## Synthesis and polymerization of 9-carbazolyl-containing 1-silacyclobutane derivatives

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Novel 9-carbazolyl-containing 1-silacyclobutane derivatives containing tri-, tetra-, and pentamethylene bridges between the nitrogen and silicon atoms and 1-methyl-1-p-[dimethyl- $\gamma$ -(9-carbazolylpropyl)silyl]phenyl-1-silacyclobutane have been synthesized. Polymerization (thermally induced and catalytic) of these monomers afforded polysiltrimethylenes having 9-carbazolyl groups in the substituents framing the main chain. The copolymerization of 9-carbazolyl-containing silacyclobutanes with silacyclobutanes of other types has been carried out.

Key words: silacyclobutanes, synthesis; carbazolyl substituents; polymerization.

Polymers with various carbazole derivatives in the side chains can be used in non-silver photography and for recording information and images by the thermoplastic method. This is due to their ability to form charge-transfer complexes with electron-withdrawing sensitizers (*e.g.*, with trinitrofluorenone). Realization of this phenomenon for the siltrimethylene chain (depending on the type of substituent at the silicon atom, polysiltrimethylenes can behave as rubbers or elastoplasts, amorphous or crystalline substances with high melting points<sup>1,2</sup>) affords elastic chains with good adhesion, strength, and sensitometric parameters.<sup>3,4</sup>

The purpose of the present work was to study the synthesis and polymerization of the hitherto unknown 1-methyl-1-(9-carbazolylalkyl)-1-silacyclobutanes with the number (n) of methylene groups separating the silicon atom in the silacyclobutane moiety from the nitrogen atom in the carbazole moiety  $n = 3 \div 5$  (compounds 1-3, respectively), as well as 1-phenyl-1-(9-carbazolylalkyl)-1-silacyclobutanes with tri- (4) and tetramethylene (5) bridges. 1-Silacyclobutane monomers were synthesized according to Scheme 1.

Compounds **6–8** were obtained using phase transfer catalysis with tetrabutylammonium bromide (TBAB) as the catalyst. The yields of 9-( $\omega$ -haloalkyl)carbazoles were within 65–85 % (at a fourfold excess of the  $\alpha, \omega$ -di-haloalkanes). The yields of methylcarbazolylalkylsilacyclobutanes (in a *one pot* synthesis, in which the solutions of compounds **6–8** were introduced into a flask in which magnesium and the necessary amount of 1-me-thyl-1-chloro-1-silacyclobutane had been previously placed) were 70–92 %, and those of phenylcarbazolyl-alkylsilacyclobutanes were 62–65 %.

In addition to the above monosilacyclobutanes with

polymethylene bridges, we also obtained 1-methyl-1-p-[dimethyl- $\gamma$ -(9-carbazolylpropyl)silyl]phenyl-1-silacyclobutane (9). The three-stage synthesis of compound 9 included the preparation of allylcarbazole (10) by the phase-transfer catalysis method (yield up to 95 %), hydrosilylation of 10 with chlorodimethylsilane to give  $\gamma$ -(9-carbazolylpropyl)chlorodimethylsilane (11) (yield 76 %), and nucleophilic substitution of the chlorine atom in the latter with a p-methylsilacyclobutylphenyl group, which proceeds on treatment with the Grignard

## Scheme 1



Translated from Izvestiya Akademii Nauk. Seriya Khimicheskaya, No. 8, pp. 1437–1441, August, 1993. 1066-5285/93/4208-1372 \$12.50 © 1994 Plenum Publishing Corporation Scheme 2



reagent prepared from 1-p-bromo(or chloro)phenyl-1methyl-1-silacyclobutane (12) (Scheme 2).

The following compounds, which were intended as comonomers for copolymerization with the carbazolylcontaining derivative 1, were also synthesized by the conventional procedure (treatment of 1-chloro-1-methyl- and 1,1-dichloro-1-silacyclobutanes with the respective Grignard reagents): 1-methyl-1-p-phenoxyphenyl-1-silacyclobutane (13) and 1,1-di-p-dimethylaminophenyl-1-silacyclobutane (14). The structures of the compounds obtained were established by mass spectrometry and <sup>1</sup>H NMR spectroscopy. The mass spectra of carbazolyl-containing silacyclobutanes comprise ions originating from the fragmentation route typical of silacyclobutanes, *i.e.*, ring cleavage with abstraction of ethylene.<sup>5</sup> However, the presence of a carbazole aromatic system with an alkyl chain at the nitrogen atom explains why the intensities of the peaks corresponding to these ions decrease for compounds 1, 2, and 3, which contain an alkyl substituent at the silicon atom; in these cases, the maximum intensity is observed for the peak of the stable ion  $C_{12}H_8NCH_2^+$  with m/z180. In the case of compounds 4 and 9, that have, besides the carbazolylalkyl system, aryl substituents at the silicon atom, the peaks of the molecular ions remain the most intense ones in the spectra. This behavior has been observed earlier in the mass spectra for aryl derivatives of silacyclobutanes.<sup>6</sup> The elemental analysis data fit well with the theoretically calculated compositions for these structures. The properties of the silacyclobutanes synthesized (1-5, 9, 13, and 14) are presented in Table 1.

The polymerization of silacyclobutane monomers occurred *via* opening of the strained four-membered ring at the endocyclic Si-C bond (Scheme 3).

The procedures for both thermally initiated and catalytic polymerization and for copolymerization of carbofunctional silacyclobutanes have been reported in detail elsewhere.<sup>1</sup> The IR spectra of all of the polymers contain no bands at 930, 1125, and 1180 cm<sup>-1</sup>, which are





characteristic of the silacyclobutane ring. The elemental analysis data for the homopolymers are in agreement with the elemental compositions of monomeric units. Also, the signals at *ca.* 1.0 and *ca.* 2.1 ppm, corresponding to the protons of  $\alpha$ - and  $\beta$ -CH<sub>2</sub> groups, respectively, in the silacyclobutane rings in the <sup>1</sup>H NMR spectra for homo- and copolymers, disappear, while the signals for the protons in the methyl groups bonded to the silicon atom in the monomers, are displaced (after ring opening) upfield.

The photo-thermoplastic registration of information and images requires polymeric materials with various molecular masses. Hence, there arises the necessity to control the molecular masses of the polymeric samples synthesized. It is known that in the absence of chain growth regulators (alcohols, halo-derivatives, amines, *etc.*), thermally initiated polymerization of silacyclobutanes ensures the maximum molecular masses of the polysiltrimethylenes.<sup>2</sup>

Table 2 presents some examples of polymerizations carried out in this way, which afforded polymers with relatively high and low molecular masses, as well as the results of polymerization of silacyclobutanes under the action of catalysts (KOH, butyllithium).

A direct dependence (as was reported earlier for dialkyl, alkylaryl and diaryl silacyclobutane derivatives<sup>2</sup>) of the molecular masses of the carbazolyl-containing polysiltrimethylenes formed on the temperature of thermally initiated polymerization is observed. The molecular masses resulting from thermal initiation were successfully controlled with the use of various higher alcohols. Polysiltrimethylenes with the required molecular masses can also be obtained by polymerization catalyzed by an alkali or butyllithium (these reactions proceed at much lower temperatures but take more time). It should be noted in conclusion that the actual copolymerization of 13 with 14 is proved by the fact that the resulting copolymer (obtained in a high yield) is soluble in heptane, whereas the homopolymer obtained from 14 is insoluble in aliphatic hydrocarbons.

## **Experimental**

<sup>1</sup>H NMR spectra were recorded in CCl<sub>4</sub> on Varian T-60 and Bruker MLS-300 spectrometers, using tetramethylsilane as

				9-Crbz-		s s <sup>R'</sup>	
					15, 9	13, 14	
R'	R	Com- po- und	Yield (%)	M.p. /°C	n <sub>D</sub> <sup>20</sup>	MS (EI), <i>m/z</i> ( <i>I</i> <sub>rel</sub> (%))	<sup>1</sup> H NMR (in CCl <sub>4</sub> vs TMS), δ
Me	(CH <sub>2</sub> ) <sub>3</sub>	1	70	_	1.6136 (viscous oil)	293 $[M]^+$ (34), 265 $[M-C_2H_4]^+$ (29), 250 $[M-CH_3-C_2H_4]^+$ (29), 180 $[C_{12}H_8NCH_2]^+$ (100)	0.18 (s, 3 H, CH <sub>3</sub> Si); 0.6–1.23 (m, 4 H, α-CH <sub>2</sub> in the ring; 2 H, SiCH <sub>2</sub> CCN); 1.6–25.15 (m, 2 H, β-CH <sub>2</sub> in the ring; 2 H, CCH <sub>2</sub> CN); 4.12 (t, 2 H, CH <sub>2</sub> N); 6.78–8.01 (m, 8 H, Crbz)
Me	(CH <sub>2</sub> ) <sub>4</sub>	2	75	_	1.6095	307 [M] <sup>+.</sup> (50), 279 [M– $C_2H_4$ ] <sup>+.</sup> (23), 180 $[C_{12}H_8NCH_2]^{+.}$ (100)	0.17 (s, 3 H, CH <sub>3</sub> Si); 0.71–2.5 (m, 6 H, CCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> Si; 6 H, $\alpha$ - and $\beta$ -CH <sub>2</sub> in the ring); 4.1 (t, 2 H, CH <sub>2</sub> N); 6.8–8.01 (m, 8 H, Crbz)
Me	(CH <sub>2</sub> ) <sub>5</sub>	3	67	16—23	1.6063	321 $[M]^+$ (41), 293 $[M-C_2H_4]^+$ (24), 278 $[M-CH_3-C_2H_4]^+$ (20), 180 $[C_{12}H_8NCH_2]^+$ (100)	0.165 (s, 3 H, CH <sub>3</sub> Si); 0.62–2.56 (m, 6 H, $\alpha$ - and $\beta$ -CH <sub>2</sub> in the ring; 8 H, Si–(CH <sub>2</sub> ) <sub>4</sub> C); 4.05 (t, 2 H, CH <sub>2</sub> N); 6.9–8.01 (m, 8 H, Crbz)
Ph	(CH <sub>2</sub> ) <sub>3</sub>	4	64	69—70.5		355 [M] <sup>++</sup> (100), 327 [M– $C_2H_4$ ] <sup>++</sup> (57), 328 [M– $C_2H_5$ ] <sup>+</sup> (34), 312 [M–CH <sub>3</sub> – $C_2H_4$ ] <sup>+</sup> (22), 180 $[C_{12}H_8NCH_2]^+$ (74)	0.91–1.44 (m, 4 H, $\alpha$ -CH <sub>2</sub> in the ring; 2 H, CH <sub>2</sub> Si); 1.73–2.38 (m, 2 H, $\beta$ -CH <sub>2</sub> in the ring; 2 H, CCH <sub>2</sub> C); 4.23 (t, 2 H, CH <sub>2</sub> N); 6.88–7.6 (m, 5 H, Ph; 6 H, Crbz without 4'-H and 5'-H); 7.98 (m, 2 H, 4'-H and 5'-H Crbz)
Ph	(CH <sub>2</sub> ) <sub>4</sub>	5	62	_	1.6183 (viscous oil)	369 $[M]^+$ (23), 341 $[M-C_2H_4]^+$ (15), 180 $[C_{12}H_8NCH_2]^+$ (100)	0.75–2.5 (m, 6 H, Si(CH <sub>2</sub> ) <sub>3</sub> C; 6 H, $\alpha$ - and $\beta$ -CH <sub>2</sub> in the ring); 4.18 (t, 2 H, CH <sub>2</sub> N); 6.95– 8.25 (m, 13 H, Crbz and Ph)
Me	p-(CH <sub>2</sub> ) <sub>3</sub> SiMe <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	9	57.5	44.5—47.0	·	427 $[M]^+$ (100), 399 $[M-C_2H_4]^+$ (18), 385 $[M-C_3H_6]_2$ (18), 180 $[C_{12}H_8NCH_2]^+$ (56)	0.2 (s, 6 H, (CH <sub>3</sub> ) <sub>2</sub> Si); 0.52 (s, 3 H, CH <sub>3</sub> Si); 0.65–1.4 (m, 2 H, SiCH <sub>2</sub> CC; 4 H, $\alpha$ -CH <sub>2</sub> in the ring); 1.5–2.35 (m, 2 H, SiCCH <sub>2</sub> CN; 2 H, $\beta$ -CH <sub>2</sub> in the ring); 4.09 (t, 2 H, CH <sub>2</sub> N); 6.83–7.48 (m, 4 H, Phn; 6 H, Crbz); 7.75–7.97 (m, 2 H, 4'-H and 5'-H Crbz)
Me	<i>p</i> -PhO—C <sub>6</sub> H <sub>4</sub>	13*	87	_	1.5800	254 [M] <sup>+•</sup> (10), 226 [M– C <sub>2</sub> H <sub>4</sub> ] <sup>+•</sup> (100)	0.5 (s, 3 H, CH <sub>3</sub> Si); 1.17 (m, 4 H, $\alpha$ -CH <sub>2</sub> in the ring); 2.1 (m, 2 H, $\beta$ -CH <sub>2</sub> in the ring); 6.52-7.52 (m, 9 H, H arom.)
<i>p</i> -Me <sub>2</sub> I	NC <sub>6</sub> H <sub>4</sub> <i>p</i> -Me <sub>2</sub> NC <sub>6</sub> H <sub>4</sub>	14	75	84.8—85.4		310 [M] <sup>+</sup> (69.5), 282 [M–C <sub>2</sub> H <sub>4</sub> ] <sup>+</sup> (100)	1.36 (m, 4 H, $\alpha$ -CH <sub>2</sub> in the ring); 2.19 (m, 2 H, $\beta$ -CH <sub>2</sub> in the ring); 2.97 (c, 12 H, CH <sub>3</sub> N); 6.7 (m, 4 H, <i>o</i> -H arom. relative to N); 7.45 (m, 4 H, <i>m</i> -H arom. relative to N)

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\* Compound **13**: b.p. 127.5–128.5 °C (0.02 Torr),  $d_4^{20}$  1.0671.

Mono- mers	С (М)	Mol. mass regulator (mass. %)	Solvent	T/°C	τ/h	Yield (%)	Mol. mass	Glass-transition or softening point/°C			
Homopolymerization											
1	2.0	_	Toluene	235	10	82.5	84000 <sup>e</sup>	63			
	2.0	_	Toluene	245	10	0 <i>)</i> 95 5	97000				
	2.0 2.5b		Vulene	230	10	83.3 70	7200				
	2.5	$n-C_6H_{13}OH$ (3.5)	Toluene	245	12	91	8300	57			
2	2.1°		Benzene	20	48	83	6300				
	2.0		Xvlene	240	10	81	72000 <sup>e</sup>	55			
	2.5	s-C <sub>10</sub> H <sub>21</sub> OH (4.1)	Xylene	245	14	77	2900	_			
	2.0 <sup>b</sup>	_	Xylene	75	72	73	3100	-			
	1.5°	$\rightarrow$	Benzene	20	48	92	3200				
3	2.0		Dicumylmethane	250	15	75	43000e	45-48			
	2.5	<i>n</i> -C <sub>6</sub> H <sub>13</sub> OH (3.5)	Toluene	245	15	72	3600				
4	2.0	_	Toluene	245	15	78	37000°	74			
	2.0	<i>n</i> -C <sub>6</sub> H <sub>13</sub> OH (3.5)	Xylene	250	15	91	4400				
5	2.0		Toluene	250	15	91.5	35000°	59-62			
C	2.5	s-C <sub>10</sub> H <sub>21</sub> OH (3.7)	Toluene	250	14	88.5	4500				
9	2.2		Xvlene	250	15	84	46500 <sup>e</sup>	65			
-	2.2	<i>n</i> -C <sub>7</sub> H <sub>15</sub> OH (3.5)	Xylene	250	10	90	6300	_			
13	2.8	<u> </u>	Toluene	230	10	87.7	720000 <sup>e</sup>	1.6 <sup>g</sup>			
Copolymerization											
1,13ª		s-C <sub>10</sub> H <sub>21</sub> OH (3.67)		240	14	90	6200				
1,14	1.3 <sup>d</sup> 0.22	s-C <sub>10</sub> H <sub>21</sub> OH (3.23)	Xylene	240	18	92	3900				
1,14	1.3 <sup>b</sup> 0.22	_	Xylene	75	80	74	2200 <sup>f</sup>	. —			
13,14	2.3 <sup>b</sup> 0.29	_	Toluene	90	96	76	7400 <sup>f</sup>	_			

Table 2. Polymerization of carbazolyl-containing silacyclobutanes and their copolymerization with other monosilacyclobutanes

<sup>a</sup> Without any solvent (molar ratio 1:13 = 1:1). <sup>b</sup> Catalysis by KOH (catalyst:monomer ratio was 1:50). <sup>c</sup> Catalysis by butyllithium (0.05 *M*). <sup>d</sup> Homopolymerization of 14 has been reported in ref. 7. <sup>e</sup> The molecular masses were determined by GPC. Molecular masses of other samples were established by measuring the thermal effects of condensation. <sup>f</sup> Copolymer compositions: 1:14 = 5.92:1; 13:14 = 8.21:1 (<sup>1</sup>H NMR data). <sup>g</sup> Measured by differential scanning calorimetry.

the internal standard. Mass spectra were recorded on LKB-2091 and Kratos MS-80 instruments. The molecular masses of high-molecular polymer samples were determined on a Waters gel-chromatograph (a column with an ultrastiragel, length 30 cm, internal diameter 7.8 mm) in toluene; calibration was performed relative to polystyrene standards. Molecular masses of other polymer samples were established on a Knauer instrument by measuring the thermal effects of condensation in benzene. The glass transition and softening points for the polymers were measured on a UIP-70 instrument and a Mettler differential scanning calorimeter.

1-Methyl- and 1-phenyl-1-chloro-1-silacyclobutanes were obtained according to the procedures in refs. 8 and 1, respectively. 1-Methyl-1-p-bromo- and 1-methyl-1-p-chloro-1silacyclobutanes were synthesized according to the method reported in ref. 9. Commercial grade  $\alpha, \omega$ -dihaloalkanes, allyl bromide, and chlorodimethylsilane were distilled prior to use. Polymerization (both thermally initiated and catalyzed by KOH or butyllithium) and copolymerization were carried out as described in ref. 1.

Synthesis of  $\alpha$ -halo- $\omega$ -9-carbazolylalkanes (general procedure). To a mixture of carbazole (1.0 mol) and 3-bromo-1chloropropane, 1,4-dibromobutane, or 1,5-dibromopentane (4-5 mol) in toluene (2.0 L), an equal volume of a 50 % KOH solution and tetrabutylammonium bromide (5-8 mol. % with respect to the carbazole) was added. The mixture was heated with stirring at 80-90 °C until the absence of carbazole (TLC test); generally, this required at least 4 h. The layers were separated; the organic layer was washed with water to a neutral pH and dried with granulated Al<sub>2</sub>O<sub>3</sub> or anhydrous

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 $Na_2SO_4$ . The solvent was removed, and the residue was chromatographed on a column with  $Al_2O_3$  or distilled *in vacuo*.

**Compound 6.** Yield 83 %, b.p. 161-165 °C (0.008 Torr). <sup>1</sup>H NMR,  $\delta$ : 2.03 (m, 2 H, CCH<sub>2</sub>C); 3.2 (t, 2 H, CH<sub>2</sub>Cl); 4.15 (t, 2 H, CH<sub>2</sub>N); 6.77-7.9 (m, 8 H, H arom.). MS, m/z( $I_{rel}$  (%)): 243/245 [M]<sup>++</sup> (100/41), 207 [M-HCl]<sup>++</sup> (14), 180 [C<sub>12</sub>H<sub>8</sub>NCH<sub>2</sub>]<sup>+</sup> (7).

**Compound 7.** Yield 78 %, m.p. 115.7–116.7 °C. <sup>1</sup>H NMR,  $\delta$ : 1.73 (m, 4 H, CCH<sub>2</sub>CH<sub>2</sub>C); 3.1 (t, 2 H, CH<sub>2</sub>Br); 4.05 (t, 2 H, CH<sub>2</sub>N); 7.18 (m, 6 H, Crbz, without 4'-H and 5'-H (*o*-H relative to C)); 7.93 (m, 2 H, 4'-H and 5'-H (*o*-H in carbazolyl relative to N)). MS, *m/z* (*I*<sub>rel</sub> (%)): 301/303 [M]<sup>++</sup> (18/18.5), 180 [C<sub>12</sub>H<sub>8</sub>NCH<sub>2</sub>]<sup>+</sup> (100).

**Compound 8.** Yield 74 %, m.p. 50.5-52.5 °C. <sup>1</sup>H NMR,  $\delta$ : 1.12-2.05 (m, 6 H, CCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>C); 3.1 (t, 2 H, CH<sub>2</sub>Br); 4.1 (t, 2 H, CH<sub>2</sub>N); 6.87-8.03 (m, 8 H, Crbz). MS, *m/z* ( $I_{rel}$  (%)): 315/317 [M]<sup>+ ·</sup> (35/32), 235 [M-HBr]<sup>+ ·</sup> (18), 180 [C<sub>12</sub>H<sub>8</sub>NCH<sub>2</sub>]<sup>+</sup> (100).

Synthesis of carbazolyl-containing silacyclobutanes (general procedure). Abs. THF (70 mL), a solution (15 mL) of an  $\alpha$ -halo- $\omega$ -9-carbazolylalkane 6, 7, or 8 (1.0 mol) in abs. THF (0.45 L), and dibromoethane (2 mL) were added to magnesium (30 g, 1.25 mol). After the reaction started, the remaining solution was added in such a way that the temperature remained within 40-55 °C. After adding the total amount of the solution, the mixture was refluxed for 1 h at 60 °C and cooled to ~20 °C. Then 1-chloro-1-methyl- or 1-chloro-1phenyl-1-silacyclobutane (1.1 mol) in THF (200 mL) was added over 1 h. The mixture was refluxed for 6 h at 60 °C, and then the solvent and excess chlorosilacyclobutane were removed in vacuo. The residue was suspended in dry benzene (0.6 L) and filtered. The latter operation was repeated, and the precipitate was washed with benzene on a filter. The combined filtrates were concentrated in vacuo, then the target product (1, 2, 3, 4, or 5) was isolated by chromatography on a column with  $Al_2O_3$  and hexane—benzene (2:1) as the eluent. If necessary, compound 4 was recrystallized from a hexane-benzene mixture (3:1, v/v).

9-Allylcarbazole (10) (the phase transfer catalysis procedure). A mixture of carbazole (1.0 mol), allyl bromide (1.5 mol), toluene (1.8 L), and TBAB (7 mass. % with respect to carbazole) with an equal volume of a 50 % aqueous KOH solution was treated similarly to the general procedure for the synthesis of haloalkylcarbazoles. The yield of carbazole 10 was 96 % after recrystallization from ethanol, m.p. 56 °C (this agrees with the data in ref. 10).

y-(9-Carbazolylpropyl)chlorodimethylsilane (11). A solution (5 mL) of allylcarbazole 10 (103.5 g, 0.5 mol) and chlorodimethylsilane (0.55 mol) in anhydrous benzene (250 mL) and 0.1 mL of a 0.1 M solution of  $H_2PtCl_6 \cdot 6H_2O$ in isopropanol were placed in a flask equipped with a reflux condenser and a dropping funnel. The mixture was heated until the reaction started, and the remaining solution was added over 12 h with continuous boiling. Then an additional 0.1 mL of fresh catalyst and chlorodimethylsilane (0.1 mol) were added, and the mixture was refluxed for a further 6 h. The residue left after removing the solvent and excess chlorodimethylsilane was distilled in vacuo. The yield of compound 11 was 76.5 %, b.p. 164.5–167 °C (0.03 Torr),  $n_D^{20}$ 1.6135 (a viscous oil). MS, m/z ( $I_{rel}$  (%)): 301/303 [M]<sup>+</sup>.  $(2.5/1), 286/288 [M-CH_3]^+ (4/1.7), 251 [M-CH_3-Cl]^+ (3.6),$ 180 [C<sub>12</sub>H<sub>8</sub>NCH<sub>2</sub>]<sup>+</sup> (100). <sup>1</sup>H NMR, δ: 0.63 (s, 6 H, CH<sub>3</sub>Si);

1.09 (m, 2 H, CH<sub>2</sub>Si); 2.04 (m, 2 H, CCH<sub>2</sub>C); 4.2 (t, 2 H, CH<sub>2</sub>N); 6.8–8.06 (m, 8 H, Crbz).

**1-Methyl-1**-*p*-[ $\gamma$ -9-(carbazolylpropyl)dimethylsilyl]phenyl-**1-silacyclobutane (9).** A solution of reagent **12** was prepared in the conventional way from magnesium (12 g, 0.5 mol) and *p*-bromo- or *p*-chlorophenylmethylsilacyclobutane (0.41 mol) in THF (400 mL). Then, a solution of compound **11** (107 g, ~0.34 mol) in THF (250 mL) was added over 2.5 h. The mixture was refluxed for 6 h at 65 °C, then toluene (0.5 L) was added. The mixture was cooled and decomposed with water. After the usual workup, the product was isolated by chromatography on a column with Al<sub>2</sub>O<sub>3</sub> (activity grade III) using hexane—benzene (3:1, v/v) as the eluent.

1-Methyl-1-*p*-phenoxyphenyl-1-silacyclobutane (13). A solution of 1-chloro-1-methyl-1-silacyclobutane (0.92 mol) in THF (120 mL) was added over 3.5 h to a solution of the Grignard reagent, which was prepared from Mg (1.2 g-at.) and *p*-bromophenylphenyl ether (0.9 mol), in THF (0.6 L). The addition was performed in such a way that the temperature remained  $\leq$ 45 °C. Heating was continued at 50 °C for 4 h, after which the mixture was decomposed with water. Normal treatment by fractionation *in vacuo* afforded compound 13 in 87 % yield.

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