the trans effect is due predominantly to a ground-state structural effect, whether the trans-directing ligand is a strong σ donor only (H^-) or whether it exerts a strong σ-donor effect because of the synergism involving its strong π-acceptor properties (olefin). Thus, the nqr frequencies reflect both the directional influence of the ligand–platinum σ bond and the isotropic effect resulting from net charge donation.

The approximately 1-MHz difference in frequencies between the cyclooctadiene and norbornadiene complexes seems too large to be accounted for entirely in terms of lattice effects. Framework molecular models of the olefins suggest that the π bonds of norbornadiene are at an angle more suitable to overlap with the dsp^2 valence-bond platinum orbitals than the π bonds of cyclooctadiene. Study of *cis*-$PtCl_2(olefin)_2$ complexes, in which the overlap optimization is not constrained as in the chelate complexes, would test the hypothesis that overlap differences account for the frequency difference.

As listed in Table II, $(d\nu/dT)_p$ for the two resonances of the norbornadiene complex differ by about 20%. It is difficult to determine if there is a discontinuity at some point between −40 and −56°, as the nonlinearity of the points suggests.

Acknowledgment.—Initial experimental work on platinum–olefin systems was carried out in these laboratories by Dr. J. L. Kirsch.

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The Reaction between Silicon Difluoride and 3,3,3-Trifluoropropyne

BY C. S. LIU AND J. C. THOMPSON*

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Silicon difluoride has been found to undergo a wide variety of reactions at low temperatures.[1–3] In reactions with alkenes and alkynes the products identified are usually consistent with a mechanism involving attack of biradicals $\cdot SiF_2(SiF_2)_nSiF_2\cdot$ (n = 0, 1, 2, etc.) on the carbon–carbon multiple bond in the unsaturated molecule. In many of the reactions a rearrangement involving the shift of a hydrogen atom is also observed, giving chain rather than cyclic products.[4]

In this note we report the results of the reaction between silicon difluoride and trifluoropropyne, which was studied since the possibilities for rearrangement might have been more limited than in the case of nonfluorinated alkynes.

Experimental Section

(i) **Preparation of $CF_3C\equiv CH$.**—Trifluoropropyne was prepared from $CF_3CCl{=}CCl_2$ (Pennisular Chemresearch Inc.) after the method of Finnegan and Norris.[5] Trace amounts of $CF_3CCl{=}CClH$ were detected by nmr but were easily removed by distillation through a trap cooled to −95°. $CF_3C\equiv CH$ was collected at −196° and stored in a stainless steel cylinder.

(ii) **Reaction of SiF_2 with $CF_3C\equiv CH$.**—SiF_2 was generated, as previously described,[6] by the reaction of SiF_4 with silicon metal at about 1150°. Approximately equimolar amounts of SiF_2, SiF_4, and $CF_3C\equiv CH$ were cocondensed at −196° to give a light brown deposit, which on warming to room temperature evolved volatile products and left a bright yellow involatile residue. The latter ignited explosively on contact with moist air.

(iii) **Volatile Products.**—The mixture of volatile products was subjected to vacuum-line fractional distillation. Excess, unreacted SiF_4 and $CF_3C\equiv CH$ were removed at −95°. The $CF_3C\equiv CH$ was trapped at −132° and used in subsequent reactions. Two compounds were obtained on further distillation of the material trapped at −95°.

A fraction trapped at −64°, volatile at −45°, contained mainly a species of formula $C_3HSi_2F_7$ (I) and a small amount of another compound of formula $C_6H_2Si_2F_{10}$ (II) as shown by the mass spectrum (Table I).

A second fraction trapped at −45°, volatile at −22°, contained apparently pure II.

The yield of these two compounds based on $CF_3C\equiv CH$ used, but not recovered after the reaction, was less than 5%. I was about twice as abundant as II.

A greaseless vacuum system was used for the manipulation of volatile compounds.

Nmr spectra were obtained on a Varian A-56/60D spectrometer using medium-walled tubes sealed under vacuum. Mass spectra were obtained on an MS-902 spectrometer with samples introduced by evaporation at room temperature. Infrared spectra were obtained on the Perkin-Elmer 521 spectrometer using a 10-cm gas cells with KBr windows. The spectroscopic results are discussed in the Results section.

(iv) **Involatile Residue.**—The bright yellow residue was heated cautiously to 150° in the vacuum system. The color became paler and small amounts of II were evolved. Because of the danger of explosion of this and similar polymers[4] the heating was not continued.

Results

The fraction collected between −45 and −64° was a colorless liquid. The mass spectrum (Table I) suggested that it was mainly compound I with a molecular formula $C_3HSi_2F_7$. The infrared spectrum showed characteristic bands for CH stretching (2950 cm^{-1} (w)), C=C stretching (1550 cm^{-1} (m)), CF stretching (1000–1300 cm^{-1} (s)), and SiF stretching (800–1000 cm^{-1} (s)). Details of the nmr spectra are given in Table II and Figure 1. The proton nmr spectrum shows only a triplet of six-line multiplets centered at τ 1.69, which may arise from coupling to one SiF_2 group and further smaller coupling to the second SiF_2 group and to the CF_3 group. Two areas of resonance were found in the fluorine spectrum: that at 65.66 ppm upfield from CCl_3F is assigned to the CF_3 group and consists of 11 lines which may be explained from the partial overlap of a triplet of doublets of triplets. The complex resonance between 131.3 and 132.7 ppm is assigned to two nonequivalent SiF_2 groups. The spectrum shows an AA'BB'X pattern.

All these data are in agreement with a four-membered ring structure (I) for $C_3HSi_2F_7$. A calculated nmr pattern for the CF_3 group based on the coupling constants J_{CF-H} = 1.6 Hz, J_{CF-SiF} = 2.4 Hz, and $J_{CF-SiSiF}$ = 0.8 Hz is shown in Figure 1. There is ex-

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

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

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[5] W. G. Finnegan and W. P. Norris, *J. Org. Chem.*, **28**, 1139 (1963).

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

TABLE I

MASS SPECTROMETRIC ION ABUNDANCES FOR I AND II

m/e	Assignment	Ion abundance I	II
19	F^+	<1	⩽1
31	CF^+	40.0	18.0
47	SiF^+	31.0	17.0
50	CF_2^+	6.2	3.5
51	CF_2H^+	11.0	18.0
56	C_3HF^+	12.0	15.0
57	$C_3H_2F^+$	8.0	11.0
66	SiF_2^+	6.0	7.0
67	SiF_2H^+	16.7	17.0
69	CF_3^+	43.0	17.0
75	$C_3HF_2^+$	47.0	37.0
85	SiF_3^+	100.0	100.0
91	$C_2HSiF_2^+$	32.0	56.0
93	$C_3F_3^+$	37.0	<1
94	$C_3HF_3^+$	62.0	<1
122	$C_3HSiF_3^+$	13.0	11.0
123	$C_3H_2SiF_3^+$	11.5	13.0
135	$CF_3SiF_2^+$	18.5	33.0
141	$C_3HSiF_4^+$	10.0	17.0
160	$C_3HSiF_5^+$	45.4	20.0
179	$C_3HSiF_6^+$	24.0	...
182	$C_4H_2Si_2F_4^+$	...	3.5
194	$C_5H_2Si_2F_4^+$	...	3.5
213	$C_5H_2Si_2F_5^+$	...	26.0
226	$C_3HSi_2F_7^+$	2.5	...
232	$C_5H_2Si_2F_6^+$	...	18.0
245	$C_3HSi_2F_8^+$	~1.0	13.0
263	$C_6H_2Si_2F_7^+$	...	33.0
282	$C_6H_2Si_2F_8^+$	...	33.0
301	$C_6H_2Si_2F_9^+$	...	~1.0
320	$C_6H_2Si_2F_{10}^+$	...	⩽1.0

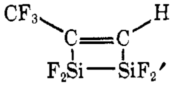
TABLE II

NMR DATA OF PRODUCTS OF THE SiF_2–$CF_3C{\equiv}CH$ REACTION

Chem shifts[a]	Value, ppm	Coupling const	Value, Hz
	Compound I		
H	1.69	J_{CF-H}	1.6
CF_3	65.66	J_{CF-SiF}	2.4
SiF_2 or	131.25 or	$J_{H-SiF'}$	16.5
SiF_2'	132.68	$J_{H-SiSiF}$	1.6
		$J_{CF-SiSiF'}$	0.8
	Compound II		
H	1.99	J_{CF-H}	0.6
CF_3	65.86	J_{CF-SiF}	0.6
SiF_2	140.00		

[a] All ^1H nmr chemical shifts were measured with internal reference TMS in τ values. All ^{19}F nmr chemical shifts were measured with internal reference CCl_3F.

cellent agreement with the observed spectrum in both the splitting pattern and line intensities.



I

The fraction collected between −22 and −45° was a colorless liquid. The mass spectrum (Table I) suggested a molecular formula $C_6H_2Si_2F_{10}$. The infrared spectrum was very similar to that of $C_3HSi_2F_7$. The proton nmr spectrum showed only one broad peak at τ 1.99. In the fluorine spectrum, one quartet (at 65.86 ppm) was observed in the region expected for a CF_3 group, and one broad peak (at 140.0 ppm) was seen in the region of SiF resonances. The broad peaks in proton and fluorine spectra were not resolvable.

The results strongly support the ring structure as shown (II), with the assignment as the 2,3-bistrifluoromethyl isomer.

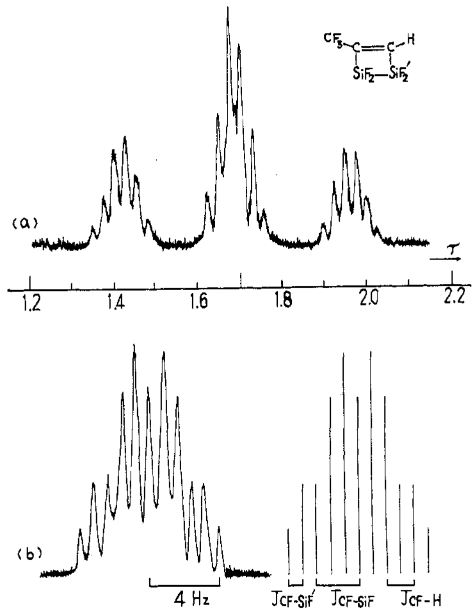
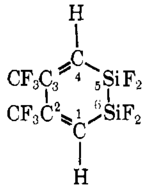


Figure 1.—(a) The ^1H nmr spectrum of I. (b) Observed and calculated ^{19}F nmr spectra of I. Only the resonance of CF_3 is shown.

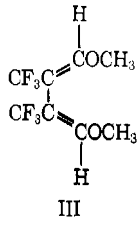


II

We can rule out the 1,3 isomer on the basis of the number of areas of resonance in the nmr spectra of the compound. In addition, based on the magnitudes of the coupling constants observed from I, we believe that the 1,4 isomer is also unlikely. In the case of I, the coupling constant between CF_3 and the "closer" SiF_2 group J_{CF-SiF} = 2.4 Hz, while the coupling constant between CF_3 and the "remote" SiF_2 group $J_{CF-SiSiF}$ = 0.8 Hz. In II, the observed coupling constant between CF_3 and SiF_2 was 0.6 Hz, indicating that CF_3 groups may be on the 2,3 rather than on the 1,4 positions. The nmr data are listed in Table II.

Compound II remained stable after heating to 100° and after uv irradiation (from a Hanovia 1 L photochemical uv source) for 15 hr.

When II was treated with CH_3OH–KOH solutions in a vacuum-sealed tube, a colorless liquid was separated from excess methanol and a white unidentified solid. The ^1H nmr spectrum of this liquid showed a quartet at τ 3.25 and a singlet at τ 6.70 with intensity ratio 1:3. The ^{19}F nmr spectrum showed a doublet at 66.1 ppm upfield from CCl_3F. No fluorine resonance was found in the region expected for Si–F. The observed coupling constants of the quartet (in ^1H nmr) and the doub-

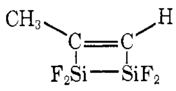


III

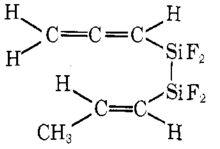
let (in ^{19}F nmr) were the same (1.0 Hz). The mass spectrum of this compound showed the highest mass peak at *m/e* 250. These data suggest that the compound may be III and support the postulated ring structure of compound II.

Discussion

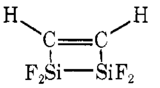
The two compounds from this reaction may be compared with the products identified in other related reactions. In the reaction between SiF_2 and propyne,[4] IV and V were obtained. In the reaction between SiF_2 and acetylene,[4] VI and VII were obtained. In all the three reactions, four-membered ring compounds were obtained. In the reaction of 3,3,3-trifluoropropyne, no open-chain products were observed. Both V and VII were formed by the addition of $\cdot SiF_2SiF_2\cdot$ biradicals on two acetylene molecules. The formation of V involved a hydrogen atom migration from one methyl group, whereas the formation of VII presumably involved the migration of an acetylenic hydrogen. From the facts that there are no methyl hydrogens available for rearrangement in $CF_3C{\equiv}CH$ and that the presence of CF_3 groups may facilitate the ring-closure process,[7] the formation of the six-membered ring product II is reasonable in this case.



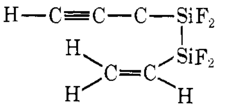
IV



V



VI



VII

Acknowledgment.—We are grateful to the National Research Council of Canada and the Ontario Department of University Affairs for financial support. C. S. L. thanks the Ontario Department of University Affairs for an Ontario Graduate Fellowship.

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Kinetic Study of the Chromium(II) Reduction of Azidopentaamminechromium(III)

BY R. DAVIES AND R. B. JORDAN*[1]

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Studies on the rates of reduction of pentaaminechromium(III) complexes by chromium(II) provide an interesting and possibly mechanistically useful comparison to the more widely studied pentaaminecobalt(III) complexes. The reaction of chromium(II) with the fluoro, chloro, bromo, and iodo complexes of $(NH_3)_5$-Cr^{3+} has been studied by Ogard and Taube.[2] The rate trends with the various bridging ligands follow those found in the $(NH_3)_5Co^{3+}$ series;[3,4] however the rate constants are ~10^8 times greater in the cobalt series. It seems worthwhile to extend this study to the rather different azide bridging ligand and to determine if the trends observed previously can be extended more generally.

Experimental Section

All solutions used in the kinetic study were prepared in water which had been distilled from alkaline permanganate solution in an all-glass apparatus. Lithium perchlorate solutions were prepared by dissolving reagent grade lithium perchlorate (G. F. Smith Chemical Co.) in water and were filtered through a 5-μ Millipore filter (Millipore Filter Corp.). The lithium perchlorate solutions were standardized by titration, with standard sodium hydroxide, of the hydrogen ion eluted from a cation ion exchange column initially in the hydrogen ion form.

Chromous perchlorate solutions were prepared by dissolving electrolytic grade chromium (99.999% purity, United Mineral and Chemical Corp.) in dilute perchloric acid–lithium perchlorate solutions. The solution was standardized periodically by reaction of an aliquot with a known excess of ferric ammonium sulfate and then determining the excess ferric ion iodometrically.

All solutions used to study the chromium(II) reduction were degassed with high-purity argon and handled using standard syringe techniques.

A sample of $(NH_3)_5CrN_3(ClO_4)_2$ was prepared as described by Linhard and Berthold[5] and purified by ion-exchange chromatography[6] on Rexyn 102 (H) weak-acid cation-exchange resin (Fisher Scientific Co.) in the sodium ion form. The ion-exchange procedure was carried out at ~2° by immersing the ion-exchange column in a cold bath. The eluent was aqueous sodium chloride in increasing concentration up to 0.50 *M*. The band of ion-exchange resin containing the required complex was separated physically from the remainder of the resin, collected, and washed with water and then treated with sufficient dilute (~0.1 *M*) perchloric acid to free the complex from the resin. The resin was filtered off and sufficient 70% perchloric acid was added to the filtrate to make it ~1 *M* in perchloric acid. The mixture was cooled for 4 hr in a refrigerator and then the product was collected and washed with ethanol and ether and dried under vacuum. The sample was stored in a refrigerator. *Anal.* Calcd for $(NH_3)_5CrN_3(ClO_4)_2$: Cr, 13.76; H, 3.97; N, 29.63. Found: Cr,[7] 13.80; H, 3.76; N, 29.71.

The absorption spectrum of $(NH_3)_5CrN_3(ClO_4)_2$ dissolved in water shows maxima at 382 nm (ϵ 93.4 M^{-1} cm^{-1}) and 500 nm (ϵ 154 M^{-1} cm^{-1}). These values are in reasonable agreement with those previously reported,[8] 382 nm (ϵ 93.4 M^{-1} cm^{-1}) 498 nm (ϵ 145 M^{-1} cm^{-1}).

The kinetics of the chromium(II) reduction of $(NH_3)_5CrN_3^{2+}$ was followed spectrophotometrically at 500 nm on a Bausch and Lomb precision spectrophotometer. The reaction was initiated by adding the required amount of a solution of chromium(II) from a syringe to a solution of the azido complex plus $HClO_4$ and $LiClO_4$ to give a final ionic strength (*I*) of 1.0 *M* in a 5-cm path length spectrophotometer cell. The temperature of the reaction solution was controlled as described previously.[9]

In all cases the reactions were carried out with at least a 25-fold excess of reducing agent over oxidizing agent. Rate constants were determined from the usual plot of log $(A_t - A_\infty)$ *vs.* time, where A_t and A_∞ are the absorbances at time *t* and after the reaction is complete, respectively.

The chromium(III) product of the reduction was characterized spectrophotometrically after ion-exchange separation. A reaction solution containing 5.35×10^{-3} *M* $(NH_3)_5CrN_3^{2+}$,

(1) Author to whom correspondence should be addressed.

(2) A. E. Ogard and H. Taube, *J. Amer. Chem. Soc.*, **80**, 1084 (1958).

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(5) M. Linhard and W. Berthold, *Z. Anorg. Allg. Chem.*, **279**, 173 (1955).

(6) This purification step was found to be necessary in order to remove a significant fraction of lower (<2+) charged species from the sample, as well as some higher (>2+) charged species.

(7) Chromium was determined spectrophotometrically as chromate after oxidation with alkaline hydrogen peroxide.

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