this research was partially supported by grants from the Fund for the Promotion of Research, the New York Metropolitan Fund, and a generous allocation of computer time. We thank Y. Arnon at the Technion Computer Center for technical assistance with some of the larger calculations. A partial travel grant to B. H. from the Technion's Vice President of Research greatly facilitated the collaboration between the experimentalists and theoreticans and it is gratefully acknowledged.

The Preparation and Characterization of Radical Cation Salts Derived from Perfluorobenzene, Perfluorotoluene, and Perfluoronaphthalene

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Abstract: The salts $C_6F_6{}^+AsF_6{}^-$ (yellow), $C_6F_5CF_3{}^+AsF_6{}^-$ (lime green), and $C_{10}F_8{}^+AsF_6{}^-$ (dark green) may be prepared by electron oxidation of the appropriate perfluoro aromatic molecule with $O_2{}^+AsF_6{}^-$. Other $O_2{}^+$ salts can be similarly employed as can the more strongly oxidizing transition-metal hexafluorides, but salts of the latter are more labile than their $AsF_6{}^-$ relatives. $C_6F_6{}^+AsF_6{}^-$ is a convenient electron oxidizer ($C_6F_6AsF_6 + C_{10}F_8 \rightarrow C_{10}F_8AsF_6 + C_6F_6$) since that which remains from the reaction decomposes at room temperature to volatile products ($2C_6F_6AsF_6 \rightarrow C_6F_6 + 1{,}4\text{-}C_6F_8 + 2AsF_5$). Magnetic susceptibilities for $C_6F_6AsF_6$ and $C_{10}F_8AsF_6$ approximate to Curie law behavior, and *g* values are close to free-electron values. X-ray diffraction data (single crystal) show $C_6F_6AsF_6$ to be primitive rhombohedral with $a_0 = 6.60$ (1) Å, $\alpha = 106.0$ (1)°, $V = 246.1$ Å^3, $Z = 1$, probable space group $R\bar{3}$, and (powder data) $C_{10}F_8AsF_6$ to be tetragonal with $a_0 = 8.27$ (5) Å, $c_0 = 18.57$ (s) Å, $V = 1270$ Å, $Z = 4$. Salts derived from the monocyclic perfluoro aromatics are thermally unstable but can be kept below −15 °C. The perfluoronaphthalene salts are indefinitely stable at room temperatures. All hydrolyze rapidly. The products of thermal decomposition of the hexafluoroarsenates of the monocyclic cation salts parallel the products of the attack by F^-. The latter reaction products are in the molar ratios indicated by the following equations: $2C_6F_6{}^+ + 2F^- \rightarrow C_6F_6 + 1{,}4\text{-}C_6F_8$; $2C_6F_5CF_3{}^+ + 2F^- \rightarrow C_6F_5CF_3 + 1{,}3\text{-}C_6F_7CF_3$. The $1{,}3\text{-}C_6F_7CF_3$ isomerizes to a 1:1 mixture with $1{,}4\text{-}C_6F_7CF_3$ over several days in the presence of fluoro acids. Mechanisms for the formation of the dienes are discussed.

Radical cations derived from perfluoro aromatic molecules were first described by Bazhin et al.[1,2] The species were made in super acid or oleum solutions and were unambiguously characterized by ESR spectroscopy.[1-5] Such species have also been proposed as intermediates in the oxidative fluorination of aromatic molecules by high-valent metal fluorides[6] such as cobalt trifluoride, by bromine trifluoride,[7] and by xenon difluoride.[8] They have also been invoked in the electrochemical fluorination[9] of aromatic molecules in the presence of F^-. Salts of such radical cation species were unknown prior to the synthesis of $C_6F_6{}^+AsF_6{}^-$ in these laboratories.[10,11]

An earlier attempt by Jha[12] to prepare $C_6F_6{}^+PtF_6{}^-$ from C_6F_6 and PtF_6 yielded a promising orange-yellow solid at low temperatures. A similar material obtained[11] using IrF_6, decomposed well below 0 °C. Kinetically stable salts sufficiently stable to be manipulated at room temperatures were first obtained[10,11] by exploiting dioxygenyl salts as oxidizers:

$$C_6F_6 + O_2AsF_6 \rightarrow C_6F_6AsF_6 + O_2$$

$$C_6F_6 + O_2Sb_2F_{11} \rightarrow C_6F_6Sb_2F_{11} + O_2$$

The range of salts has been extended since the preliminary report.[10] Utilization of the low-melting solvent SO_2ClF has improved yields and provided access to less thermally stable perfluoro aromatic radical cation salts. Less powerful oxidizers than $O_2{}^+$ salts are needed for the synthesis of $C_{10}F_8{}^+$ and polycyclic cation salts which have much higher thermal stability than their monocyclic relatives. The preparation and characterization of monocation salts derived from C_6F_6, C_6F_5 CF_3, and $C_{10}F_8$ is reported here. The preparation and some properties of the pentafluoropyridine radical cation salts have been described elsewhere.[13]

Particular attention has been given to the products of thermal decomposition of the radical cation salts and the products of F^- attack, since the sets of products are related. Salts of the single-ring aromatics are thermally unstable at room temperature but can be kept below 258 K. Their thermal decomposition gives an equimolecular mixture of the parent fluoro aromatic and a perfluorocyclohexadiene. The initial diene product is a specific isomer. This provides clean high-yield syntheses for those dienes and provides insight into the reaction mechanisms.

Results and Discussion

Composition of the Salts and Structural and Magnetic Properties. The high ionization potential of C_6F_6 (~10 eV)[14] requires

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anions of very high ionization potential to stabilize the $C_6F_6^+$ cation in a salt. Clearly both PtF_6 (as shown earlier by Jha[12]) and IrF_6 (as shown in this study) bring about salt formation. If these salts have the formulation $C_6F_6^+MF_6^-$ (which is probable), the lattice energies would be[15] approximately -115 kcal mol^{-1}. The electron affinities of IrF_6 and PtF_6 have been determined[16,17] to be 160 and 184 kcal mol^{-1}, respectively, which means that the enthalpy of formation from the gaseous reactants

$$\Delta H°(C_6F_6 + MF_6 \rightarrow C_6F_6^+MF_6^-) \qquad (1)$$

should be -45 and -69 kcal mol^{-1} respectively for the IrF_6^- and PtF_6^- salts. These anticipated reaction enthalpies are greatly in excess of those required to offset the unfavorable entropy change[18] associated with (1). The inability of OsF_6 or the less powerfully oxidizing hexafluorides to form $C_6F_6MF_6$ salts is a consequence of their lower electron affinities ($\leq$130 kcal mol, see below). The instability of $C_6F_6MF_6$ (M = Ir, Pt) appears to be due to the relative ease of transfer of F^- from the anion to the cation in such instances (see below). Indeed this is a general problem in the stabilization of cations of the monocyclic perfluoro cations, and the AsF_6^-, SbF_6^-, and $Sb_2F_{11}^-$ anions appear to provide the best kinetic stability for such salts.

The first effective synthesis[11] of $C_6F_6AsF_6$ employed O_2AsF_6 as the oxidizer of C_6F_6 dissolved in liquid WF_6. This solvent not only provided the desirable diluent effect for this hot reaction but its relatively high heat capacity also aided in preservation of a lower temperature. These are essential requirements for high-yield syntheses of $C_6F_6AsF_6$ and its monocyclic relatives, since all are thermally unstable at ordinary temperatures. In more recent work sulfuryl chloride fluoride has been used as the diluent and moderator and the low working temperatures have resulted in greatly improved yields. Nevertheless, even with SO_2ClF, pyrolysis products from the salts are always observed and a quantitative yield has never been obtained for any of the monocyclic cation salts. For these and other reasons[19] the salt composition in each case has been determined from the stoichiometry of the salt pyrolysis products and other reaction stoichiometries.

The spontaneous interaction of nitric oxide with $C_6F_6AsF_6$ is in harmony[20] with the ionization potentials (I(NO) = 213 kcal mol^{-1}, $I(C_6F_6)$ = 230 kcal mol^{-1}) and lattice energies[15] (LE($C_6F_6AsF_6$) = -115 kcal mol^{-1}, LE($NOAsF_6$) = -130 kcal mol^{-1}).

$$NO + C_6F_6AsF_6 \rightarrow C_6F_6 + NOAsF_6 \qquad (2)$$

When this reaction is carried out by admitting nitric oxide very slowly to the $C_6F_6AsF_6$, the thermal decomposition products are present only in traces. Then the yield of $NOAsF_6$ is almost quantitative on the basis of the salt formulation $C_6F_6AsF_6$. This salt stoichiometry is also indicated by the ^{19}F NMR spectra of the pyrolysis products. The spectra show C_6F_6 and 1,4-C_6F_8 to be present in 1:1 stoichiometry consistent with the reaction

$$2C_6F_6AsF_6 \rightarrow C_6F_6 + 1,4\text{-}C_6F_8 + 2AsF_5 \qquad (3)$$

The product distribution in the decomposition of the perfluorotoluene cation salt similarly indicates that the stoichiometries are as follows

$$2C_6F_5CF_3AsF_6 \rightarrow C_6F_5CF_3 + 1,3\text{-}C_6F_7CF_3 + 2AsF_5 \qquad (4)$$

With extension of the π systems from one ring to two there is a large decrease in ionization potential[14] ($I(C_{10}F_8)$ = 204 kcal mol^{-1}), and as the system becomes more extended the ionization enthalpy approaches that of graphite. But the lattice energy of salts of all of these cations must depend primarily upon the closest approach of cation and anion, and since all of the cations have essentially the same thickness (that of the van der Waals' distance[21] between nearest-neighbor rings, which is ~3.3 Å), the lattice energy probably does not decrease as much as the greater size of the more extended cations would suggest. By comparison with C_6F_6 and $C_6F_5CF_3$, therefore, the electron oxidation of $C_{10}F_8$ and polycyclic aromatic relatives[22] is comparatively easy. Not surprisingly then, $C_{10}F_8AsF_6$ can be prepared from the $C_6F_6AsF_6$ salt

$$C_{10}F_8 + C_6F_6AsF_6 \rightarrow C_{10}F_8AsF_6 + C_6F_6 \qquad (5)$$

Since the thermal decomposition products of $C_6F_6AsF_6$ are all volatile whereas the $C_{10}F_8AsF_6$ is thermally stable and involatile at room temperature, a quantitative conversion of $C_{10}F_8$ to the salt can be achieved. This has settled the composition as $C_{10}F_8AsF_6$. It is not, however, necessary to employ $C_6F_6AsF_6$ as the oxidizer. A convenient, clean synthesis uses a mixture of AsF_5 and F_2 in SO_2ClF.

$$C_{10}F_8 + AsF_5 + \tfrac{1}{2}F_2 \rightarrow C_{10}F_8AsF_6 \qquad (6)$$

Perfluoronaphthalene is also oxidized by AsF_5 alone according to the equation

$$2C_{10}F_8 + 3AsF_5 \rightarrow 2C_{10}F_8AsF_6 + AsF_3 \qquad (7)$$

This reagent is unable to oxidize the monocyclic perfluoro aromatics because the electron affinity[23]

$$-\Delta H°(\tfrac{3}{2}AsF_{5(g)} + e^- \rightarrow AsF_{6(g)}^- + \tfrac{1}{2}AsF_{3(g)}) \approx 120 \text{ kcal mol}^{-1} \qquad (8)$$

is too low. Nor, for similar reasons, will the hexafluorides of tungsten (E = 81 kcal mol^{-1}),[24] rhenium (E = 106 kcal mol^{-1}),[25] or osmium (E = 130 kcal mol^{-1})[25] oxidize the single-ring perfluoroaromatics. In the case of $C_{10}F_8$, however, ReF_6 rapidly and quantitatively oxidizes it

$$C_{10}F_8 + ReF_6 \rightarrow C_{10}F_8ReF_6 \qquad (9)$$

although WF_6 is unable to do so. It is therefore probable that

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(15) In their study of the fluoride ion affinities of various fluoroacids Mallouk et al. (Mallouk, T. E.; Rosenthal, G. L.; Muller, G.; Brusasco, R.; Bartlett, N. *Inorg. Chem.* **1984**, *23*, 3167–3173) employed the linear dependence of lattice energy upon the inverse of the cube root of the formula unit volume to determine the lattice energies of salts of unknown structure. From that empirical relationship which is U_L (kcal mol^{-1}) = 556.3 (molar volume in Å^3)$^{-1/3}$ + 26.3, $U_L(C_6F_6AsF_6)$ = 115 kcal mol^{-1} and $U_L(C_{10}F_8AsF_6)$ = 108 kcal mol^{-1}.

(16) Bartlett, N.; Yeh, S.; Kourtakis, K.; Mallouk, T. *J. Fluorine Chem.* **1984**, *26*, 97–116.

(17) Nikitin, M. I.; Sidorov, L. N.; Korobov, M. W. *Int. J. Mass Spectrom. Ion Phys.* **1981**, *37*, 13–16.

(18) The standard entropies of a large number of simple AB salts have been shown to be in simple relationship to the formula unit volume, the relationship being $S°$ (cal mol^{-1} K^{-1}) = 0.44 × molar volume (in Å^3). From this $S°(C_6F_6MF_6)$ is estimated to be ~108 cal mol^{-1} K^{-1}. The standard entropies of gaseous MF_6 are ca. 80 cal mol^{-1} K$^-$ [NBS Technical Notes 270-3, 1968, and 270(4), 1969, and JANAF Tables to 1971 (Dow Chem. Co., Michigan)] and that of $C_6F_{6(gas)}$ is 92 cal K^{-1} (Counsell, J. F.; Green, J. H. S.; Hales, J. L.; Martin, J. F. *Trans Faraday Soc.* **1965**, *61*, 212–218). This means that $\Delta S°(C_6F_{6(g)} + MF_{6(g)} \rightarrow C_6F_6MF_{6(c)}) \approx -64$ cal mol^{-1} K^{-1}, and, at 300 K, $T\Delta S° \approx -19$ kcal mol^{-1}.

(19) Fluoroarsenates are notoriously difficult to analyze because of the kinetic stability of AsF_6^-, which persists even in aqueous solution in the presence of H_2S reagent. In addition the C–F bond is a very stable one and conventional combustion analysis cannot normally be applied to such fluorocarbon materials as these.

(20) The entropy change for the reaction represented in eq 2 is approximately zero, but the enthalpy change could be less exothermic than indicated by these ionization potentials and lattice energies. The lattice energy given here for $C_6F_6AsF_6$ may have underestimated the dispersion energy contribution by as much as 5 kcal mol^{-1}, bringing the $C_6F_6AsF_6$ lattice energy to a possible value of ~120 kcal mol^{-1}.

(21) The face-to-face contact between aromatic hydrocarbons such as that which occurs in the $(C_{10}H_8)_2PF_6$ structure (loc. cit.) of 3.2 Å and that in TCNQ complexes of 3.24 Å (Fritchie, C. J., Jr. *Acta Crystallogr.* **1966**, *20*, 892–898. Kobayachi, H. *Bull. Chem. Soc., Jpn.* **1975**, *48*, 1373–1377) is comparable with the sheet-to-sheet separation in graphite of ~3.3 Å.

(22) Coronene and other polycyclic hydrocarbons are electron oxidized by $C_6F_6AsF_6$, and weaker oxidizers such as AsF_5, to yield highly conducting salts (e.g., $C_{24}H_{12}^+AsF_6^-$). Richardson, T. J.; Tanzella, F. L.; Bartlett, N., to be published.

(23) Rosenthal, G. L.; Mallouk, T. E.; Bartlett, N. *Synth. Met.* **1984**, *9*, 433–440.

(24) George, P. M.; Beauchamp, J. L. *Chem. Phys.* **1979**, *36*, 345–351.

(25) On the basis of the electron-oxidizing properties of the sequence of third transition series hexafluorides it has been argued (see: Bartlett, N. *Angew. Chem., Int. Ed. Engl.* **1968**, *7*, 433–439) that the electron affinity increases approximately by 1 eV (23.06 kcal mol^{-1}) for each unit increase in atomic number from WF_6 to PtF_6. With WF_6 (ref 24) and PtF_6 (ref 17) as fixed points, the increment becomes approximately 25 kcal mol^{-1} and this yields $E_a(ReF_6) \approx 106$ and $E_a(OsF_6) \approx 130$ kcal mol^{-1}.

AsF_5 or ReF_6, although not particularly powerful oxidizers, will generate radical cation salts from any of the multiring perfluoro (or perhydro) aromatics.

Although the crystal structure of $C_6F_6AsF_6$ has not been defined with satifactory precision because of the degradation of single crystals in the X-ray beam (even at 143 K), the structure has a rhombohedral unit cell containing one formula unit, $C_6F_6AsF_6$. The probable space group is $R\bar{3}$, and the site symmetry for each ion is D_{3d}. Indeed the cation could be essentially of D_{6h} symmetry in this lattice, but the anticipated Jahn–Teller distortion should generate D_{2h} symmetry. The latter distortion could be present and masked by a random placement of the distorted species in the cation sites. The structural arrangement is one of cesium chloride type with each ion surrounded by a rhombically distorted cube of ions of the other kind. Unfortunately, Raman spectra were not obtained for the $C_6F_6AsF_6$ salt, and the infrared spectra are confused by the presence of pyrolysis products. The infrared spectra do indicate AsF_6^- (ν_3 and ν_4 are observed) and fit a slightly modified C_6F_6 behavior consistent with the cationic formulation. Others have observed[26] a Jahn–Teller distortion in $C_6F_6^+$, but there is nothing to indicate that such a distortion is present in crystalline $C_6F_6AsF_6$.

The thermal stability of $C_6F_5CF_3AsF_6$ is even lower than that of the perfluorobenzene relative, and because of this it is even less well characterized structurally, but the similarity of the *g* value from the ESR spectrum to that of $C_6F_6AsF_6$ points to the magnetic behavior being similar to that salt. The *g* value for the broad unresolved resonance observed for crystalline $C_6F_6AsF_6$ was centered at 2.0063. A septet similar to that reported earlier by Bazhin et al.[2] for $C_6F_6^+$ in superacid solutions was observed for a dilute solution of $C_6F_6^+Sb_2F_{11}^-$ in SbF_5 at 77 K with a $g = 2.003$ also in agreement with the value given by the earlier workers. These free electron-like *g* values are in harmony with the simple Curie law paramagnetism observed for $C_6F_6AsF_6$. Although the presence of thermal decomposition products in the samples prevented reliable determination of the magnetic moment, the susceptibility dependence upon temperature followed the simple Curie law. This shows that the radical cations, which are well separated and screened from one another in the $C_6F_6AsF_6$ lattice, are not interacting measurably at 4 K. The same Curie law behavior is also observed in $C_{10}F_8AsF_6$, where the magnetic interactions between the cations must again be negligible.

Even though $C_{10}F_8AsF_6$ is readily soluble in anhydrous HF and other solvents, all efforts to grow single crystals have failed. The X-ray powder data, however, were indexed and indicate a tetragonal unit cell (see Experimental Section). The dimensions of this cell suggest that the cations are aligned with their long axes parallel to the long axis of the unit cell, two such molecules being related by a 4_2 screw axis parallel to the long axis. The exact arrangement of cations and anions is not known, but packing and symmetry considerations indicate that the anions must be symmetrically placed between facing cations and the cations thus screened well from one another, in accord with the observed simple paramagnetism.

In none of the $C_{10}F_8^+$ salt syntheses had there been any indication of the existence of a polymeric-cation salt analogous to the $(C_{10}H_8)_2^+PF_6^-$ salt described by Fritz and his co-workers.[27] Face-to-face bonding of $C_{10}F_8$ with $C_{10}F_8^+$ appears not to be energetically favorable. This may be a consequence of the repulsive interaction of the electron-rich F ligands (particularly because of those electrons occupying the orbitals[28] of carbon–fluorine π-bonding character). The failure of the partially occupied π orbitals of the perfluoroaromatic cations to provide for effective bonding of the cations to one another has great impact on the physical properties of the salts. Thus the perfluoro cation salts are electrical insulators (and simple paramagnets) whereas perhydropolycyclic relatives,[22] and such salts[27] as $(C_{10}H_8)_2^+PF_6^-$, are metallic.

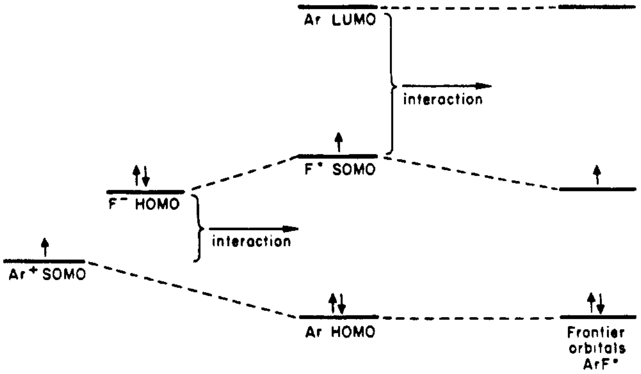

Figure 1. The interaction of Ar^+ with F^-.

Relationship of Thermal Degradation to F^- Attack Products. That the interaction of the radical cations with nucleophiles has the potential of providing a special derivative chemistry is indicated by the products of F^- attack found in this work. One specific diene is obtained in quantitative yield in each instance. The thermal degradation of the salts yields the same fluorocarbon products as the F^- attack, indicating that the first step of the pyrolysis involves F^- transfer from anion to cation.

The interaction of F^- with the radical cation Ar^+ (see Figure 1) involves[29] interaction of the HOMO of the F^- with the SOMO of the cation and electron transfer from the former to the latter. The subsequent step is equivalent to the interaction of $F^\bullet$ radical with the aromatic molecule Ar. In this the interaction is strongest at the atom of Ar which makes the largest contribution to the LUMO. This initiates formation and location of the new C–F bond.

The ^{19}F NMR spectra of the reaction products from the attack on $C_6F_6AsF_6$ by F^- show that the fluorocarbon products are C_6F_6 and the 1,4-diene in a 1:1 molar ratio. These products are exactly the same as in the pyrolysis of the salt. The production of equimolar quantities of C_6F_6 and the diene C_6F_8 in both of these reactions is in harmony with rapid transfer of an electron from the addition product radical, $C_6F_7^\bullet$, to another $C_6F_6^+$ ion.[30]

$$C_6F_7^\bullet + C_6F_6^+ \rightarrow C_6F_7^+ + C_6F_6 \qquad (10)$$

The nature of the diene formed in the interaction of a second F^- with the $C_6F_7^+$ is determined by the LUMO of the latter. The π system of the cyclohexadienyl cation is essentially that of a pentadienyl entity. The π orbitals of an idealized pentadienyl system, simply represented, are

I II III IV V

In the cation, the nonbonding orbital (III) is the LUMO. However, the situation is a little more complex in the case of $C_6F_7^+$ because of the high electronegativity of the carbon atom of the CF_2 group which causes the nodes to be swung toward the electronegative center. This amounts to a mixing of I and III and the LUMO has the form VI. Thus the interaction of F^- with the

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(26) Bondybey, V. E.; Miller, T. A.; English, J. H. *J. Am. Chem. Soc.* **1979**, *101*, 1248–1252. Sears, T. J.; Miller, T. A.; Bondybey, V. E. *J. Chem. Phys.* **1981**, *74*, 3240–3448.

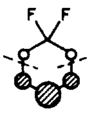
(27) Fritz, H. P.; Gebauer, H.; Friedrich, P.; Schubert, U. *Angew. Chem.* **1978**, *90*, 305–306.

(28) Hexafluorobenzene has two sets of π orbtials: the lowest energy set (six orbitals) is primarily of C–F π-bonding character and is fully occupied; the higher energy set (six orbitals) is C–F π-antibonding but the occupied orbitals (three) also have ring π-bonding character (see Yim and Brundle (Yim, M. B; Wood, D. E. *J. Am. Chem. Soc.* **1976**, *98*, 2053–2057. Brundle, C. R.; Robin, M. B.; Kuebler, N. A. *J. Am. Chem. Soc.* **1972**, *94*, 1466–1475) for evidence on the relative energies of the molecular orbitals).

(29) We are indebted to Professor A. Streitwieser, Jr., for pointing out the details of the transition state for the $Ar^+ + F^-$ interaction, which are crucial to the understanding of the F^- addition ortho to E in the interaction with $C_5EF_5^+$.

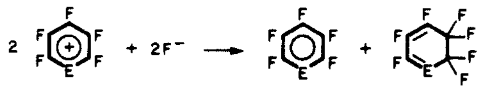
(30) Arsenic pentafluoride is a strong fluoride ion acceptor (ref 15) with $\Delta H°(AsF_{5(g)} + F_{(g)}^- \rightarrow AsF_{6(g)}^-) = -111 \pm 4$ kcal mol^{-1} whereas $C_6F_7^\bullet$ must be a very weak acid. Hence the F^- transfer from AsF_6^- to C_6F_7 can be ruled out.

$C_6F_7^+$ is strongest at the carbon atom para to the CF_2 group. This accounts for the 1,4-diene product.



VI

In the case of the perfluorotoluene cation salts, both F^- attack and pyrolysis again yield half a mole of the parent fluoro aromatic molecule and half a mole of diene. But now the diene is wholly the 1,3-diene. These findings are essentially the same as those for the perfluoropyridine radical cation salts,[13] where F^- attack and pyrolysis produce half a mole each of C_5NF_5 and 1,3-C_5NF_7. With representation of the more electronegative centers (C·CF_3 and N) by E, the interaction is

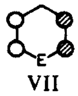


(11)

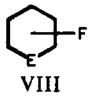
That there must be strict electronic control of the reaction course which leads to the 1,3-diene is indicated by the observation that the diene subsequently isomerizes in the toluene case[31] to a 1:1 mixture of 1,3- and 1,4-dienes.

(12)

Unlike the $C_6F_6^+$ case, the site of F^- attack at the cation $C_5EF_5^+$ is crucial to the determination of which diene can subsequently form. The SOMO of $C_5EF_5^+$ has the form VII, and this means[29]

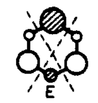


VII

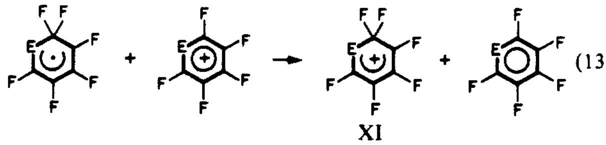


VIII

that the early transition state has F^- adding to $C_5EF_5^+$ as in VIII. The subsequent electron transfer from F^- HOMO to $C_5EF_5^+$ SOMO is followed by F• orbital interaction with the C_5EF_5 LUMO. The latter has the form IX. Since the node in SOMO VII determines the early-transition-state geometry VIII, the F• orbital (now SOMO) interaction with IX is determined by the large coefficients for the atoms ortho to E. This leads to radical X. This radical must lose an electron to another $C_5EF_5^+$. The nature of the $C_5EF_6^+$ LUMO of XI determines the site of the subsequent F^- attachment. That LUMO differs markedly from VI.



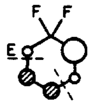
IX



(13)

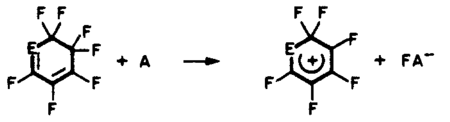
XI

Because of the high electronegativity and excellent π-bonding character of the ring atom at E the nodes of the LUMO are swung toward E relative to their situation in VI and the LUMO has the form XII (the coefficients are exaggerated to clearly illustrate the effect of the nodal planes displacement). The preference for F^- attachment at the site ortho to CF_2 and meta to E accounts for the formation of the 1,3-diene.



XII

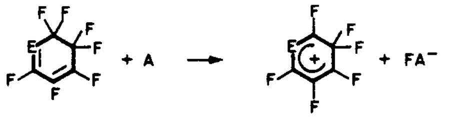
Since the isomerization of the 1,3- to the 1,4-diene represented by eq 12 leads to an approximately 1:1 mixture, these isomers must be of comparable thermodynamic stability. It appears that the isomerization requires the presence of a fluoro acid, A (AsF_5 was present in twofold molar excess of the original 1,3-diene), hence it is likely that the first step in the isomerization involves F^- abstraction. Formation of cation XI



(14)

XI

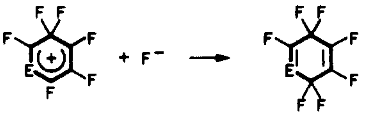
should lead to re-formation of the 1,3-diene for the reasons previously given. On the other hand, abstraction of F^- to generate cation XIII



(15)

XIII

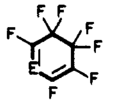
provides a new pentadienyl system. Since E is at the node of the idealized LUMO III, its influence is minimal and the LUMO of XIII closely resembles the $C_6F_7^+$ LUMO, VI. Therefore, F^- attachment at cation XIII should occur preferentially at the site para to the CF_2 group, thus providing for the observed 1,4-diene



(16)

XIV

Of course F^- abstraction from the 1,4-diene XIV at the CF_2 ortho to E merely provides for repetition of the process in eq 16. In the case of F^- abstraction from the 1,4-diene XIV at the CF_2 meta to E, cation XI is formed and this again gives rise to the original 1,3-diene. Thus by F^- abstraction from each of the dienes, followed by F^- addition, each of the two observed dienes would be generated. These mechanisms, without other rearrangements in the intermediates, do not provide for the formation of the other possible 1,3-diene XV. It is not observed as a reaction product from the $C_5EF_5^+$ salts, and its synthesis via radical cation salts appears to be ruled out.



XV

The thermal decomposition of the monocyclic cation salts must occur as a consequence of F^- transfer from anion to cation. Clearly, for the highest thermal stability, the best fluoride ion acceptors must be employed. These are SbF_5 (for SbF_6^-, $Sb_2F_{11}^-$, and $Sb_3F_{16}^-$ salts) and AsF_5 (for AsF_6^- salts).

Experimental Section

All manipulations were carried out in Kel-F, Teflon FEP, or fused silica reaction vessels attached to a stainless steel or Monel fluorine-type vacuum system and/or in a Vacuum Atmospheres inert atmosphere Dri-lab. Hexafluorobenzene, octafluorotoluene, octafluoronaphthalene (PCR Inc., Gainesville, FL), sulfur dioxide, anhydrous hydrogen fluoride (Matheson, E. Rutherford, NJ), cesium fluoride (ROC/RIC, Sun Valley, CA), trifluoroacetic acid (Aldrich, Milwaukee, WI), and tungsten hexafluoride, arsenic pentafluoride, and antimony pentafluoride (Ozark-Mahoning, Inc., Tulsa, OK) were used as received after their purity was checked by infrared spectroscopy. Dioxygenyl salts[32] and rhenium[33] and

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(31) It may be that comparable isomerization of the 1,3-diene derived from the perfluoropyridine cation is prevented by the formation of a stable N adduct with the AsF_5.

(32) (a) Shamir, J.; Binenboym, J. *Inorg. Chim. Acta* **1968**, *2*, 37–38. (b) McKee, D. E.; Bartlett, N. *Inorg. Chem.* **1973**, *12*, 2738–2740.

iridium[34] hexafluorides were prepared by literature methods. Sulfuryl chloride fluoride (Ozark-Mahoning) was distilled from O_2AsF_6 before use to convert the SO_2Cl_2 impurity to SO_2ClF, with elimination of Cl_2.

Infrared spectra were obtained with Perkin-Elmer 337 and 597 infrared spectrophotometers. Raman spectra were recorded on a J-Y Ramanor HG-2S double monochromator in conjunction with Spectra-Physics 165 Kr ion and Coherent Radiation Ar ion lasers. ^{19}F NMR spectra were recorded on a Varian Associates NV-14 NMR spectrometer. Debye–Scherrer X-ray powder photographs of samples contained in dry thin-walled quartz capillaries (Charles Supper Co.) were obtained on a General Electric Powder Camera utilizing Ni-filtered Cu radiation. Precession photographs of single crystals of $C_6F_6AsF_6$ were taken with a Polaroid cassette on an Enraf-Nonius precession camera with Zr-filtered Mo radiation. Magnetic susceptibility measurements were carried out with a Princeton Applied Research vibrating sample magnetometer. ESR spectra were recorded on Varian Associates V4500 and E-3 spectrometers.

Synthesis of Perfluoro Aromatic Radical Cation Salts. Hexafluorobenzene Hexafluoroiridate(V). Hexafluorobenzene (2.6 mmol) was dissolved in tungsten hexafluoride (2 mL) in a fused silica reactor to give a yellow-green solution. Iridium hexafluoride (2 mmol) was condensed into the reactor at 77 K. At about 273 K, the reaction mixture melted, and a bright orange solid rose to the surface of the WF_6. The solvent and excess C_6F_6 were removed under vacuum at 298 K. The dry orange solid decomposed rapidly, producing volatile carbon fluorides. Some of the iridium was reduced to the metal.

Hexafluorobenzene and Octafluorotoluene Hexafluoroarsenates(V). The bright yellow monocyclic cation hexafluoroarsenates were typically prepared (eq 17) by co-condensing at 77 K approximately 2 mmol of the

$$Ar + O_2AsF_6 \rightarrow Ar^+AsF_6^- + O_2 \qquad (17)$$

aromatic species with 2 mL of either tungsten hexafluoride or sulfuryl chloride fluoride with 1.5 mmol of dioxygenyl hexafluoroarsenate in a pre-passivated fused silica reaction vessel equipped with a Whitey 1KS4-SS valve. The vessel was warmed slowly. The vigorous reaction, which ensued as soon as the solvent began to melt, was complete at 273 K in WF_6, or at 233 K in SO_2ClF. Neither the dioxygenyl salt nor the product is soluble in either solvent; hence the product is a very fine powder. In order to ensure complete removal of unreacted reagents and volatile byproducts (these were found to be minimized by the use of SO_2ClF), the reaction vessel was evacuated at 273 K and then cooled to 195 K for storage. Purification of the hexafluoro arsenates was achieved by rapid evacuation of the storage vessel at room temperature.

Hexafluorobenzene Fluoroantimonates. Fluoroantimonate salts, prepared in a similar manner from O_2SbF_6 and $O_2Sb_2F_{11}$, proved to be somewhat more thermally stable than the hexafluoroarsenates, although partial decomposition of the former gave materials of mixed composition due to formation of bridged polyanions $Sb_2F_{11}^-$ and $Sb_3F_{16}^-$ by reaction with SbF_5 formed in the thermal degradation reaction. Yields were generally about 60% but were strongly dependent upon the effectiveness of the heat dissipation; local heating caused decomposition of the product in each case.

Octafluoronaphthalene Hexafluoroarsenate(V). Emerald green $C_{10}F_8AsF_6$ (mp 395 K) was prepared directly from O_2^+ salts (as above), by metathesis (eq 18), from arsenic pentafluoride (eq 19), or from a mixture of arsenic pentafluoride and elemental fluorine (eq 20). The last was

$$C_{10}F_8 + C_6F_6AsF_6 \xrightarrow{SO_2ClF} C_{10}F_8AsF_6 + C_6F_6 \qquad (18)$$

$$2C_{10}F_8 + 3AsF_5 \xrightarrow{SO_2ClF} 2C_{10}F_8AsF_6 + AsF_3 \qquad (19)$$

$$C_{10}F_8 + AsF_5 + (1/2)F_2 \xrightarrow{CCl_3F} C_{10}F_8AsF_6 \qquad (20)$$

found to be the most effective route to this octafluoronaphthalene salt but is inapplicable to the syntheses of the monocyclic salts due to their relative instability at the temperatures required to maintain the starting materials in solution. $C_{10}F_8AsF_6$ was prepared in quantitative yield by metathesis: $C_{10}F_8$ (2.3 mmol) was added to $C_6F_6AsF_6$ (excess) in SO_2ClF. The reaction was complete in 30 min at 233 K. Unreacted $C_6F_6AsF_6$ was decomposed at 298 K, and the decomposition product was pumped away, leaving pure $C_{10}F_8AsF_6$ (2.3 mmol).

Octafluoronaphthalene Hexafluororhenate(V). Octafluoronaphthalene (0.42 mmol) was dissolved in dry trichlorofluoromethane (0.5 mL) at 273 K in a fused silica vessel. A slight excess of rhenium hexafluoride was admitted to the reaction vessel, causing the deep green octafluoronaphthalene hexafluororhenate(V) to precipitate at the vapor–liquid interface. The reaction was complete in less than 1 min. The reaction vessel was evacuated at 295 K to remove the solvent and unreacted rhenium hexafluoride, leaving the dry, free-flowing product, $C_{10}F_8ReF_6$ (0.42 mmol, 100% yield).

Table I. Vibrational Frequencies of $C_{10}F_8^+$

	$C_{10}F_8$ (solid)		$C_{10}F_8^+$ in AsF_6^- Salt	
assignment[a]	IR	Raman	IR	Raman
		166 mw		164 w
				190 w
$\nu_{28}(b_{3g})$		291 m		284 w
$\nu_8(a_g)$		301 sh		
$\nu_{23}(b_{1u})$	317 w			
$\nu_{43}(b_{3g})$		339 mw		331 w
$\nu_{15}(b_{1g})$, $\nu_{27}(b_{2g})$		375 vs		382 m
$\nu_7(a_g)$		394 sh		396 m
$\nu_{34}(b_{2u})$	405 m			
				420 vvs
		432 vw	434 w	432 sh
$\nu_6(a_g)$		512 s		517 ms
$\nu_{42}(b_{3g})$		528 vw		540 w
$\nu_{22}(b_{1u})$	531 mw			
		577 vw		580 w
$\nu_{26}(b_{2b})$		601 mw		
		642 vw		646 s
$\nu_{45}(b_{3u})$	670 mw		675 w	
$\nu_{25}(b_{2g})$, $\nu_{41}(b_{3g})$		758 m		750 m
$\nu_{33}(b_{2u})$	784 s		790 s	784, 792 mw
$\nu_{21}(b_{1u})$	803 sh			
$\nu_{20}(b_{1u})$	946 s		940 vw	
	970 vw		977 s	
	1022 vw			
	1044 vw			
$\nu_5(a_g)$		1071 w		
$\nu_{40}(b_{3g})$		1083 vw		1097 mw
$\nu_{32}(b_{2u})$	1120 s		1118 vw	1122 m
	1145 vw		1135 w	
	1160 w		1170 s	
$\nu_{19}(b_{1u})$	1203 s	1198 w		
$\nu_4(a_g)$		1236 w	1245 s	
$\nu_3(a_g)$		1370 s	1380 s	1374 w
		1394 vw	1400 sh	1396 w
$\nu_{18}(b_{1u})$	1413 s		1415 w	1411 s
	1430 m		1450 sh	1451 m
$\nu_{30}(b_{2u})$	1480 s		1465 s	
	1547 w		1545 s	1556 m
			1580 s	
$\nu_1(a_g)$	1619, 1624 m			1629 m
$\nu_{17}(b_{1u})$	1660 s		1690 m	
	1705 w		1725 w	

s = strong, m = medium, w = weak, sh = shoulder

[a] Assignments after: Girlando, A.; Tamurini, B.; Pecile, C. *J. Chem. Soc., Faraday Trans. 2* **1974**, *70*, 6.

Table II. Magnetic Susceptibility Data for $C_6F_6AsF_6$ and $C_{10}F_8AsF_6$

T (K)	$1/\chi m$ (cgs units)	*T* (K)	$1/\chi m$ (cgs units)
	$C_6F_6AsF_6$		$C_{10}F_8AsF_6$
3.8	16.5	5.8	19.5
5.6	22.9	15.8	52.9
8.3	37.6	30.5	99.0
10.2	50.5	45.6	147.0
14.7	73.1	60.0	192.0
18.6	91.9	74.0	231.0
23.9	116.4		
29.3	136.4		
38.5	196.5		
45.6	255.0		
51.8	297.5		
71.5	375.7		

Solvents for Radical/Cation Salts. All of the perfluoro aromatic cation salts are readily soluble in anhydrous hydrogen fluoride, antimony, and iodine pentafluorides and in dry sulfur dioxide. The marked dependency of solubility in HF on temperature provided for the formation of crystals useful for single-crystal X-ray diffraction studies in the case of $C_6F_6AsF_6$. The freshly prepared salt was dissolved in anhydrous HF at room temperature and the solution cooled slowly to 195 K, when amber-colored

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(33) Malm, J. G.; Selig, H. *J. Inorg. Nucl. Chem.* **1961**, *20*, 189–197.
(34) Ruff, O.; Fischer, J. *Z. Anorg. Allg. Chem.* **1929**, *179*, 161–185.

Table III. X-ray Powder Data for $C_6F_6AsF_6$[a]

hex *hkl*	rhomb *hkl*	d_{hkl}	$10^4/d^2$-(calcd)	$10^4/d^2$-(obsd)	rel intensity
101	010	5.84	290	293	w
110	$01\bar{1}$	5.29	359	357	vvs
021	$11\bar{1}$	3.294	650	650	s
012	110	3.532	802	802	vs
211	$02\bar{1}$	3.151	1009	1007	vs
300	$\bar{1}2\bar{1}$	3.054	1078	1072	vvw
202	020	2.948	1161	1151	vw
122, 003	$12\bar{1}$, 111	2.550	1520, 1534	1537	w
131	$12\bar{2}$	2.408	1728	1725	w
113	120	2.308	1893	1877	vvw
312	$03\bar{1}$	2.118	2239	2229	m
321	$03\bar{2}$	2.021	2447	2448	w
303	030	1.955	2612	2615	w

[a] Rhombohedral unit cell: $a_0 = 6.60$ (1) Å, $\alpha = 106.0$ (1)°, $V = 246.1$ Å^3, $Z = 1$. Probable space group $R\bar{3}$, hexagonal unit cell: $a_0 = 10.55$ (1) Å, $c_0 = 7.66$ (1) Å, $V = 738.4$ Å^3, $Z = 3$ (for observed reflections $-h + k + 1 = 3n$).

Table IV X-ray Powder Data for $C_{10}F_8AsF_6$ (Cu Kα Ni Filter)[a]

	data for sample at ~20 °C			data for sample at −60 °C	
	$(1/d^2) \times 10^4$			$(1/d^2) \times 10^4$	
I/I_0	obsd	calcd	*hkl*	obsd	calcd
w	119	114	002		116
m	145	145	100	145	146.5
vvw	159[b]				
m	176	173	101	176	176
vw	261	259	102		
vw	294	290	110		
m	323	318	111	322	322
vw	372[b]				
s	406	401 404	103 112	410	408 409
mw	460	454	004	465	464
w	502[b]				
s	552	546	113	559	554
vw	572	580	200		
s	613	608	201	617	615
vvw	641[b]				
vs	699	694	202	712	702
vs	758	753	211	767	762
vvw	798[b]				
mw	844	836 836	203 212	858	847 849
vw	867	855	105		
vw	988	981	213	1008	995
vw	1021	1022	006		

[a] Tetragonal unit cells with (20 °C) $a_0 = 8.30$ (1) Å, $c_0 = 18.76$ (1) Å; (−60 °C) $a = 8.26$ (1) Å, $c_0 = 18.57$ (2) Å. [b] These lines are not indexable on the basis of a tetragonal cell and could be due to an impurity.

Table V. X-ray Powder Data for $C_{10}F_8ReF_6$ (Cu Kα Ni Filter) at 293 K

I/I_0	$(1/d^2) \times 10^4$ (obsd)	I/I_0	$(1/d^2) \times 10^4$ (obsd)
vw	119	w	1760
vs	142	mw	1814
s	245	w	1922
w	276	w	1993
m	301	m	2128
s	394	m	2227
vw	440	w	2356
s	480	m	2475
s, br	583	w	2580
s	658	w	2678
vw	731	m	2765
s	792	m	2964
ms	832	w	3177
m	905	w	3387
m, br	1114	vw	3713
w	1221	vw	3801
w	1277	vw	4100
w	1324	w	4531
w	1359	vw	4815
w	1473	vw	5148
w	1530	vw	5853
vw	1657		

needle-like crystals formed. Solvation by SO_2 prevented its use in growing single crystals of this and other radical cation salts. Poorly crystalline materials were recovered from SbF_5 and IF_5 solutions perhaps because of the loss of solvent of crystallization from the first-formed crystals.

Reactions of Perfluoro Aromatic Cation Salts. Nitric Oxide. The reaction

$$C_6F_6{}^+AsF_6 + NO \rightarrow NO^+AsF_6{}^- + C_6F_6 \qquad (21)$$

was always accompanied by some decomposition due to local heating. The controlled reduction of $C_6F_6{}^+$ salts with nitric oxide was, however, useful in establishing the stoichiometry of these materials. Freshly prepared $C_6F_6AsF_6$ (0.66 mol) was exposed to dry NO gas in a fused silica reactor, producing $NOAsF_6$ (0.64 mol, identified by its Raman spectrum and X-ray powder pattern) and C_6F_6 (0.68 mol, identified by NMR spectroscopy). The octafluorotoluene salt behaved similarly. $C_{10}F_8AsF_6$ did not react with NO.

Thermal Decomposition. $C_6F_6AsF_6$ decomposes smoothly at room temperature with a half-life of 15–20 min to arsenic pentafluoride and a colorless liquid, shown by infrared and ^{19}F NMR spectroscopy to be a 1:1 mixture of hexafluorobenzene and octafluoro-1,4-cyclohexadiene, C_6F_8.[35]

$C_6F_5CF_3AsF_6$ decomposes in a similar fashion to give arsenic pentafluoride and initially a 1:1 mixture of octafluorotoluene and 1,2,3,5,5,6,6-heptafluoro-4-(trifluoromethyl)-1,3-cyclohexadiene, $C_6F_7CF_3$ [NMR shifts[36] relative to internal CCl_3F: 58.8 (3), 104.1 (2), 113.5 (2), 114.9 (1), 153.2 (1), 159.0 (1)]. This 1,3-diene isomerized over a period of 3 days at room temperature in the presence of trifluoroacetic acid and AsF_5 to a 1:1 mixture of the 1,3-diene and 1,2,3,3,4,6,6-heptafluoro-5-(trifluoromethyl)-1,4-cyclohexadiene[37] [58.4 (3), 110.0 (1), 118.2 (2), 125.9 (2), 150.4 (1), 152.1 (1)].

$C_{10}F_8AsF_6$ is stable at room temperature, melting with slow decomposition at 395 K. The products of thermal decomposition are arsenic pentafluoride, octafluoronaphthalene, and a complex residue containing traces of decafluoro-1,4-dihydronaphthalene, $C_{10}F_{10}$ (identified by its ^{19}F NMR spectrum).[38]

Cesium Fluoride. Closely related to the thermal decomposition reactions are the interactions of the aromatic cation salts with cesium fluoride (see Discussion). $C_6F_6AsF_6$ in HF solution reacts rapidly with excess cesium fluoride, producing cesium hexafluoroarsenate and the 1:1 mixture of C_6F_6 and 1,4-C_6F_8 described above. $C_{10}F_8AsF_6$ reacts more slowly with CsF, the green color of the radical cation persisting for up to 1 h. The products found were the same as in the thermal decomposition.

Hydrolysis of $C_{10}F_8AsF_6$. Octafluoronaphthalene hexafluoroarsenate (1.1 mmol) reacted with excess water in the presence of CCl_4 (5 mL) to give a yellow solid. The ^{19}F NMR of this solid dissolved in methanol and benzene (1:1) showed it to be a 1:1 mixture of octafluoronaphthalene and hexafluoro-1,4-naphthalenedione, $C_{10}F_6O_2$.[39]

Vibrational Spectra. Infrared spectra were obtained by pressing the freshly prepared powders between silver chloride plates. In the case of $C_6F_6AsF_6$, products of thermal decomposition were present in each spectrum. By recording spectra at successive stages of decomposition, however, it was possible to distinguish those features due to the radical cation salt. In addition to the characteristic absorptions due to $AsF_6{}^-$,

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(35) Burdon, J.; Whiffen, D. H. *Spectrochim. Acta* **1958**, *12*, 139–142. Hoehn, H. H.; Pratt, L.; Watterson, K. F.; Wilkinson, G. *J. Chem. Soc.* **1961**, 2738–2745.

(36) Integrated relative intensities in parentheses. Peak assignments and multiplicities are as follows: CF_3 (doublet of triplets), 5-F (multiplet), 60F (quartet), 3-F (multiplet), 2-F (septet), 1-F (multiplet). The composition C_7F_{10} is established by peak intensity integration. The large coupling constant J_{65} (22 Hz) for the alicyclic (CF_2) groups confirms the 1,3-diene structure. Coupling is also observed between the trifluoromethyl group and 5-F but not 6-F, thus ruling out the 3-CF_3 isomer.

(37) Integrated relative intensities in parentheses. Peak assignments and multiplicities are as follows: CF_3 (triplet), 4-F (multiplet), 6-F (multiplet), 3-F (triplet), 1-F (quartet), 2-F (triplet). This composition is also shown to be C_7F_{10} by peak integration. Here no coupling is observed between the CF_2 groups. The similarity in the chemical shifts of the CF_3 groups in the two dienes indicates a similar CF_3 environment in each case.

(38) Feast, W. J.; Hughes, R. R.; Musgrave, W. K. R. *J. Fluorine Chem.* **1977**, *10*, 585–604.

(39) Blum, Z.; Nyberg, K. *Acta Chem. Scand.* **1979**, *B33*, 73–75.

J. Am. Chem. Soc. **1986**, *108*, 4943–4952

two strong bands appeared at 1490 and 1030 cm^{-1}, which correspond to similarly strong absorptions at 1530 cm^{-1} and at 1019 and 994 cm^{-1} in neutral hexafluorobenzene. The infrared spectrum of $C_6F_5CF_3AsF_6$ was too complex to allow absorption due to the cation to be distinguished from those due to decomposition products. Intense fluorescence and thermal instability of the monocyclic cations prevented the recording of their Raman spectra even at very low temperatures. The Raman spectrum of $C_{10}F_8AsF_6$ was obtained by employing a Teflon rotating sample cell with a sapphire window. While the majority of vibrational modes in the cation are shifted only slightly in frequency from those in the neutral molecule, the relative intensities of some IR absorptions and Raman lines are greatly changed. In addition, the most intense feature in the Raman spectrum of $C_{10}F_8AsF_6$ (the band at 420 cm^{-1}) has no observed counterpart in $C_{10}F_8$. The absence in the Raman spectrum of $\nu_1(AsF_6^-)$ (which is ordinarily a strong band) hints at absorption enhancement of the cation Raman spectrum. On the whole, however, the overall framework of the molecule appears to be altered little by ionization. Moreover, the mutual exclusion of the IR and Raman activity appears to hold for the $C_{10}F_8^+$ ion (see Table I). Therefore, it is likely that the cation is at least approximately centrosymmetric in its lattice site. It may retain the D_{2h} symmetry of the parent molecule.

Magnetic Susceptibility and ESR Spectra. The magnetic susceptibility of $C_6F_6AsF_6$ (Table II) obeys the Curie law down to 3.8 K. The low effective moment of 1.3 μ_B is probably due, at least in part, to decomposition of the pressure- and temperature-sensitive compound during manipulation to the degradation products which are diamagnetic. A higher moment was obtained for the more stable $C_{10}F_8AsF_6$, which also exhibits Curie law behavior over the range 74 to 5.8 K. For that salt μ (eff) = 1.68 μ_B.

ESR spectra of dilute solutions of $C_6F_6Sb_2F_{11}$ in SbF_5 at 77 K consist of a septet (J = 20 Hz) centered at g = 2.003, in agreement with results reported by Bazhin et al.[1] for solutions of C_6F_6 in superacid media. ESR spectra of $C_{10}F_8AsF_6$ in anhydrous HF or SbF_5 at 4 K were unresolved, symmetrical resonances with g = 2.004.

X-ray Diffraction. The Debye–Scherrer X-ray powder pattern of $C_6F_6AsF_6$ is given in Table III. Single crystals of $C_6F_6AsF_6$ were grown as described above. Due to thermal degradation and resultant fragmentation of these crystals, it proved impossible to collect sufficient high-quality diffractometer data for a complete structure determination. Precession photographs did, however, establish the identity of the crystals and the bulk powder from which they were prepared. The data are consistent with a rhombohedral unit cell: a = 6.60 (1) Å, α = 106.0 (1)°, ν = 246.1 Å, Z = 1. Efforts to grow single crystals of $C_{10}F_8AsF_6$ were unsuccessful. The powder diffraction pattern, however, has been indexed (Table IV) on the basis of a tetragonal unit cell: (293 K) a_0 = 8.30 (1) Å, c_0 = 18.76 (1) Å, V = 1292 Å^3; (213 K) a_0 = 8.26 (1) Å, c_0 = 18.57 (3) Å, V = 1267 Å^3. Since AsF_6^- has an effective volume of ~105 Å^3 and the effective packing volume of $C_{10}F_8$ in its crystal[40] is 226 Å, the anticipated formula unit volume for the 1:1 salt is ~330 Å^3. The observed unit cell volume is therefore consistent with four formula units. Moreover, the dimensions of the unit cell indicate that the $C_{10}F_8^+$ species may be aligned with its long molecular axis[41] (~9.6 Å) parallel to C. (The c_0 dimension is consistent with the molecules being arranged head to tail on a fourfold axis 4_2.) The X-ray powder data for $C_{10}F_8ReF_6$ have not been fully indexed and are given in Table V. Similarity of the low-angle d spacings with the data for $C_{10}F_8AsF_6$ suggests a close structural relationship, but the salts are not isomorphous.

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Registry No. O_2SbF_6, 12361-66-9; $O_2Sb_2F_{11}$, 12592-38-0; $C_{10}F_8AsF_6$, 71715-93-0; AsF_5, 7784-36-3; $NOAsF_6$, 18535-07-4; C_6F_8, 775-51-9; $C_6F_7CF_3$, 27943-60-8; $C_{10}F_6O_2$, 1024-60-8; C_6F_6, 392-56-3; CsF, 13400-13-0; octafluorotoluene, 434-64-0; octafluoronaphthalene, 313-72-4; iridium hexafluoride, 7783-75-7; hexafluorobenzene hexafluoroiridate(V), 102781-69-1; dioxygenyl hexafluoroarsenate, 12370-43-3; hexafluorobenzene hexafluoroarsenate(V), 53863-36-8; octafluorotoluene hexafluoroarsenate(V), 76097-35-3; hexafluorobenzene·$Sb_2F_{11}^-$, 54189-38-7; hexafluorobenzene·SbF_6^-, 54532-41-1; octafluoronaphthalene hexafluororhenate(V), 102747-22-8; rhenium hexafluoride, 10049-17-9; nitric oxide, 10102-43-9; 1,2,3,3,4,6,6-heptafluoro-5-(trifluoromethyl)-1,4-cyclohexadiene, 31665-17-5; hexadiene, 31665-17-5; CsF, 13400-13-0.

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L-Aspartic Acid in Acyclic Stereoselective Synthesis. Synthetic Studies on Amphotericin B

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Abstract: The development of a potentially general approach to the synthesis of polyketide nature products is presented that features the use of L-aspartic acid as a synthetic equivalent to an asymmetric 1,3-dicarbonyl fragment. Illustrations of the manner in which the rational application of covalent, chelation, and stereoelectronic control can be used to afford products of complementary stereochemistries are given. Thiol ester **9** has been featured as a particularly valuable synthetic intermediate for the preparation of a variety of structural units found in propionate-derived compounds. This methodology has been utilized in a synthesis of the C21–C37 fragment (**35**) of amphotericin B.

The polyene macrolide class of antibiotics have attracted considerable attention for their potent fungicidal properties.[1,2] While the skeletal features of most of the compounds in this group have been determined, a complete structural description has been

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