Journal of Organometallic Chemistry, 204 (1981) 13—19
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

THE SYNTHESIS AND SOME PROPERTIES OF 1-THIA-3-SILACYCLOBUTANES AND 1-THIA-3-SILACYCLOPENTANE

M.G. VORONKOV *, S.V. KIRPICHENKO, E.N. SUSLOVA and V.V. KEIKO

Institute of Organic Chemistry, Siberian Division of the USSR Academy of Science, 664033 Irkutsk (U.S.S.R.)

(Received June 10th, 1980)

Summary

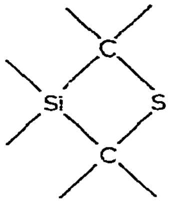
3,3-Dimethyl-1-thia-3-silacyclobutane has been obtained by the reaction of $Me_2Si(CH_2Cl)_2$ with potassium hydrosulfide in abs. ethanol. Intramolecular hydrosilylation of isomeric vinylthioethyldiethylsilanes, $HEt_2Si{-}X{-}SCH{=}CH_2$ ($X = CH(CH_3)$ or CH_2CH_2) proceeds selectivity as α-addition to afford cyclic compounds, $Et_2\overline{SiCH(CH_3)SC}HCH_3$ and $Et_2\overline{SiCH_2CH_2SC}HCH_3$, respectively. This ring closure reaction is catalyzed by $(Ph_3P)_3RhCl$. The endocyclic Si—C bond of 3,3-dimethyl-1-thia-3-silacyclobutane undergoes cleavage upon treatment with ethanolic KOH leading to $Me_2(EtO)SiCH_2SCH_3$ and $O(SiMe_2CH_2SCH_3)_2$. The reaction of 3,3-dimethyl-1-thia-3-silacyclobutane with ethanolic $HgCl_2$ involves ring opening and formation of a complex, $O[SiMe_2CH_2S(HgCl_2)CH_2HgCl]_2$.

Introduction

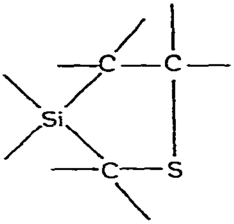
Silicon heterocyclic compounds containing sulfer in the ring are rather well studied [1]. Most of them, however, contain ring systems where the silicon is bonded to the sulfer atom [2,3]. The data on the simplest heterocycles in which the silicon and sulfer atoms are separated by at least one methylene group are scarce and concern only six to eight-membered rings. Thus, 5,5-diorganyl-1-thia-5-silacyclooctanes have been prepared by photochemical addition of H_2S to diorganyldiallylsilanes [4,5]. An analogous ring system is formed by photolysis of 3-mercaptopropylallyldimethylsilane [5]. 3,3-Dimethyl-1-thia-3-silacyclohexane and -cycloheptane have been obtained upon treating the corresponding dimethylhalomethylhaloalkylsilanes with Na_2S [6,7]. However, it was not possible to prepare 3,3-dialkyl-1-thia-3-silacyclopentanes in such a manner due to the unstability of the initial chloromethylhaloethyldialkylsilanes [6].

Results and discussion

The purpose of this work was to synthesize a series of four- and five-membered heterocyclic systems containing separated atoms of silicon and sulfur (structures A and B, respectively) and to study the properties of compounds of this type.



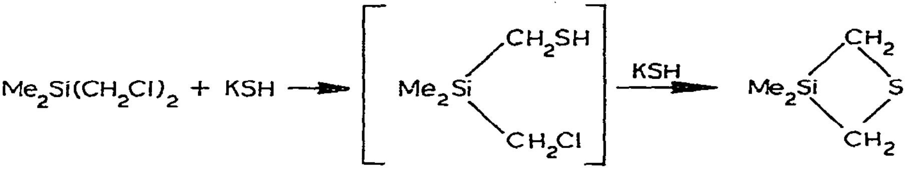
(A)



(B)

The reaction of Na_2S with α,ω-dihalogen derivatives is a common method for the synthesis of cyclic sulfides in organic chemistry [8]. However, this sulfide causes cleavage of the CH_2Cl group of 1,2-bis(chloromethyl)-1,1,2,2-tetramethyldisiloxane instead of cyclization [9]. Only the use of a less alkaline sulfurating agent, potassium hydrosulfide, allowed 2,2,6,6-tetramethyl-2,6-disila-4-thia-1-oxane to be prepared in good yield [9].

We thought this method to be a simple way for the synthesis of silethane systems (structure A). Indeed we have found that the reaction of bis(chloromethyl)dimethylsilane with KSH in dry ethanol at 20°C affords 3,3-dimethyl-1-thia-3-silacyclobutane (II) in 55% yield.



(I) (II)

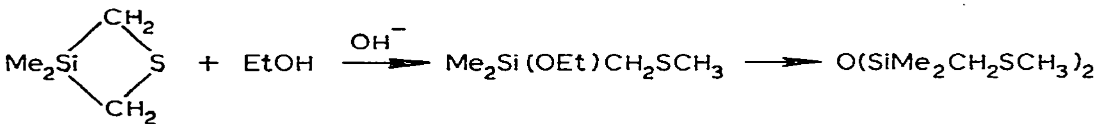
Chloromethylmercaptomethyldimethylsilanes (I), containing CH_2Cl and SH groups at the silicon, seems to be an intermediate. Intramolecular abstraction of HCl by KSH from I leads to compound II. The formation of bis(mercaptomethyl)dimethylsilane as an intermediate is unlikely since the ring closure reaction due to elimination of H_2S does not proceed readily and required a catalyst in most cases [10].

If the reaction is carried out at 60°C no compound II is observed among the products *. The main reaction products are $Me_2(EtO)SiCH_2SCH_3$ and O(SiMe₂-

---

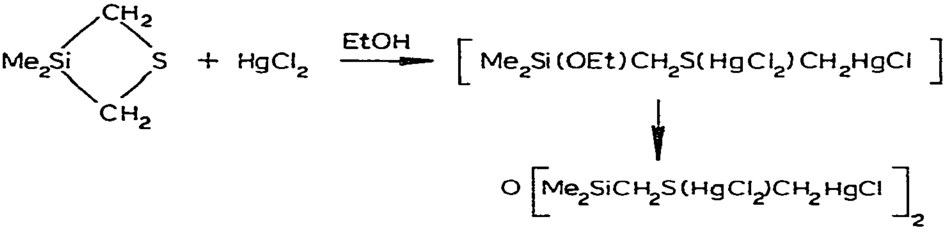
* Heating of the reaction mixture causes evolution of H_2S, displacement of equilibrium $KSH \rightleftharpoons K_2S$ and increase in basicity of the medium.

$CH_2SCH_3)_2$, formed by rupture of the endocyclic Si—C bond in II. The same compounds III and IV are obtained upon treating $Me_2Si(CH_2)_2S$ with an ethanolic solution of KOH. In this case an exothermic reaction, similar to that found for base-catalyzed cleavage of silacyclobutane [11] takes places.



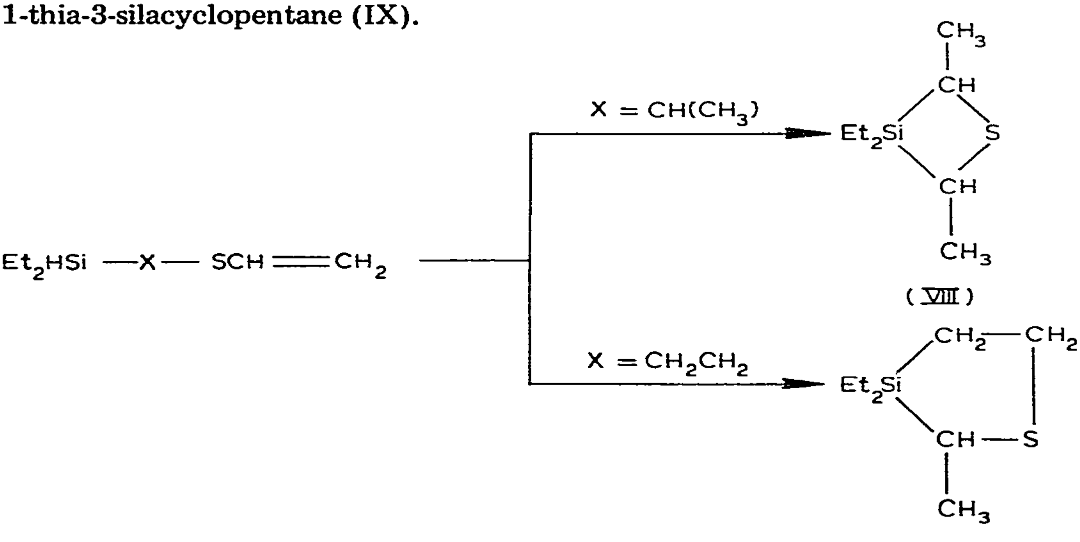
(III) (IV)

Ring opening also occurs when compound II is treated with an ethanolic solution of $HgCl_2$. The white crystalline product, insoluble in organic solvents, has an elemental composition corresponding satisfactorily to the formula in $C_8H_{20}Si_2OS_2Hg_4Cl_6$. Thus, the reaction of 3,3-dimethyl-1-thia-3-silacyclobutane with $HgCl_2$ involves both formation of a complex through the sulfur atom and cleavage of the endocyclic Si—C bond common to silacyclobutane systems [12].



(V)

An alternative method for the synthesis of thiasilethane and thiasilolane derivatives (structures A and B, respectively) is based on the ring closure reaction of isomeric dialkylvinylthioethylsilanes, $R_2HSi–X–SCH{=}CH_2$ (VI, X = $CH(CH_3)$, VII, X = CH_2CH_2). As we have already reported, these alkenylthio derivatives undergo intramolecular hydrosilylation in the presence of $H_2PtCl_6 \cdot 6\ H_2O$ resulting in heterocyclic compounds [13]. In such a way we have obtained 2,4-dimethyl-3,3-diethyl-1-thia-3-silacyclobutane (VIII) and 2-methyl-3,3-diethyl-1-thia-3-silacyclopentane (IX).



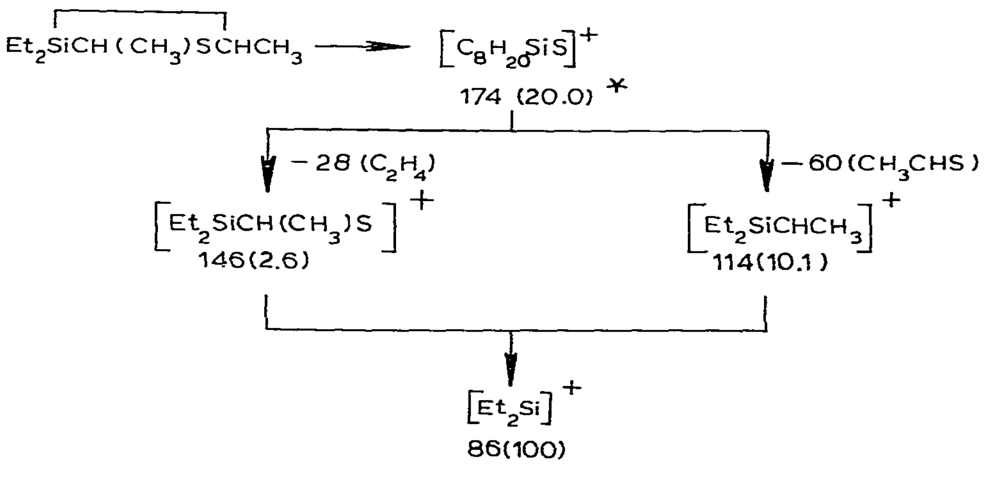
(VIII)

(IX)

We have found that $(Ph_3P)_3RhCl$ catalyzed the above cyclization more readily than H_2PtCl_6 does. In the presence of the former catalyst the ring closure reactions of compounds VI and VII proceed more rapidly affording heterocycles VIII and IX in higher yields. The difference in activity of the catalysts is more noticeable when a five-membered cycle is formed. Thus, in the presence of the rhodium complex the yield of IX amounts to 48% (12 h, 100° C). Under the same conditions only traces of IX are observed with H_2PtCl_6.

It should be noted that the ring closure reaction of $Me_2HSi(CH_2)_nCH{=}CH_2$ ($n = 1, 2$) could not be used for the synthesis of silacyclobutane derivatives [14]. When $n = 1$ polymeric material was formed, with $n = 2$, only 1,1-dimethyl-1-silacyclopentane was obtained. This was explained by the increase in strain in going from a five-membered intermediate complex to the four-membered silacyclobutane. By contrast, a more ready formation of a four-membered ring (VIII) as compared with a five-membered ring (IX) is observed in the heterocyclic system. No compound IX is obtained when ring closure of $Et_2HSiCH(CH_3)SCH{=}CH_2$ occurs. Evidently, the smaller C—S—C valence angle (100°) as compared to that of C—C—C and, consequently its smaller deformation in going from the linear to the cyclic structure favours the formation of the four-membered ring (compound VIII). Thus, the intramolecular hydrosilylation of $Et_2HSiCH(CH_3)SCH{=}CH_2$ proceeds selectivity as α-addition in the presence of both H_2PtCl_6 and $(Ph_3P)_3RhCl$. A similar mechanism is observed for the ring closure of $Et_2HSiCH_2CH_2SCH{=}CH_2$, its cyclization affords no compound containing a six-membered ring.

However, the intramolecular hydrosilylation of diorganylalkenylsilanes, $R_2HSi(CH_2)_nCH{=}CH_2$ in most cases results in the formation of a mixture of silacycloalkanes with $n + 1$ and $n + 2$ carbon atoms in the ring [14,15]. This difference is likely to be due to a different charge distribution in the vinyl moiety of alkenyl- and alkenylthioalkyl-silanes. The terminal carbon of the vinylthio group has a smaller electron density owing to π,σ-acceptor character of the sulfer atom [16]. This favours the addition of the hydrogen atom of the



---

* Figures in parentheses are relative intensities.

initial silane (which carries a high electron density: $Si^+—H^-$) to the above carbon and leads to the selectivity seen in the intramolecular hydrosilylation.

The mass spectral fragmentation behavior of thiasilacyclobutane and thiasilacyclopentane derivatives (compound VII and IX, respectively) is rather different. The mass spectrum of compound VIII has the maximum peak at m/e 86 corresponding to the $[Et_2Si]^+$ ion. This pattern can be formed by cleavage of the endocyclic Si—C bonds of VIII according to the above scheme.

Loss of the ethyl radical from silicon due to cleavage of the exocyclic Si—C bond leads to a low intensity ion of m/e 145. In contrast, this fragmentation pathway prevails for compound IX. Its mass spectrum shows the most intense peak at m/e 145. The peak at m/e 86 has a low intensity (10.9).

$$\mathrm{Et_2SiCH_2CH_2SCHCH_3} \rightarrow \underset{174(23.9)}{[\mathrm{C_8H_{20}SiS}]^+} \xrightarrow{-29(\mathrm{C_2H_5})} \underset{145(100)}{[\mathrm{EtSiCH_2CH_2SCHCH_3}]^+}$$

More detailed mass spectral data on silicon heterocyclic compounds with four- and five-membered rings will be published later.

Experimental

In most cases reactions were carried out in an argon atmosphere. Analytical gas chromatography (GLC) was carried out on a Chrom-4 instrument with a catharometer having a stainless steel 2.4 m × 3 mm column packed with 5% Silicone XE-60 on 45—60 mesh Chezasorb AW or a 1.2 m × 3 mm column packed with 10% Lukopren G-1000 on 45—60 mesh Chromaton N-AW. A PACHV-07 gas chromatograph was used for GLC separation. The mixture were quantified using peak areas.

NMR spectra were recorded on a Tesla BS 487 B spectrometer (80 MHz). Mass spectra were obtained on a AEI MS 902 spectrometer operating at 70 eV.

Isomeric vinylthioethylsilanes were prepared by the published method [13].

3,3-Dimethyl-1-thia-3-silacyclobutane (II)

5.8 g (0.037 mol) of bis(chloromethyl)dimethylsilane was added dropwise to a potassium hydrosulfide solution (prepared by saturation with hydrogen sulfide of 90 ml dry ethanol with 9.3 g (0.016 mol) of potassium hydroxide). After stirring the mixture at room temperature for 1 h, water was added and the product was extracted with pentane. The pentane solution was dried over magnesium sulfate. Removal of the solvent by distillation followed by preparative GLC (5% Silicone E 301 on 45—60 mesh Chromaton at 90°C) gave 2.6 g (59% yield) of compound II, n_D^{20} 1.5005. Anal. Found: C, 40.41; H, 8.52; Si, 23.14; S, 26.51. $C_4H_{10}SiS$ calcd.: C, 40.68; H, 8.47; Si, 23.73; S, 27.12%. ^1H NMR spectrum (δ, ppm/TMS, solvent CCl_4): 0.36 (s, 6H, CH_3); 2.28 (s, 4H, CH_2).

When the above reaction was run under reflux for 1.5 h different major products were formed. Fractional distillation afforded 0.51 g of impure $Me_2Si(OEt)CH_2SCH_3$ (III, 6% yield), b.p. 75—90°C (30 mm), 0.89 g of impure $O(SiMe_2CH_2SCH_3)_2$ (IV, 10% yield), b.p. 100—130°C (30 mm) and 1.2 g of oily residue. Analytical samples were obtained by preparative GLC (5% Silicone E 301 on Chromaton N-AW at 110° C and 160° C for compounds III and IV, respectively). Physical properties and analyses of the compounds were as follows:

$Me_2Si(OEt)CH_2SCH_3$, n_D^{20} 1.4439. Found: C, 44.13; H, 10.38; Si, 16.83; S, 19.01. $C_6H_{16}SiSO$ calcd.: C, 43.90; H, 9.76; Si, 17.07; S, 19.51%.

$O(SiMe_2CH_2SCH_3)_2$, n_D^{20} 1.4720 (lit. n_D^{20} 1.4742 [17]). Found: C, 38.13; H, 8.87; Si, 21.28; S, 24.23. $C_8H_{22}Si_2S_2O$ calcd.: C, 37.78; H, 8.66; Si, 22.05; S, 25.19%. ^1H NMR spectrum (δ, ppm/TMS, solvent CCl_4): 0.17 (s, 6H, $SiCH_3$); 1.70 (s, 4H, SCH_2); 2.07 (s, 6H, SCH_3). IR, ν(Si—O—Si) at 1060 cm^{-1}.

After more prolonged heating of the reaction mixture (6 hours) GLC analysis followed by preparative GLC gave one major product in 26% yield identified as 1,3-bis(methylthiomethyl)-1,1,3,3-tetramethyldisiloxane (IV).

Reaction of 3,3-dimethyl-1-thia-3-silacyclobutane with ethanolic alkali

A solution of 0.15 g (2.85 mmol) of potassium hydroxide in 8 ml of ethanol was added dropwise to 0.58 g (4.92 mmol) of $Me_2Si(CH_2)_2S$. When the exothermic reaction was over, the mixture was neutralized with several drops of dilute HCl. GLC analysis showed that the organic layer contained three components in a ratio of 1 : 1 : 1. Comparison of retention times of the second and third peaks with those of compounds III and IV proved the presence of $Me_2Si(OEt)CH_2SCH_3$ and $O(SiMe_2CH_2SCH_3)_2$ in the reaction mixture *. Treatment of the reaction mixture with $HgCl_2$ in ethanol gave the complex $O(SiMe_2CH_2SCH_3)_2 \cdot 2\,HgCl_2$, m.p. 138° C. Anal. Found: C, 12.37; H, 3.01; Si, 6.80; Hg, 50.98. $C_8H_{22}Si_2S_2Hg_2Cl_4O$ calcd.: C, 12.06; H, 2.76; Si, 7.03; Hg, 50.31%.

Reaction of 3,3-dimethyl-1-thia-3-silacyclobutane with mercury chloride

0.43 g (3.64 mmol) of thiasilacyclobutane (II) was treated with 0.7 g (2.58 mmol) of $HgCl_2$ in 5 ml of ethanol. A white precipitate was formed immediately. The solid was filtered off, washed with a small amount of ethanol and dried in vacuo. 0.50 g (46% yield) of compound was isolated, but it could not be obtained sufficiently pure due to the insolubility of the compound in aliphatic hydrocarbons, ether, THF and CCl_4. In C_6H_6 solution the solid decomposed to form metallic mercury. Anal. Found: C, 7.12; H, 1.43; Hg, 66.21; Cl, 12.46; Si, 3.83; S, 6.18. $C_8H_{20}Hg_4Si_2S_2Cl_6O$ calcd.: C, 7.58; H, 1.59; Hg, 63.23; Cl, 16.78; Si, 4.43; S, 5.05%. IR, ν(Si—O—Si) at 1055 cm^{-1}.

2,4-Dimethyl-3,3-diethyl-1-thia-3-silacyclobutane (VIII)

0.92 g (5.3 mmol) of $Et_2HSiCH(CH_3)SCH{=}CH_2$ was heated in a sealed tube (100° C, 12 h) with 5.2 mg (5.3×10^{-3} mmol) of $(Ph_3P)_3RhCl$ in 15 ml of benzene. After evaporation of the solvent on a rotary evaporator, purification of the residue by preparative GLC (20% Carbowax 20 M on Chromaton N-AW) gave 0.67 g (73% yield) of compound VIII having n_D^{20} 1.4920. Anal. Found: C, 54.30; H, 10.36; Si, 16.42; S, 18.14. $C_8H_{20}SiS$ calcd.: C, 55.10; H, 10.40; Si,

---

* Identification of the reaction mixture components was also made by comparison of their retention times with those of samples of an authentic mixture prepared by the reaction of $Me_2Si(OEt)CH_2Cl$ with sodium methyl mercaptide in hexane.

16.11; S, 18.39%. Compound VIII is a mixture of *cis*- and *trans*-isomers in a 1 : 1 ratio. ^1H NMR spectrum (δ, ppm/HMDS, solvent CCl_4): 0.81—1.15 (m, 10H, SiC_2H_5); *cis*-isomer: 1.35 (d, 6H, CH_3); 2.59 (q, 2H, CH, $^3J(CHCH_3)$ = 7.0 Hz); *trans*-isomer: 1.40 (d, 6H, CH_3); 2.75 (q, 2H, CH, $^3J(CHCH_3)$ = 7.0 Hz).

2-Methyl-3,3-diethyl-1-thia-3-silacyclopentane (IX)

1.10 g (6.3 mmol) of $Et_2HSiCH_2CH_2SCH{=}CH_2$ was heated (100°C, 12 h) with 9.4 mg (10×10^{-3} mmol) of $(Ph_3P)_3RhCl$ in 10 ml of C_6H_6 in a sealed tube. Evaporation of the solvent left a residue which was separated by preparative GLC (20% Carbowax 20 M on Chromaton N-AW) to give 0.5 g (48% yield) of $Et_2\overline{SiCH_2CH_2SC}HCH_3$ having n_D^{20} 1.4970. Anal. Found: C, 55.06; H, 10.35; Si, 16.14; S, 18.05. $C_8H_{18}SiS$ calcd.: C, 55.10; H, 10.40; Si, 16.11; S, 18.39%. ^1H NMR (δ, ppm/HMDS, solvent CCl_4): 0.75 (m, 6H, CH_2Si); 1.05 (m, 6H, CH_3CSi); 1.30 (d, 3H, CH_3CS) 2.21 (q, 1H, CH); 2.79 (m, 2H, SCH_2, ^3J-($CHCH_3$) 7.0 Hz).

Acknowledgements

We thank Dr. A.I. Albanov for recording the NMR spectra. We are grateful to Dr. V.A. Pestunovich for helpful discussions on the ^1H NMR spectra. We are indebted to Dr. A.A. Tatarinova for the microanalytical results reported here.

References

1 S.N. Borisov, M.G. Voronkov and E.Ya. Lukevits. Organosilicon Derivatives of Phosphorus and Sulfur. Plenum Press, New York, London, 1971, pp. 167—208, 252—254.
2 W. Wojnowski, Zeszyty Naukowe Politechniki Gdanskij, Chemia, 21, No 172 (1971) 23.
3 D. Brandes, J. Organometal. Chem. Libr., 7 (1979) 257.
4 K.E. Koenig and W.P. Weber, Tetrahedron Lett., (1973) 3151.
5 K.E. Koenig, R.A. Felix and W.P. Weber, J. Org. Chem., 39 (1974) 1539.
6 R.J. Fessenden and M.D. Coon, J. Org. Chem., 29 (1964) 2499.
7 R.J. Fessenden and M.D. Coon, J. Org. Chem., 29 (1964) 1607.
8 D. Martinez, Z. Chem., 16 (1974) 1.
9 M. Schmidt, M. Wieber, Chem. Ber., 94 (1961) 1426.
10 S. Patai, The Chemistry of the Thiol Group, Part I, J. Wiley and Sons, New York, 1974.
11 N.S. Nametkin, E.D. Babich, V.N. Karelski and V.M. Vdovin, Izv. Akad. Nauk SSSR, Ser. Khim., (1971) 1033.
12 N.S. Nametkin, V.M. Vdovin, M.V. Pozdnyakova, E.D. Babich and I.V. Silkine, Izv. Akad. Nauk SSSR, Ser. Khim., (1973) 1681.
13 M.G. Voronkov, T.J. Barton, S.V. Kirpichenko, V.V. Keiko and V.A. Pestunovich, Izv. Akad. Nauk SSSR, Ser. Khim., (1976) 611.
14 J.W. Swisher and H.-H. Chen, J. Organometal. Chem., 69 (1974) 83.
15 K.I. Kobrakov, T.I. Chernysheva and N.S. Nametkin, Dokl. Akad. Nauk SSSR, 193 (1971) 1340.
16 O. Kajimoto, M. Kobayashi and T. Fueno, Bull. Chem. Soc. Japan, 46 (1973) 2316.
17 G.D. Cooper, J. Amer. Chem. Soc., 76 (1954) 3713.