insufficient to convert the gold(III) to a class a or hard coordination center. Likewise, neither counterion[9] nor solvent[10] control of the thiocyanate's bonding mode is operative in this case. As originally prepared, the potassium salt exhibits an additional thiocyanate CN stretching band at 2060 cm^{-1}, along with strong water absorption bands at 3640, 3560, and 1620 cm^{-1}. As the water absorption bands diminish in intensity when the salt is dried *in vacuo*, the thiocyanate band at 2060 cm^{-1} also diminishes in intensity, suggesting that it is due to an aquo complex impurity which contains an ionic thiocyanate, *e.g.*, $[Au(CN)_2(H_2O)_2]SCN$, the thiocyanate entering the coordination sphere as the water is removed. The 2060-cm^{-1} band also disappears when the potassium salt is washed thoroughly with water, leaving a compound whose spectrum is virtually identical with that of the tetramethylammonium salt, except for water absorption bands and the bands due to the latter cation. As mentioned earlier, drying this compound results in its beginning to decompose. We have also observed that the tetramethylammonium salt immediately turns red when placed on a cesium iodide plate, indicating the ease with which the thiocyanate groups can be replaced by iodide ions.

Both the potassium and tetramethylammonium salts of the thiocyanate complex develop red colors as they decompose in ethanolic solution. We were unable, after repeated attempts, to isolate an analytically characterizable sample of the red substance. However, it is now clear that it is *not* a linkage isomeric form of the yellow complex.

Although the infrared data indicate[7] that the selenocyanate complex contains Se-bonded groups in the solid state (the $\nu_{\text{AuSe}-\text{CN}}$ frequency is lowered relative to the free-ion value[7]), the appearance of the third selenocyanate CN stretching band at 2117 cm^{-1} indicates that a solvent-induced[10,11] partial Se→N-bonded isomerization takes place in nitromethane solution.

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[9] D. F. Gutterman and H. B. Gray, *J. Amer. Chem. Soc.*, **91**, 3105 (1969).

[10] J. L. Burmeister, R. L. Hassel, and R. J. Phelan, *Chem. Commun.*, 679 (1970).

[11] J. L. Burmeister, R. L. Hassel, and R. J. Phelan, *Inorg. Chem.*, **10**, 2032 (1971).

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Silicon-Fluorine Chemistry. VI. The Reaction of Silicon Difluoride with Butadiene

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A number of recent studies have been concerned with the reactions between silicon difluoride and unsaturated compounds.[1-6] This report describes the reaction between 1,3-butadiene and silicon difluoride. The system was of interest in comparison with the reactions with benzene,[2] which apparently acts as a 1,3-diene in its addition to silicon difluoride, and some of the other olefinic or acetylenic species[4-6] where not only do addition reactions occur but also specific hydrogen migrations are observed forming rearranged products.

Experimental Section

Silicon difluoride was prepared as previously described[7] by the reaction of silicon tetrafluoride with silicon at 1150°. Commercially available 1,3-butadiene (Matheson) was used without further purification. An approximately 2:1 molar excess of butadiene (based on 50% conversion of SiF_4 to SiF_2) was used, since this ratio appeared to give the best yields of volatile products, which were, however, only about 2% based on olefin used.

Volatile compounds were manipulated in a conventional greaseless vacuum system and studied by mass spectrometry (Bendix 14-107 Time-of-Flight instrument), by infrared spectrometry (Beckman IR-20), and by nmr spectroscopy (Varian A-56/60 and HA-100 instruments).

$C_4H_6Si_2F_4$ was separated at room temperature on a 6 ft × $^3/_8$ in. column containing 10% Kel-F-10 oil on Chromosorb W, using helium as carrier gas.

A sample of 1-vinyl-2,2,3,3-tetrafluorocyclobutane was kindly donated by Dr. J. J. Drysdale of Du Pont (Jackson Laboratory). This was passed at low pressures through a Vycor tube heated to 700°, and from the volatile products samples of the tetrafluorocyclohexenes IV and V were obtained by gas chromatographic separation.[8] They were identified by their mass and nmr spectra (see below).

Results

At −196° the cocondensed reaction mixture of SiF_4, SiF_2, and butadiene was olive green, while on warming to room temperature a pale yellow involatile solid remained and volatile products were given off. The solid residue was not spontaneously inflammable but burned readily with a smoky flame on ignition. It dissolved fairly readily in dilute alkali but was attacked very slowly by dilute HF solution, without liberation of spontaneously inflammable silicon hydrides.

The volatile products, after separation of excess SiF_4 and butadiene, were found to consist of colorless crystals and a rather oily liquid; this mixture proved to be inseparable by vacuum distillation. However an apparently pure crystalline solid (mp 29.5°) was obtained by gas chromatographic separation at room temperature; none of the liquid emerged from the column at this temperature and the use of higher temperatures apparently caused rapid decomposition since there was continuous evolution of SiF_4 from the column above 40°.

The mass spectrum of the crystalline solid, Table I, showed the heaviest ion at *m/e* 186, corresponding to a formula of $C_4H_6Si_2F_4$ (I). Gas-phase molecular weight determinations were hampered by the low vapor pressure of the compound at room temperature (∼22 mm);

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[1] J. C. Thompson, P. L. Timms, and J. L. Margrave, *Chem. Commun.*, 566 (1966).

[2] P. L. Timms, D. D. Stump, R. A. Kent, and J. L. Margrave, *J. Amer. Chem. Soc.*, **88**, 940 (1966).

[3] C. S. Liu and J. C. Thompson, *Inorg. Chem.*, **10**, 1100 (1971).

[4] C. S. Liu, J. L. Margrave, J. C. Thompson, and P. L. Timms, *Can. J. Chem.* in press.

[5] C. S. Liu, J. L. Margrave, and J. C. Thompson, *ibid.*, in press.

[6] C. S. Liu and J. C. Thompson, *J. Organometal. Chem.*, in press.

[7] P. L. Timms, R. A. Kent, T. C. Ehlert, and J. L. Margrave, *J. Amer. Chem. Soc.*, **87**, 824 (1965).

[8] J. J. Drysdale, U. S. Patent 2,831,025, assigned to E. I. du Pont de Nemours and Co., Wilmington, Del., Nov 1958.

Table I

Mass Spectrum of $C_4H_6Si_2F_4$ (I) (50 eV)

Mass	Rel intens (mass 54 = 100)	Assignment	Mass	Rel intens (mass 54 = 100)	Assignment
186	13.2	$C_4H_6Si_2F_4^+$	85	2.1	SiF_3^+
167	2.4	$C_4H_6Si_2F_3^+$	66	4.7	SiF_2^+
120	21.7	$C_4H_6SiF_2^+$	54	100	$C_4H_6^+$
101	11.3	$C_4H_6SiF^+$	47	54.7	SiF^+
93	5.6	$C_2H_3SiF_2^+$	39	34.0	$C_3H_3^+$
91	5.6	$C_2HSiF_2^+$			

from five determinations a value of 183 ± 9 was found, which confirms the empirical formula of $C_4H_6Si_2F_4$.

Nmr spectra of $C_4H_6Si_2F_4$ were obtained from solutions in $CDCl_3$, containing small amounts of TMS and $CFCl_3$ as internal standards. The main features of the spectra are given in Table II. The spectra are considerably complicated by the presence of 10 magnetically active nuclei in the molecule and a complete analysis has not been attempted. The spectra are however very similar in appearance to those of the symmetrical tetrafluorocyclohexene IV.

Table II

Proton and Fluorine Nmr Spectra of I and IV[a]

		I	IV	Description (intens)
Proton	(a)	$\tau = 4.17$	$\tau = 4.45$	Complex triplet (1)
	(b)	$\tau = 8.08$	$\tau = 7.27$	Complex multiplet (2)
		$J_{ab} \approx 5$ Hz	$J_{ab} \approx 1.5$ Hz	
Fluorine	(c)	$\phi = 141.2$	$\varphi = 120.5$	Complex multiplet (. . .)

[a] ^{1}H (TMS), $\tau = 10$; ^{19}F ($CFCl_3$) $\phi = 0$. All peaks symmetrical about a midpoint.

$C_4H_6Si_2F_4$ is stable in $CDCl_3$ solution at room temperature for several months; no changes were observed in the nmr spectra after this time.

The infrared spectrum obtained in a 10-cm gas cell (KBr windows) at a pressure of about 22 mm is described in Table III.

Table III

Infrared Spectrum (Gas Phase) of $C_4H_6Si_2F_4$

Freq, cm^{-1}	Intens	Assignment	Freq, cm^{-1}	Intens	Assignment
3050	m	CH str	1030[a]	s	SiF str
2960	mw		980	vs	
2890	mw		940	vs	
2240	vw		915	vs	
1690	vw		890	s (sh)	
1620	w	C=C str	870	vs	
1415	m	CH def	790	s	Skeletal and SiF def modes
1180	ms		740	vs	
1140	s		715	s	
			650	ms	
			610	m	

[a] In part, due to SiF_4 impurity.

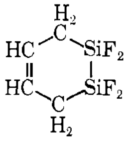
Hydrolysis of $C_4H_6Si_2F_4$ was conducted in a sealed tube with 10% HF solution. The sample was heated at 80° for 24 hr. On opening the tube some noncondensable gas (H_2) was found together with *cis*-2-butene as the sole volatile organic product of the hydrolysis. The olefin was identified by comparison of its nmr spectrum with an authentic sample (Matheson).

The mass spectrum of the unseparated mixture indicates that, in addition to I, a major component of the mixture is a compound of formula $C_8H_{12}Si_2F_4$, which has prominent fragment ion peaks based on C_4H_5 and C_4H_7 units. The proton nmr spectrum shows complex areas of resonance in the regions associated with protons bound to unsaturated ($\tau \sim 4$) and saturated ($\tau \sim 8$) carbon atoms and the fluorine nmr shows one complex unsymmetrical peak, in addition to the symmetrical resonance of I. A structure which is consistent with these observations and can thus be tentatively proposed for one of the additional compounds is the open-chain derivative II.

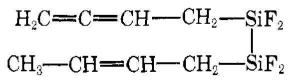
The mass spectrum also indicates a compound of formula $C_4H_6Si_3F_6$ in small amount, but no structural information has been obtained about this species.

Discussion

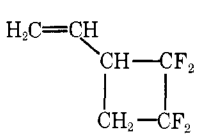
The types of product found in this reaction follow a similar pattern to those found in reactions with other unsaturated hydrocarbons,[5,6] in that both ring and open-chain (tentatively) compounds are formed and that the compounds are based on Si_2F_4 units rather than single SiF_2 groups. The latter observation supports a mechanism in which the most reactive silicon difluoride species is the dimeric biradical[9,10] and in which this unit reacts with the unsaturated organic reagent to form an unstable intermediate: $H_2\underset{\cdot}{C}{-}CH{=}CH{-}CH_2{-}SiF_2{-}\underset{\cdot}{S}iF_2$. This may then undergo ring closure to form the disilacyclohexene derivative I. The net result is that of 1,4 addition of Si_2F_4 to the conjugated double bonds of butadiene. The addition of tetrafluoroethylene to 1,3-butadiene[8] has been shown to give initially the 1,2-addition product III, but this rearranges on heating to form the two isomeric tetrafluorocyclohexenes IV and V. We have studied the proton and fluorine nmr spectra of III–V and find that III and V show very complex, asymmetric peaks from each of the nonequivalent magnetic nuclei,[11] whereas the spectra of IV though complex show that each peak is symmetrical about a midpoint as was also found for I (Table II). Thus the silicon fluoride derivative I is identified as the symmetrical disilacyclohexene rather than as either of the silicon analogs of III or V. The formation of *cis*-2-butene on hydrolysis of I is a further confirmation of the symmetrical structure.



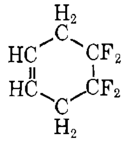
I



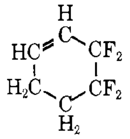
II



III



IV



V

The nature of the second compound, $C_8H_{12}Si_2F_4$ (II), though only tentatively established, is also consistent with the types of product formed in other reactions, since the formation of allenic groups during reactions of silicon difluoride with unsaturated hydrocarbons is not now an unexpected event.[5]

Acknowledgments.—This work has been supported by the U. S. Army Research Office (Durham) and by the National Research Council of Canada.

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(9) H. P. Hopkins, J. C. Thompson, and J. L. Margrave, *J. Amer. Chem. Soc.*, **90**, 901 (1968).

(10) J. M. Bassler, P. L. Timms, and J. L. Margrave, *Inorg. Chem.*, **5**, 729 (1966).

(11) J. C. Thompson, unpublished observations.