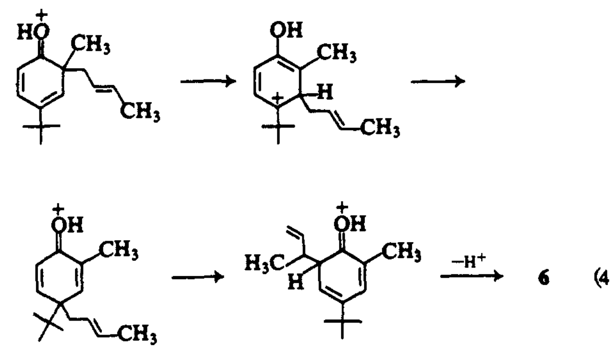
(4)

formed more conventionally by the mechanism shown as process 4. Both the twofold Wagner–Meerwein migration of the crotyl group to a position substituted by a *t*-butyl group[3,5] and the subsequent acid-catalyzed Cope rearrangement[2] have excellent precedent.

If process 4 for formation of **6** is correct, all the observed rearrangements proceed in accordance with the Woodward–Hoffmann rules for suprafacial "thermal" migrations,[4] provided protonation can occur on either n or π electrons of the oxygen atom. The possibility that the rearrangement of **3** to **5** proceeds by a direct [1,5] migration is of particular interest, since no examples of migration of a group other than a hydrogen atom in a [1,5] sigmatropic shift are known.[6,7]

Acknowledgment. This work was supported by Petroleum Research Foundation Grant 3551-A1, 4, administered by the American Chemical Society.

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(5) B. Miller, *J. Am. Chem. Soc.*, **87**, 5111 (1965).

(6) The possibility has been suggested that migration of C-7 around cycloheptatriene rings may involve [1,5] migrations, but it is not yet known whether these reactions proceed by concerted or free-radical paths. See J. A. Berson and M. R. Willcott, III, *Record Chem. Progr.*, **27**, 139 (1966); J. A. Berson, *Accounts Chem. Res.*, **1**, 152 (1968).

(7) Note Added in Proof. A probable [1,5] shift of a methyl group has recently been reported: V. Boekelherde and E. Storm, *J. Am. Chem. Soc.*, **91**, 902 (1969).

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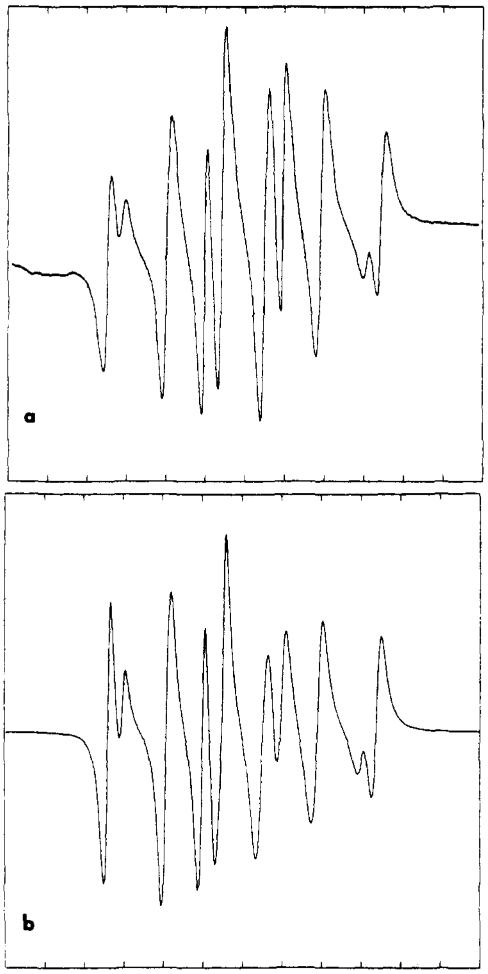

Figure 1 (a). First derivative epr spectrum of the chlorine monofluoride radical cation **2** formed by the reaction of ClF_5 with HF–SbF_5 (6:1 *M*). The base line is distorted because of the presence of an impurity. The marker spacing is 10 G. (b) Simulated spectrum of ClF^+ (75.4% ^{35}ClF, 24.6% ^{37}ClF) with 100% Lorentzian line shape and with coupling constants $a(^{35}Cl) = 14.75$ G, $a(^{37}Cl) = 12.25$ G, and $a(^{19}F) = 24.0$ G. The line width (full width at half-height of zeroth derivative absorption) equals 3.25 G for the left half and 4.50 G for the right half. The marker spacing is 10 G.

Radical Cations. II.[1] The Chlorine Monofluoride Molecule Cation, ClF^+

Sir:

Recently we reported the formation and observation of the chlorine molecule cation Cl_2^{+1} (**1**) and the further observation that under the appropriate conditions, the radical cation **1** was in equilibrium with a second paramagnetic species. We now wish to report that this second species is the chlorine monofluoride molecule cation ClF^+ (**2**) and that the formation of **2** can be achieved directly in the reaction mixture of chlorine trifluoride or chlorine pentafluoride with antimony pentafluoride.

Cl_2^+ ClF^+
1 **2**

When chlorine trifluoride is allowed to react with antimony pentafluoride at room temperature, the chlorine monofluoride radical cation **2** is formed. The formation of **2** can also be achieved by the reaction of chlorine trifluoride or chlorine pentafluoride with HF–SbF_5 or with FSO_3H–SbF_5 at or below room temperature. Figure 1 is the first derivative epr spectrum of a solution of the chlorine monofluoride radical cation **2** obtained by the reaction of chlorine pentafluoride with HF–SbF_5 (6:1 *M*) at −60°. The spectrum was obtained at −60°. The assignment of Figure 1 to the chlorine monofluoride molecule cation **2** follows from the comparison of Figure 1 with the simulated spectrum[2] of **2** (Figure 1b) and from the fact that the *g* value of **2** (2.006) is different from that of the (averaged) *g* value (2.02) of the chlorine monofluoride molecule anion[4] ClF^-.[5]

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(1) Part I: G. A. Olah and M. B. Comisarow, *J. Amer. Chem. Soc.*, **90**, 5033 (1968).

(2) Spectra were calculated using a modified form of Fritsch's[3] program on a Univac 1108 computer and plotted with CalComp plotter.

(3) J. M. Fritsch, Ph.D. Thesis, University of Kansas, Lawrence, Kan., 1965.

(4) J. Wilkens and J. R. Gabriel, *Phys. Rev.*, **132**, 1950 (1963).

The spectral line widths of ClF^+ (**2**) (Figure 1a) are not constant, the outer and high-field lines being broadened.[6] This is a phenomenon characteristic of species with a residual line width due to nonaveraging of the g and hyperfine tensors.[7,8]

The Raman spectrum of the chlorine monofluoride radical cation **2** shows in addition to solvent bands a very strong band at 819 cm^{-1}. Unfortunately gas-phase spectra of ClF^+ have not been reported, but comparison with the vibrational frequencies of the isoelectronic species ClO (ground state $\omega_e = 868\ cm^{-1}$)[9] and with the vibrational frequency of ClF (758 cm^{-1})[10] is possible. Since the vibrational frequency of ClO should be lowered on passing from the gas phase into solution[11] and since a π^*-antibonding electron is removed from ClF to form ClF^+, the observed vibrational frequency of ClF^+ would seem to be consonant with those of ClF and ClO.[12]

When solutions of the chlorine molecule cation **1** are heated to 60°, the chlorine monofluoride molecule cation **2** is formed, and when solutions containing **1** and **2** are heated and cooled between the temperatures -80 to $+60°$, the relative amounts of **1** and **2** change reversibly with **1** predominating at low temperature and **2** predominating at high temperature.[13] Thus Cl_2^+ (**1**) can be

$$\underset{\mathbf{1}}{Cl_2^+} \rightleftarrows \underset{\mathbf{2}}{ClF^+}$$

formed from chlorine monofluoride[1] at or below room temperature with the complete nonformation of **2**, but

$$ClF \xrightarrow{SbF_5} Cl_2^+$$

once any of the radical cation **2** is formed by heating the sample to $+60°$, the equilibrium is rapidly established. So far we have only been able to obtain the chlorine monofluoride radical cation **2** in the absence of **1** by the reaction of chlorine pentafluoride with SbF_5

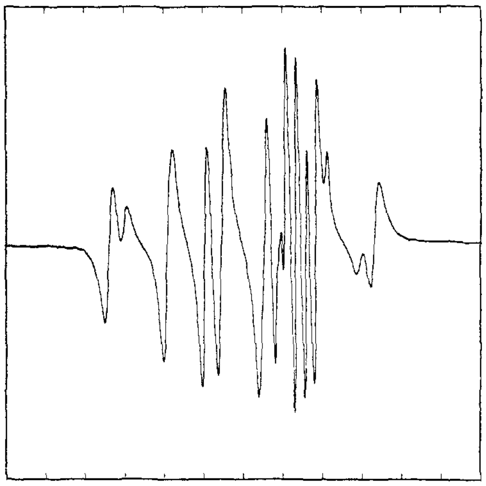

Figure 2. Epr spectrum of an equilibrium mixture of ClF^+ (**2**) and Cl_2^+ (**1**) at $-40°$. The marker spacing is 10 G.

$$ClF_5 \xrightarrow{SbF_5} ClF^+$$

the reaction of chlorine trifluoride always yielding the equilibrium mixture of **1** and **2**.

$$ClF_3 \xrightarrow{SbF_5} ClF^+ \rightleftarrows Cl_2^+$$

Figure 2 is a typical spectrum of the equilibrium mixture at $-40°$.

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(5) (a) Since ClF^+ would be expected to have a $^2\pi$ ground state, the g value near that of the free-spin value indicates that strong quenching of the orbital angular momentum in ClF^+ is present. This could be due to a strong (bonding) interaction with the solvent.[5b] Thus it is a somewhat moot point if the observed paramagnetic species should be called ClF^+. Similar comments apply to Cl_2^+. In solution, of course, any ion strongly interacts with its solvent environment. (b) The averaged g value for chlorine atoms adsorbed on silica is 2.009 and the isotopic coupling is about 10 G: C. L. Gardner, *J. Chem. Phys.*, **45**, 2991 (1967).

(6) The line widths in Figure 1a are approximately 3.25 G (central), 4.00 G (low field), and 4.50 G (high field).

(7) G. E. Pake, "Paramagnetic Resonances," W. A. Benjamin, Inc., New York, N. Y., 1962, p 110.

(8) The line widths for typical Cl_2^+ spectra monotonically increase from high field to low field. Matching of experimental spectra with simulated spectra for Cl_2^+ yields coupling constants of $a(^{35}Cl) = 2.59$ G and $a(^{37}Cl) = 2.15$ G. The highest resolution spectra we have as yet obtained for Cl_2^+ have maximum line widths (low field) of about 1.5 G. The previously published spectrum of Cl_2^+ (Figure 1 of ref 1) has a maximum line width of about 2.5 G.

(9) G. Porter, *Discussions Faraday Soc.*, **9**, 60 (1950).

(10) E. A. Jones, T. F. Parkinson, and T. G. Burke, *J. Chem. Phys.*, **18**, 235 (1950).

(11) H. Stammreich, P. Forneris, and Y. Taveres, *Spectrochim. Acta*, **17**, 1173 (1967).

(12) (a) Assuming the stretching frequencies of ClO would be about 20 cm^{-1} lower in solution than in the gas phase still leaves a difference of 30 cm^{-1} between the vibrational frequencies of ClO and ClF^+. This difference is consonant with strong interaction with the solvent mentioned in footnote 5 which would weaken the (formally bond and a half) Cl–F bond. (b) It has been reported [K. O. Christe and W. Sawodny, *Inorg. Chem.*, **6**, 313 (1967)] that ClF_2^+ possesses a Raman band at 818 cm^{-1}. While the presence of the diamagnetic species ClF_2^+ in the solutions described in present work must be considered, the band at 819 cm^{-1} can also be assigned to ClF^+ based on the above discussion.

(13) At $-80°$ the equilibrium contains about 90% **1** and 10% **2**, and at $+60°$ the equilibrium mixture contains about 5% **1** and 95% **2**.

A Three-Carbon Carborane Analog.
1-Stanna-2,3-dicarba-*closo*-dodecaborane(11)

Sir:

Molecular orbital calculations originally suggested that the $B_{12}H_{12}^{2-}$ ion would be stable[1] and that the icosahedral framework was held together by 26 electrons. The formal substitution of two electronically equivalent carbon atoms for two boron atoms in $B_{12}H_{12}^{2-}$ produces $B_{10}C_2H_{12}$, carborane. A further substitution of carbon for boron so as to maintain 26 electrons in the icosahedral framework would yield the unknown cation $[B_9C_3H_{12}]^+$, or if the species lost a proton, $B_9C_3H_{11}$. We would like to report the preparation and characterization of $B_9C_2SnH_{11}$ (I), a species related to $B_9C_3H_{11}$ by the formal replacement of C by another main-group IV element, Sn.

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(1) H. C. Longuet-Higgins and M. de V. Roberts, *Proc. Roy. Soc.* (London), **A230**, 110 (1955).