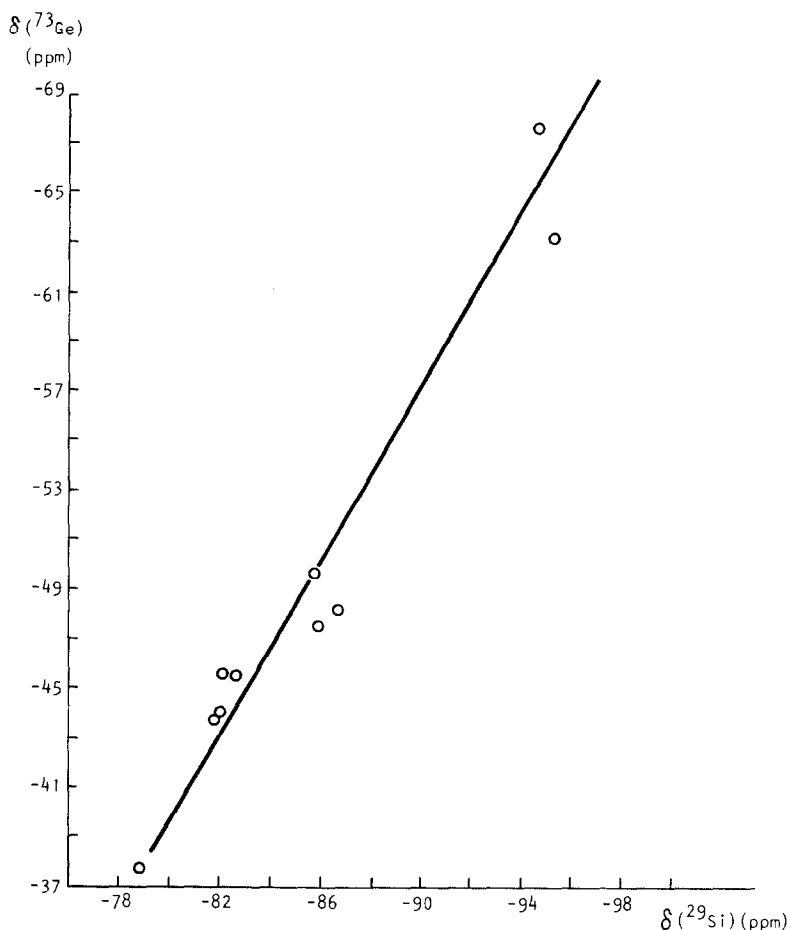
Fig. 1. Correlation of ^{73}Ge chemical shifts in tetraalkoxygermanes $Ge(OR)_4$ with ^{29}Si chemical shifts in their silicon analogues.

expression for paramagnetic screening, in particular, by the factor characterizing the extent of double bonding of the germanium and silicon atoms. The experimental evidence available at the moment is not sufficient to provide a satisfactory explanation of the factors regulating chemical shift variations in germanium compounds.

^{17}O Chemical shifts

^{17}O resonance signals of the alkoxygermanes studied are located over a range of 60 ppm and, as a rule, are wider than those of the corresponding alkoxysilanes, but narrower than those of alkoxymethanes.

We failed to find any satisfactory correlation between the ^{17}O chemical shift and the σ^* and E_s constants of the substituent in the alkoxy radical (correlation coefficient $r = 0.78$) in the tetraalkoxygermanes under study. Nevertheless, the ^{17}O signal of $Ge(OR)_4$ compounds quite definitely tends to shift to higher fields as the electron acceptor properties of substituent R increase. Introduction of a methyl group in the α-position to the oxygen atom causes a sharp downfield shift of the ^{17}O

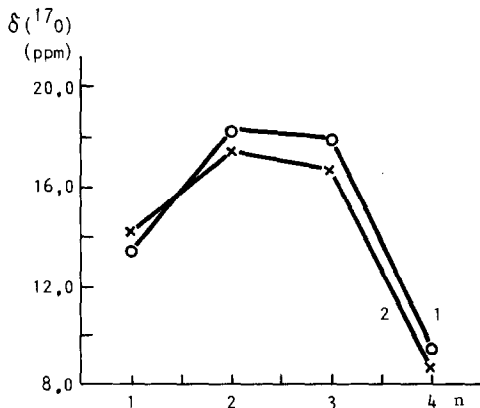Fig. 2. The dependence of ^{17}O chemical shifts in alkoxygermanes $Me_{4-n}Ge(OR)_n$ on the number of alkoxy groups n; $R = Pr$ (1), $CH_2CH=CH_2$ (2).

resonance signal, indicating a strong steric effect of the substituent. The dependence of the ^{17}O chemical shift on the number of alkoxy groups in alkoxygermanes shows a non-linear pattern (Fig. 2) resembling that in the alkoxysilanes [20]. This enables one to assume that, apart from the inductive and steric effects of substituents other effects, for example, $(p-d)_\pi$-interaction between the germanium and oxygen atoms, operate in alkoxygermanes.

A correlation (eq. 4) has been found between the ^{17}O shift of tetraalkoxygermanes and the corresponding alcohols, suggesting that the ^{17}O shifts of $Ge(OR)_4$ are generally determined by the properties of the substituent at the oxygen atom. On the other hand, a linear correlation (eq. 5) is observed between the ^{17}O chemical shifts of the $M(OR)_4$ (M = Ge, Si) indicating a similar sensitivity of ^{17}O shifts to the influence of substituent R.

$$\delta\left(^{17}O[Ge(OR)_4]\right) = 9.3(\pm 0.04) + 1.02(\pm 0.03)\delta\left(^{17}O(ROH)\right) \qquad (4)$$
$$(r = 0.99; \ n = 9)$$

$$\delta\left(^{17}O(Ge)\right) = 0.6(\pm 2.4) + 1.1(\pm 0.2)\delta\left(^{17}O(Si)\right) \ (r = 0.96; \ n = 7) \qquad (5)$$

As follows from eq. 5, the extent of double bonding is almost the same for each oxygen atom in tetraalkoxygermanes and -silanes. The points corresponding to di- and tri-alkoxy derivatives deviate from the correlation in eq. 5, the deviation being greater for compounds with $n = 3$ (Fig. 3). It would be logical to explain the above results by the different extent of double bonding between the oxygen atom and the silicon or germanium atoms [13,14]. It should be expected that the deviations of values for monoalkoxy derivatives would exceed those at $n = 2$ and $n = 3$. This has not been observed experimentally (Fig. 3). Obviously, differences in the M–O (M = Ge, Si) additional bonding are most pronounced in dialkoxy and trialkoxy derivatives.

^{13}C Chemical shifts

^{13}C resonance signals of the methyl group at the germanium atom are shifted to lower fields as compared with alkoxysilanes [20]. This is in accordance with the inductive effects of GeOR and SiOR groups [12].

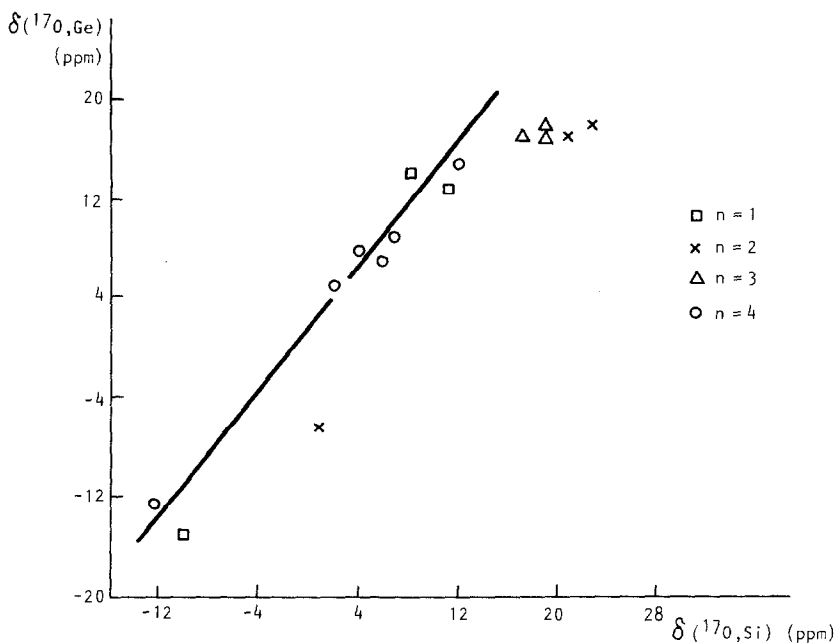Fig. 3. Correlation of ^{17}O chemical shifts in alkoxygermanes $R^1_{4-n}Ge(OR)_n$ and their silicon analogues.

On the other hand, the ^{13}C chemical shifts of C_α and C_β atoms of the alkoxy groups in monoalkoxygermanes Me_3GeOR are also located in lower fields as compared to the corresponding silicon analogues. If the inductive effects of Me_3Si and Me_3Ge groups [23,24] alone were operating, an opposite location of the ^{13}C resonance signals of the alkoxy groups would be expected. Such discrepancies in relation to the general notions concerning the experimental values of ^{13}C shifts in the molecules containing Si–O–C and Ge–O–C groups are explained in the literature by geminal interaction of silicon and germanium atoms with the O–C bond [11,25,26].

When comparing the values of ^{13}C NMR for alkoxy derivatives of germanium and silicon, a linear relationship between the ^{13}C shifts of the methyl groups at germanium and silicon atoms was found:

$$\delta\left(^{13}C_{Me}(Ge)\right) = 0.6(\pm 0.4) + 0.73(\pm 0.08)\delta\left(^{13}C_{Me}(Si)\right) \qquad (6)$$
$$(r = 0.96; \ n = 11)$$

Applying the literature data [17,27–30], we also found a similar equation for the ^{13}C chemical shift of the methyl groups at the central atom in the alkyl derivatives $Me_{4-n}MR_n$ (M = Ge, Si):

$$\delta\left(^{13}C_{Me}(Ge)\right) = -0.4(\pm 0.4) + 0.9(\pm 0.1)\delta\left(^{13}C_{Me}(Si)\right) \qquad (7)$$
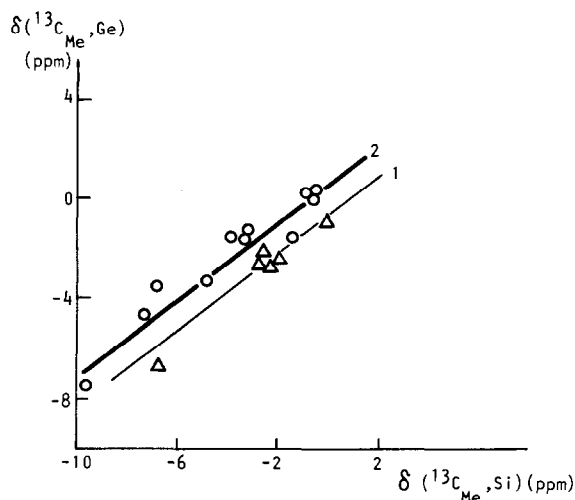$$(r = 0.98; \ n = 6)$$

Fig. 4. Correlation of methyl group ^{13}C chemical shifts in alkyl (1)- and alkoxy (2)-germanes and silanes.

A similar linear correlation also exists for the chemical shifts of ^{13}C$_\alpha$ atoms in the alkoxy groups:

$$\delta\left(^{13}C_{OC_\alpha}(Ge)\right) = 0.31(\pm 1.3) + 1.02(\pm 0.02)\delta\left(^{13}C_{OC_\alpha}(Si)\right) \tag{8}$$
$$(r = 0.998; \; n = 16)$$

The value of coefficient ρ in eq. 8 indicates equal overall influence of substituents on the $^{13}C_{OC_\alpha}$ shift of alkoxy-silanes and -germanes, i.e., a change in the central atom does not alter the mechanism of transmission of the substituent effects to the alkoxy group atoms. This can take place when: (i) No additional $(p-d)_\pi$-bonding occurs between the central atom M and the oxygen. (ii) The changes in this bonding with different substituents are similar for M = Ge and M = Si. The fact that the ^{13}C chemical shifts of the methyl groups in MeGeX$_3$ and MeSiX$_3$ (X = alk) (eq. 7) fall on a different correlation plot (Fig. 4) located somewhat lower than the plot obtained for alkoxy derivatives (eq. 6) demonstrates that $(p-d)_\pi$-bonding does take place. Therefore we may assume that the extent of $(p-d)_\pi$-bonding in alkoxygermanes and alkoxysilanes displays equal variations under the effects of substituents in the molecule. The correlation between the $^{13}C_{OC_\alpha}$ shifts in alkoxygermanes and -silanes (eq. 8) also supports this conclusion. At the same time, the $^{13}C_{Me}$ shift of alkoxygermanes are less sensitive to the effects of substituents (see coefficient ρ in eq. 6) than in the silicon analogues. This suggests that the extent of double bonding in the Si–O bond is higher than that in the Ge–O bond.

Experimental

^{73}Ge NMR spectra were obtained using a Bruker WH-90/DS spectrometer operating at 3.135 MHz, pulse width 50 μs; chemical shifts were measured and reported relative to external tetramethylgermanium, the accuracy was estimated as $\pm\Delta\nu_{1/2}/100$ ppm, where $\Delta\nu_{1/2}$ is the halfwidth of signals in ppm.

TABLE 2

PHYSICAL PROPERTIES OF ALKOXYGERMANES

No.	Compound	M.p. (°C/mmHg)	n_D^{20}
1	Me_3GeOPr	122–125	1.4145
2	$Me_3GeOCH_2CH=CH_2$	122–124	1.4263
3	Bu_3GeOPr	131/7	1.4465
4	$Me_3GeOCH_2CF_3$	96–100	1.3720
5	$Bu_3GeOCH_2CH=CH_2$	106/2	1.4550
6	$Me_2Ge(OCH_2CF_3)_2$	52–56/12	1.3570
7	$MeGe(OPr)_3$	93–97/12	1.4240
8	$Ge(OCH_2CH=CH_2)_4$	123–124.5/12	1.4560
9	$Ge(OCH_2CH_2OMe)_4$	184/12	1.4390
10	$Ge(OCH_2CF_3)_4$	73–74/15	1.3250

^{17}O NMR spectra were obtained using a Bruker WM-360 spectrometer operating at 48.82 MHz, pulse width 40 μs, number of scans 10^4 to 10^5; the accuracy of CS measurements was ± 0.3 relative to external H_2O.

^{13}C NMR spectra were obtained using a Bruker WH-90/DS spectrometer operating at 22.63 MHz with complete proton decoupling, pulse width 5 μs; CS were measured relative to internal TMS, accuracy ± 0.07 ppm.

The temperature of samples was 313 K (^{17}O NMR) and 298 K (^{13}C, ^{73}Ge NMR). All spectra were registered for 50% solutions in $CDCl_3$.

All the studied alkoxygermanes were prepared from the corresponding organylchlorogermanes and alcohols in the presence of triethylamine. The constants of new compounds are listed in Table 2.

Acknowledgement

References

1 A.N. Egorochkin, M.L. Khidekel, V.A. Ponomarenko, G.Ya. Zueva and G.A. Razuvaev, Izv. Akad. Nauk SSSR, Ser. Khim., (1964) 373.
2 A.N. Egorochkin, M.L. Khidekel and G.A. Razuvaev, Izv. Akad. Nauk SSSR, Ser. Khim., (1966) 437.
3 C.W.N. Cumper, A. Melnikoff, E.F. Mooney and A.I. Vogel, J. Chem. Soc. B, (1966) 874.
4 R. Rivière and J. Satgé, J. Organomet. Chem., 49 (1973) 157.
5 J.E. Drake, B.M. Glavinčevsky and H.E. Henderson, Can. J. Chem., 56 (1978) 465.
6 J. Dubac, P. Mazerolles and J. Cavezzan, Tetrahedron Lett., (1978) 3255.
7 J.E. Drake, B.M. Glavinčevsky, R.E. Humpries and A. Majid, Can. J. Chem., 57 (1979) 1426.
8 A.I. Gren' and N.E. Yasinenko, Ukr. Khim. Zh., 47 (1981) 629.
9 J. Dubac, J. Escudie, C. Couret, J. Cavezzan, J. Satgé and P. Mazerolles, Tetrahedron, 37 (1981) 1141.
10 J. Barrau, M. Bouchaut, H. Lavayssiere, G. Dousse and J. Satgé, J. Organomet. Chem., 243 (1983) 281.
11 V.P. Feshin, L.D. Khamaganova, M.G. Voronkov, G.Ya. Zueva, G.V. Lipatova, Ya.B. Yasman and R.A. Kuramshin, Izv. Akad. Nauk SSSR, Ser. Khim., (1981) 915.
12 V.I. Glukhikh, M.G. Voronkov, O.G. Yarosh, S.N. Tandura, N.V. Alekseyev, N.Yu. Khromova and T.K. Gar, Dokl. Akad. Nauk SSSR, 258 (1981) 387.

13 A.N. Egorochkin, N.S. Vyazankin and S.Ya. Khorshev, Usp. Khim., 41 (1972) 828.

14 A.N. Egorochkin and S.Ya. Khorshev, Usp. Khim., 49 (1980) 1687.

15 J. Kaufmann, W. Sahm and A. Schwenk, Z. Naturforsch. A, 26 (1971) 1384.

16 A.A. Vashman and I.S. Pronin, Yadernaya magnitnaya relaksatsya i eyo primeneniye v khimicheskoi fizike, Nauka, Moscow, 1979.

17 I. Zicmane, E. Liepiņš, E. Lukevics and T.K. Gar, Zh. Obshch. Khim., 52 (1982) 896.

18 Y. Takeuchi, T. Harazono and N. Kakimoto, Inorg. Chem., 23 (1984) 3835.

19 P.J. Watkinson and K.M. Mackay, J. Organomet. Chem., 275 (1984) 39.

20 E. Liepiņš, I. Zicmane and E. Lukevics, J. Organomet. Chem., 306 (1986) 167.

21 G. Zelčāns, A. Lapsiņa, I.I. Solomennikova, E. Lukevics, E. Liepiņš and Ē. Kupče, Zh. Obshch. Khim., 53 (1983) 1069.

22 C.J. Jameson and H.S. Gutowsky, J. Chem. Phys., 40 (1964) 1714.

23 W. Adcock, J. Alste, S.Q.A. Rizvi and M. Aurangzeb, J. Am. Chem. Soc., 98 (1976) 1701.

24 W. Adcock and G.L. Aldous, J. Organomet. Chem., 202 (1980) 385.

25 V.P. Feshin, L.D. Khamaganova, M.G. Voronkov, Ya.B. Yasman and R.A. Kuramshin, Izv. Akad. Nauk SSSR, Ser. Khim., (1980) 569.

26 V.P. Feshin, L.D. Khamaganova, M.G. Voronkov, E.I. Dubinskaya, V.G. Komarov, Ya.B. Yasman and R.A. Kuramshin, Zh. Obshch. Khim., 52 (19820 1401.

27 J. Schraml, V. Chvalovsky, M. Mägi and E. Lippmaa, Collect. Czech. Chem. Commun., 43 (1978) 3365.

28 J. Schraml, V. Chvalovsky, M. Mägi and E. Lippmaa, Collect. Czech. Chem. Commun., 46 (1981) 377.

29 L. Delmulle and G.P. Van der Kelen, J. Mol. Struct., 66 (1980) 315.

30 B.E. Mann and B.F. Taylor, ^{13}C NMR Data for Organometallic Compounds, Academic Press, New York, 1981.