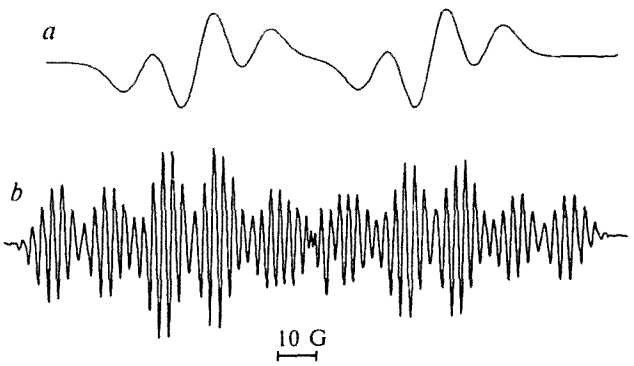

Fig. 1. ESR spectra of radicals **4a** (*a*) and **4b** (*b*).

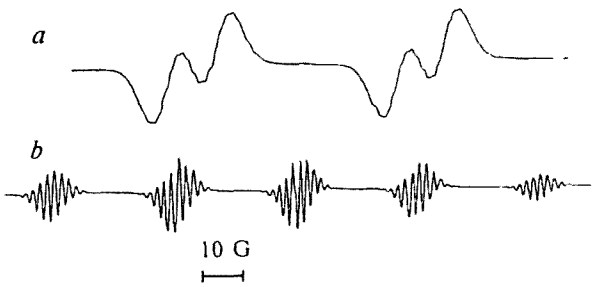

Fig. 2. ESR spectra of radicals **5a** (*a*) and **5b** (*b*). The decrease in the intensity of multiplets in the high-field spectral region is associated with the slow decay of the radical (time of recording is 4 min).

parameters of radical **5a** (Fig. 1, *b*) coincide with those of the radical obtained[6] by the fluorination of olefin **3a**: $a_{\alpha\text{-}F}$(1 F) = 67.0, $a_{\beta\text{-}F}$ (1 F) = 14.0, $a_{\beta\text{-}F}$(2 F) = 29.9, $a_{\gamma\text{-}F}$(9 F) = 2.6 G. Radicals **4b** and **5b** (Fig. 2, *a*) are characterized by the following parameters: **4b**. $a_{\alpha\text{-}F}$(1 F) = 61.5, $a_{\beta\text{-}F}$(1 F) = 10.5 G. **5b**. $a_{\alpha\text{-}F}$(1 F) = 64.5, $a_{\beta\text{-}F}$(2 F) = 33.2 G.

Thus, the new data obtained show that the substitution of the FSO_3 group by fluorine in β-fluorosulfonyloxyperfluoroalkyl radicals under the action of SbF_5 has a general character. It is based on the stabilization of the positive charge on the carbon atom, at which the substitution occurs, by the paramagnetic center, which provides the anionoid mobility of the fluorosulfate group.

This work was financially supported by the International Science Foundation (Grant MO 2300) and the Russian Foundation for Basic Research (Project No. 95-0308795).

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Received December 6, 1995;
in revised form January 25, 1996

A new cage metalloorganosiloxane

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Cage metalloorganosiloxanes (MOS) synthesized to the present time contain Ni,[1] Co,[2,3] Zr,[4] Sn,[5] and other metals and both metallosiloxane (M—O—Si) and pure siloxane (Si—O—Si) fragments. We have synthesized a cage MOS containing only M—O—Si fragments by the consecutive addition of alternating Si—O and M—O

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 4, pp. 1031—1032, April, 1996.

fragments to the branching center. The order of introduction of the reagents specified and their ratio (see below) make it possible to "close" the branched polyfunctional molecule into the polyhedral structure at the final stage. The synthesis was performed by the following scheme.

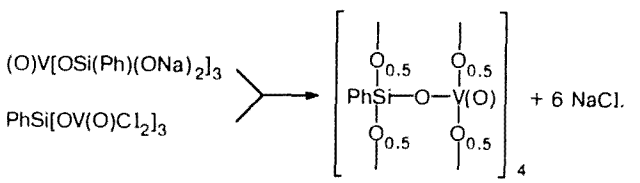
The first stage, the synthesis of branched vanadiumsiloxane with the terminal Si—O—Na groups, is the reaction of vanadium oxychloride with excess crystallosolvate $PhSi(ONa)_3 \cdot 6Pr^nOH$ (see Ref. 6) in benzene:

$$3PhSi(ONa)_3 + V(O)Cl_3 \longrightarrow (O)V[OSi(Ph)(ONa)_2]_3 + 3NaCl.$$

The second stage, the synthesis of branched vanadiumsiloxane with the terminal V(O)Cl groups, is the reaction of the same reagents in benzene, but in the opposite ratio (excess vanadium oxychloride):

$$3V(O)Cl_3 + PhSi(ONa)_3 \longrightarrow PhSi[OV(O)Cl_2]_3 + 3NaCl.$$

The third stage is the reaction of the compounds obtained at the first and second stages in equimolar ratio in benzene:



After separation of NaCl formed, the solution was concentrated, and a finely crystalline light-yellow precipitate was filtered off. Yield 14 %. Found (%): C, 33.02; H, 2.32; Si, 11.9; V, 22.8. $C_{24}H_{20}Si_4O_{16}V_4$. Calculated (%): C, 32.74; H, 2.29; Si, 12.76; V, 23.14. Molecular weight: found (cryoscopy, benzene): 864—889; calculated: 880.52. IR, ν/cm^{-1}: 1139 (Si—Ph), 950—960 (Si—O—V). ^{29}Si NMR (39.76 MHz, $CDCl_3$), δ: 31.70 (s).

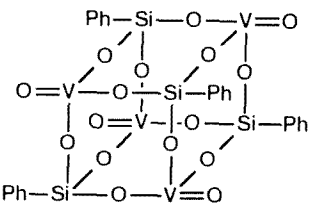


Fig. 1. Structure of vanadiumphenylsiloxane.

The data obtained altogether, *viz.*, molecular mass measurements and spectral data (the equivalence of the Si atoms according to the NMR and the absence of the Si—O—Si groups (ν(SiOSi) 1100—1000 cm^{-1}) according to the IR spectra, allow one to suggest the cubic cage structure for the compound synthesized (Fig. 1).

This work was financially supported by the International Science Foundation (Grant NDQ 000).

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Received December 9, 1995