Nucleophilic Reactions of Pyridines and Imidazoles with Vinyl and Aromatic Halides

Andrew S. Koch, Amy S. Feng, Traci A. Hopkins, and Andrew Streitwieser*

Department of Chemistry, University of California, Berkeley, California 94720

Received September 11, 1992

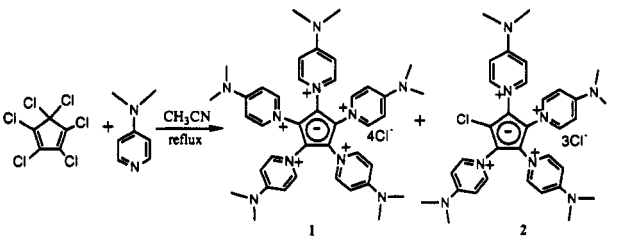
The reaction of 4-(dimethylamino)pyridine (DMAP) with hexachlorocyclopentadiene gives two products, 1,2,3,4,5-pentakis(4-(dimethylamino)pyridinium-1-yl)cyclopentadienyl anion (1) and 1-chloro-2,3,4,5-tetrakis(4-(dimethylamino)pyridinium-1-yl)cyclopentadienyl anion (2). The pK_a of the conjugate acid of 1, with protonation occurring on the cyclopentadienyl ring, is approximately −6. The reaction of DMAP with hexafluorobenzene gives 1,2,4,5-tetrafluoro-3,6-bis(4-(dimethylamino)-pyridinium-1-yl)benzene (3); its X-ray single crystal structure is presented. Upon further treatment of 3 with DMAP, 1-fluoro-2,3,4,5,6-pentakis(4-(dimethylamino)pyridinium-1-yl)benzene (4) is produced. The nucleophiles DMAP, 4-phenylpyridine, 1-methylimidazole, and 1-phenylimidazole were used with 1,2-dichlorotetrafluorocyclobutene to produce, respectively, 1,2-bis(4-(dimethylamino)-pyridinium-1-yl)tetrafluorocyclobutene (5), 1,2-bis(4-phenylpyridinium-1-yl)tetrafluorocyclobutene (6), 1,2-bis(3-methylimidazolium-1-yl)tetrafluorocyclobutene (7), and 1,2-bis(3-phenylimidazolium-1-yl)tetrafluorocyclobutene (8). The electrochemistry of some of these compounds is described.

Several years ago we reported the preparation of the first perpyridinium substituted compounds from the reaction of tetrachlorocyclopropene and 4-(dimethylamino)pyridine (DMAP): 1,2,3,3-tetrakis(4-dimethylamino)-pyridinium-1-yl)cyclopropene and 1,1,2,3,3-pentakis(4-(dimethylamino)pyridinium-1-yl)allylide.[1] The latter was found to form a room-temperature, air-stable allylide radical with a variety of oxidizing agents.[2] This discovery led us to explore related charged systems that could potentially form the basis of novel polymers, for use as modified electrode coatings and as semiconductors. Since the initial report, we have prepared and characterized several types of pyridinium- and imidazolium-substituted compounds derived from perhalogenated unsaturated compounds. Electrochemical experiments were done on the multiply charged products to determine whether they undergo reversible oxidation/reduction. In this paper we report the reactions of some pyridines and imidazoles with hexafluorobenzene, hexachlorocyclopentadiene, and 1,2-dichloro-3,3,4,4-tetrafluorocyclobutene.

Results and Discussion

Hexachlorocyclopentadiene. When hexachlorocyclopentadiene and excess DMAP were heated at reflux in acetonitrile for 4 days, 25% of 1 and 12% of 2 were obtained after recrystallization (Scheme I). Assignments are based on the following data. The ^{1}H NMR spectrum of 1 shows only one type of pyridinium and its ^{13}C NMR spectrum shows one type of pyridinium and one other signal in the aromatic region at 112.6 ppm. UV–vis spectroscopy shows λ_{max} = 308.4 nm (ϵ = 83 600) in water, and the elemental analysis was consistent with the assigned structure, assuming 4.5 waters of crystallization. The ^{1}H NMR spectrum of 2 showed two types of pyridinium, while its ^{13}C NMR spectrum showed two types of pyridinium and three other weak signals in the aromatic region. Compound 2 has λ_{max} at 305.6 nm (ϵ = 58 600) in water. The elemental analysis is consistent with the structure, assuming four molecules of water. Reaction of hexachlorocyclopentadiene with excess DMAP at 120 °C in adiponitrile gave a higher yield of 1, about 80%, in the crude reaction mixture, but the impurities were difficult to remove and reduced the effectiveness of these conditions. It should be noted that formation of 1 and 2 requires a reduction of the cyclopentadiene at some stage, perhaps via nucleophilic attack by DMAP on ring-bound chlorine.

Scheme I. Reaction of Hexachlorocyclopentadiene with DMAP



1 2

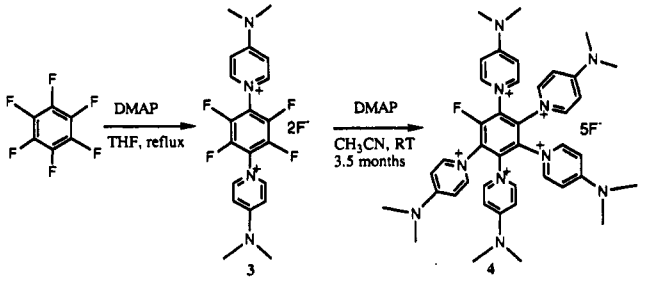
The ^{1}H NMR spectrum of the sulfate salt of 1 in 16 M D_2SO_4 showed the α-protons of the DMAP units splitting to three signals in a 1:2:2 ratio. The β-protons split into a doublet of doublets and the dimethylamino methyl protons split into three overlapping signals. The pronounced change of the α-protons indicates that protonation occurs on the cyclopentadienyl ring. Compound 1 was completely unprotonated in 10 M DCl, and a 1:1 ratio of the protonated and nonprotonated species, as determined by integration of the α-protons of the DMAP units, was observed in 12.5 M D_2SO_4. This medium has H_0 of about −6.4,[3] hence the pK_a of the protonated 1 is about −6. This pK_a value falls between those of pentakis(trifluoromethyl)-cyclopentadiene[4] and pentacyanocyclopentadiene,[5] pK_a = −2 and −11, respectively. Both 1 and 2 are thermally stable in both the solid state and in solution, even in the presence of base, but 1 decomposed in concd D_2SO_4 over several days.

Hexafluorobenzene. Reaction of hexafluorobenzene with 5 equiv of DMAP in refluxing THF gave a yellow

(1) Waterman, K. C.; Streitwieser, A. *J. Am. Chem. Soc.* **1984**, *106*, 3874.
(2) DiMagno, S. G.; Waterman, K. C.; Speer, D. V.; Streitwieser, A. *J. Am. Chem. Soc.* **1991**, *113*, 4679.
(3) Rochester, C. H. *Acidity Functions*; Academic Press: London, 1970.
(4) Laganis, E. D.; Lemal, D. M. *J. Am. Chem. Soc.* **1980**, *102*, 6633.
(5) Webster, O. W. *J. Am. Chem. Soc.* **1966**, *88*, 3046.

0022-3263/93/1958-1409$04.00/0 © 1993 American Chemical Society

Scheme II. Reactions of Hexafluorobenzene with DMAP



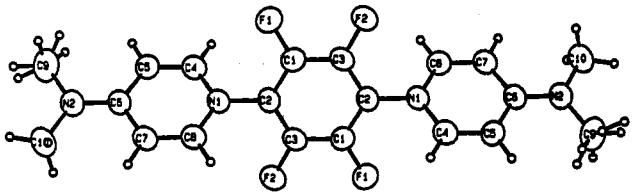


Figure 1. ORTEP drawing of 3.

Table I. Selected Bond Distances of 3

atom 1	atom 2	distance, Å	atom 1	atom 2	distance, Å
C1	F1	1.342 (2)	C1	C2	1.373 (2)
C2	N1	1.428 (2)	N1	C4	1.362 (2)
C4	C5	1.344 (2)	C5	C6	1.421 (2)
C6	N2	1.328 (2)	N2	C9	1.441 (2)

precipitate in 20% yield whose ^{1}H NMR spectrum was indicative of 1,2,4,5-tetrafluoro-3,6-bis(4-(dimethylamino)-pyridinium-1-yl)benzene difluoride (3) (Scheme II). When the reaction was allowed to stir under reflux longer than 1 day, significant amounts of other higher substituted products were formed that complicated the reprecipitations and thus lowered the isolated yield of 3. The ^{1}H NMR spectrum of 3 shows only one type of DMAP, and its ^{19}F NMR spectrum indicates two types of fluorines. Upon ion exchanging to the chloride ion, the ^{19}F NMR signal at −146 ppm disappeared, showing only one peak at −165 ppm for the covalently bound fluorine. It should be noted that the chemical shift of the fluoride ion appears to be concentration dependent. The ^{13}C NMR spectrum shows one type of DMAP and one other carbon at 93.1 ppm. All attempts to find the other ring carbon failed. UV–vis spectroscopy showed λ_{max} at 314 nm (ϵ = 42 000). Elemental analysis was consistent with the assigned structure, assuming three waters of crystallization.

Crystal Structure of 3. Columnar orange-yellow crystals of 3 (BF_4^-) were obtained by slow crystallization from acetonitrile/water at room temperature and the structure was determined by X-ray crystallography. Figure 1 shows the ORTEP drawing of 3. Hydrogen atoms, where represented, are given as arbitrary small spheres. Each unit cell has a crystallographic center of inversion. The BF_4^- counterions are also related by the inversion center. Selected bond lengths and angles are given in Table I. One interesting feature is the dihedral angle of 54.9° between the pyridinium moieties and the benzene ring. This noncoplanarity understandably arises from steric interactions between the pyridinium ring and the ring fluorines. Both pyridinium rings are twisted in the same direction as seen in Figure 1. Note also the disorder shown by two of the methyl groups.

An interesting feature of the pyridinium moieties is that they have a substantial degree of quinoidal character. The bond length between the α- and β-carbons of the pyridinium ring is significantly shorter (1.34 Å) than the bond length between the β- and γ-carbons (1.41 Å). The γ-carbon-to-amino nitrogen distance, 1.33 Å, is between a carbon–nitrogen single and double bond, 1.47 and 1.27 Å, respectively, indicative of significant conjugation. Such conjugation has also been observed for other pyridinium compounds such as 1,2,3,3-tetrakis(4-(dimethylamino)-pyridinium-1-yl)cyclopropene[6] and methyl 3,3-bis(4-(dimethylamino)pyridinium-1-yl)propenoate dichloride.[7] Bond distances within the benzene ring are approximately equal, indicating no distortion of the ring due to the pyridinium groups. The BF_4^- counterions are held tightly between pyridinium groups of different molecules as shown in the unit cell in Figure 2.

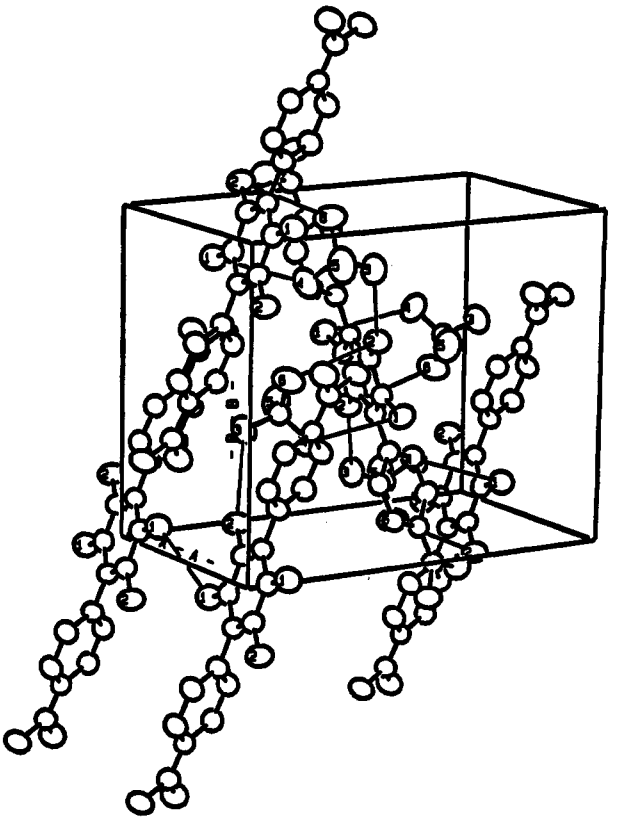


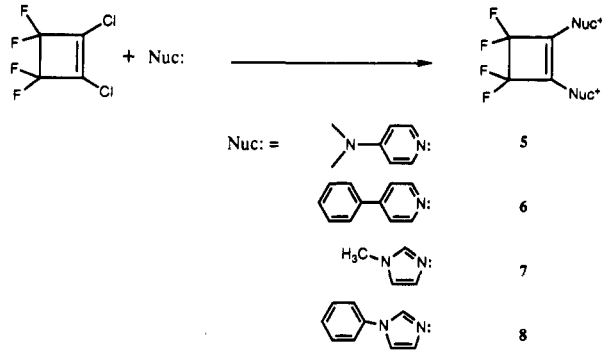
Figure 2. Unit cell of 3.

There are numerous close interactions between the gegenion fluorines and ring-bound fluorines, in addition to the relatively short distances of the ring-bound fluorines of two different molecules. The distance between two fluorines on different phenyl rings is 3.18 Å. There are no solvent molecules associated with the single crystal, unlike the chloride salt of methyl 3,3-bis(4-(dimethylamino)-pyridinium-1-yl)propenoate, in which the chloride ions are heavily solvated by water.[8]

Reaction of DMAP with hexafluorobenzene in more polar solvents gave highly substituted products. In refluxing acetonitrile a compound assigned as 1-fluoro-2,3,4,5,6-pentakis((4-dimethylamino)pyridinium-1-yl)benzene pentafluoride (4) was isolated in low yield from a black tarry product mixture. The reaction proceeded

(6) Feng, A. S.; Speer, D. V.; DiMagno, S. G.; Konings, M. S.; Streitwieser, A. *J. Org. Chem.* **1992**, *57*, 2902.
(7) Koch, A. S.; Waterman, K. C.; Bank, K.; Streitwieser, A. *J. Org. Chem.* **1990**, *55*, 6166.
(8) Waterman, K. C. Ph.D. Dissertation, University of California at Berkeley, 1985.

Scheme III. Nucleophilic Reactions of 1,2-Dichlorotetrafluorocyclobutene



slowly, taking several days before a significant amount of the black tarry precipitate formed that contained 15% of 4, based on the ^{1}H NMR spectrum. When 1,3-dimethyl-2-imidazolidinone (DMEU) or *N*-methyl-2-pyrrolidone (M-Pyrol) was used as the solvent, the reaction occurred facilely at room temperature but also produced more side products.

Assignments are based on the following data. Compound 4 has a λ_{max} at 297 nm, ϵ = 36 000, and a shoulder at 340 nm. The ^{1}H NMR spectrum shows three types of DMAP in a 1:2:2 ratio with no other protons, while its ^{19}F NMR spectrum indicates two types of fluorine. The broad-band decoupled ^{13}C NMR spectrum of 4 (BF_4^- salt) shows signals that are consistent with three different DMAP rings. The signal at 41.00 ppm is broad and unsymmetrical and is assumed to be two different dimethylamino groups overlapping. Elemental analysis of 4 was consistent with the assigned structure assuming one water molecule of crystallization.

Gram quantities of 3 were cleanly converted to 4 by dissolving 3 in a minimum amount of methanol to which was then added a solution of DMAP in acetonitrile or M-Pyrol. The resulting solution left to stand for several weeks gave a 36% yield of 4 after recrystallization. As the reaction proceeded, the disappearance of 3 and the appearance of 4 was followed by ^{1}H NMR spectroscopy, with no sign of the formation of other pyridinium compounds. Thus, the intermediate tri- and tetrasubstituted benzenes necessarily formed are clearly too reactive to accumulate in any appreciable amount. When the reaction of hexafluorobenzene with DMAP was carried out at a pressure of 15 KBar, other uncharacterized products containing pyridinium moieties were observed along with some 4. There was no sign of further addition of DMAP to 4, even when 4 and DMAP were heated to 60 °C at 15 KBar.

1,2-Dichlorotetrafluorocyclobutene. Nucleophiles have been found to react readily with 1,2-dichlorotetrafluorocyclobutene to give the mono- or disubstituted cyclobutene products.[9-11] The reactions of DMAP and 1-methylimidazole with 1,2-dichlorotetrafluorocyclobutene in acetonitrile at 0 °C produced two light yellow precipitates, 1,2-bis(4-(dimethylamino)pyridinium-1-yl)tetrafluorocyclobutene (5) and 1,2-bis(3-methylimidazolium-1-yl)tetrafluorocyclobutene (7), respectively (Scheme III). The ^{1}H NMR spectra of 5 and 7 show only one type of pyridinium and imidazolium groups. Both the ^{13}C decoupled NMR and ^{19}F NMR spectra of 5 and 7 are consistent with the assigned structures. Elemental analyses of the hexafluorophosphate salts of 5 and 7 show no waters of crystallization, whereas the dichloride salt of 5 has one such water. Similar reaction of 1,2-dichlorotetrafluorocyclobutene with 4-phenylpyridine in acetonitrile at 55 °C produced a yellow precipitate in 17% yield. Recrystallization from acetonitrile/diethyl ether produced 1,2-bis(4-phenylpyridinium-1-yl)tetrafluorocyclobutene (6) as yellow plates. The ^{1}H NMR and ^{19}F NMR spectra are consistent with the assigned structure. While both 5 and 7 readily precipitated out of solution, the synthesis and purification of 1,2-bis(3-phenylimidazolium-1-yl)tetrafluorocyclobutene (8) proved to be more difficult. Two crystallizations from diethyl ether/acetonitrile were needed to isolate 8 (BF_4^- salt) as an off-white waxy solid. Its ^{1}H NMR and ^{19}F NMR spectra and elemental analysis are consistent with the assigned structure, assuming two molecules of water.

Table II. Oxidation/Reduction Potentials vs SCE for 1-8 in Acetonitrile

compound (salt)	E^0_{oxid} (V)	E^0_{red} (V)
1 (BF_4^-)		−1.76
2 (BF_4^-)		−1.76
3 (BF_4^-)		−2.20, −1.85, −1.66, −1.10
4 (BF_4^-)		−2.65, −2.40, −2.23, −2.03, −1.24
5 (PF_6^-)	1.32, 1.58	−0.82, −1.02
5 (BF_4^-)		−0.82, −1.05
6 (PF_6^-)		−0.94, −0.79
7 (PF_6^-)		−0.75, −0.45
7 (BF_4^-)		−0.76, −0.52
8 (BF_4^-)		−1.15 V, −0.76

[a] Note that the electrochemical reaction conditions are described in the experimental General section.

Electrochemistry. The results of the electrochemical experiments performed on compounds 1–8 are shown in Table II. Neither 1 nor 2 could be oxidized electrochemically. Irreversible reduction of the pyridinium rings was observed at −1.76V vs SCE. Compound 3 was found to undergo four irreversible reductions at −2.20, −1.85, −1.66, and −1.10 V vs SCE. Since 3 undergoes four reductions and only has two pyridinium moieties, it seems reasonable to assume that the benzene ring is also undergoing reduction. These reductions were found to be irreversible even when scanning was done just up to the point of reduction. Compound 4 was found to undergo five irreversible reductions in acetonitrile with tetrabutylammonium tetrafluoroborate as the supporting electrolyte. Reductions occurred at −2.65, −2.40, −2.23, −2.03, and −1.24 V vs SCE. ($E^0 \cong E_{1/2}$). Each of the substituted cyclobutenes 5–8 underwent irreversible reductions, which usually disappeared after the first five scans. The cyclobutenes tend to adhere to the glassy carbon electrode surface, so that eventually no reduction waves can be seen. It should be noted that the DMAP-substituted cyclobutene 5 (PF_6^- salt) also underwent two irreversible oxidations at 1.32 and 1.58 V vs SCE.

Conclusion

Highly halogenated alkenes and benzenes react with nucleophilic amines such as DMAP and N-substituted imidazoles to give multiply charged products. Many of these products, such as 1–8, undergo irreversible reductions in acetonitrile and show that the resulting radical ions are

(9) Kimoto, H.; Muramatsu, H.; Inukai, K. *Bull. Chem. Soc. Jpn.* **1977**, *50*, 2815–16.
(10) Bauer, G.; Haegele, G. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1979**, *34B*, 1252–9.
(11) Park, J. D.; Pearson, G. G. *J. Flourine Chem.* **1972**, *1*, 277–82.

unstable to the reaction conditions. Accordingly, this result means that these structures have diminished promise as potential monomers for electron-conducting polymers and electrode coatings. Nevertheless, each of the cyclic systems presented is the first pyridinium- or imidazolium-substituted molecule of its type to be reported. They extend the generality of multiply charged compounds in which heterocyclic onium cation rings are joined by conjugating groups.

Experimental Section

General. General experimental procedures, spectroscopy, and materials are as described in our previous work.[6,7,12]

UV-visible spectra were determined with a Hewlett-Parkard 8452A diode array spectrophotometer, for which we thank Professor Mark Bednarski; results are expressed as (solvent), λ_{max} in nm (extinction coefficient).

Gas chromatography (GC) was done with a Hewlett-Packard series 5880 gas chromatograph, with a 0.125 in., 6 ft, SE 30 on Chromosorb column. Thin-layer chromatography (TLC) was performed in 50% hexane/50% ethyl acetate or 100% ethyl acetate. The buffer solutions were calibrated with a Fisher Accumet Model 805 MP pH meter.

Columnar orange-yellow single crystals of **3**, suitable for X-ray analysis, were grown by slow evaporation from acetonitrile/water. Preliminary cell constants and space-group analyses were obtained from precession photographs on an Enraf-Nonius precession camera. Data collection was performed on a CAD4 diffractometer at room temperature. Data were collected by monitoring three intensity standards (4 3 3, 2 7 2, 1 4 $\bar{8}$) every 1 h and by checking three orientation standards (4 3 3, 2 7 2, 1 4 $\bar{8}$) every 200 reflections. Crystal orientation was redetermined if any of the reflections were offset by more than 0.10° from their predicted positions. Reorientation was not needed during data collection.[13] A total of 1606 raw intensity data were collected which were converted to structure factor amplitudes and their ESD's by correction for scan speed, background, and Lorentz and polarization effects. Inspection of the intenstiy standards revealed a reduction of 4% of the original intensity. The data were corrected for this decay. Inspection of the azimuthal scan data showed a random variation $I_{min}/I_{max} = \pm 1\%$ for the average curve. No correction for absorption was applied. Inspection of the systematic absences indicated uniquely space group $P2_1/n$. Removal of systematically absent data left 1506 unique data in the final set. Structure of **3** was solved by direct methods (MULTAN) and refined via standard least-squares and Fourier techniques. Peaks corresponding to the positions of all of the hydrogen atoms were calculated following the refinement of all non-hydrogen atoms with anisotropic thermal parameters in a difference Fourier map. Hydrogen atoms were included in the structure at their calculated positions with d(C–H) = 0.95 Å and with an isotropic thermal parameter 1.2 times the equivalent isotropic thermal parameter of the carbon to which they are attached. The final cycle of least-squares refinement yielded R = 2.98%, R_w = 4.32%, and GOF = 2.19. The R value for all 1506 data was 4.00%.

Cyclic voltammetry was performed on a EG&G Princeton Applied Research (PAR) Model 173 potentiostat/galvanostat, with a Model 176 current follower, driven by a Model 175 universal programer. Cyclic voltammograms were recorded on a Houston Instruments Model 200 XY recorder. For compounds **1–4**, best results were obtained using glassy carbon for both the working and counter electrodes. For compounds **5–8**, the working electrode was glassy carbon, while the counter electrode was platinum wire. A silver wire placed in a capillary tube to minimize contact with any decomposition products was used for the pseudo-reference electrode for all samples. Aqueous samples were run at a concentration of about 10 mM in 0.1 M KCl as a supporting electrolyte. Samples **1–4** run in acetonitrile used either 0.1 M tetrabutylammonium tetrafluoroborate or 0.1 M tetrabutylammonium hexafluorophosphate. Samples **5–8** run in acetonitrile used either 0.25 M tetrabutylammonium tetrafluoroborate or 0.25 M tetrabutylammonium hexafluorophosphate as the electrolyte. All nonaqueous potentials were referenced to ferrocene as an internal standard. Multiple scans were recorded for each compound with little or no variation between scans.

Prior to submission for elemental analyses, all samples were weighed in tared vials and dried for at least 24 h under a minimum vacuum of 0.01 mmHg. All samples in the vials were then stored in argon, which was first passed through a drying tube of fresh Drierite. Elemental analyses were performed by the Microanalytical Laboratory, operated by the College of Chemistry, University of California, Berkeley, CA.

1,2,3,4,5-Pentakis(4-(dimethylamino)pyridinium-1-yl)cyclopentadienyl Anion Pentachloride (1) and 1-Chloro-2,3,4,5-tetrakis(4-(dimethylamino)pyridinium-1-yl)cyclopentadienyl Anion Tetrachloride (2). To a solution of 0.77 g (2.83 mmol) of hexachlorocyclopentadiene in 5 mL of acetonitrile was added a solution of 4.14 g (33.92 mmol) of 4-(dimethylamino)-pyridine (DMAP) in 70 mL of acetonitrile. The reaction mixture was kept for 100 h at 82 °C. Upon addition of 5 drops of water a brownish precipitate formed. The precipitate was collected via suction filtration and reprecipitated from methanol with acetone. The solid was collected again via suction filtration, dissolved in a minimal amount of methanol, and reprecipitated slowly from a 50/50 mixture of 2-propanol and *tert*-butyl alcohol to give 237 mg (0.331 mmol, 12%) of **2**; mp 233 °C dec: ^{1}H NMR (250 MHz, D_2O, CH_3CN internal standard) δ 3.03 (12 H, s), 3.09 (12 H, s), 6.64 (4 H, d, J = 7.8 Hz), 6.76 (4 H, d, J = 7.8 Hz), 7.80 (4 H, d, J = 7.8 Hz), 7.87 (4 H, d, J = 7.8 Hz); ^{13}C NMR (75 MHz, CD_3OD) δ 157.7, 157.6, 145.5, 114.2, 112.2, 109.1, 108.9, 97.0, 40.6; IR (KBr), 3050 (b, m), 2625 (w), 1630 (sh, s), 1570 (b, s), 1440 (w), 1400 (sh, s), 1340 (w), 1210 (b, s), 1150 (sh, s), 1080 (sh, w), 1060 (w), 1020 (w), 970 (sh, w), 935 (sh, w), 820 (sh, s), 755 (sh, w); UV-vis (H_2O) λ 305.6 (ε 58 600); (concd H_2SO_4) λ 298.4, 335 shoulder, 385 shoulder.

Anal. Calcd for $C_{33}H_{40}N_8Cl_4 \cdot 4H_2O$: C, 51.97; H, 6.34; N, 14.69; Cl, 18.60. Found: C, 52.25; H, 6.53; N, 14.62; Cl, 19.31.

The mother liquor from the first reprecipitation of **2** was evaporated to dryness. The resulting solid was dissolved in a minimal amount of methanol and slowly precipitated from a 50/50 mixture of 2-propanol and *tert*-butyl alcohol to give 639 mg (0.715 mmol, 25%) of **1**; mp 281 °C dec: ^{1}H NMR (250 MHz, D_2O, CH_3CN internal standard) δ 3.06 (30 H, s), 6.67 (10 H, d, J = 7.8 Hz), 7.86 (10 H, d, J = 7.8 Hz); (D_2SO_4, no standard). The NMR spectrum of the yellow solution shows four types of pyridinium, one being very weak. Upon dilution with 4 equiv of D_2O, the solution became colorless and showed only one type of pyridinium: ^{1}H NMR (250 MHz, D_2O, CH_3CN internal standard) δ 3.00, (30 H, s), 6.61 (10 H, d, J = 6.3 Hz), 7.67 (10 H, d, J = 6.3 Hz); ^{13}C NMR (75 MHz, CD_3OD) δ 157.7, 145.4, 112.6, 109.0, 40.7; IR (KBr) 3010 (b, m), 2630 (w), 1630 (b, m), 1580–1510 (b, s), 1400 (sh, s), 1340 (w), 1320 (w), 1220 (sh, s), 1150 (sh, s), 935 (sh, m), 830 (sh, s); UV-vis (H_2O) λ 308 (ε = 83 600); (concd H_2SO_4) λ 300, 340 shoulder, 400 shoulder.

Anal. Calcd for $C_{40}H_{50}N_{10}Cl_4 \cdot 4.5H_2O$: C, 53.75; H, 6.65; N, 15.67; Cl, 15.87. Found: C, 53.72; H, 6.52; N, 15.50; Cl, 16.49.

Acidity Determination of 1. A standard base solution was prepared by diluting 5.66 g (0.101 mol) of KOH to 100 mL and diluting 50 mL of this solution to 500 mL. Concentration of KOH solution was determined by a three-point titration with potassium acid phthalate. NMR solutions were prepared by diluting concd D_2SO_4 with D_2O, and molarity was determined by three-point titration using the above standard base solution. Since no standard is known for D_2SO_4 the strongest upfield absorption was set to 3.0 ppm. Peaks were severely broadened, and spectra were obtained in 17.5, 14.4, 13.6, 12.8, and 11.7 M D_2SO_4.

1,2,4,5-Tetrafluoro-3,6-bis((4-dimethylamino)pyridinium-1-yl)benzene Difluoride (3a). To a solution of 0.51 g (2.77 mmol) of hexafluorobenzene in 3 mL of THF was added 2.03 g

(12) Waterman, K. C.; Speer, D. V.; Streitwieser, A.; Look, G. C.; Nguyen, K. O.; Stack, J. G. *J. Org. Chem.* **1988**, *53*, 583.

(13) Diffraction data for the crystal structure was collected by Dr. Fred Hollander, director of the UCB X-ray facility. The authors have deposited atomic coordinates for this structure with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge, CB2 1EW, UK.

(16.61 mmol) of DMAP in 40 mL of THF. The reaction mixture was stirred at reflux under a N_2 atm for 24 h and cooled to room temperature, and the resulting yellow precipitate was collected via suction filtration to give 0.32 g of crude product. Its ^1H NMR spectrum showed the product to be about 56% **3** (NMR yield, 13%). The crude material was reprecipitated from methanol, acetone, and THF to give 0.073 g of pure **3** (5% yield). The original reaction mixture was refluxed for 48 h to give 0.47 g of a yellowish brown solid which proved to be 22% **3** by ^1H NMR spectroscopy; NMR yield 7.7%. When the reaction was allowed to proceed for more than 24 h, **3** underwent further reaction to give a variety of higher substituted products. ^1H NMR (250 MHz, D_2O, CH_3CN internal standard): δ 3.23 (12 H, s), 7.00 (4 H, d, J = 8.0 Hz), 8.03 (4 H, d, J = 7.6 Hz). ^{19}F NMR (250 MHz, CD_3OD, $CFCl_3$ internal standard): δ −146.5, −164.8. UV–vis (H_2O): λ 314 (ϵ = 42 000).

Anal. Calcd for $C_{20}H_{20}N_4F_6 \cdot 3H_2O$: C, 49.59; H, 5.41; N, 11.57. Found: C, 49.89; H, 4.92; N, 11.28.

1,2,4,5-Tetrafluoro-3,6-bis((4-dimethylamino)pyridinium-1-yl)benzene Bis(tetrafluoroborate) (3b). The X-ray single crystal structure of **3b** was obtained by first dissolving **3a** in a minimal amount of water and acetonitrile. Excess sodium tetrafluoroborate was added to the solution. To keep the solution free of dust particles, the vial was then covered with a Kimwipe tissue, fastened with a rubber band. Over a period of several days, acetonitrile slowly evaporated to afford crystals of **3b** in the remaining aqueous solution.

1-Fluoro-2,3,4,5,6-pentakis((4-dimethylamino)pyridinium-1-yl)benzene Pentafluoride (4a). Under High Pressure. A solution of 0.21 g (1.12 mmol) of hexafluorobenzene and 0.75 g (6.15 mmol) of DMAP in 8 mL of 1:3 (v:v) THF–CH_3CN was placed in a 10-mL syringe. The end was sealed with a hot spatula and the plunger arm was cut off. The syringe was then pressed to 15 Kbar for 4 h in a high pressure piston press.[14] The syringe was then allowed to stand at room pressure for 4 d before collecting 0.24 g of brown solid via suction filtration. Precipitation from a mixture of methanol, acetonitrile, and THF was followed by multiple recrystallizations from methanol and 2-propanol to give 0.072 g (0.090 mmol, 8%) of **4**: ^1H NMR (250 MHz, CD_3OD, CH_3CN internal standard) δ 3.04 (6 H, s), 3.06 (12 H, s), 3.11 (12 H, s), 6.67 (2 H, br d), 6.72 (4 H, d, J = 7.5 Hz), 6.82 (4 H, d, J = 7.6 Hz), 7.88 (10 H, complex mult); ^{19}F NMR (250 MHz, CD_3OD, $CFCl_3$ internal standard) δ −130, −149; UV–vis (H_2O) λ 297 (ϵ 36,000), 340 nm shoulder.

Thermally. A 27% THF in acetonitrile solution containing 0.70 g (3.78 mmol) of hexafluorobenzene and 2.82 g (23.1 mmol) of DMAP was heated at reflux for 2 h and allowed to stand at room temperature for 4 days. Filtering the solution gave 0.25 g of a black solid which appeared to be mostly **4** by ^1H NMR spectroscopy. Addition of 4 drops of water to the mother liquor produced 0.28 g of an off-white precipitate that appeared to be a mixture of **4** and other pyridinium-substituted benzenes. Multiple recrystallizations from methanol and 2-propanol gave 14 mg (0.5%) of **4**.

1-Fluoro-2,3,4,5,6-pentakis((4-dimethylamino)pyridinium-1-yl)benzene Pentakis(tetrafluoroborate) (4b). From 3. To a solution of 1.00 g (2.32 mmol) of **3** in 8 mL of methanol was added a solution of 1.13 g (9.29 mmol) of DMAP in 35 mL of acetonitrile. The reaction mixture was sealed and allowed to stand at rt for 3.5 months. The resulting solid was collected via suction filtration and washed with 3 × 2 mL of acetonitrile and 3 × 5 mL of acetone to give 1.64 g (2.01 mmol) of **4**, yield 80%. Fluoride ions were exchanged for tetrafluoroborate ions by dissolving the sample in a minimum amount of water and adding a solution of 1.55 g (14.1 mmol) of $NaBF_4$ in 30 mL of water. The resulting precipitate was collected via suction filtration and reprecipitated from acetonitrile/water: yield, 1.05 g (0.835 mmol, 36%); mp 285–355 °C dec; ^1H NMR (250 MHz, CD_3OD, CH_3CN internal standard) δ 3.04 (6 H, s), 3.06 (12 H, s), 3.11 (12 H, s), 6.67 (2 H, br d), 6.72 (4 H, d, J = 7.5 Hz), 6.82 (4 H, d, J = 7.6 Hz), 7.88 (10 H, complex mult); ^{19}F NMR (250 MHz, CD_3OD, $CFCl_3$ internal standard) δ −130, −149; UV–vis (H_2O) λ 297 (ϵ = 36 000), 340 shoulder; ^{13}C NMR (75 MHz, CD_3CN) δ 164.57, 157.40, 157.30, 157.22, 143.92, 143.77, 141.77, 137.67, 132.34, 114.06, 109.60, 109.05, 41.01, 40.96, 40.82; ^{13}C DEPT (100 MHz, CD_3CN) 135° δ 143.92, 143.77, 141.77, 109.60, 109.05, 41.01, 40.96, 40.82.

Anal. Calcd for $C_{41}H_{50}N_{10}B_5F_{21} \cdot H_2O$: C, 42.68; H, 4.54; N, 12.14; B, 4.68. Found: C, 42.52; H, 4.83; N, 12.56; B, 4.95.

1,2-Bis(4-dimethylamino)pyridinium-1-yl)tetrafluorocyclobutene Dichloride (5a). To a stirring solution of 1.48 (7.59 mmol) of 1,2-dichlorotetrafluorocyclobutene in dichloromethane (50 mL) was added 1.78 g (14.6 mmol) of DMAP over a 3-h period. The reaction mixture immediately turned yellow, and a yellow solid precipitated. As the DMAP was added, more precipitate formed at the bottom of the flask. Any unreacted 1,2-dichlorotetrafluorocyclobutene and dichloromethane solvent were removed by rotary evaporation. The remaining yellow solid was dried overnight under vacuum; yield, 2.1 g (63%); mp 103–105 °C; ^1H NMR (300 MHz, D_2O, CH_3CN internal standard) δ 7.95 (d, 4, J = 8.0 Hz), 7.01 (d, 4, J = 8.0 Hz), 3.28 (s, 12); ^{19}F NMR (250 MHz, D_2O, $CFCl_3$ internal standard) δ −114.07; ^{13}C NMR (75.8 MHz, D_2O, CH_3OH internal standard) δ 165.1, 146.0, 145.8, 145.6, 117.6, 117.5, 117.3, 49.0.

Anal. Calcd for $C_{18}H_{20}N_4F_4Cl_2 \cdot H_2O$: C, 47.28; H, 4.85; N, 12.25. Found: C, 47.60; H, 4.69; N, 12.13.

1,2-Bis(4-(dimethylamino)pyridinium-1-yl)tetrafluorocyclobutene Bis(hexafluorophosphate) (5b). To a stirring solution of 1.49 g (7.64 mmol) of 1,2-dichlorotetrafluorocyclobutene in acetonitrile (25 mL) was added 1.82 g (14.9 mmol) of DMAP over a 3-h period. The reaction mixture immediately turned yellow, and an orange solid precipitated. As the DMAP was added, more precipitate formed at the bottom of the flask. The yellow mixture was stirred at rt under N_2 for 9 h. Any unreacted 1,2-dichlorotetrafluorocyclobutene and acetonitrile solvent were removed by rotary evaporation. The remaining orange solid was dissolved in water (25 mL), to which was added a solution of 2.69 g (16.0 mmol) of $NaPF_6$ in water (10 mL). The resulting yellow precipitate was vacuum filtered and dried overnight under vacuum: yield, 4.27 g (85%); ^1H NMR (400 MHz, CD_3CN) δ 7.87 (dd, 4, J = 8.0, 2.3 Hz), 7.03 (dd, 4, J = 8.0, 2.1 Hz), 3.34 (s, 12); ^{19}F NMR (400 MHz, CD_3CN, $CDCl_3$ internal standard) δ −1.87, −42.94; ^{13}C NMR (100 MHz, CD_3CN) δ 158.0, 138.8, 118.4, 110.5, 42.0.

Anal. Calcd for $C_{18}H_{20}N_4P_2F_{16}$: C, 32.84; H, 3.06; N, 8.51. Found: C, 32.66; H, 2.95; N, 8.56.

1,2-Bis(4-(dimethylamino)pyridinium-1-yl)tetrafluorocyclobutene Bis(tetrafluoroborate) (5c). Hexafluorophosphate ions were exchanged for tetrafluoroborate ions by dissolving **5b** in a minimum amount of acetonitrile and running it down a column of Amberlyst A-21 resin with 50% aqueous methanol as eluant. (The Amberlyst A-21 column had been previously flushed three times with an aqueous solution of saturated sodium tetrafluoroborate.) After the yellow solution was collected from the column, methanol was removed by rotary evaporation, and water was removed by lyophilization. The resulting yellow solid was dried overnight under vacuum: ^1H NMR (300 MHz, CD_3CN) δ 7.89 (d, 4, J = 0.75 Hz), 7.04 (t, 4, J = 1.8 Hz), 3.34 (s, 12); ^{19}F NMR (400 MHz, CD_3CN, $CDCl_3$ internal standard) δ −114.1, −151.7.

1,2-Bis(4-phenylpyridinium-1-yl)tetrafluorocyclobutene Dichloride (6). To a stirring solution of 0.307 g (1.57 mmol) of 1,2-dichlorotetrafluorocyclobutene in acetonitrile (25 mL) was added 0.49 g (3.16 mmol) of 4-phenylpyridine. The reaction was stirred under N_2 at 55 °C for 12 h. Upon cooling, yellow needles precipitated. The crystals were filtered and dried in vacuo to yield 0.127 g (16%) of product. Crystallization from acetonitrile/diethyl ether afforded 0.105 g of yellow plates: mp 324–325 °C dec; ^1H NMR (300 MHz, acetone-d_6) δ 8.82 (2 H, dd, J = 1.53, 5.26 Hz), 8.26 (2 H, dd, J = 1.57, 5.25 Hz), 7.97 (2 H, ddd, J = 2.12, 3.51, 4.75 Hz), 7.62 (3 H, m); ^{19}F NMR (400 MHz, CD_3CN, $CFCl_3$ internal standard) δ −118.6.

1,2-Bis(3-methylimidazolium-1-yl)tetrafluorocyclobutene Dichloride (7a). To a stirring solution of 1.22 g (6.24 mmol) of 1,2-dichlorotetrafluorocyclobutene in acetonitrile (25 mL) was added 1.17 g (14.2 mmol) of 1-methylimidazole. The reaction solution was stirred at rt under a N_2 atm and turned from pale yellow to orange. After 2 min, a yellow precipitate formed. After vacuum filtration, the yellow solid was dissolved

(14) Dauben, W. G.; Krabbenhoft, H. O. *J. Org. Chem.* **1977**, *42*, 282.

in a minimal amount of methanol, precipitated with acetone to form a cloudy mixture, and then redissolved with methanol to form a clear solution. After chilling the solution overnight, white crystals were isolated by vacuum filtration: yield, 1.6 g (70%); mp 134–136 °C; ^{1}H NMR (300 MHz, D_2O, CH_3CN internal standard) δ 9.64 (s, 2), 7.84 (d, 2, J = 2.2 Hz), 7.75 (d, 2, J = 2.2 Hz), 3.96 (s, 6); ^{19}F NMR (250 MHz, D_2O, $CFCl_3$ internal standard) δ −115.01; ^{13}C NMR (75.8 MHz, D_2O, CH_3CN internal standard) δ 126.9, 126.8, 126.7, 126.54, 126.49, 121.73, 121.71, 115.0, 37.4.

Anal. Calcd for $C_{12}H_{12}N_4F_4Cl_2$: C, 40.13; H, 3.37; N, 15.60. Found: C, 39.98; H, 3.39; N, 15.45.

1,2-Bis(3-methylimidazolium-1-yl)tetrafluorocyclobutene Bis(hexafluorophosphate) (7b). To a solution of 1.22 g (6.24 mmol) of 1,2-dichlorotetrafluorocyclobutene in acetonitrile (25 mL) was added 1.17 g (14.2 mmol) of 1-methylimidazole. After 3 min, a yellow precipitate formed. The reaction solution was stirred for 9 h at rt under N_2. Rotary evaporation was used to removed excess starting reagents and acetonitrile. The yellow solid was dissolved in water (15 mL), to which was added a solution of 2.19 g (13.1 mmol) of $NaPF_6$ in water (15 mL). After the PF_6^- salt precipitated, it was vacuum filtered and dried overnight under vacuum: yield, 3.17 g (88%); ^{1}H NMR (400 MHz, CD_3CN) δ 9.04 (s, 2), 7.70 (t, 2, J = 2.2 Hz), 7.64 (t, 2, J = 2.2 Hz), 2.85 (s, 6); ^{19}F NMR (400 MHz, CD_3CN, $CDCl_3$ internal standard) δ −115.05, −73.24, −71.36; ^{13}C NMR (100 MHz, CD_3CN) δ 138.5, 127.5, 122.3, 38.2.

Anal. Calcd for $C_{12}H_{12}N_4P_2F_{16}$: C, 24.93; H, 2.09; N, 9.69. Found: C, 24.55; H, 2.11; N, 9.89.

1,2-Bis(3-methylimidazolium-1-yl)tetrafluorocyclobutene Bis(tetrafluoroborate) (7c). Hexafluorophosphate counterions were exchanged for tetrafluoroborate ions as previously described for **5c**. The resulting yellow solid was dried overnight under vacuum: ^{1}H NMR (300 MHz, CD_3CN) δ 8.81 (s, 2), 7.57 (dd, 4, J = 1.8, 7.1 Hz), 3.89 (s, 6); ^{19}F NMR (400 MHz, CD_3CN, $CFCl_3$ internal standard) δ −71.5, −73.3, −152.06.

1,2-Bis(3-phenylimidazolium-1-yl)tetrafluorocyclobutene Bis(tetrafluoroborate) (8). To a solution of 1.11 g (5.67 mmol) of 1,2-dichlorotetrafluorocyclobutene in 80% diethyl ether/20% CH_2Cl_2 (25 mL) was added 1.68 g (11.7 mmol) of 1-phenylimidazole. After 1 h of stirring at 0 °C, the reaction solution was allowed to stand at 0 °C overnight. Clusters of an off-white precipitate were removed by vacuum filtration. Because the dichloride salt was extremely hygroscopic, the solid was immediately converted to the tetrafluoroborate salt. The sample (1.10 g, 2.28 mmol) was dissolved in a minimal amount of water, to which was added a solution of 0.51 g (4.62 mmol) of $NaBF_4$ in 15 mL of water. After the BF_4^- salt precipitated, it was vacuum filtered and dissolved in a minimal amount of acetonitrile. Drops of diethyl ether were added until the solution became cloudy, and then drops of acetonitrile were added to produce a clear solution again. The solution was chilled at 0 °C for 9 h to produce a light yellow precipitate. This solid was vacuum filtered and recrystallized from acetonitrile/diethyl ether as previously described. The off-white waxy solid was vacuum filtered and dried overnight under vacuum: yield, 0.56 g (17%); ^{1}H NMR (400 MHz, CD_3CN) δ 8.97 (s, 2), 7.77 (t, 2, J = 2.1 Hz), 7.62 (t, 2 J = 2.2 Hz), 7.55 (d, 4, J = 7.1 Hz), 7.43 (m, 6); ^{19}F NMR (400 MHz, CD_3CN, $CFCl_3$ internal standard) δ −142.09, −77.33.

Anal. Calcd for $C_{22}H_{16}N_4B_2F_{12}\cdot 2H_2O$: C, 42.48; H, 3.24; N, 9.01. Found: C, 42.79; H, 3.47; N, 8.77.

Acknowledgment. This research was supported in part by National Science Foundation Grants CHE82-05696 and DMR87-19302 and by the Committee on Research, UCB. We thank Professor William G. Dauben and his research group for the use of their high pressure equipment. We also thank Reilly Tar and Chemical Co. and Nepera Chemical Co. for their gifts of chemicals.

Supplementary Material Available: All available ^{1}H NMR, ^{13}C NMR, and ^{19}F NMR spectra for the 1,2,3,4,5-pentakis(4-(dimethylamino)pyridinium-1-yl)cyclopentadienyl anion (**1**), 1-chloro-2,3,4,5-tetrakis(4-(dimethylamino)pyridinium-1-yl)cyclopentadienyl anion (**2**), 1,2,4,5-tetrafluoro-3,6-bis(4-(dimethylamino)pyridinium-1-yl)benzene (**3**), 1-fluoro-2,3,4,5,6-pentakis-(4-(dimethylamino)pyridinium-1-yl)benzene (**4**), 1,2-bis(4-(dimethylamino)pyridinium-1-yl)tetrafluorocyclobutene (**5**), 1,2-bis-(4-phenylpyridinium-1-yl)tetrafluorocyclobutene (**6**), 1,2-bis(3-methylimidazolium-1-yl)tetrafluorocyclobutene (**7**), and 1,2-bis(3-phenylimidazolium-1-yl)tetrafluorocyclobutene (**8**) (35 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.