well be the influence of the methyl groups of DMSE. The only calculation that has been carried out on DMSE[3b] indicates that the methyl groups lengthen the carbon-silicon double bond by 0.04 Å.

Finally, it should be noted that the measured value of r_g(C═Si) and the product distributions of Table I are in good agreement[16] with recent carbon-silicon π-bond energy measurements,[17] force fields derived from spectroscopic studies of matrix-isolated silaalkenes,[4] and the second-order rate constant for the dimerization of DMSE.[18]

Supplementary Material Available: Experimental conditions for plates I-IV; raw intensity data for DMSCB, TMDSCB, ethylene, and plates I-IV; theoretical models for DMSB, TMDSCB, and ethylene; error and correlation matrices; intensity curves and radial distribution curves for plates I-IV (23 pages). Ordering information is given on any current masthead page.

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Production of Dixenon Cation by Reversible Oxidation of Xenon[1,2]

Sir:

Dixenon cation, Xe_2^+, is a principal product of the reduction of xenon(II) in antimony pentafluoride solutions. The bright green, paramagnetic ion has been characterized by its Raman, UV-visible, and ESR spectra[3] and has been shown to be formed as an intermediate product in reactions of elemental xenon with dioxygenyl salts. We have found that the cation can also be produced by adding xenon gas to a solution of $XeF^+Sb_2F_{11}^-$ in antimony pentafluoride and can be decomposed by pumping off the gas. At 20 °C, the solution frequently separates into two liquid phases, a pale green upper phase containing low concentrations of Xe_2^+, XeF^+, and $Sb_2F_{11}^-$ ions and a dark green bottom phase containing high concentrations of these ions. We report here the results of a preliminary study of this reaction—the first to produce a noble-gas species by reversible oxidation at ambient temperature.

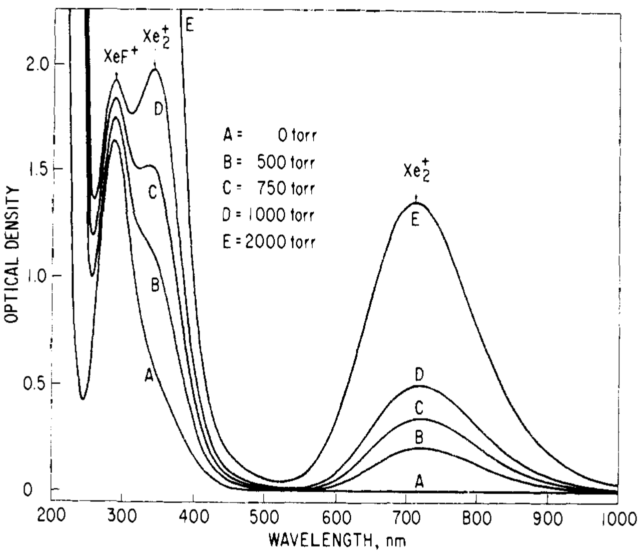

Figure 1. The effect of xenon pressure upon the UV–visible spectrum of a solution of $XeF^+Sb_2F_{11}^-$ in antimony pentafluoride at 25 °C: curve A, 0.404 M $XeF^+Sb_2F_{11}^-$ in the absence of xenon gas (yellow); curves B, C, D, and E, the same solution in equilibrium with xenon at partial pressures shown in the figure (green). The bands at 287 and 335 nm are off scale in curve E. The spectra were obtained with a Cary 14 spectrometer, using a 0.1-cm-path-length cell.

A thoroughly degassed solution of $XeF^+Sb_2F_{11}^-$ is pale yellow and exhibits only a single band of XeF^+ cation at 287 nm in its UV-visible spectrum, as shown in curve A, Figure 1. When xenon gas is added to a pressure of 500 Torr and the solution is stirred until equilibrium is reached (~ 30 min), the solution turns green and a new spectrum is obtained (curve B). Bands of Xe_2^+ cation then become visible at 335 and 720 nm.[4] As the xenon pressure is increased, these bands increase in intensity but very little change occurs in the band at 287 nm. (The apparent increase in height of this band is due to overlap with the adjacent Xe_2^+ band.) Upon removal of the xenon, the bands of Xe_2^+ disappear and the spectrum reverts to its original shape. The Raman band of Xe_2^+ at 123 cm^{-1} and the ESR signal of Xe_2^+ also appear and disappear in corresponding fashion in Raman and ESR spectra, respectively. We have found that this process can be repeated many times and is highly reproducible. A reversible reaction therefore occurs in this system between xenon and $XeF^+Sb_2F_{11}^-$.

The dependence of the optical density of the band at 720 nm upon xenon pressure and upon the concentration of $XeF^+Sb_2F_{11}^-$ does not correspond to that which would be expected for the simplest possible equilibrium

$$3Xe + XeF^+Sb_2F_{11}^- + 2SbF_5 \rightleftarrows 2Xe_2^+Sb_2F_{11}^- \tag{1}$$

This requires that the concentration of Xe_2^+ be proportional to the $\frac{3}{2}$ power of the xenon pressure (inasmuch as Henry's Law is obeyed by xenon in antimony pentafluoride), the square root of the $XeF^+Sb_2F_{11}^-$ concentration, and the first power of the antimony pentafluoride concentration. Instead, we find

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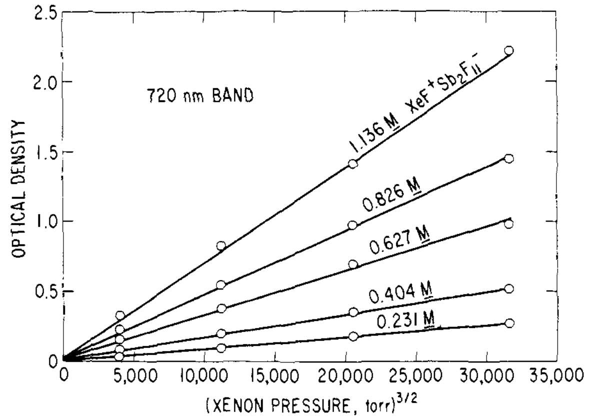

Figure 2. Optical density of the 720-nm band plotted as a function of the 3/2 power of xenon pressure. Each line was obtained at a constant concentration of $XeF^+Sb_2F_{11}^-$, shown in the figure. The spectra were recorded with a Cary 14 spectrometer, using a 0.1-cm-path-length cell for all measurements except those of the most dilute solution. Measurements of the 0.231 M solution were made with a 1.0-cm-path-length cell and were divided by 10 for purposes of representation in this figure.

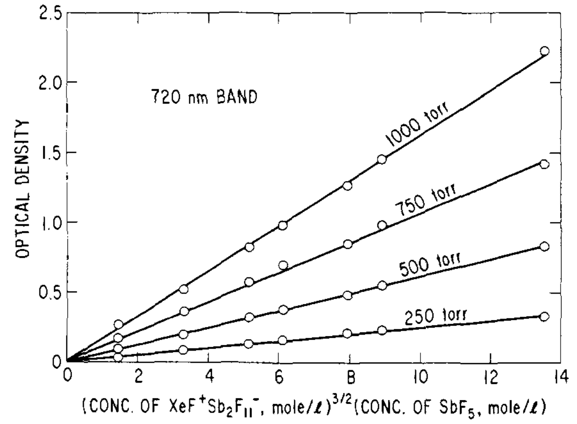

Figure 3. Optical density of the 720-nm band plotted as a function of the product of the 3/2 power of $XeF^+Sb_2F^{11-}$ concentration and first power of the SbF_5 concentration; the latter concentration is not an independent variable but is required for the equilibrium in eq 3. Each line was obtained at a constant pressure of xenon, shown in the figure. The measurements were made in the same manner as those described in Figure 2.

that the concentration of Xe_2^+, measured by the optical density at 720 nm, is proportional to approximately the 3/2 power of both the xenon pressure (Figure 2) and the $XeF^+Sb_2F_{11}^-$ concentration (Figure 3), and the first power of the antimony pentafluoride concentration. We therefore conclude that the cation is strongly bound in a complex with excess oxidant (eq 2). The overall reaction resulting from both oxidation and complexation is shown in eq 3. Our spectral data yield a uniform equilibrium constant for this reaction over a sixteenfold range of xenon pressure and fourfold range of $XeF^+Sb_2F_{11}^-$ concentration, when an arbitrary value for the molar extinction coefficient of dixenon cation is used. We are currently endeavoring to measure the extinction coefficient and establish a value for this constant.

$$Xe_2^+Sb_2F_{11}^- + XeF^+Sb_2F_{11}^- \rightleftarrows Xe_2^+Sb_2F_{11}^-\cdot XeF^+Sb_2F_{11}^- \quad (2)$$

$$3Xe + 3XeF^+Sb_2F_{11}^- + 2SbF_5 \rightleftarrows 2Xe_2^+Sb_2F_{11}^-\cdot XeF^+Sb_2F_{11}^- \quad (3)$$

The original methods for the production of dixenon cation[3]—reduction of xenon(II) with metals or water—involve irreversible reactions. A number of new reductants, including lead monoxide, arsenic trioxide, finely divided silica, glass wool, sulfur dioxide,[5] phosphorus trifluoride, and carbon monoxide, have been found to react in analogous fashion with solutions of $XeF^+Sb_2F_{11}^-$ in antimony pentafluoride. These irreversible reactions produce both Xe_2^+ and elemental xenon in various nonequilibrium ratios. Hence they proceed independently of the reversible reaction described in this communication.

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References and Notes

(1) Work performed under the auspices of the Office of Basic Energy Sciences, Division of Chemical Sciences, U.S. Department of Energy.

(2) This method for the production of dixenon cation was first described in a paper presented at the Fourth Winter Fluorine Conference, Daytona Beach, Fla., Jan 28–Feb 2, 1979, by L. Stein in collaboration with J. R. Norris, A. J. Downs, and A. R. Minihan; it has more recently been described in greater detail by the present authors at the Ninth International Symposium on Fluorine Chemistry, Avignon, France, Sept 3–7, 1979.

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(4) The band at 720 nm is very broad and has a non-Gaussian shape, which suggests that it may encompass two overlapping bands. However, this is an artifact caused by the nonlinearity in energy of the wavelength scale; when converted to a wavenumber scale, the band assumes a Gaussian shape. The center of this band was previously reported at 710 nm in ref 3.

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Transition Metal Catalyzed Reactions of Alkynes and Boron Hydrides: Synthesis of 2-(*cis*-2-Butenyl)pentaborane(9) and Its Conversion into Monocarbon Carboranes

Sir:

Conventional small carborane syntheses have usually involved the thermal reactions[1a] of pentaborane(9) with alkynes and have generally resulted in both cage fragmentation and the formation of numerous products.[1b] The initial step in these reactions has been proposed[2] to be the hydroboration of the alkyne to produce the corresponding alkenyl-substituted pentaborane(9) derivative, although no such compounds have heretofore been isolated. We now report the development of a transition metal catalyzed synthesis of these compounds under mild conditions and that, furthermore, these alkenyl-substituted pentaborane(9) derivatives can be converted in high yields into monocarbon carboranes.

In a typical reaction equimolar amounts of pentaborane(9) and dimethylacetylene are heated in the liquid phase at 75 °C in the presence of 10 mol % of dimethylacetylene dicobalthexacarbonyl, $(CH_3)_2C_2Co_2(CO)_6$. After 1 h, vacuum line fractionation of the reaction products revealed a 22% conversion[3] of pentaborane(9) into 2-(*cis*-2-butenyl)-pentaborane(9) (I). This compound, which has not been detected in uncatalyzed experiments, can then be further purified by GLC[4] to give an air-sensitive liquid which slowly decomposes to polymeric material under vacuum.

The composition of I is supported by exact mass measurements on the parent ion (mass calculated, 118.1643; found, 118.1650) and its proposed structure is consistent with the spectroscopic data. Thus, the ^{11}B NMR[5] consists of three doublets at −14.4 (J = 160 Hz), −18.6 (J = 167 Hz), and −50.9 (J = 174 Hz) and a singlet at 3.2 ppm with relative intensities of 2:1:1:1, confirming substitution at the 2 boron position. Likewise, the ^{11}B spin decoupled ^1H NMR spectrum[6] is in agreement with this formulation showing broad resonances from the protons bound to the boron cage at 2.52

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