in large excess, leads to the production of dimethylfluoronium ion, $CH_3FCH_3^+$. Subsequent methyl cation transfer equilibrium, eq 6, establishes the methyl cation affinity of CH_3F as 59.2 ± 2.0 kcal mol^{-1}.[11]

This accurate determination of the methyl cation affinity of CH_3F has subsequently been used in this laboratory to provide a reference point for determination of further methyl cation affinities by ion cyclotron resonance spectroscopic observation of methyl cation transfer equilibria involving CH_3F, eq 7.[14] Included

$$(CH_3)_2F^+ + B \rightleftharpoons CH_3B^+ + CH_3F \qquad (7)$$

in these experiments is the observation of methyl cation transfer equilibria involving CH_3F and Xe, eq 8, which may be used to

$$(CH_3)_2F^+ + Xe \rightleftharpoons CH_3Xe^+ + CH_3F_3 \qquad (8)$$

determine the methyl cation binding energy to Xe. Verification that the species observed is in fact CH_3Xe^+ may be seen in Figure 1 where identical isotopic distributions for Xe^+ and CH_3Xe^+ are shown. A typical methyl cation transfer equilibrium between CH_3F and Xe is illustrated in Figure 2.

In order to unambiguously ascertain the value of the equilibrium constant for eq 8, K_8, several replicate experiments were carried out in which the CH_3F:Xe pressure ratio was varied by a factor of 3. The data obtained from these equilibrium observations yield a value for K_8 of 0.16 ± 0.05 which allows a value of $\Delta G_8°$ of 1.1 ± 0.2 kcal mol^{-1} to be calculated. The low pressures involved in ICR experiments preclude determination of the entropy change, $\Delta S_8°$, by examination of the temperature dependence of K_8. However, it has been shown in the past that absolute entropies of ions may be reliably estimated from known entropies of isoelectronic neutrals.[15] Thus $S°((CH_3)_2F^+)$ may be estimated as 63.7 cal mol^{-1} K^{-1} from the experimental value for $(CH_3)_2O$ and $S°(CH_3Xe^+)$ may be estimated to be 60.5 cal mol^{-1} K^{-1} from data for CH_3I.[16] The maximum uncertainty in the ionic entropy estimates is probably ±0.5 cal mol^{-1} K^{-1}. These estimates and known entropy data for Xe and CH_3F establish $\Delta S_8°$ as 9.6 ± 1.0 cal mol^{-1} K^{-1}. Combining this entropy data with the value of $\Delta G_8°$ measured at ambient temperature (298 K) which gives the enthalpy change, $\Delta H_8°$, as 4.0 ± 0.5 kcal mol^{-1} allows a calculation of the methyl cation affinity of Xe of 55.2 ± 2.5 kcal mol^{-1}.

It is interesting to note the relative proton affinities and methyl cation affinities of Xe and a variety of other weak bases. For example equilibrium measurements establish the methyl cation affinity of Xe as 1.5 kcal mol^{-1} less than that of N_2O and 1.4 kcal mol^{-1} greater than that of CO_2.[11] This order is different than the order of proton affinities for these compounds in which Xe is found to be a weaker base than CO_2.[17] The principle attractive interactions in CH_3^+ adducts with weak bases will be electrostatic (ion-induced dipole) and covalent while the interaction in H^+ adducts will be much more predominantly covalent. The reversal in basicities of Xe and CO_2 toward H^+ and CH_3^+ may then be understood in terms of the increased relative importance of the electrostatic component of interaction in CH_3^+–Xe due to the much greater polarizability of Xe (4.02 $Å^3$) relative to CO_2 (2.59 $Å^3$). It should be noted, however, that the covalent component of interaction in CH_3–Xe^+ must still be appreciable.[18]

In summary, a method for establishing CH_3^+ binding energetics has been presented and applied to Xe to give a C–Xe bond strength of 55.2 ± 2.5 kcal mol^{-1} in CH_3Xe^+. Recent efforts in this laboratory have resulted in generation of CH_3Kr^+ and initial evidence indicates that a C–Kr bond strength in this ion may also be obtainable.[19] These data lead to the suggestion that CH_3Xe^+ and CH_3Kr^+ may be observable in CH_3F, SbF_5, and Xe or Kr mixtures by NMR.[20]

Acknowledgment. Financial support of the Natural Sciences and Engineering Research Countil of Canada is gratefully acknowledged in the form of an operating grant (T.B.M.) and fellowship support (J.K.H.).

Registry No. $XeCH_3^+$, 34176-86-8; CH_3N_2, 20404-06-2; CH_3F, 593-53-3; $(CH_3)_2F^+$, 64710-12-9; N_2, 7727-37-9.

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[14] All experiments were carried out at 298 K using an ion cyclotron resonance spectrometer of basic Varian V-5900 design, extensively modified to permit operation in both conventional drift and trapped ion modes. Both marginal oscillator and capacitance bridge detection systems were used in these experiments. Accurate partial pressure ratios of Xe and CH_3F were obtained with a Validyne capacitance manometer. Benson, S. W. "Thermochemical Kinetics", 2nd ed.; Wiley: New York, 1976.

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One-Step Synthesis of a 9-Phosphabarbaralane. Close Approach to a Bishomoaromatic System in the Solid State

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Phosphenium ions (R_2P^+) exhibit an interesting and diversified reactivity[1] and have been recently reported to undergo 1,4-addition to 1,3-dienes to yield 3-phospholenium ions.[1b,c] We now report the following: (i) the addition of a phosphenium ion to cyclooctatetraene to effect a one-step synthesis of a 9-phosphabarbaralane (**1**), (ii) the first structural information on a heteroatom-substituted barbaralane, and (iii) a solid-state structure closely approaching the geometry of the transition state for a Cope rearrangement.

Cyclooctatetraene (10.8 mmol, about 5M in CH_2Cl_2) is added dropwise to a stirred solution of $[(Me_2N)(Cl)P][AlCl_4]^2$ (10.8 mmol, about 0.5 M in CH_2Cl_2) cooled by an ice-water bath. The ice is allowed to melt and the reaction mixture warmed to room temperature. The reaction is monitored by ^{31}P NMR spectroscopy and after about 3 h appears to be complete with only one signal observed (80.8 ppm). The solvent is removed and the crude solid recrystallized by allowing heptane to diffuse into a methylene chloride solution at −35 °C. The product, **1**, is a colorless solid (mp dec 262 °C).[3]

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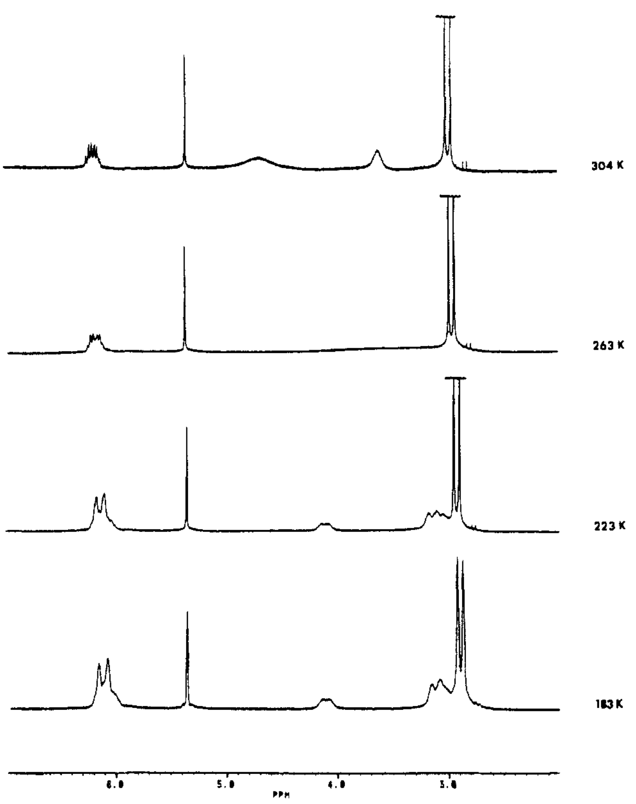

Figure 1. Variable-temperature ^{1}H NMR spectra for **1** in CD_2Cl_2. The signal at δ 5.35 is due to the residual protons in the solvent.

Table I. Selected Interatomic Distances (Å) and Angles (deg) for **1**

C(1)–C(2)	1.490 (10)	C(2)–C(8)	1.949 (7)
C(2)–C(3)	1.402 (14)	C(4)–C(6)	2.054 (7)
C(3)–C(4)	1.337 (10)	P–C(1)	1.829 (11)
C(4)–C(5)	1.541 (8)	P–C(5)	1.732 (9)
C(5)–C(6)	1.395 (7)	P–Cl(5)	1.972 (9)
C(6)–C(7)	1.370 (2)	P–N	1.616 (8)
C(7)–C(8)	1.477 (3)	N–C(9)	1.426 (6)
C(8)–C(1)	1.496 (10)	N–C(10)	1.524 (6)
C(1)–C(2)–C(3)	127.4 (8)		
C(2)–C(3)–C(4)	124.0 (1)	C(6)–C(5)–P	111.4 (5)
C(3)–C(4)–C(5)	122.9 (7)	C(1)–P–C(5)	103.8 (5)
C(4)–C(5)–C(6)	88.7 (4)	C(1)–P–Cl(5)	106.3 (5)
C(5)–C(6)–C(7)	125.9 (3)	C(5)–P–Cl(5)	108.5 (4)
C(6)–C(7)–C(8)	123.1 (2)	C(1)–P–N	110.7 (5)
C(7)–C(8)–C(1)	120.2 (4)	C(5)–P–N	113.3 (5)
C(8)–C(1)–C(2)	81.5 (5)	Cl(5)–P–N	113.5 (5)
C(2)–C(1)–P	109.1 (6)	P–N–C(9)	122.0 (5)
C(8)–C(1)–P	110.3 (7)	P–N–C(10)	119.9 (4)
C(4)–C(5)–P	112.7 (4)	C(9)–N–C(10)	115.2 (4)

The results of a variable-temperature ^{1}H NMR study of **1** are shown in Figure 1. The low-temperature spectrum (183 K) is assigned as follows: H(1), H(2), and H(8), δ 2.9–3.2 (m); H(3), H(4), H(6), and H(7), δ 5.9–6.2 (m); H(5), δ 4.1 (d, br); Me_2N δ 2.9 (d). In principle, the two allyl moieties are symmetry-nonequivalent and should be distinguishable. In fact, the absorptions at δ 2.9–3.2 and 5.9–6.2 exhibit some fine structure; however, this probably results from unresolved coupling. On raising the temperature, H(1) and H(5) exchange, as do H(2) and H(4) and H(6) and H(8). We assign the absorption at δ 3.6 to H(1) and H(5), that at δ 4.7 to H(2), H(4), H(6), and H(8), and that at δ 6.2 to H(3) and H(7). Again, it is impossible to distinguish allyl nonequivalence. These spectra are analogous to those of 9-ethyl-9-phenyl-9-phosphoniatricyclo[3.3.1.0^{2,8}]nona-3,6-diene tetrafluoroborate[4] and thus establish that the solution-phase ground state of **1** corresponds to a localized structure for which the Cope rearrangement becomes facile at room temperature. We estimate a barrier of 12 ± 1.7 kcal/mol for the Cope rearrangement of **1** in solution.

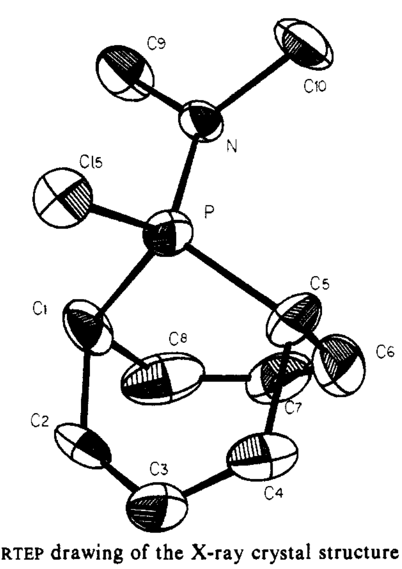

Figure 2. ORTEP drawing of the X-ray crystal structure of **1**.

Theoretical predictions,[5] notably by Hoffmann et al.[5a] and Dewar et al.[5b–d] have inspired attempts to achieve a bishomoaromatic system as exemplified by **1′** through substitution of semibullvalene[6] and barbaralane.[7] By means of X-ray crystallography it has been determined that a number of substituted semibullvalenes possess unusually long C_2–C_8 bonds and short C_4–C_6 distances.[8] These geometric anomalies have been described as "consistent with a structure that is approaching the transition state for Cope rearrangement".[6p] The only barbaralane geometry available for comparison, however, corresponds to a localized structure with C(2)–C(8) and C(4)–C(6) distances of 1.585 and 2.370 Å, respectively.[7d] It was therefore surprising that the X-ray diffraction study of **1**[9] (Figure 2 and Table I) revealed that the

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[3] Anal. Calcd for $C_{10}H_{14}AlCl_5NP$: C, 31.32; H, 3.68; N, 3.65. Found: C, 31.06; H, 3.96; N, 3.47.

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[8] See, for example, ref 6l, o, p, s, u, w.

C(2)–C(8) and C(4)–C(6) distances are extremely close (1.949 (7) and 2.054 (7) Å, respectively) as are the corresponding C-(2)–C(1)–C(8) and C(4)–C(5)–C(6) bond angles (81.5 (5)° and 88.7 (4)°, respectively). Collectively, the solid-state structure of **1** represents the closest approach to a bishomoaromatic system (**1′** in this case) thus far reported. Scrutiny of the nonbonded distances indicates that there are no unusually short contacts involving, e.g., the $AlCl_4^-$ gegenion. However, the thermal ellipsoids of C(6) and C(8) are significantly larger than those of the other atoms. The delocalized solid-state structure of **1** stands in sharp contrast to its localized solution-phase structure. Since the barrier to the Cope rearrangement for **1** is similar in magnitude to that of other barbaralanes,[7] we are reluctant to invoke any special solvent interactions in the solvation of **1**. The structural differences are, therefore, most probably due to crystal packing forces.

Acknowledgment. We are grateful to the National Science Foundation (Grant CHE-8506029), the Robert A. Welch Foundation, and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for financial support.

Supplementary Material Available: Tables of bond lengths, bond angles, torsional angles, atomic coordinates, and thermal parameters for **1** (6 pages). Ordering information is given on any current masthead page.

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(9) Crystal data for **1**: $C_{10}H_{14}AlNPCl_5$, M_r = 383.45, monoclinic, space group $P2_1/c$ (No. 14), a = 6.667 (1) Å, b = 17.149 (3) Å, c = 14.976 (3) Å, β = 93.50 (2)°; V = 1709.0 Å^3, Z = 4; D_c = 1.491 g cm^{-3}; λ (Mo Kα) = 0.7107 Å, μ(Mo Kα) = 9.8 cm^{-1}. An empirical absorption correction was applied. The intensities of 2766 reflections were measured on an Enraf-Nonius CAD-4F diffractometer at room temperature ($3.00 \leq 2\theta \leq 48.00$). The structure was solved by direct methods and refined by full-matrix least squares using 1306 unique observed reflections ($I \gtrsim 3.0\sigma(I)$). The reflection to parameter ratio was 8:1. The final residuals were R = 0.0730 and R_w = 0.0750. All calculations were performed using the SDP-Plus program package.[10]

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Selenoformaldehyde Phosphorescence Observed in the Reaction of Molecular Fluorine with Dimethyl Diselenide

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The spectroscopy and chemistry of formaldehyde analogues have recently become of wide interest.[1,2] Chemiluminescence (CL) methods have been successful in obtaining useful spectral data on the difficult-to-study formaldehyde analogues thioformaldehyde (CH_2S)[3] and silanone (SiH_2O).[4] The only previous study of the optical spectrum of selenoformaldehyde (CH_2Se) was that of Judge and Moule.[5] These workers obtained absorbance spectra of CH_2Se ($\tilde{a}^3A_2$) over a 68-m path length after pyrolysis of dimethyl selenide. The microwave spectrum[6] and photoelectron spectrum[7] of CH_2Se have also been studied only within the last several years.

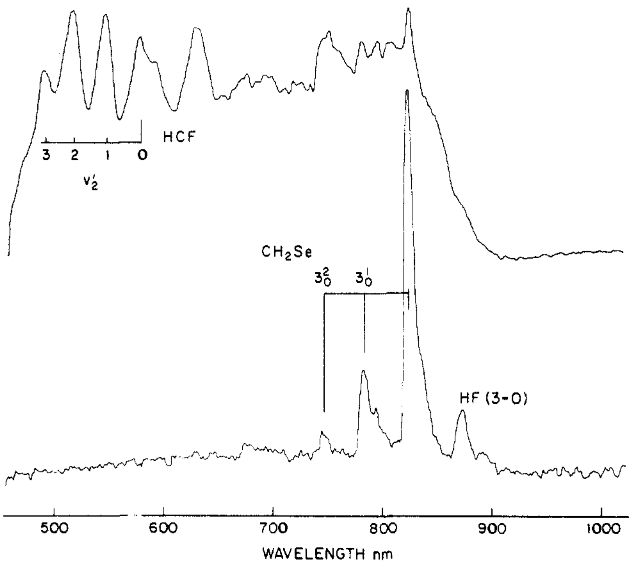

Figure 1. Uncorrected diode array spectra obtained in the reactions of dimethyl diselenide with a 10% F_2/He mixture. Upper trace: 10 mtorr of DMDSe and 330 mtorr of F_2/He. Lower trace: 60 mtorr of DMDSe and 270 mtorr of F_2/He. Although a short progression in ν'_3 is labeled in the lower trace, other transitions may account for some intensity in those bands (see text). The precision of the wavelength measurement is ±1 diode or ±1.2 nm.

Reactions of molecular fluorine with organosulfur compounds generate rich, gas-phase CL spectra. Vibrationally excited HF and electronically excited HCF and CH_2S have been identified in emission spectra from the reactions of F_2 with a number of organosulfur compounds under various conditions.[3,8-10] In addition, the novel species FCS has also been tentatively identified.[10]

In a CL study similar to that which has yielded a CH_2S phosphorescence spectrum,[3] we have obtained emission spectra from the reaction of $(CH_3Se)_2$ with F_2 corresponding to the $\tilde{a}^3A_2 \rightarrow \tilde{X}^1A_1$ transition in CH_2Se. We have also obtained spectral evidence for the production of $HF^{\dagger}$, HCF^*, and a fourth unidentified intense emitter from the $F_2/(CH_3Se)_2$ reaction.

The CL was observed as it occurred in our chromatography detector cell that has been described in detail elsewhere.[8,9] The entrance slit to the 512 channel intensified diode array spectrophotometer (focal length 0.25 m) was set close to a quartz window at one end of the cell.

Emission spectra recorded during the reaction of a 10% F_2/helium mixture (Matheson) with dimethyl diselenide (DMDSe, Alfa Products) under two different conditions of reactant pressure are presented in Figure 1. The lower trace was obtained with 60 mtorr of DMDSe and 270 mtorr of F_2/He. The location of three prominent bands, not assignable to $HF^{\dagger}$, is consistent with expected selenoformaldehyde phosphorescence features on the basis

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