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Highly Unsaturated Macrocyclic Silahydrocarbons Containing Exocyclic Phenyl Groups

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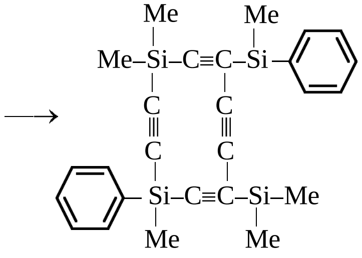
Abstract — A series of 12- and 18-membered macrocycloethynes and macrocyclosilethenesilethynes, containing peripheral methyl and phenyl groups was prepared by organomagnesium sysnthesis under conditions of high dilution. One of these compounds contains an endocyclic 1,4-phenylene bridge.

Until now octaphenylcyclotetrasilethyne and dodecaphenylcyclohexasilethyne, prepared in 1 and 23%, respectively, have been the only reported representatives of cyclosilethynes with exocyclic phenyl groups [1].

Proceeding with research on highly unsaturated macrocyclic silahydrocarbons [2, 3] we have synthesized a series of cyclosilethynes and cyclosilethenesilethynes containing exocyclic methyl and phenyl groups **I**–**III**. The first macrocyclic highly unsaturated aliphatic silahydrocarbon with an exocyclic 1,4-phenylene bridge has also been prepared (compound **IV**).

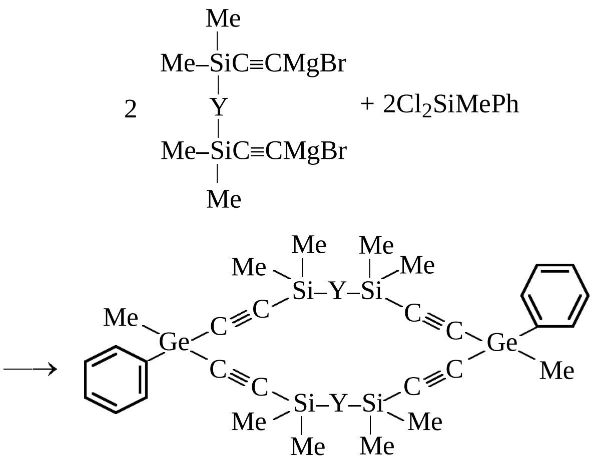
The reaction of bis(bromomagnesioethyl)dimethylsilane with dichloro(methyl)(phenyl)silane gave 1,4,4,7,10,10-hyxamethyl-1,7-diphenyl-1,4,7,10-tetrasilacyclododeca-2,5,8,11-tetrayne (**I**).

$2Me_2Si(C{\equiv}CMgBr)_2 + 2Cl_2SiMePh$



I

Similarly, by reacting bis[(bromomagnesioethynyl)dimethylsilyl]ethyne or (*E*)-bis[(bromomagnesioethynyl)dimethylsilyl]ethene with dichloro(methyl)(phenyl)silanes we obtained 1,4,4,7,7,10,13,13,16,16-decamethyl-1,10-diphenyl-1,4,7,10,13,16-hexasilacyclooctadeca-2,5,8,11,14,17-hexayne (**II**) and (*E*,*E*)-1,4,4,7,7,10,13,13,16,16-decamethyl-1,10-diphenyl-1,4,7,10,13,16-hexasilacyclooctadeca-5,14-diene-2,8,11,17-tetrayne (**III**), respectively.



II, III

Y = C≡C (**II**), (*E*)-CH=CH (**III**).

Finally, the reaction of (*E*)-bis[(bromomagnesioethynyl)dimethylsilyl]ethene with 1,4-bis(methyldifluorosilyl)benzene was used to synthesize a unique 18-membered macrocyclosilethenesilethyne containing a 1,4-phenylene bridge inside the macroring, (*E*,*E*)-1,4,4,7,7,10,13,13,16,16-decamethyl-1,10(1',4'-phenylene)-1,4,7,10,13,16-hexasilacyclooctadeca-5,14-diene-2,8,11,17-tetrayne (**IV**).

The reactions all formed great amounts of polymers. Their structure, properties, and transformations are presently under investigation.

Compounds **I**–**IV** are colorless high-melting crystals poorly soluble in hexane and readily soluble in benzene and chloroform. Their melting points, yields, elemental analyses, and mass spectral characteristics are given in Table 1. The ^1H, ^{13}C, and ^{29}Si NMR spectra of compounds **I**–**IV** are presented in Table 2.

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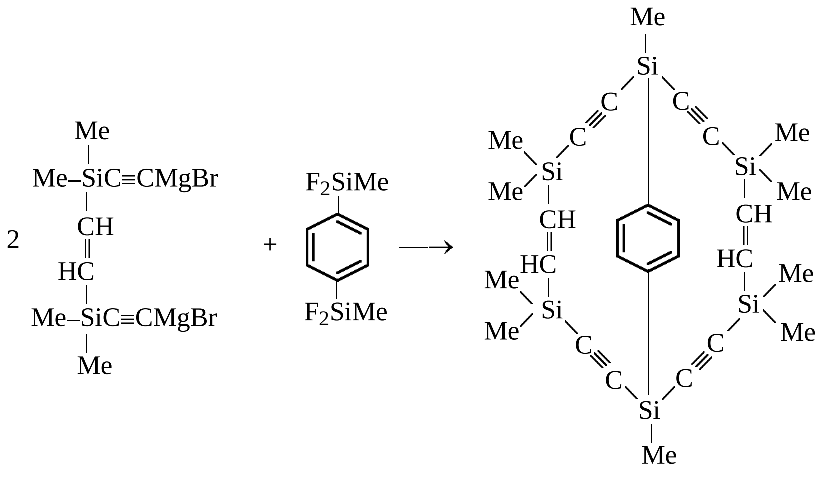
Table 1. Properties of compounds **I–IV**

Comp. no.	Yield, %	mp, °C	Mass spectrum, *m/z* (I_{rel}, %)	Found, %			Formula	Calculated, %		
				C	H	Si		C	H	Si
I	5.5	230	452 (20)	68.95	6.42	24.29	$C_{26}H_{28}Si_4$	68.98	6.23	24.80
II	4.3	232	616 (16)	65.97	6.50	26.57	$C_{34}H_{40}Si_6$	66.16	6.53	27.30
III	10	203	620 (100)	65.92	7.25	26.88	$C_{34}H_{44}Si_6$	65.3	7.14	27.11
IV	4.5	240	542 (20)	62.08	7.28	31.33	$C_{28}H_{38}Si_6$	61.92	7.05	31.03

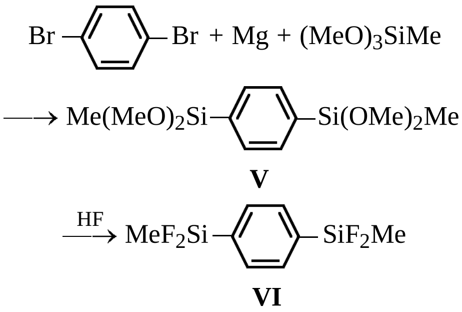
Table 2. ^1H, ^{13}C, and ^{29}Si spectra of compounds **I–IV**

Comp. no.	^1H NMR spectrum, δ, ppm				^{13}C NMR spectrum, δ_C, ppm					^{29}Si NMR spectrum, δ_{Si}, ppm	
	$Si^1_1CH_3$	$Si^2_1CH_3$	C_6H_5	CH=CH	$Si^1_1CH_3$	$Si^2_1CH_3$	C_6H_5	SiC≡	SiCH=	Si_1	Si_2
I	0.36	0.55	7.41, 7.70	–	–0.86	–1.33	128.08, 130.28, 132.49, 134.18	112.39, 115.69	–	–41.12	–46.25
II	0.36	0.56	7.40, 7.71	–	–0.13	–0.48	134.03, 129.95, 127.85	112.39 110.63, 108.84	–	–41.10	–46.08
III	0.26	0.60	7.40, 7.75	6.74	–1.84, –1.78	–1.65, –1.69	128.02, 130.00, 134.03	109.40, 114.68	148.44, 148.83	–25.26	–46.76
IV	0.26	0.56	7.52, 7.57	6.71	–0.24	–0.30	125.11, 131.31, 135.75	108.96, 115.39	148.56	–25.05	–46.52



IV

Previously unknown 1,4-bis[difluoro(methyl)silyl]benzene was synthesized by the reaction of 1,4-dibromobenzene with methyltrimethoxysilane and magnesium in ether, followed by fluorination of the resulting 1,4-bis(methyldimethoxysilyl)benzene with 40% HF.



EXPERIMENTAL

The mass spectra were obtained on an LKB-2091 GC–MS system with direct inlet (250°C), ionizing energy 60 eV. The NMR spectra were measured on a Bruker DRX-400 instrument for 15% solutions in $CDCl_3$, internal reference TMS.

1,4,4,7,10,10-Hexamethyl-1,7-diphenyl-1,4,7,10-tetrasilacyclododeca-2,5,8,11-tetrayne (I). To 50 ml of ether we simultaneously added dropwise with stirring $Me_2Si(C{\equiv}CMgBr)_2$ prepared from 2.43 g of Mg, 10.9 g of EtBr, and 5.4 g of $Me_2Si(C{\equiv}CH)_2$ in 75 ml of THF, and 9.5 g of $MePhSiCl_2$ in 75 ml of ether. The mixture was heated for 30 min and then decomposed with water and 5% HCl. After conventional workup and drying over calcined $CaCl_2$, the solvents were removed at reduced pressure, and the residue was subjected to high-vacuum distillation (5×10^{-5} mm) to isolate 0.93 g (5.5%) of compound **I**.

Compounds **II**–**IV** were prepared in a similar way.

1,4-Bis[difluoro(methyl)silyl]benzene (VI). To 15.0 g of Mg and 68 g $MeSi(OMe_3)_3$ in 500 ml of ether, we added dropwise with stirring 59 g of $BrC_6 \cdot H_4Br$ in 250 ml of ether. The mixture was refluxed for 12 h. The precipitate and unreacted magnesium were filtered off and washed with ether on the filter. The ether was distilled off, and the residue was distilled in a vacuum to obtain 50.5 g of compound **V**. After repeated distillation the latter was treated with 40% HF. The resulting 1,4-bis[difluoro((methyl)silyl]-benzene was separated and distilled in a vacuum. Yield 10.1 g (20%), bp 80–81°C (8 mm), d_4^{20} 1.1348, n_D^{20} 1.4870.

ACKNOWLEDGMENTS

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