by passing dry nitrogen over the solution and out through the condenser during the last 30 min of the reflux period. The mixture was then allowed to cool and the excess sodium hydride separated. The supernatant tetrahydrofuran solution of Na$_2$(C$_6$H$_5$)B$_9$C$_2$H$_{10}$ was then ready for further use.

Preparation of 3,6-Diphenyl-1,2-dicarbaclovododecaborane(12) (VIII). The 6-phenyl-(3)-1,2-dicarbollide ion, prepared as described above, was allowed to react with 2.5 g (0.0157 mole) of phenylboron dichloride using the previously described insertion reaction procedure. The reaction mixture filtrate was concentrated in the usual manner to a yellow semisolid which was crystallized from methanol-water. The air-stable white product was collected, dried, and recrystallized twice from heptane as fluffy plates. The yield of product was 1.51 g (35%), mp 173.5–174.5°.

Preparation of 3,6-Diphenyl-1,2-dimethyl-1,2-dicarbaclovododecaborane(12) (IX). The procedure for the synthesis of 3,6-diphenyl 1,2-dimethyl-1,2-dicarbaclovododecaborane(12) (IX) was employed in the preparation of VIII. This procedure was followed using 3.00 g (0.0101 mole) of the trimethylammonium salt of II and 0.84 g (0.0126 mole) of phenylboron dichloride. After the reaction mixture filtrate had been evaporated, the resulting yellow oil was dissolved in a minimum amount of methylene chloride and purified by chromatography on a silica gel column. Hexane, 100 ml, and then 50:50 hexane–benzene were used as the eluents. After removal of the eluent, an air-stable white crystalline material remained. This residue was twice recrystallized from heptane or 75:25 heptane–benzene to yield analytically pure needles of IX. The yield of product was 0.70 g (22%), mp 214–216°.

Piperidine Reactions with 3,6-Diphenyldicarbaclovododecaborane(12) Derivatives. Both VIII and IX were treated with piperidine as described below. A solution of 0.25 g (0.845 mmole) of 3,6-diphenyl-1,2-dicarbaclovododecaborane(12) (VIII) dissolved in 3 ml of piperidine was heated at the reflux temperature under nitrogen for 1 week. The piperidine was removed *in vacuo* and a yellow semisolid resulted. The yellow residue was dissolved in 10 ml of hot heptane and the solution filtered. No perceptible precipitate was obtained and the filtrate upon cooling to 0° yielded white crystals which were collected. A second crop was obtained upon concentration of the heptane solution. Based upon infrared spectral and melting point data (213–215°), the recovered material, 0.18 g (72%), was the starting material, 3,6-diphenyl-1,2-dicarbaclovododecaborane(12). Identical results were obtained with IX.

Preparation of Bis-π-6-phenyl-(3)-1,2-dicarbollylcobalt (III) (X). A tetrahydrofuran solution of 6-phenyl-(3)-1,2-dicarbollide ion was prepared in the previously described manner using 1.80 g (0.0067 mole) of the trimethylammonium salt of V and 0.0188 mole (0.80 g of a 56% dispersion in mineral oil) of sodium hydride. Anhydrous cobaltous chloride was prepared by heating its hexahydrate under vacuum at 120° over phosphorus pentoxide for 48 hr. The anhydrous cobaltous chloride (0.70 g, 0.0054 mole) was washed with 25 ml of tetrahydrofuran into a 300-ml, three-necked, round-bottom flask equipped with a mechanical stirrer, condenser, addition funnel, and nitrogen bubbler. The solution of 6-phenyl-(3)-1,2-dicarbollide ion in tetrahydrofuran was rapidly added from the addition funnel to the cobaltous chloride. The color of the reaction mixture immediately changed from blue to black as cobalt metal formed. After the addition was complete, the mixture was heated at reflux for 0.5 hr, cooled, and filtered through Celite. The Celite layer was washed twice with two 20-ml portions of tetrahydrofuran and discarded. The filtrate was concentrated to a dry solid in the usual manner. The yellow residue was dissolved in hot water and the resulting solution filtered through Celite. A 50% aqueous solution of tetramethylammonium chloride was added to the filtrate to produce a light yellow precipitate. The product was recrystallized three times as yellow needles from ethanol-water. The yield of product was 1.13 g (62%), mp 275–277°.

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Electron Spin Resonance Studies of Silicon Difluoride

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Abstract: Electron spin resonance studies of SiF$_2$–SiF$_4$ mixtures condensed with various diluents over the range 20°K to room temperature show the presence of paramagnetic species, probably (SiF$_2$)$_n$ diradicals where n = 2, 3, ...

Most of the gas-phase properties of the extremely stable, carbene-like molecule silicon difluoride have been established by mass spectrometric studies[1] and microwave,[2] infrared,[3,4] and electronic spectral measurements.[5] Little is known, however, about the reddish brown solid formed when SiF$_2$ is condensed at low temperatures.[1,6] Upon warming to room temperature, the solid turns white and can be cracked to yield perfluorosilanes up to at least Si$_{16}$F$_{34}$. SiF$_2$ is comparatively unreactive in the gas phase, oxygen being the only molecule with which it combines rapidly,[1,7] but many chemical reactions can be performed by the cocondensation of the species with a particular reactant at low temperatures. The majority of compounds[8] formed in this way contain (SiF$_2$)$_n$ units where n ranges from 2 to at least 11. The low-temperature chemistry and reddish-brown color of condensed SiF$_2$–SiF$_4$ mixtures suggest that polymeric species are present with unsatisfied valences; esr studies have been performed on the low-temperature form of SiF$_2$ and confirm the existence of unpaired electrons.

Experimental Section

A Varian V4500-10A esr spectrometer, with Fieldial Mark II field regulation and a multipurpose cavity operating in the TE$_{102}$

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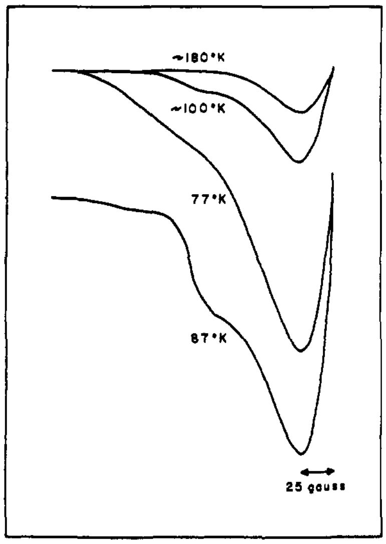


Figure 1. Esr spectrum of SiF_2–SiF_4 condensate. Only half of the various totally symmetric spectra are shown.

mode at a frequency of approximately 9200 Mc, was used to observe and record the spectra.

A mixture of SiF_2 and SiF_4 was produced as previously described[1a] by allowing SiF_4 to pass at low pressure through a quartz tube packed with lumps of silicon metal and heated to approximately 1100°. The SiF_4 was prepurified by passing it through steel wool heated to 800°.

To observe the esr spectrum of condensed SiF_2, a specially constructed liquid nitrogen dewar, containing a quartz cold finger reaching down into the cavity of the spectrometer, was used to condense the SiF_2–SiF_4 mixture.

Results and Discussion

No esr signal over a wide range of magnetic field was observed when the mixture of SiF_2 and SiF_4 was allowed to flow through the system without condensation, even at the highest possible pressures usable in such a flow system. The concentration of a radical species in the gas phase is apparently very low and beyond the limit of detection of the spectrometer. Since no complex gaseous species except SiF_2 or SiF_4 have been observed previously in the reaction of SiF_4 with silicon,[1] the most likely radical species which could be present is the triplet state of SiF_2. The failure to observe this, and thus the implied low concentration of triplet SiF_2, is in agreement with the results from the microwave[2] and electronic[5] absorption spectral studies.

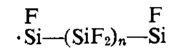
When the mixture of SiF_2 and SiF_4 was condensed at 77°K in the cavity, a broad esr signal was observed after several minutes which became increasingly intense as deposition continued. When the flow was stopped and the esr signal was examined over a period of 8 hr, it was found that there was only a very slight decrease in intensity during this time. No absolute intensity measurements were attempted, and the small decrease could possibly be attributed to variations in the spectrometer operation.

The signal obtained at 77°K is shown in Figure 1. The g factor for the resonance was determined by comparison with DPPH as $g = 2.003 \pm 0.002$; the observed g factor is very close to that usually found for a free electron. When the SiF_2–SiF_4 mixture was condensed at 20°K, a virtually identical signal was found. A further experiment was performed at 87°K (liquid argon) and the spectrum is included in Figure 1. An attempt to dilute the reactive species was made by operating the furnace at lower temperatures, to provide a higher SiF_4/SiF_2 ratio in the mixture. The signal did not change except in intensity after a given period of deposition, even at temperatures as low as 700°. This latter temperature is about 200° lower than has been previously reported for the formation of SiF_2 by the reaction of SiF_4 with silicon.[1]

A matrix-isolation experiment was attempted with liquid hydrogen in the dewar using argon as the matrix. Above a ratio of 50:1 of Ar/SiF_2–SiF_4 no esr signal could be discerned. Warm-up was too rapid to observe the formation of any intermediate radical species which may possibly have been expected from the infrared studies.[4] At a dilution ratio of 20:1 the characteristic broad signal was observed. This is a further indication that the ground electronic state of SiF_2 monomer is a singlet. In all experiments the esr signal rapidly decayed as room temperature was approached. It was not possible to control the warm-up process, but measurements were made on the sample as the warm-up process occurred. These spectra are also shown in Figure 1; the temperatures given are not equilibrium values, and it is probable that the intensity of the signal shown in the figure is not an equilibrium intensity for that particular temperature because of kinetic factors.

The existence of a strong esr spectrum for condensed SiF_2–SiF_4 mixtures at low temperatures proves experimentally that radical polymeric species exist, and this explains the observed chemical reactivity. The disappearance of this signal on warming the condensed species to room temperature, and the fact that signal could not be regenerated by cooling, shows that the polymerization is irreversible and complete.

The most likely species giving rise to the observed esr spectrum are diradicals of the type



$$\cdot\overset{F}{\underset{F}{Si}}—(SiF_2)_n—\overset{F}{\underset{F}{Si}}\cdot$$

where $n = 0, 1, 2, \ldots$. Several studies have been made on irradiated organic polymers, such as Teflon, and give spectra that are comparable to those found here.[9]

The broad unresolved nature of the resonance is most likely due to a combination dipolar broadening and anisotropic coupling of the fluorines not averaged out by molecular motion. The general shape of the signal appears to contain three features which could not be resolved. At 87°K, the two outer wings are more pronounced as is shown in Figure 1.

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