It has been observed, however, that 1,2′-$(B_5H_8)_2$ rapidly decomposes in air.

Other examples of boranes in which several polyhedra or polyhedral fragments are attached by a single B–B bond include B_8H_{18}, which most probably consists of two tetraborane units bound by a B–B bond between the 2,2′ positions,[9–11] $B_{20}H_{26}$, which is assumed to consist of two $B_{10}H_{13}$ units (from $B_{10}H_{14}$) bound together by a B–B bond,[2] and all three possible isomers of $B_{20}H_{18}{}^{4-}$.[12]

Experimental Section

A nearly empty B_5H_9 cylinder was attached to the vacuum line and the remaining volatile materials were distilled into a trap at −196° over a period of several days. The materials less volatile than pentaborane(9) were separated by fractional condensation in a U trap at −45°. The materials condensing in this trap were transferred to a high-vacuum reflux cold-finger assembly. The cold finger was cooled to −12° (salt-ice bath) and the bulb of the reflux assembly was heated with a beaker of warm water. The materials were allowed to reflux in the closed apparatus for some time; then the stopcock connecting the reflux assembly to the vacuum line was opened and materials distilling past the cold finger were collected in several fractions. The initial samples had infrared spectra characteristic of alkyl-substituted boron hydrides; these compounds were not characterized. Subsequent samples showed decreasing absorptions in the C–H stretching region of the infrared spectrum, but no samples could be obtained without this absorption. When the amount of liquid material in the reflux assembly became negligible, a solid material began to collect on the cold finger. The solid was subsequently identified as $B_{10}H_{14}$ by its ^{11}B nmr spectrum.

Several samples from the reflux distillation, with only a small C–H stretch absorption, were combined and further purified using a low-temperature, high-vacuum spinning-band distillation column.[4] The first samples collected again showed a strong absorption in the C–H stretching region of the infrared spectrum, but this absorption disappeared as successive fractions were collected. Several samples of material having no absorption in the C–H stretching region of the infrared spectrum were combined and analyzed (Schwarzkopf Microanalytical Laboratories). *Anal.* Calcd for $B_{10}H_{16}$: B, 87.03; H, 12.98. Found: C, 0.00; B, 86.93; H, 12.96.

A gas chromatogram of these samples showed that they were mixtures containing about 85% of one component and 15% of a second component.

Other similar samples, containing approximately 20% of the second component, were purified by preparative gas chromatography using a Loenco Model 160-PMT-2 gas chromatograph. Separation of the components is effected using a $^3/_8$ in. × 10 ft column of 20% Kel-F on Chromosorb W at 60° and a helium flow rate of 200 cm^3/min, with the samples being collected at −196°. Samples were injected as 50% hexane solutions. Owing to severe overloading characteristics of these compounds, sample sizes were restricted to 5 μl or less. The observed retention times were about 6 min for the smaller component and 7.5 min for the major component, compared to about 0.5 min for the hexane solvent. The larger of the two components was subsequently identified as 2-[2′-pentaboran(9)yl]pentaborane(9), 2,2′-$(B_5H_8)_2$, and the smaller as 1-[2′-pentaboran(9)yl]pentaborane(9), 1,2′-$(B_5H_8)_2$. Melting points of both isomers were obtained in sealed capillaries: 1,2′-$(B_5H_8)_2$, 18.4°; 2,2′-$(B_5H_8)_2$, −22.8 to −20.5°.

Nmr Spectra. **1,2′-$(B_5H_8)_2$.**—The 32.1-MHz ^{11}B nmr spectrum of the 1,2′-$(B_5H_8)_2$ has a low-field group that appears to be a composite of a singlet of intensity 1 at about 3.58 ppm (from $BF_3 \cdot O(C_2H_5)_2$), B(2′), and a sharp, well-resolved doublet, B(2–5 and 3′–5′), of intensity 7 at 12.6 ppm, with a coupling constant of 168 Hz (Figure 1). The high-field group appears to be a composite of a singlet of intensity 1, B(1), at 57.3 ppm and a doublet of intensity 1, B(1′), at 50.5 ppm, with a coupling constant of 180 Hz.

The 60- and 100-MHz ^1H nmr spectra of 1,2′-$(B_5H_8)_2$ show both bridging and terminal hydrogens but give no structural information. The following chemical shifts were obtained: H(2–5, 3′–5′), τ 7.82 ppm, J = 165 Hz; H(bridge), τ 12.2 ppm.

2,2′-$(B_5H_8)_2$.—The 32.1-MHz ^{11}B nmr spectrum of 2,2′-$(B_5H_8)_2$ (Figure 1) has a low-field group of intensity 8 which appears to be a doublet, B(3–5, 3′–5′), and a singlet, B(2, 2′), overlapping with the low-field member of the doublet. The resulting two peaks are at 9.6 and 13.4 ppm. The high-field doublet of intensity 2, B(1, 1′), is at 49.9 ppm with a coupling constant of 180 Hz.

The 60- and 100-MHz ^1H nmr spectra of 2,2′-$(B_5H_8)_2$ exhibit two kinds of terminal hydrogens as well as bridging hydrogens. The following chemical shifts and coupling constants were obtained: H (3–5, 3′–5′), τ 7.46 ppm, J = 156 Hz; H(1, 1′), τ 9.5 ppm, J = 171 Hz; H(bridge), τ 12.0 ppm.

Infrared Spectra.—Infrared spectra were obtained in the gas phase, using a Perkin-Elmer 700 spectrometer. In the case of 2,2′-$(B_5H_8)_2$, a thin-film spectrum was also obtained. The infrared spectra of 1,2′-$(B_5H_8)_2$ and 2,2′-$(B_5H_8)_2$, respectively, are (cm^{-1} ± 10 cm^{-1}) as follows: 1,2′-$(B_5H_8)_2$: 2595 (s), 1840 (w), 1790 (vw), 1440 (w), 1395 (m), 1085 (vw), 1010 (w), 890 (m); 2,2′-$(B_5H_8)_2$: 2595 (s), 1805 (m, b), 1495 (sh), 1465 (sh), 1395 (s), 1350 (sh), 1110 (w), 1035 (sh), 1010 (s), 975 (m), 905 (s), 890 (sh), 880 (s), 850 (m), 800 (w).

Mass Spectra.—Mass spectra were obtained using an MS-902 spectrometer. For both isomers, the mass spectra at 70 eV cut off at m/e 126 as expected for $B_{10}H_{16}$. Exact mass measurement gave the following results: calcd for $B_{10}H_{16}$, 126.2183; found, 126.2172. The overall appearance of the spectra of both isomers is nearly identical with the previously reported spectrum of decaborane(16).[5] Mass spectra, obtained at a number of different ionizing voltages in the range 10–20 eV, showed only very slight differences between the two isomers. None of these differences was judged useful in distinguishing between the two isomers on the basis of their mass spectra.

Acknowledgments.—This work was supported in part by the National Science Foundation and the Office of Naval Research. We thank Bill Stebbings for the mass spectra. The mass spectrometer and nmr facilities were purchased in part with funds supplied by National Science Foundation equipment grants.

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Chlorine Nuclear Quadrupole Resonances in Platinum(II)–Olefin Complexes[1]

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The trans effect in the substitution reactions of square-planar metal complexes, particularly of platinum(II), has been of interest for many years. The variety of ligands which exert a strong trans effect is quite remarkable. Hydride, H^-, presumably capable of interacting with Pt only through a σ bond, exerts a kinetic effect comparable to that of ethylene,[2] in which interaction with Pt is generally agreed to consist in both σ and π bonding to comparable degrees.

In attempts to account for the kinetic trans effect,

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(1) This research was supported in part by the Advanced Research Projects Agency of the Department of Defense under Contract SD-131 and in part by the donors of the Petroleum Research Fund, administered by the American Chemical Society.

(2) C. H. Langford and H. B. Gray, "Ligand Substitution Processes," W. A. Benjamin, New York, N. Y., 1965.

the question arises whether the trans-directing ligand owes its effect principally to the weakening of the trans platinum–ligand bond in the ground state of the molecule or whether it operates more importantly in stabilizing the transition state. This question is of particular significance in comparing the trans effects due to such diverse groups as H^- and olefin. The number of observations of ground-state properties which bear upon the question in a meaningful way is limited. We present here recent measurements of chlorine nuclear quadrupole resonances in Zeise's salt and analogous monoolefin complexes, cyclooctadieneplatinum(II) chloride and norbornadieneplatinum(II) chloride.

Experimental Section

The cyclooctadiene and norbornadiene complexes were prepared by literature methods[3,4] and recrystallized, and their purities were established by satisfactory elemental analysis. Zeise's salt, $K[PtCl_3(C_2H_4)]\cdot H_2O$, and $K[PtCl_3($*cis*-$CH_3CH{=}CHCH_3)]$ were prepared by bubbling the appropriate olefin through a concentrated solution of $K_2[PtCl_4]$ in 3% HCl with 5 mol % $SnCl_2$ as a catalyst and evaporating the solution to crystallize the yellow or orange product. The composition and purity in each case were established by elemental analysis. The styrene complex was also prepared by two methods previously described.[5]

The nqr spectra were obtained on a Wilks NQR-1A superregenerative nqr spectrometer, using Zeeman modulation. Sample volumes used were about 3 cm³. Signals were generally weak; many olefin complexes examined did not yield resonances, and only in the case of Zeise's salt and cyclooctadieneplatinum(II) chloride could the weaker ^{37}Cl resonances be observed at the expected frequencies. In most cases the central absorption was easily distinguishable from the side bands spaced at intervals of approximately 20 kHz (the quench frequency) on either side. Measurement of frequencies was accomplished using a Drake R4-A receiver equipped with a crystal converter and calibrated crystals. Time constants of 10 and 30 sec were used during frequency measurements; the scan rate was the slowest possible, to minimize the time between frequency measurement and recorder response. The accuracy of the frequency measurements is approximately ±5 kHz, assuming the center absorption has been correctly identified. The frequencies reported in this work for $K[PtCl_3(C_2H_4)]\cdot H_2O$ differ by as much as 80 kHz from the values reported recently;[6] the lowest frequency was not identified in that work.

Temperature-dependence data were obtained by regulating the boil-off rate from liquid nitrogen and allowing the cold gas to flow inside a double-walled plastic box enclosing the sample.[7] Changes in frequency were measured to within ±2 kHz; the temperature measurements, using an iron–constantan thermocouple, are accurate to ±1°.

Results and Discussion

The most conspicuous common feature in the spectra of the monoolefin complexes (Table I) is the presence of a pair of higher frequencies and one lower frequency. Each of these in turn may be split by crystallographic inequivalence (the observation of three instead of four upper frequencies in the styrene complex could result from a weak resonance not detected or from two nonresolved signals). Although an attempt to assign the frequencies by preparing the trans-bromo-substituted Zeise's salt and searching for the ^{35}Cl frequencies was unsuccessful, assignment of the lowest frequency to the trans Cl is justified by two observations. First, in complexes of the type $PtCl_2L_2$, ^{35}Cl nqr frequencies in the trans form (containing no Cl trans to L) occur higher than those in the cis form.[8] The difference is most pronounced in ligands with a strong trans effect. Second, if the lowest frequency were not due to the trans Cl, then a difference of about 4 MHz between the two cis chlorines would need to be ascribed to lattice inequivalence in Zeise's salt and molecular and lattice inequivalence in the styrene and butene complexes (see Figure 1).

TABLE I

^{35}Cl NQR FREQUENCIES IN $K[PtCl_3($OLEFIN$)]$ AND $PtCl_2($OLEFIN$)$

Complex	Temp, °C	^{35}Cl freq, MHz	Charge on Cl, $-(1-\sigma)$
$K_2[PtCl_4]$[a]	0	17.93	−0.68
$K[PtCl_3(C_2H_4)]\cdot H_2O$	13	16.001	−0.71
		20.137	−0.63
		20.370	−0.63
$K[PtCl_3($*cis*-but-2-ene$)]$	22	16.007	−0.71
		16.525	−0.70
		19.872	−0.64
		20.125	−0.63
		20.920	−0.62
		21.078	−0.62
$K[PtCl_3($styrene$)]$	22	16.639	−0.70
		16.933	−0.69
		20.338	−0.63
		20.606	−0.62
		20.772	−0.62
(1,5-cyclooctadiene)$PtCl_2$	22	19.772	−0.64
(norbornadiene)$PtCl_2$[b]	30	18.573	−0.66
		18.799	−0.66

[a] E. P. Marram and E. J. McNiff, *J. Phys. Chem.*, **67**, 1719 (1963). [b] Norbornadiene = bicyclo[2.2.1]hepta-2,5-diene.

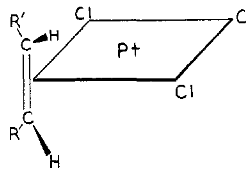

Figure 1.—Schematic drawing of a platinum–olefin complex, showing the origin of nonequivalence in the cis chlorines.

This seems very improbable, since the frequency difference is so marked and approximately constant.

Accepting the assumption that the lowest frequencies are due to the trans Cl, it is not possible in the styrene and butene complexes to distinguish which pairs of resonances in the upper multiplet are due to lattice effects and which to molecular inequivalence. The temperature-dependence data for Zeise's salt (Table II and Figure 2) indicate that the higher frequency cis Cl has a $(d\nu/dT)_p$ considerably less negative than the other cis Cl. The crystal structure[9] reveals hydrogen bonds to each of the cis Cl's, and they appear to be effectively equivalent. Assuming the same effective torsional frequencies for all three chlorines, Bayer's theory[10] predicts a nearly linear temperature dependence, as is observed in Figure 2, and a single value for $(1/\nu_0)(d\nu/dT)_p$ (ν_0 is the nqr frequency in the rigid

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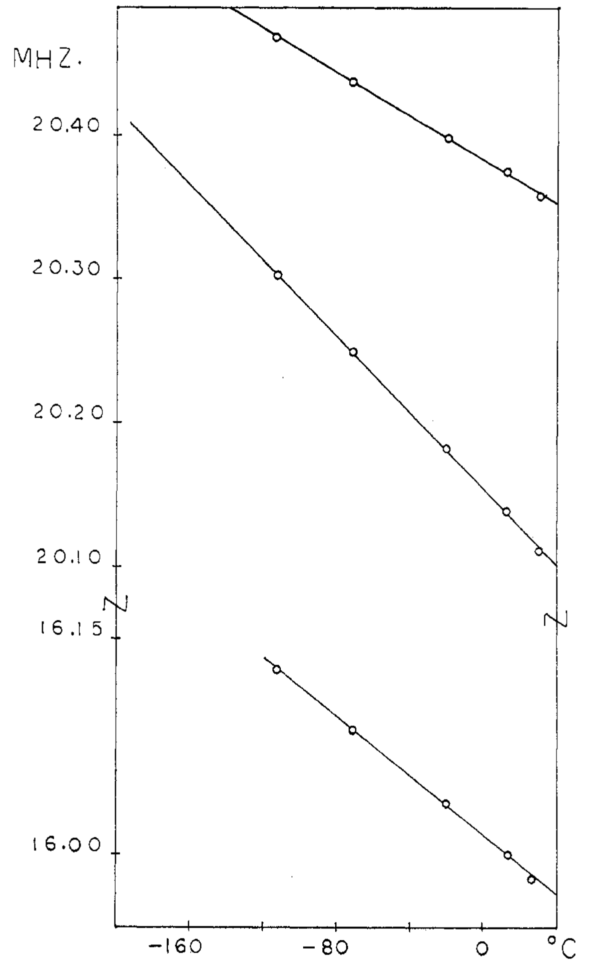

Figure 2.—Temperature dependence of ^{35}Cl nqr frequencies in Zeise's salt, $K[PtCl_3(C_2H_4)] \cdot H_2O$.

TABLE II

TEMPERATURE DEPENDENCE OF ^{35}Cl NQR FREQUENCIES IN $K[PtCl_3(C_2H_4)] \cdot H_2O$ AND (NORBORNADIENE)$PtCl_2$

$\nu(^{35}Cl)$, MHz	Temp, °C	$(d\nu/dT)_p$, kHz/deg	$\nu(^{35}Cl)$, MHz	Temp, °C	$(d\nu/dT)_p$, kHz/deg
		$K[PtCl_3(C_2H_4)] \cdot H_2O$			
16.129	−113	−1.03	20.137	13	−1.34
16.089	−71		20.109	31	
16.037	−20		20.465	−110 ± 2	−0.76
16.001	13		20.434	−71	
15.984	28		20.394	−21	
20.300	−110 ± 2	−1.34	20.370	13	
20.247	−71		20.354	31	
20.180	−21				
		(Norbornadiene)$PtCl_2$[a]			
18.713	−115	−0.98	18.916	−115	−0.80
18.685	−79		18.892	−79	
18.654	−56		18.866	−56	
18.646	−40		18.828	−8	
18.609	−8		18.799	30	
18.573	30				

[a] The order of measurement was 30, −8, −56, −115, −40, and −79°. The identification of the center peak in some cases was very questionable, and the kinetics of any phase change may render the low-temperature measurements invalid, if two phases were present during measurement or if the unstable phase existed during the measurement.

lattice, approximated from experimental data by extrapolation of the observed frequencies to 0°K). Evaluating this expression for the chlorines from the lowest to the highest frequency yields, in units of 10^{-5}/deg, the values −6.3, −6.5, and −3.7. The significantly less negative value for the highest frequency Cl suggests that it may be involved in hydrogen bonding to a different degree that the other cis chlorine.

Charges on the Cl atoms listed in Table I have been computed using the simplifying assumptions of the Townes and Dailey theory.[8] The presence of a 0.5-MHz crystallographic splitting in the butene complex suggests that a relative ordering is perhaps all that is currently justified. The observed order of increasing ^{35}Cl frequencies, ethylene < butene < styrene, is probably influenced by both the inductive and steric character of the substituents on the ethylene.

The ^{35}Cl nqr frequencies of the *cis*-$PtCl_2$(olefin) complexes listed in Table I occur at higher values than those for the analogous amine and phosphine complexes reported.[8] That the complexes with strong trans effects exhibit higher resonance frequencies in both cis and trans forms may be due to back-bonding between the phosphine or olefin ligand and platinum.[11] Thus, the net charge donated by the ligand actually decreases and the ^{35}Cl frequency increases with increasing back-bonding, while the σ covalent bond is strengthened by the synergic effect. Moore calculates the population of the olefin π^* (back-bonding) orbital in Zeise's salt to be 0.36 and the reduction of the occupied π-orbital population due to σ bonding to be 0.33, which implies a nearly neutral ethylene.[12] Concomitant with this increased back-bonding is an increased σ-overlap integral in the order of $N < Cl < P \approx C$, as calculated by McWeeny, *et al.*[13] Increased covalency in the ligand–platinum bond, according to Syrkin's account of the trans effect,[14] induces extra covalency in the cis Cl but reduces the covalency in the trans Cl. This would have the effect of lowering the nqr frequencies in the *cis*-$PtCl_2$(olefin) complexes from the high values expected on the basis of total charge donation. It would also account for the observed frequencies in the $K[PtCl_3$(olefin)] series, in which the trans Cl is considerably more ionic than the cis Cl, given the assumptions that the hybrid character of the σ orbital from cis and trans chlorines is the same and that chlorine-to-platinum π bonding is small. This explanation is similar to ones recently offered;[6,11] the observation of cis and trans influences in the same complex, as in Zeise's salt, further supports this interpretation.

A structural trans influence in Zeise's salt has been evidenced by X-ray data, which indicate a longer Pt–trans Cl bond distance than normal.[9,15] Infrared studies indicate that the Pt–trans Cl stretching frequency is lower than the average for the Pt–cis Cl modes.[16] A lowering of the ^{35}Cl nqr frequency thus correlates with decreasing bond order, as was found in other Pt(II) complexes. Especially interesting is the low ^{35}Cl nqr frequency in *trans*-$(P(CH_3)_2C_6H_5)_2PtHCl$,[11a] approximately 14.4 MHz, compared to the value of 21.0 MHz observed in *trans*-$((C_2H_5)_3P)_2PtCl_2$. This suggests that

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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

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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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