mmoles (II) in 10 ml toluene was added to a solution of 1 g (2 mmoles) (XII) in 10 ml toluene. The solution becomes violet at the end of the reaction and 12 ml of the solvent was distilled off at reduced pressure. Violet needle crystals of (XV) and (XVI) (Table 2) precipitated out of the solution upon standing for 24 h. The crystals were filtered and dried in vacuum. The ESR spectra were recorded on an RÉ-1301 radiospectrometer.

CONCLUSIONS

1. New cuprous o-semiquinolate complexes with phosphine ligands were obtained and studied by ESR spectroscopy. The paramagnetic cuprous complexes with 1,4-bis(diphenylphosphine)benzene were isolated and characterized for the first time.

2. The effect of the electron-withdrawing properties of the phosphorus substituent in the neutral ligand on the coupling constants was established.

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REACTION OF LITHIUM DIPHENYLPHOSPHIDE WITH MONOSILACYCLOBUTANES

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Monosilacyclobutanes (SCB) are capable of reacting with alkyllithium and aryllithium compounds in ethereal and hydrocarbon media to form addition products with ring opening in accord with the polarity of the endocyclic Si—C bond [1]. In the case of insufficient alkyllithium, opening of a second, third, and subsequent molecule occurs after the initial addition, i.e., SCB undergoes polymerization by the "living chain" mechanism [2].

In order to clarify the scope of this reaction for obtaining the C—Li bond at the end of a silotrimethylene chain attached to the surface of an inorganic oxide support, in which the silicon atom is bound to a PPh_2 group, we studied the reaction of SCB with lithium diphenylphosphide (LDP) in THF.

LDP (obtained according to Capka [3]) reacts with 1,1-dimethyl- (I) and 1-methyl-1-m-tolyl-1-silacyclobutanes (II) in THF at 20-80°C to form polymers even with a fivefold excess of LDP. The dependence of the polymer yield and the molecular masses (or intrinsic viscosities) on the LDP/SCB ratio is given in Table 1, which indicates that even for equimolar LDP/SCB ratio, the polymer yield is about 90%, while an increase in this ratio to 5/1 leads to a decrease in yield only to 40%. The molecular masses of the polymers formed in this case also decrease but not by more than a factor of 2. Apparently, this behavior is related to the significantly slower addition of LDP to SCB than the alkyllithium fragment formed as a result of the initial addition, which reproduces itself after each new addition to an SCB

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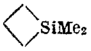
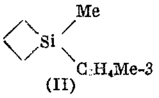
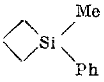
TABLE 1. Reaction of Monosilacylobutanes with Ph_2PLi in THF

Experiment No.	Monomer	Ph_2PLi/SCB ratio	Reaction time, h	T., °C	Polymer yield, %	[η], dl/g (mol. mass)*
1	 (I)	1,6/1	16	40	89,0	0,24 (–)
2†		1/100	0,5	20	44,0	0,055 (–)
3	 (II)	1/1	16	40	86,0	0,33 (7600)
4		3/1	16	40	66,0	0,16 (–)
5		5/1	16	40	40,0	0,12 (2100±50)
6		5/1	0,5	40	8,0	– (400±10)
7†		1/200	10	20	89,5	0,2 (–)

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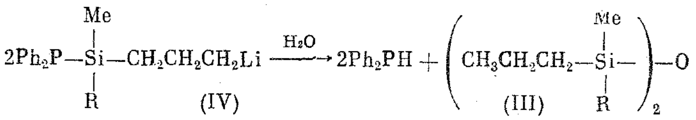
*Molecular masses determined ebullioscopically. The viscosity indices were found in toluene at 25°C.

†Polymerization in benzene with n-BuLi [2].

molecule and consumes monomer in a polymerization process until chain termination. This hypothesis is also supported by the finding that the molecular masses of the polymers formed are somewhat higher (i.e., the chain nucleation sites are less) than for polydimethylsilotrimethylene obtained by polymerization with n-BuLi in hydrocarbon solvent for 1/100 monomer–initiator ratio. The properties of the polymers obtained, including solubility and appearance as well as their IR spectra, do not differ from those for the analogous polymers obtained in our previous work [2, 4]. However, after precipitation of the polymers (see Table 1, experiment 3), their separation, and concentration of the filtrate by removal of the solvent, starting (II) was not found in the residue, i.e., the monomer is completely consumed. Mass spectral analysis of the residue indicates the presence of dimethyldi-n-propyldi-m-tolyldisiloxane (III) (ions with m/z 327 $[M - C_3H_7]^+$, 355 $[M - CH_3]^+$; a molecular ion for siloxanes is not characteristic [5]). Product (III) is formed by hydrolysis induced by the precipitating agent (the Si–P bond is unstable toward hydrolysis [6])

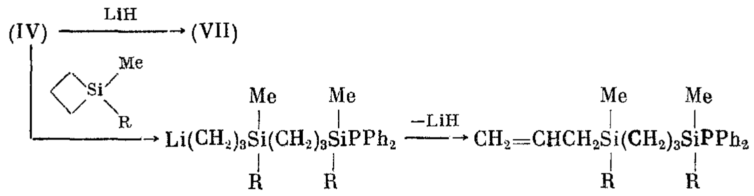


$$2Ph_2P-\overset{\overset{\displaystyle Me}{|}}{\underset{\underset{\displaystyle R}{|}}{Si}}-CH_2CH_2CH_2Li \underset{(IV)}{} \xrightarrow{H_2O} 2Ph_2PH + \left(CH_3CH_2CH_2-\overset{\overset{\displaystyle Me}{|}}{\underset{\underset{\displaystyle R}{|}}{Si}}- \right)_2 O \quad (III)$$

In all cases, R = $3\text{-}MeC_6H_4$. In addition, dimethyldiallyldi-m-tolyldisiloxane (V) (peaks with m/z 325, $[M - C_3H_5]^+$, 351 $[M - CH_3]^+$, and 285 $[RSi(Me)OSiHRMe]^+$) and dimethyldi-m-tolyl-n-propylallyldisiloxane $PrSi(Me)(R)OSi(Me)(R)CH_2CH{=}CH_2$ (VI) (with peaks m/z 327 $[M - C_3H_5]^+$, 325 $[M_2 - C_3H_7]^+$, 353 $[M - CH_3]^+$). Siloxanes (V) and (VI) are formed as a consequence of the hydrolysis of $H_2C{=}CHCH_2Si(Me)(R)PPh_2$ (VII) formed by the removal of LiH from $Li(CH_2)_3 \cdot Si(Me)(R)PPh_2$ (VIII) and its cohydrolysis with (IV). The IR spectrum of this product with bands at 1050 cm^{-1} (Si–O), 1640 cm^{-1} (C=C), 907, 964, 1406, 1600 cm^{-1} (C=C), 3020 cm^{-1} (=C–H), and 3061 cm^{-1} (=CH_2) is in accord with this composition of the residue.

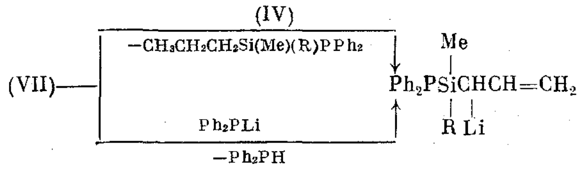
The formation of dipropylsiloxane (III) may formally be represented as the result of the addition of the precipitating agent (methanol) and subsequent hydrolysis of the propylmethoxy derivative by the water present in the methanol sample. Hence, in order to confirm the addition of LDP to SCB, the terminal lithium atom should be replaced, for example, by the trimethylsilyl group by the action of Me_3SiCl. This requires the reaction of 5 equiv. Ph_2PLi with 1 equiv. (II) in THF at 40°C for 30 min in a dry argon atmosphere followed by the addition of 5.5 equiv. Me_3SiCl (upon complete conversion of SCB, the concentration of the primary addition products may be negligible due to loss of LiH). In this case, we would expect both products of the reaction with Me_3SiCl at the retained C–Li bonds and products of the hydrolysis of the Ph_2PSi group (after the addition of aqueous methanol) and their cohydrolysis with excess Me_3SiCl. Treatment with methanol gives about 8% polymer. The THF and methanol solvents were removed together with the hexamethyldisiloxane formed and then distillation in higher vacuum gave about 80% unreacted monomer.

Mass spectral analysis of the residue indicated that even for relatively low conversion both after opening of the first and second monomer molecules, the reaction giving loss of LiH with the formation of allyl groups makes a very significant contribution [2]

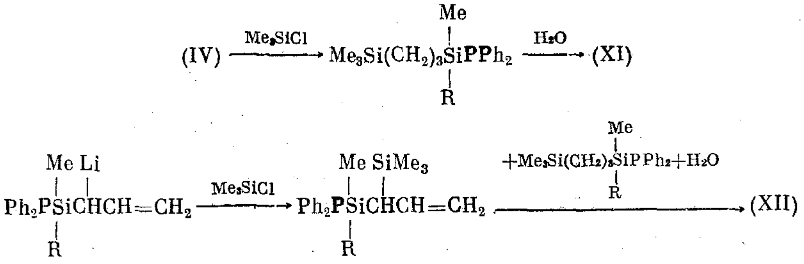


The products of the hydrolysis of the reaction mixture after the addition of Me_3SiCl are siloxanes (V), (VI), $CH_2{=}CHCH_2Si(Me)(R)(OSiMe_3)$ (IX), and $CH_2{=}CHCH_2Si(Me)(R)(CH_2)_3Si(Me)\cdot(R)OSiMe_3$ (X) identified by mass spectral peaks with m/z 325 $[M - C_3H_5]^+$, 351 $[M - CH_3]^+$, 285 $[RMeSiOSiRMeH]^+$ for (V), 223 $[M - C_3H_5]^+$, 249 $[M - CH_3]^+$, and 209 $[RMeSiOSiMe_2H]^+$ for (VI), 327 $[M - C_3H_5]^+$, 325 $[M - C_3H_7]^+$, 353 $[M - CH_3]^+$ for (XI), and 425 $[M - CH_3]^+$, 223 $[Me_3SiOSiMeR]^+$ for (X). In the latter case, the chain termination (loss of LiH) occurs after opening of the second monomer molecule. The multiplet at 4.80-5.75 ppm in the PMR spectrum also indicates the presence of a significant amount of allyl groups in the reaction products after hydrolysis (the ratio of the integral intensities of the signals for the aromatic multiplets at 6.5-7.5 ppm and of the allylic multiplets is 4.0:2.5).

The allyl groups formed may be metallated by C—Li fragments or



In this case, the product with an n-propyl group at the silicon atom is formed. This product undergoes hydrolysis to give 1,1,1,3-tetramethyl-3-propyl-3-tolyldisiloxane (VIII) with mass spectral peaks m/z 251 $[M - CH_3]^+$ and 223 $[M - C_3H_7]^+$ in addition to (III) which has peaks at m/z 327 $[M - C_3H_7]^+$ and 355 $[M - CH_3]^+$. The peaks with the greatest mass at m/z 499 and 497 correspond to siloxanes $[Me_3Si(CH_2)_3SiRMe]_2O$ (XI) and $Me_3Si(CH_2)_3Si(R)(Me)OSi\cdot(R)(Me)CH(SiMe_3)CH{=}CH_2$ (XII), respectively. In addition, (XI) has peaks with m/z 441 $[M - Me_3Si]^+$ and 399 $[M - Me_3Si(CH_2)_3]^+$ while (XII) has peaks with m/z 399 $[M - Me_3SiCHCH{=}CH_2]^+$ and 397 $[M - Me_3Si(CH_2)_3]^+$. Both these products are the result of the reaction of Me_3SiCl with C—Li fragments and subsequent hydrolysis



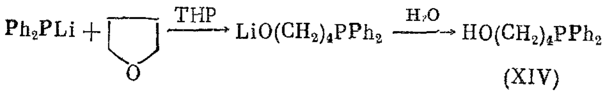
$$(IV) \xrightarrow{Me_3SiCl} Me_3Si(CH_2)_3\overset{Me}{\underset{R}{Si}}PPh_2 \xrightarrow{H_2O} (XI)$$

$$Ph_2P\overset{Me}{\underset{R}{Si}}\overset{Li}{C}HCH{=}CH_2 \xrightarrow{Me_3SiCl} Ph_2P\overset{Me}{\underset{R}{Si}}\overset{SiMe_3}{C}HCH{=}CH_2 \xrightarrow{+Me_3Si(CH_2)_3\overset{Me}{\underset{R}{Si}}PPh_2 + H_2O} (XII)$$

The same behavior is found for $Me_3Si(CH_2)_3Si(Me)(R)OSi(Me)(R)CH_2CH{=}CH_2$ (XIII). This siloxane has mass spectral peaks with m/z 425 $[M - CH_3]^+$, 399 $[M - C_3H_5]^+$, 325 $[M - Me_3Si(CH_2)_3]^+$, and 285 $[RMeSiOSiRMeH]^+$.

Thus, the results obtained indicate that LDP in THF is capable, similar to organolithium compounds, of opening the monosilacyclobutane ring although it is less active.

In conclusion, we note that the sample of LDP should be freshly prepared in a well-dried inert gas atmosphere since Ph_2PH may react with the C—Li bond and LDP may react with the THF solvent upon prolonged storage (see scheme on next page). After maintenance of a solution of LDP in THF for 1.5 months and subsequent hydrolysis, we found δ-hydroxybutyldiphenylphosphine (XIV) in the hydrolysis by mass spectroscopy in addition to Ph_2PH. Product (XIV) has mass spectral peaks with m/z 258 $[M]^+$, 241 $[M - OH]^+$, 240 $[M - H_2O]^+$, and 185 $[M - Ph_2P]^+$.



(XIV)

EXPERIMENTAL

The IR spectra were taken on a UR-20 spectrometer and the PMR spectra were taken on a Varian T-60 spectrometer with TMS internal standard. The mass spectra were taken on an LKB-2091 mass spectrometer.

Samples of 1,1-dimethyl-1-silacyclobutane and 1-methyl-1-m-tolyl-1-silacyclobutane were synthesized according to Ushakov [4] and Ushakov and Vdovin [7], respectively. A commercial sample of Me_3SiCl was used with purity greater than 99%. Commercial methanol was used for precipitation of the polymers without additional treatment. THF was dried by the usual method.

Reaction of Monosilacyclobutanes with Ph_2PLi. a) A freshly prepared solution of 0.5-0.65 M Ph_2PLi was added to an ampul and degassed by freezing in vacuum. Then, purified and dried (I) was added. The ampul was sealed and maintained for 16 h at 40°C. Then the ampul was opened and the contents were poured into methanol. The precipitated polymer was separated, washed with methanol, dried to constant weight, and analyzed. The methanol solution was concentrated in vacuum at not more than 20°C and the residue was analyzed.

b) A weighed sample of (II) was added to an ampul and degassed in a dry argon atmosphere. Then, the required amount of a solution of Ph_2PLi in THF was added and the solution was again degassed by evacuation. The ampul was sealed and maintained for 16 h at 40°C. The further treatment was the same as described in procedure a).

c) A solution of Ph_2PLi in THF and degassed sample of (II) in 5/1 ratio were added to a flask previously heated in vacuum and filled with pure, dry argon. The mixture was heated for 0.5 h at 40°C and then 5.5 equiv. Me_3SiCl was added in an argon stream and stirred for 15 min. Upon cooling, methanol was added to the mixture. The polymer precipitate was separated, dried to constant weight, and analyzed. The methanol solution was concentrated in vacuum at about 20 mm Hg to constant weight and the residue was analyzed.

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CONCLUSIONS

1. Lithium diphenylphosphide added to monosilacyclobutanes by ring opening with the formation of Si—P and C—Li bonds which cause further polymerization of the monosilacyclobutanes.

2. Polymer chain termination occurs by the loss of lithium hydride. This process is significant even in the initial polymerization steps. Molecules are formed with allyl groups at the silicon atom.

ppm

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