computer. Convergence of the calculations was monitored using control functions as described previously,[6,7] and elsewhere.[15] The solvent averaged force on the solute is clearly oscillatory as a function of R. The force vanishes at $R \simeq 4.2$, 5.15, and 7.0 Å and these distances should correspond to the calculated extrema in the $W(R)$ for the system. The extremum at 4.2 Å falls at the geometry $\sim 2R_{CH_4}$ expected for contact hydrophobic bonding. The average coordination number of the $[(CH_4)_2]_{aq}$ complex at the contact hydrophobic bonding distance is 24.5.

We infer that a maximum in $W(R)$ develops at 5.15 Å, followed by a second minimum at ~7.0 Å. This latter minimum distance corresponds to $\sim R_{CH_4} + 2R_{H_2} + R_{CH_4}$, two methanes approximately separated by a water molecular diameter. The average solvent coordination number of the $[(CH_2)_2]_{aq}$ complex at the solvent-separated hydrophobic bonding distance is 29.6. Our calculations thus support the possibility of a solvent-separated as well as contact hydrophobic bond.

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Evidence for the Synthesis of a "Stable" σ-Bonded Xenon–Carbon Compound: Bis(trifluoromethyl)xenon

Sir:

A target of prime interest since the pioneering work of Bartlett in xenon chemistry[1] has been the synthesis of a compound in which carbon is σ bonded to xenon. Such a species is a definite possibility in view of the recent synthesis of $FXeN(SO_2F)_2$[2] and evidence from ion cyclotron resonance experiments which estimate the strength of a xenon–carbon bond to be in the range of 43 ± 8 kcal/mol for $Xe(CH_3)^+$.[3] The less stable species $FXeCF_3$ has also been proposed as a reaction intermediate.[4]

Previously in our laboratory we have developed a general synthesis for trifluoromethyl organometallic compounds employing reactions of plasma generated radicals with metal halides:[5]

$$C_2F_6 \rightarrow 2CF_3\cdot$$

$$nCF_3\cdot + MX_n \rightarrow M(CF_3)_n + {}^n/_2X_2$$

$$X = I, Br, Cl$$

Considering the fact that xenon–fluorine bond strengths in XeF_2 are on the order of 31 kcal/mol, i.e. weaker than many of the halogen–metal bonds which have been broken in previous syntheses, synthesis of a xenon–carbon compound in this manner was thought to be a reasonable possibility. Crucial factors for the success of such a synthesis are (1) that the electronic rearrangement lifetime of the radical FXe· be long with respect to the collision frequency with an excess of trifluoromethyl radicals and (2) that, once formed in the free-radical process, the molecular species $Xe(CF_3)_2$ be stable enough to withstand collision and condensation.

By this synthetic method we were able to obtain a volatile, waxy, white solid which has a half-life of ~30 min when contained in a Kel-F container at room temperature. It has a much longer half-life (~2 weeks) at liquid nitrogen temperatures and decomposition is catalyzed by oxygen, glass, and moisture. This new compound, believed to be $Xe(CF_3)_2$, sublimes under vacuum with a vapor pressure significantly greater than that of XeF_2 and has very different physical properties. Thermal decomposition in the solid state while contained in a Kel-F tube gives xenon difluoride and at least six (GLC evidence) fluorocarbon products, presumably by a difluorocarbene elimination mechanism:

$$Xe(CF_3)_2 \xrightarrow{20\ °C} XeF_2 + C_nF_m$$

The XeF_2 produced appears as a highly crystalline solid on the Kel-F tube in contrast to the original waxy solid and the fluorocarbon layer separates over a 30-min period. Decomposition in the gas phase produces xenon and fluorocarbons including C_2F_6.

The synthetic procedure is identical with that reported previously[5] except that the entire plasma system is constructed of Teflon and other vacuum components are stainless steel and Kel-F. Xenon difluoride is bled into the tail of the trifluoromethyl radical plasma and the product is collected along with XeF_2 and fluorocarbons in a stainless steel trap at −196 °C. After the reaction is terminated the trap is warmed to −80 °C to remove unreacted C_2F_6. The white, waxy material is then separated from XeF_2 which is retained in a −35 °C trap on a Kel-F vacuum line. The product of interest condenses in a −78 °C trap and fluorocarbons pass on into a −196 °C trap. Separation may be performed several times and no significant quantities of XeF_2 are found after the initial separation. About 10 mg of product is produced in a 4-h time period.

One of the most compelling pieces of evidence for this compound is elemental analyses on samples of 1.88 and 0.85 mg for fluorine done after transporting the material at −196 °C to Schwarzkopf's Laboratories which gave 42.53 and 43.58% fluorine on duplicate samples. (Calcd for $Xe(CF_3)_2$: 42.33.)

The catalytic effect of polar surfaces such as AgCl, KBr, and CsI salt windows, resulting in the decomposition of $Xe(CF_3)_2$, leads to difficulty in obtaining an IR spectrum of the compound. Even when a CsI window was cooled to 35 K before sample deposition, decomposition to fluorocarbon products occurred as shown in Figure 1. By first depositing a layer of Xe and then a layer of $Xe(CF_3)_2$ at 35 K, we were able to ob-

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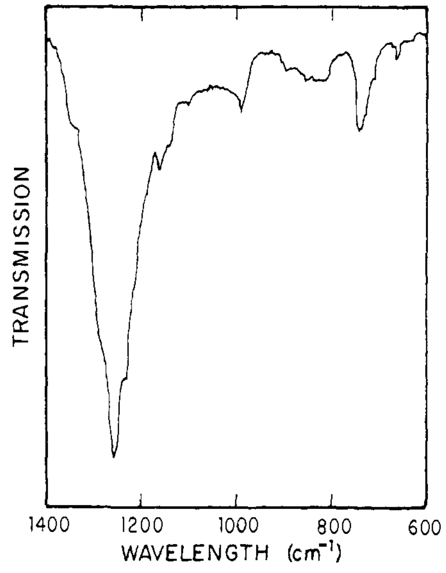

Figure 1.

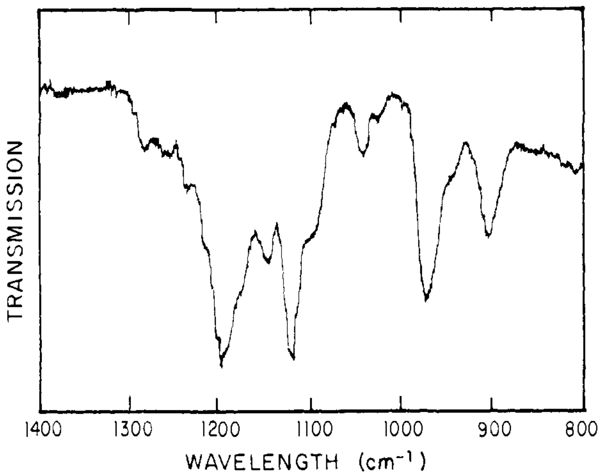

Figure 2.

tain the spectrum in Figure 2 which has a number of similarities to the spectrum of $Hg(CF_3)_2$. A complete vibrational analysis has not yet been possible because decomposition occurs with a Raman laser source.

Electron impact mass spectra of the $Xe(CF_3)_2$ showed peaks for Xe^+, Xe^{2+}, CF_3^+, and $C_2F_5^+$. Samples of the compound introduced through a 150 °C heated inlet gave Xe^+, Xe^{2+}, and a large number of fluorocarbon peaks ranging as high as *m/e* 498. Chemical ionization mass spectra of the compound using methane gas gave peaks representing Xe^+, CF_3^+, $C_2F_5^+$, XeF^+, XeF_2H^+, and a small amount of $C_2F_4^+$. Samples which had been stored at liquid nitrogen temperatures for several days showed, in addition, peaks representing $C_2F_4H^+$ and $C_3F_8H^+$. The ions XeF^+ and XeF_2H^+ are also observed in the chemical ionization mass spectra of XeF_2, but in this case the XeF^+/XeF_2H^+ ratio is 10, while that ratio is 1.6 for the $Xe(CF_3)_2$ compound. This result is consistent with the thermal decomposition of $Xe(CF_3)_2$ to XeF_2. Isobutane was unsuccessful in producing a chemical ionization spectra.

Acquisition of ^{19}F NMR evidence has been greatly hampered by lack of a suitable solvent. Although over 20 solvents have been considered, two categories have been observed: those in which decomposition occurs rapidly, and those (mostly fluorocarbons) in which the new fluorocarbon material is insoluble. In methylene chloride the compound decomposes rapidly to give xenon difluoride and fluorocarbons. A Fourier transform ^{19}F spectrum was obtained very rapidly during the process of decomposition in methylene chloride at −85 °C in FEP tubing. This ^{19}F NMR spectrum shows a peak at δ −9.6 ppm relative to $CFCl_3$ with two side bands indicative of the xenon-129 isotope (spin = $^1/_2$, 26.44% natural abundance). The $^{19}F-^{129}Xe$ two-bond coupling constant observed for this is 1940 Hz. This is smaller than the one-bond coupling of 5550 Hz in XeF_2[6] and larger than the three-bond coupling of 18 Hz in $FXeN(SO_2F)_2$.[2]

Confirmation of these observations awaits ^{19}F and ^{13}C or ^{129}Xe spectra in a suitable solvent.

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Evidence of Vibronic State “Selectivity” in the Photoracemization of Tris(1,10-phenanthroline)chromium(III) Ion in Solution

Sir:

Photoracemization of (+)-tris(1,10-phenanthroline)-chromium(III) ((+)-$Cr(phen)_3^{3+}$) has been observed to be partially quenched by I^- and O_2, but there is a residual nonquenchable limit which was assigned to immediate reaction from the initially excited ^4T state (approximate octahedral microsymmetry) preceding intersystem crossing to the quenchable ^2E state.[1] Subsequently, it has become clear that intersystem crossing from ^4T states in Cr(III) complexes is a fast (picosecond) process[2,3] and that intersystem crossing shows wavelength dependence indicating a common time scale for intersystem crossing and vibrational relaxation.[3,4] If there is a fraction of reaction which proceeds from the quartet prior to intersystem crossing, this reactivity might be expected to occur in competition with vibrational relaxation, i.e. to display vibronic state selectivity. This point can be tested by examining wavelength dependence at high quencher concentrations where only the direct quartet reaction is observed.

First-order plots of decay of optical activity of (+)-$Cr(phen)_3Cl_3$ were obtained for irradiation at argon ion laser wavelengths of 457.9, 465.8, 488.0, and 514.5 nm. Data quality and precision is illustrated by the runs presented in Figure 1. The experimental procedure included the following features: (i) (+)-$Cr(phen)_3^{3+}$ solutions were prepared gravimetrically

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