Journal of Organometallic Chemistry, 201 (1980) 123—136
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

Ar-MATRIX STABILIZATION AND IR SPECTRA OF 1,1-DIMETHYL-1-SILAETHYLENE AND ITS DEUTEROMETHYL DERIVATIVE *

O.M. NEFEDOV *, A.K. MALTSEV, V.N. KHABASHESKU and V.A. KOROLEV

Institute of Organic Chemistry, Academy of Sciences of the U.S.S.R., Leninsky Prospect 47, Moscow 117913 (U.S.S.R.)

(Received May 23rd, 1980)

Summary

The IR spectra of the unstable silaethylenes $(CH_3)_2Si{=}CH_2$ and $(CD_3)_2Si{=}CH_2$ formed in the gas phase from monosilacyclobutanes have been recorded in an argon matrix at 10° K. An assignment of the spectral bands to the unstable species is established by experiments with pyrolysis at higher temperatures and pressures or with a controlled warm-up of the matrix, and also by recording spectra of the same species produced from various precursors. The assignment of the frequency 1003.5 cm^{-1} to the stretching vibration of the Si=C bond in $(CH_3)_2Si{=}CH_2$ is in agreement with force field calculations.

Introduction

The long search for Si=C intermediates [1,2] has entered upon a new phase by their direct spectroscopic identification. The spectral studies include both relatively stable silaethylenes with large substituents found to be in a mobile equilibrium with their dimers in solution [3] and the species isolated in inert matrices at low temperatures [4—9].

The first communication [4] on the IR spectrum of 1,1-dimethyl-1-silaethylene (I) in an Ar matrix at 10° K has been confirmed [5,6] and completed by observation of the matrix IR spectra of 1,1,2-trimethyl-1-silaethylene [7—9] **. Later, a new IR spectrum of I was presented in a review [2, p. 537] and the IR and UV bands of matrix-isolated silabenzene were reported [11]. Recently, unexpected stabilization of $H_2Si{=}CH_2$ and $CH_3SiH{=}CH_2$ has been

---

[*] Dedicated to Prof. G.A. Razuvaev on the occasion of his 85th birthday on August 23rd, 1980.

[**] The assignment of the IR band at 1407 cm^{-1} to 1,1-dimethyl-1-silaethylene [10] was found to be incorrect [7].

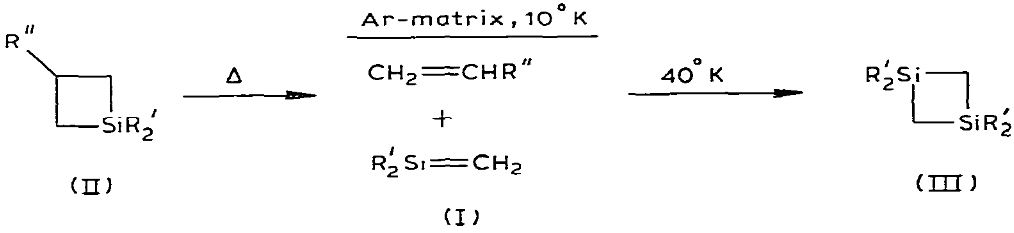
claimed (without a matrix, at 77° K) and their IR spectra published [12].

In several studies [4—9,11] the spectral bands of the unstable molecules containing the Si=C bond have been identified mainly through a controlled warm-up of the matrix to diffusion conditions. This process facilitates secondary reactions of the active species with consequent decrease and disappearance of their bands. Otherwise the set of frequencies found can be confirmed by producing the same species from another precursor [6,11] or under varied conditions.

The present study reports an application of the different approaches to obtain the IR spectra of the molecules $(CH_3)_2Si{=}CH_2$ and $(CD_3)_2Si{=}CH_2$. Preliminary reports on various parts of this work have been published [4—6,13].

Experimental

For the IR investigation of silaethylenes $R'_2Si{=}CH_2$ (I) we trapped these intermediates in an inert matrix from the gas phase, which has been shown to be a useful method to study the mechanism of the thermal decomposition reactions [14]. The species I were formed in gas phase pyrolysis of silacyclobutanes (II) [15] carried out in vacuum (10^{-2}—10^{-4} Torr) in the temperature range of 650—1000° C.



(a, $R' = CH_3$, $R'' = H$; b, $R' = R'' = CH_3$;
c, $R' = CD_3$, $R'' = H$; d, $R' = CD_3$, $R'' = CH_3$)

The products of pyrolysis were deposited at 10° K with an excess of argon (1000—5000:1) on a CsI window cooled by a continious flow of liquid helium. The IR spectra were recorded on a Hitachi—Perkin-Elmer 225 spectrophotometer; wavenumber accuracy is ±0.2 cm^{-1}. A controlled change in coolant flow allowed a repeatable cycle of raising matrix temperature from 10 to 35—40° K and recooling down to 10° K.

The parent monosilacyclobutanes (II,a—d) were prepared by cyclization of the appropriate γ-halopropylchlorosilane with Mg followed by methylation with $CH_3(CD_3)MgI$. 1,3-Disilacyclobutanes IIIa and IIIc were obtained by gas phase pyrolysis of IIa and IId, respectively. The samples were vacuum distilled bulb-to-bulb and their purity was determined from GLC and GC-MS data to be >99%.

Results and discussion

The IR spectrum of $(CH_3)_2Si{=}CH_2$ (Ia)

The IR spectra of the matrix-isolated products obtained by pyrolysis of IIa

TABLE 1

THE VIBRATIONAL FREQUENCIES (cm^{-1}) OF IIa, IIb, THEIR PYROLYSIS PRODUCTS AND IIIa IN AN Ar MATRIX AT 10°K

IIa ν	IIIa ν	Pyrolysis products of IIa at 750°C		IIb ν	Pyrolysis products of IIb at 820°C	
		ν	Assignment		ν	Assignment
1460.0		1460.0	IIa	1451.0	1453.0	C_3H_6
1444.0						
		1440.0	C_2H_4		1439.0	C_3H_6
					1416.0	C_3H_6
1395.0				1396.0	1396.0	IIb
					1374.0	C_3H_6
	1330.0			1368.0	1368.0	IIIb
				1325.0	1325.0	IIb
		1304.5	CH_4		1303.5	CH_4
		1259.0	Ia *		1259.0	Ia *
1254.0	1253.5	1254.0	IIa	1256.0	1256.0	IIb
		1251.0	Ia *		1251.0	Ia *
1248.8	1248.5	1248.5	IIa	1249.0	1249.0	IIb
1214.0				1194.0	1194.0	IIb
1184.0		1184.0	IIa	1136.0	1136.0	IIb
1123.0		1123.0	IIa	1045.0	1045.0	C_3H_6
		1003.5	Ia *		1003.5	Ia *
					997.0	C_3H_6
		958.2	C_2H_4		991.0	C_3H_6
		946.8	C_2H_4	955.0	955.2	IIb
	938.0	938.0	IIIa			
	935.4	935.6	IIIa		935.0	IIIa
					932.0	C_3H_6
921.5		920.8	IIa		914.0	C_3H_6
905.9		905.0	IIa		908.2	C_3H_6
					890.0	?
884.1		884.0	IIa	885.6	885.3	IIb
878.7		878.6	IIa		868.2	
	870.3	869.7	IIIa	861.0	861.2	IIb
				851.4	851.7	IIb
839.7		839.8	IIa	840.1	841.0	IIb
	828.6	828.8	IIIa		828.0	IIIa
		825.2	Ia *		825.2	Ia *
	821.3	821.3	IIIa	820.3	821.0	IIIa + IIb
		817.5	Ia *		817.5	Ia *
813.2		813.2	IIa	810.0	810.0	IIb
807.8		807.8	IIa	805.6	805.6	IIb
728.0		728.0	IIa	720.0	720.0	IIb
706.1; 703.6	714.3	706.0; 704.6	IIa	711.0	711.0	IIb
	692.9	692.8	IIIa		692.8	IIIa
		663.2 661.7	CO_2		664.0 662.0	CO_2
648.0		647.7	IIa	657.0	656.0	IIb
		642.9	Ia *		643.0	Ia *
609.0		609.0	IIa	621.8	621.8	IIb
	574.2					

are characterized by the set of frequencies given in Table 1. Besides the bands belonging to IIa and ethylene, new absorptions (labelled *) are seen in Fig. 1a at 642.9, 817.5, 825.2, 1003.5, 1251.0 and 1259.0 cm^{-1}. The intensities of these

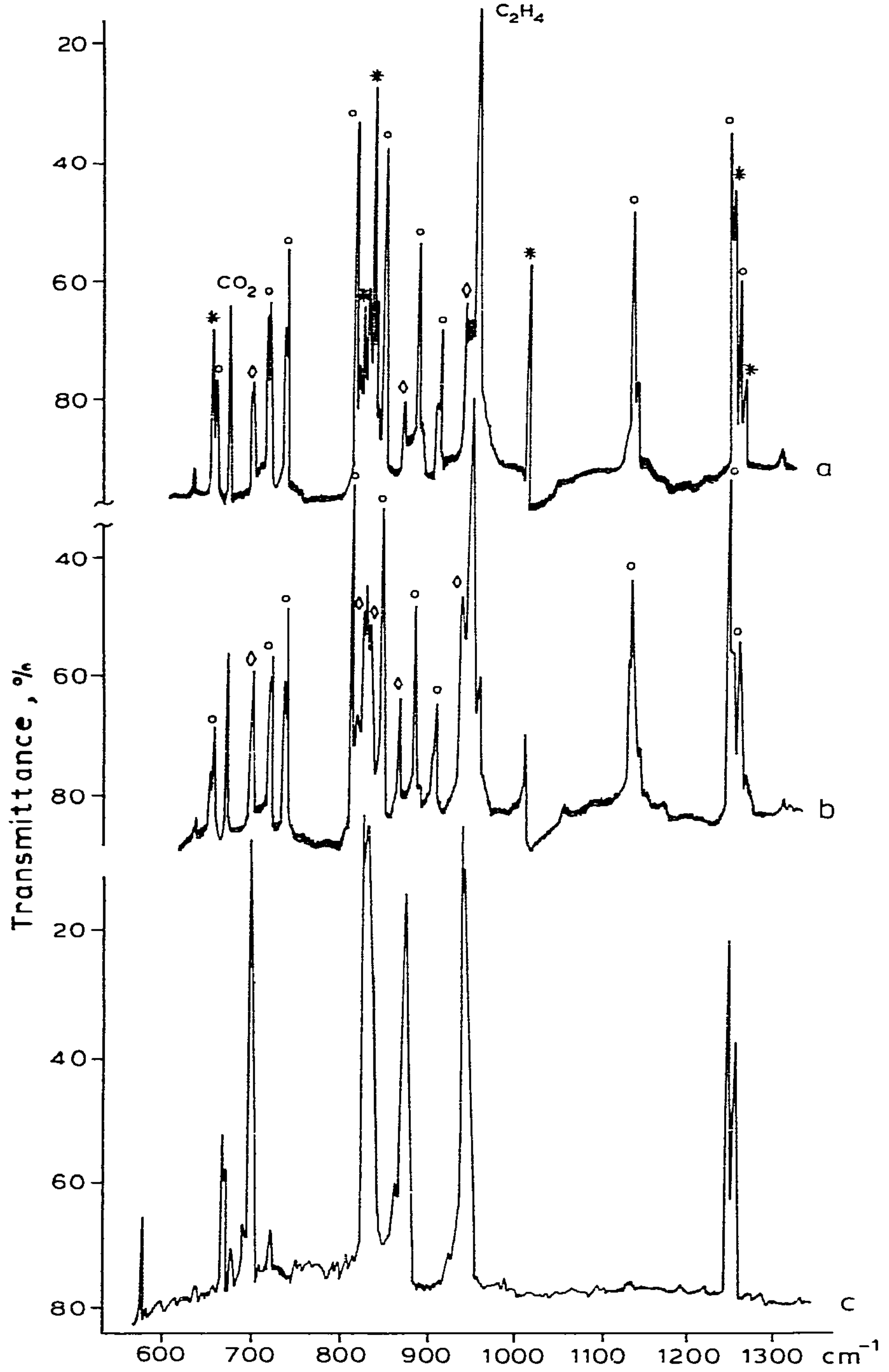


Fig. 1. a) The IR spectrum of the pyrolysis products of IIa (750°C, 10^{-3} Torr) in an Ar matrix at 10°K b) The same after warming the matrix up to 35°K and recooling to 10°K. c) The IR spectrum of the dimer IIIa in an Ar matrix at 10°K. Here and in Figs. 2—5: *, Ia; ○, IIa, ◊, IIIa.

six bands decrease markedly and uniformly (Fig. 1b) when the matrix is warmed up to 35°K, proving that the bands can be attributed to the same unstable species. Simultaneously, the increase of the absorptions at 692.8, 821.3, 828.6, 870.3 and 935.4 cm^{-1} assigned [5,16] to 1,1,3,3-tetramethyl-1,3-disilacyclobutane (IIIa), a dimer of molecule Ia, is observed (compare Fig. 1c).

The pressure increase in the pyrolysis zone (that is a growing number of the collisions) should facilitate dimerization and other secondary reactions of the reactive intermediates. Accordingly, the six absorptions of the unstable species mentioned above were much weaker when pyrolysis pressure rose up to 1—10^{-1} Torr, the bands of the cyclodimer (IIIa) again appearing with greater intensity (Fig. 2). These observations have shown that the unstable species in question is silaethylene (Ia).

Additional evidence for the correct assignment was provided by matrix stabilization of Ia generated from the precursor (IIb). In Fig. 3 the Ar-matrix IR spectrum of IIb is compared with one of the pyrolysis products. The absorptions at 577.8, 908.2, 915.1, 932.1, 991.0, 997.6, 1439.0, and 1453.0 (Fig. 3b) are attributed to the propylene molecules in accordance with ref. 17. New spectral features (labelled *) coincide within 0.2 cm^{-1} with the band positions of Ia found in the pyrolysis study of IIa (Table 1). The data obtained confirm all the six frequencies first reported for Ia [4,5].

In a recent review [2] the IR spectra are shown where five out of these six bands can be seen. Of the two bands we identified in the region of 1250—1260 cm^{-1} (Fig. 1a), one adsorption was not detected in ref. 2 probably because of insufficient resolution and low (Ia) band intensities.

Three frequencies at 696, 932 and 992 cm^{-1} were given additionally for Ia in

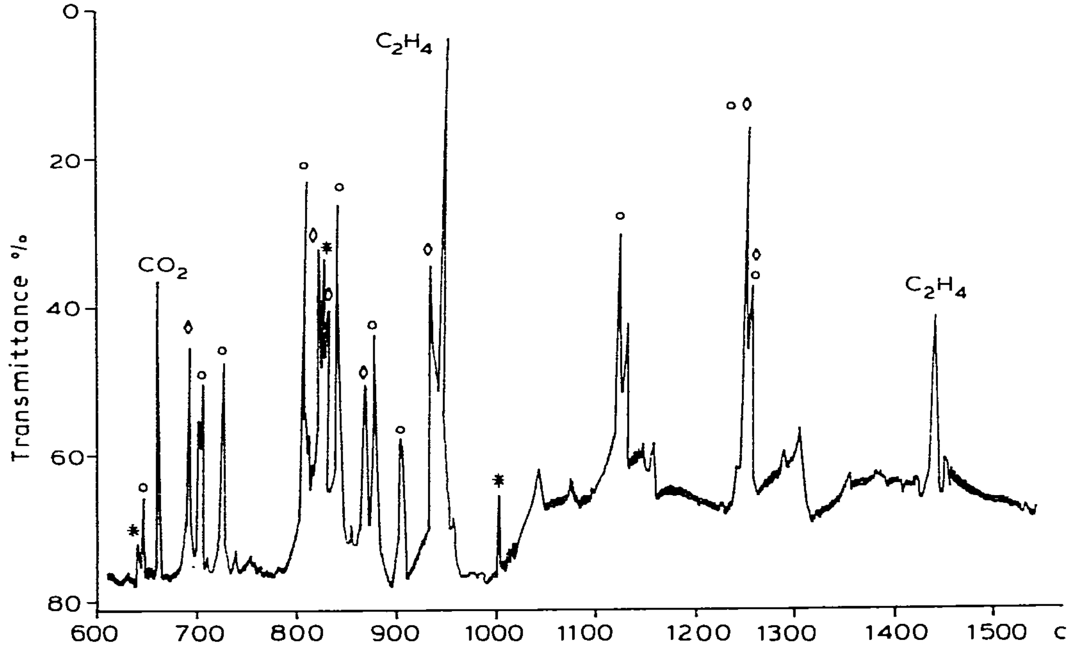


Fig. 2. The IR spectrum of the pyrolysis products of IIa (700°C, 10^{-1} Torr) in an Ar matrix at 10°K.

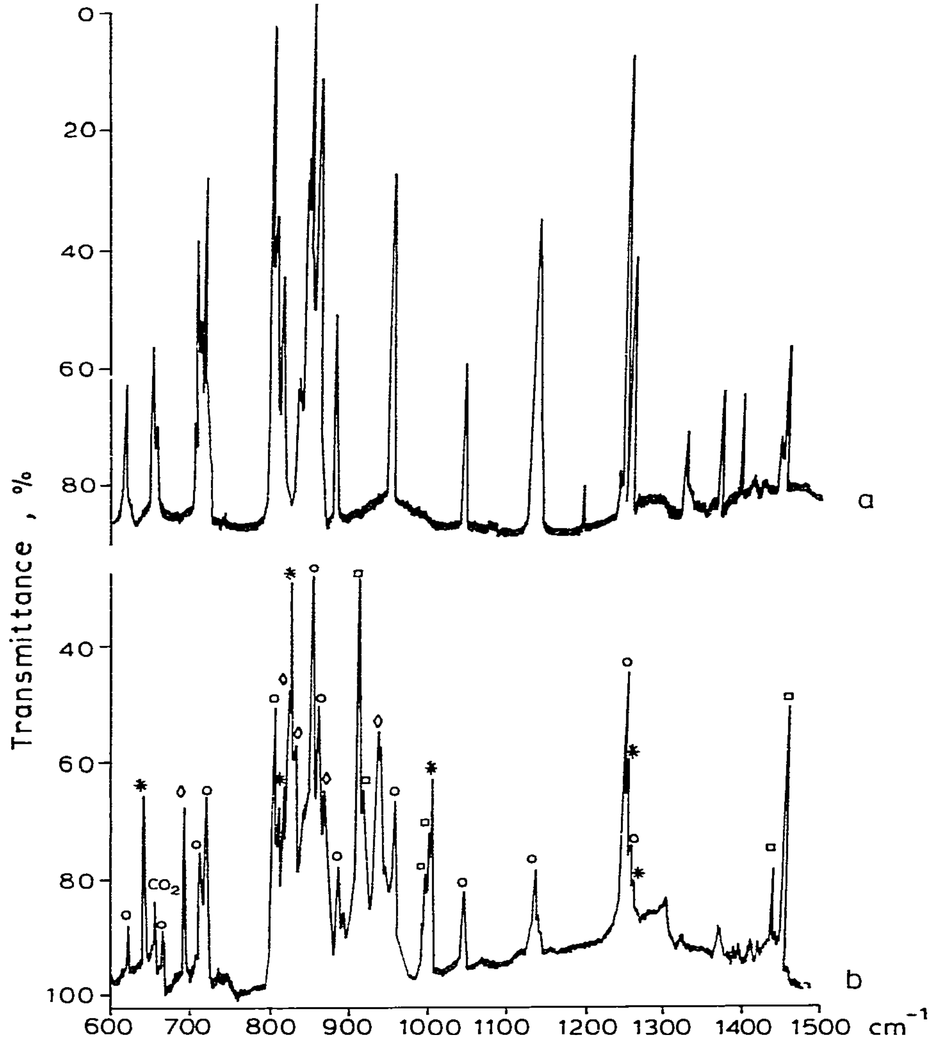


Fig. 3. a) The IR spectrum of IIb in an Ar matrix at 10°K. b) The IR spectrum of the pyrolysis products of IIb (820°C, 10^{-3} Torr) in an Ar matrix at 10°K. □, C_3H_6.

ref. 2. However we recorded at these positions only the bands of the dimer IIIa at 692.8 and 935.4 cm^{-1} and those of C_3H_6 at 932.1 and 991.0 cm^{-1}. These three bands do not belong to an unstable species because their intensities increased after warm-up of the matrix. Propylene is not formed in pyrolysis of IIa and there are no bands near 990 cm^{-1} in Fig. 1a.

The very intense band of C_2H_2 near 735 cm^{-1} is observed in the spectra of the products from pyrolysis of IIa and IIb given in ref. 2. In marked contrast, in our experiments, non-selective formation of C_2H_2 (the matrix IR bands at 736.2 and 3287 cm^{-1}), CH_4 (1304.0 and 3030 cm^{-1}) and CH_3 radical (616.0 cm^{-1}) become prominent only at pyrolysis temperature above 800—850°C (Fig. 4). These fragmentation products are practically missing at lower temperatures (Fig. 1a and 3b).

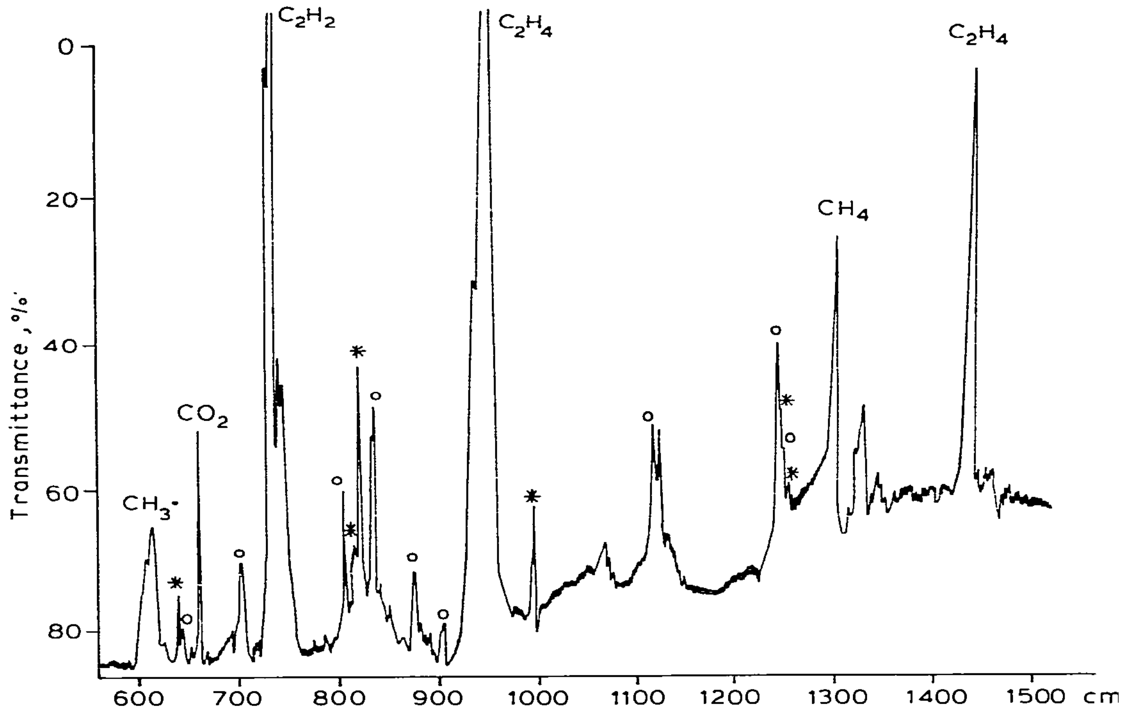


Fig. 4. The IR spectrum of the pyrolysis products of IIa (1000°C, 10^{-3} Torr) in an Ar matrix at 10°K.

Silaethylene Ia turned out to be a very active molecule at even the lowest temperatures, dimerizing to IIIa when diffusing in a solid argon matrix. Cyclodimerization of Ia takes place at 10—15°K in the absence of large excess of the matrix gas. All our attempts to discover the bands of Ia in the IR spectra of the pyrolysis products of IIa at 77°K were unsuccessful. Only the stable com-

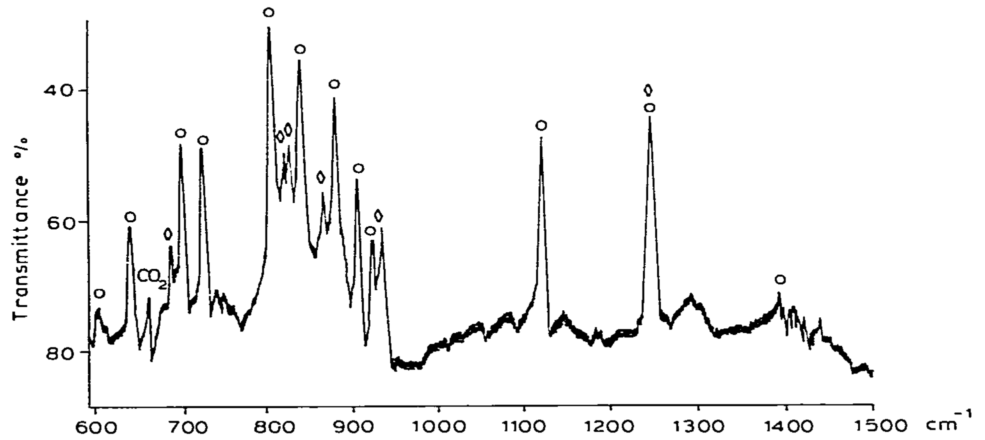


Fig. 5. The IR spectrum of the pyrolysis products of IIa (750°C, 10^{-3} Torr) trapped at 77°K without an inert matrix.

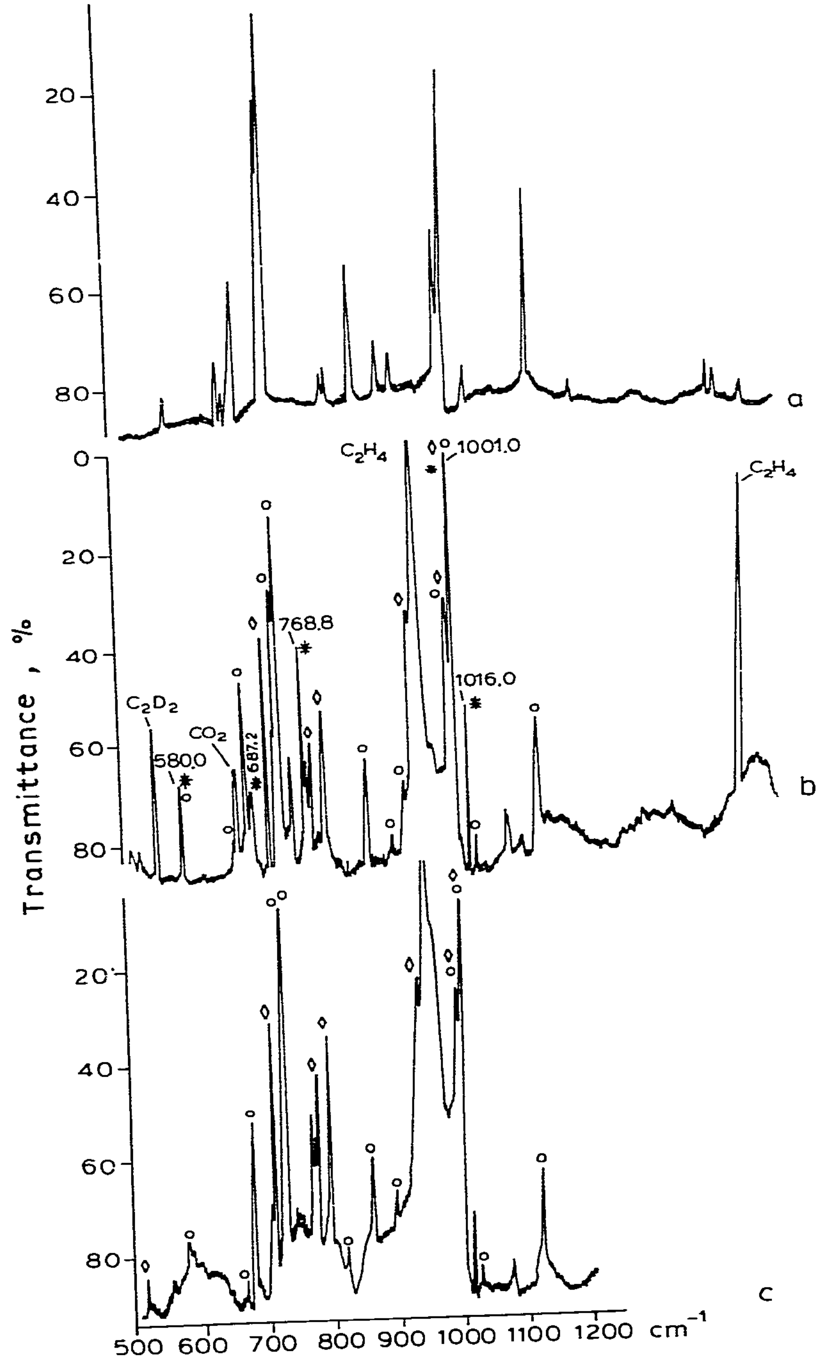


Fig. 6. a) The IR spectrum of IIc in an Ar matrix at 10°K. b) The IR spectrum of the pyrolysis products of IIc (780°C, 10^{-3} Torr) in an Ar matrix at 10°K. c) The same after warming the matrix up to 35°K and recooling to 10°K. *, Ic; o, IIc; ◇, IIIc.

pounds IIa and IIIa have been found (Fig. 5). This was also observed in the matrix studies of other silaolefines and silabenzene [7,11]. These results do not confirm the conclusions drawn on possible stabilization of Ia [18], $H_2Si{=}CH_2$ and $CH_3SiH{=}CH_2$ [12] without an inert matrix at 77° K.

The IR spectrum of $(CD_3)_2Si{=}CH_2$ (Ic)

The spectrum of the deuteromethyl derivative Ic was recorded with the

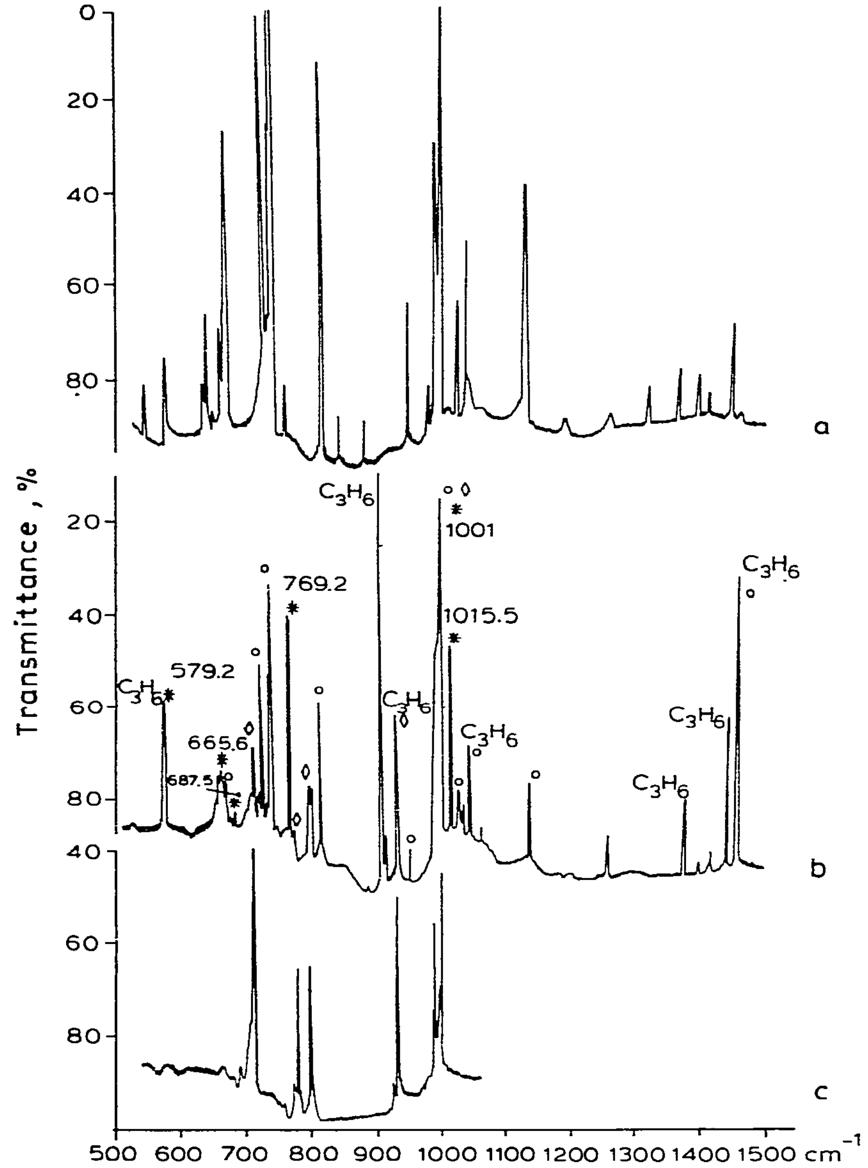


Fig. 7. a) The IR spectrum of IId in an Ar matrix at 10° K. b) The IR spectrum of the pyrolysis products of IId (840° C, 10^{-4} Torr) in an Ar matrix at 10° K. c) The IR spectrum of the dimer IIIc in an Ar matrix at 10° K. Here and in Figs. 8, 9: *, Ic; o, IId; ◇, IIIc.

TABLE 2

THE VIBRATIONAL FREQUENCIES (cm^{-1}) OF IIc, IId, THEIR PYROLYSIS PRODUCTS AND IIIc IN AN Ar MATRIX AT 10°K

IIc ν	IIIc ν	Pyrolysis products of IIc at 780°C		IId ν	Pyrolysis products of IId		
		ν	Assignment		At temperature		Assignment
					840°C	970°C	
1450				1451	1453		C_3H_6 + IId
		1440	C_2H_4				
					1438.5		C_3H_6
1412					1416		C_3H_6
1399				1396	1397		C_3H_6
		1334	IIIc		1373		C_3H_6
				1325			
1184					1254		?
				1136	1136		IId
1124		1124	IIc				
						1073	?
					1065		?
					1043	1043.5	C_3H_6 + IId
				1030	1028		IId
1026		1029	IIc + Ic?				
		1016.0	Ic *		1015.5	1015.0	Ic *
		1001.0	Ic + IIc + IIIc		1001.4		Ic *
1001				1001	1000.9		IId
	1001				1000.0	1000.5	IIIc
					996.8	996.9	C_3H_6
				993.6			
	992.4	992.4	IIIc			992.7	IIIc
991.2		962.0	?				
				952.1	951.0		IId
		946.6	C_2H_4			944.7	C_2H_4?
	932.9	931.4	IIIc		932.0	932.0	C_3H_6 + IIIc
	924						
919		920	IIc				
					915.0	914.5	C_3H_6
					908.3	908.0	C_3H_6
897.8		898.0	IIc				
					892.0	891.9	?
861.2		862.4	IIc				
				884.7			
				844.4			
				817.1	816.9	816.5	IId
				802.3			
	798.1	798.0	IIIc		797.8	798.5	IIIc
					795.4		?
					791.7	791.6	?
	778.4	778.0	IIIc		777.8	777.5	IIIc
	774.0	772.7	IIIc				
		768.8	Ic *		769.2		Ic *
					761.9	761.5	?
		749.0	?			749.1	?
				740.7	740.2		IId
				737.6	737.6		IId
					736.1	736.3	C_2H_2
						734.0	C_2H_2
732.0		731.6	IIc				
						731.0	C_2H_2?
727.6		727.6	IIc				
				726.9	726.0		IId

TABLE 2 (continued)

IIc	IIIc	Pyrolysis products of IIc at 780°C		IId	Pyrolysis products of IId		
					At temperature		Assignment
ν	ν	ν	Assignment	ν	840°C	970°C	
		722.0	?			722.7	?
		718.0	?		718.7	718.9	?
	711.6	711.5	IIIc		711.0	711.5	IIIc
		687.2	Ic *		687.5		Ic *
		683.0	C_2HD		683.4	683.3	C_2HD
					677.5	677.8	?
677.0		678.2	IIc				
				671.7	671.4		IId
		666.0	?		666.8		?
		662.4	CO_2		665.4		Ic *?
656.0		658.0	IIc				
				639.3			
628.0						628.7	?
		580.0	Ic + IIc		579.2		Ic *
578.0				578.0			
					577.6	577.9	C_3H_6
		541.0	C_2D_2			541.9	C_2D_2
524.0							
		518.0	C_2HD			518.6	C_2HD
		505.6	?				

general aim of assigning the frequencies to the molecular vibrations of I and to obtain information on Si=C bonding. The IR spectrum of Ic was taken from the pyrolysis products of both IIc and IId. The IR spectra of the parent compounds and those of the products are given in Fig. 6 and 7 and the frequencies are listed in Table 2. Additionally we have recorded the matrix IR spectrum of the deuterated cyclodimer IIIc, presented in Fig. 7c.

The vibration frequencies of Ic were determined by both an analysis of the changes in the band intensities upon warming the matrix and coincidence of the band positions on the spectra from pyrolysis of IIc and IId. Thus, the bands near 579, 687, 769, 1001 and 1016 cm^{-1} present in both spectra (Fig. 6b and 7b) diminish when the temperature of the matrix rises from 10 to 35° K (Fig. 6c).

The absorptions of Ic at 579.2, 1001.4 cm^{-1} and the somewhat less reliable one at 665.6 cm^{-1} can be seen only in the well-resolved spectra (Fig. 8). The former band in the regular spectrum is largely overlapped with the neighbouring absorptions belonging to the stable molecules: C_3H_6 at 577.8 cm^{-1} and IIc at 578.0 cm^{-1} (or IId also at 578.0 cm^{-1}). In the 980—1000 cm^{-1} region of the spectrum there are no less than ten bands of the stable compounds IIc, IId, IIIc and C_3H_6. The band at 1001.4 cm^{-1}, weakening markedly on warm-up relative to the bands of IId and IIIc, in Fig. 8b is assigned to silaethylene Ic.

The bands near 540, 749 and 962 cm^{-1} shown for Ic in our preliminary communication [13] appear only under the elevated temperature or pressure conditions of pyrolysis. In such a case a nonselective decomposition of IIc and

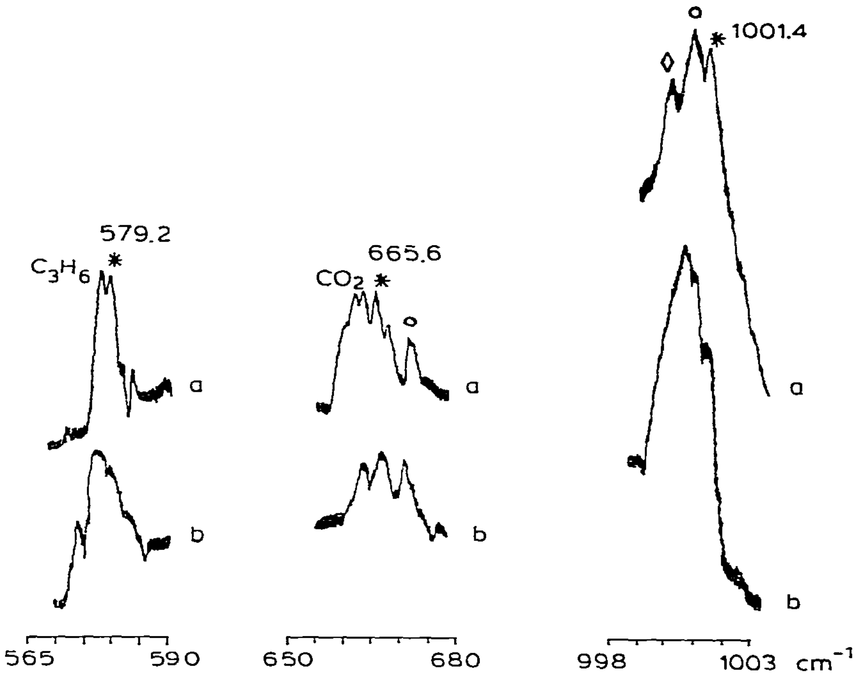


Fig. 8. The IR spectra of the pyrolysis products of IId (840°C, 10^{-4} Torr) in the 565—590, 650—680 and 998—1003 cm^{-1} regions in an Ar matrix. a) At 10°K. b) After warming to 35°K and recooling to 10°K.

IId occurred similar to that of IIa and IIb with formation of C_2H_2 (736.2 cm^{-1}), C_2HD (683.3 and 518.6 cm^{-1}) and C_2D_2 (541.9 cm^{-1}). Also it is clear from the experiments that the bands at 677.8, 718.9, 722.7, 749.1 and 891.9 cm^{-1} (Fig. 9) belong to the stable molecules produced because of extensive fragmentation of parent silacyclobutanes. Besides those bands in the spectrum one can see the features of propylene and the cyclodimer IIIc, particularly the band near 930 cm^{-1} which turns out to reflect the superimposed modes of both molecules. On the other hand, the bands of silaethylene (Ic) seem to be very small in Fig. 9 pointing out that concentration of Ic is negligible under the severe pyrolysis conditions.

The vibration frequency of the Si=C bond

The frequencies determined here for deuterated silaethylene Ic: 579.2, 687.5, 769.2, 1001.4 and 1015.5 cm^{-1} were used together with those of Ia and $CH_3(CD_3)Si{=}CH_2$ [13] for a vibration assignment. The latter was based upon the deuterium isotopic shifts in I in comparison with the respective shifts in the methylsilanes and isobutylene molecules.

We have assigned the 1003.5 cm^{-1} frequency in the spectrum of Ia to the Si=C stretching vibration [19,13] in contrast to our preliminary assignment to the $\rho(CH_2)$ mode [5]. This conclusion is confirmed by normal coordinate calculations which were done by the central force field approximation with a modified program of Schachtschneider [20].

The calculations [21] give a substantially higher value for the stretching force

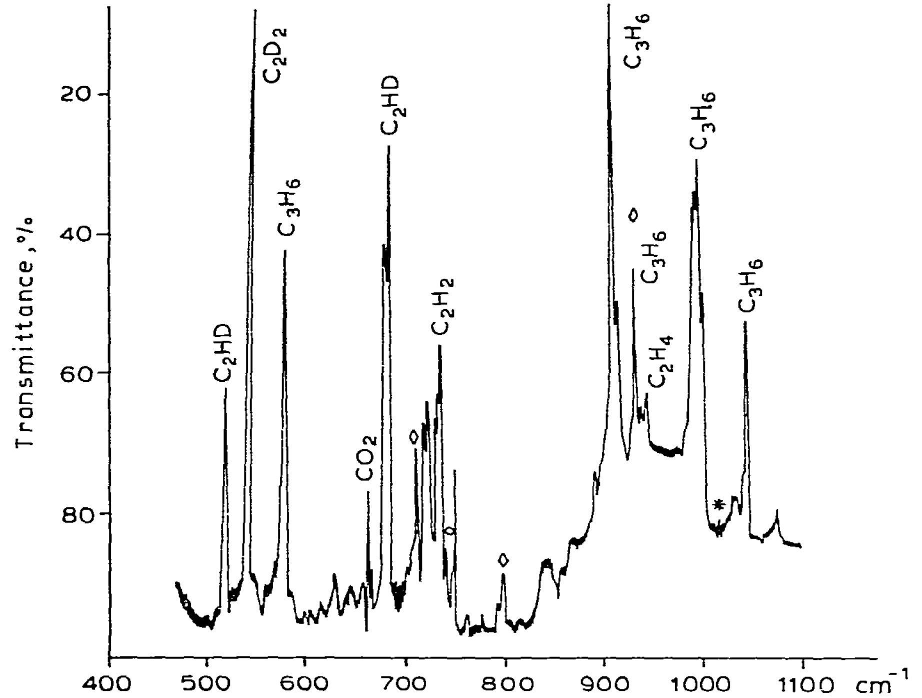


Fig. 9. The IR spectrum of the pyrolysis products of IId (970°C, 10^{-4} Torr) in an Ar matrix at 10°K.

constant, k(Si=C) = 5.6 mdyn/Å than that for the ordinary Si—C bond (3.0—3.5 mdyn/Å). The experimental Si=C bond frequency, 1003.5 cm^{-1}, in Ia may be compared with the calculated ones of 1140 cm^{-1} [22] and 1156 cm^{-1} [23] for the $H_2Si{=}CH_2$ molecule. The latter shifts to 1044 cm^{-1} upon substituting the protons on the silicon atom with heavier D atoms [23].

It is of interest that both the vibrational frequency and the force constant are practically the same for the Si=C bond in Ia and the $\overset{+}{P}—\overset{-}{C}$ bond in the simple phosphorus ylid molecule $(CH_3)_3\overset{+}{P}—\overset{-}{C}H_2$ [24]. Our analysis of the structural and chemical properties of silaethylenes compared to ylids [25] emphasized their clear similarity and allows one to consider silaolefines as C-ylids of silicon.

References

1 L.E. Gusel'nikov, N.S. Nametkin and V.M. Vdovin, Acc. Chem. Res., 8 (1975) 18.

2 L.E. Gusel'nikov and N.S. Nametkin, Chem. Rev., 79 (1979) 529.

3 A.G. Brook, J.W. Harris, J. Lennon and M. El Sheikh, J. Amer. Chem. Soc., 101 (1979) 83; A.G. Brook, S.C. Nyburg, W.F. Reynolds, Y.C. Poon, Y.-M. Chang and J.-S. Lee, J. Amer. Chem. Soc., 101 (1979) 3750.

4 A.K. Maltsev, V.N. Khabashesku and O.M. Nefedov, Izv. Akad. Nauk SSSR, Ser. Khim., (1976) 1193; Chem. Abstr., 85 (1976) 122861g.

5 A.K. Maltsev, V.N. Khabashesku and O.M. Nefedov, Dokl. Akad. Nauk SSSR, 233 (1977) 421.

6 A.K. Maltsev, V.N. Khabashesku and O.M. Nefedov, Izv. Akad. Nauk SSSR, Ser. Khim., (1979) 2152.

7 O.L. Chapman, C.-C. Chang, J. Kolc, M.E. Jung, J.A. Lowe, T.J. Barton and M.L. Tumey, J. Amer. Chem. Soc., 98 (1976) 7844.

8 M.R. Chedekel, M. Skoglund, R.L. Kreeger and H. Shechter, J. Amer. Chem. Soc., 98 (1976) 7846.

9 A.K. Maltsev, V.A. Korolev, V.N. Khabashesku and O.M. Nefedov, Dokl. Akad. Nauk SSSR, 251 (1980) 1166.
10 G. Maier, G. Mihm and H.P. Reisenauer, Angew, Chem., 92 (1980) 58.
11 N. Auner and J. Grobe, Z. Anorg. Allgem. Chem., 459 (1979) 15.
12 T.J. Barton and C.L. McIntosh, J. Chem. Soc. Chem. Commun., (1972) 862.
13 A.K. Maltsev, V.N. Khabashesku, E.G. Baskir and O.M. Nefedov, Izv. Akad. Nauk SSSR, Ser. Khim., (1980) 222.
14 A.K. Maltsev, R.G. Mikaelyan and O.M. Nefedov, Dokl. Akad. Nauk SSSR, 201 (1971) 901.
15 N.S. Nametkin, V.M. Vdovin, L.E. Gusel'nikov and V.I. Zav'yalov, Izv. Akad. Nauk SSSR, Ser. Khim., (1966) 584.
16 V.N. Khabashesku, A.K. Maltsev and O.M. Nefedov, Izv. Akad. Nauk SSSR, Ser. Khim., (1980) 837.
17 W.A. Guillory and S.G. Thomas, J. Phys. Chem., 79 (1975) 692.
18 N.S. Nametkin, L.E. Gusel'nikov, E.A. Volnina, E.N. Burdasov and V.M. Vdovin, Dokl. Akad. Nauk SSSR, 214 (1974) 818.
19 A.K. Maltsev and O.M. Nefedov, Plenary Lecture at 4th International Symposium on Analytical and Applied Pyrolysis. Budapest, Hungary, June 11—15, 1979; V.N. Khabashesku, Dissertation, Institute of Organic Chemistry, Moscow, 1979.
20 J.H. Schachtschneider, Vibrational Analysis of Polyatomic Molecules, Tech. Rept. 231—64, Shell Development Company. Emeryville, California, U.S.A., 1964.
21 A.K. Maltsev, E.G. Baskir, V.N. Khabashesku and O.M. Nefedov, in preparation.
22 H.B. Schlegel, S. Wolfe and K. Mislow, J. Chem. Soc. Chem. Commun., (1975) 246.
23 N. Auner, R. Demuth, J. Grobe and H. Rathmann, in preparation, see ref. 12.
24 W. Sawodny, Z. Anorg. Allg. Chem., 368 (1969) 284.
25 O.M. Nefedov, A.K. Maltsev and V.N. Khabashesku, Angew. Chem., in press.