From **29** were prepared in this manner (in order of decreasing R_f on silica gel) olefin **30** [oil; IR (neat) 2946, 2868, 1734, 1709, 1665, 1613 cm^{-1}; ^1H NMR δ 0.72 (s, 3 H), 0.9–3.0 (m, 33 H), 3.61 (d, J = 3 Hz, 1 H), 3.77 (s, 3 H), 3.90 (br s, 1 H), 4.81 (s, 1 H), 5.03 (s, 1 H), 5.70 (s, 1 H); HRMS calcd for $C_{29}H_{44}O_3$ 440.3289, found 440.3285] and alcohol **31** [oil; IR (neat) 3486, 2947, 2870, 1740, 1705, 1645, 1611 cm^{-1}; ^1H NMR δ 0.70 (s, 3 H), 0.96 (s, 3 H), 0.8–3.0 (m, 34 H), 3.67 (d, J = 3 Hz, 1 H), 3.70 (d, J = 3 Hz, 1 H), 3.78 (s, 3 H), 5.86 (s, 1 H); HRMS calcd for $C_{29}H_{46}O_4$ 458.3395, found 458.3391.

Ortho Ester 25. A solution of **16** (100 mg, 0.46 mmol) in 50 mL of anhydrous dioxane was purged with argon and then irradiated in the usual manner for a period of 30 min. Irradiation was discontinued, and methanol (10 mL) was introduced. The mixture was allowed to stand in the dark for 10 min. Evaporation gave a crude product, which was purified by PTLC on silica gel (40% EtOAc in hexane) to give (in order of decreasing R_f) **17** (29 mg, 29%) and **25** (59 mg) as an unstable oil: IR (neat) 2940, 1699, 1136 cm^{-1}; ^1H NMR δ 1.04 (s, 3 H), 1.4–2.95 (m, 8 H), 3.05 (d, J = 8 Hz, 1 H), 3.22 (s, 3 H), 3.32 (s, 3 H), 3.77 (d, J = 8 H, 1 H), 5.71 (br s, 1 H); HRMS calcd for $C_{14}H_{20}O_4$ 252.1361, found 252.1367.

Cyclopropyl Ketone 40 and Phenol 41. A solution of dienone **39**[34] (55 mg, 0.30 mmol) in 15 mL of dry dioxane was purged with nitrogen and placed in a Rayonet photochemical reactor equipped with low-pressure mercury lamps. After 25 min, irradiation TLC indicated the disappearance of starting material and the formation of two higher running products. The solvent was removed under reduced pressure and PTLC on silica gel (25% EtOAc in hexane) gave (in order of decreasing R_f) phenol **41** (8 mg, 15%) [IR (neat) 2955, 1663 cm^{-1}; ^1H NMR δ 2.22 (s, 3 H), 2.41 (s, 3 H), 3.96 (s, 3 H), 6.75 (d, J = 8.4 Hz, 1 H), 7.18 (d, J = 8.4 Hz, 1 H), 10.56 (br s, 1 H); HRMS calcd for $C_{10}H_{12}O_3$ 180.0786, found 180.0790] and cyclopropyl ketone **40** (17 mg, 31%) [oil; IR (neat) 2957, 1720, 1705 cm^{-1}; ^1H NMR δ 1.19 (s, 3 H), 1.36 (s, 3 H), 2.94 (dd, J = 3 Hz, 1 H), 3.77 (s, 3 H), 5.99 (d, J = 5.5 Hz, 1 H), 7.40 (dd, J = 5.5, 3 Hz, 1 H), HRMS calcd for $C_{10}H_{12}O_3$ 180.0786, found 180.0788].

Acknowledgment. We thank the Research Board of the University of Illinois, Research Corporation, and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for their support of this work.

Registry No. (±)-**10**, 60815-97-6; (±)-**10** (allyl ether), 112042-27-0; (±)-**10** (allyl ether, ketone), 112042-28-1; (±)-**11**, 112042-31-6; (±)-**12**, 112042-32-7; (±)-**13**, 25435-10-3; (±)-(*E*)-**14**, 112042-33-8; (±)-(*Z*)-**14**, 112042-25-8; (±)-*cis*-**15**, 112042-26-9; (±)-*trans*-**15**, 112042-34-9; (±)-**16**, 112042-35-0; (±)-**17**, 112042-36-1; (±)-**18**, 112042-37-2; *carbonyl*-^{18}O-(±)-**18**, 112042-39-4; (±)-**19**, 112042-38-3; (±)-**23**, 112042-42-9; (±)-**24**, 112068-66-3; (±)-**25**, 112042-43-0; (±)-**27**, 112042-45-2; (±)-**27** (CD_3 ester), 112042-30-5; (±)-**28**, 112042-46-3; **29**, 112042-47-4; **30**, 112042-48-5; **31**, 112042-49-6; (±)-**36**, 112042-40-7; **37**, 112042-41-8; (±)-**38**, 112042-44-1; **39**, 65595-92-8; (±)-**40**, 112042-50-9; **41**, 5628-60-4; $NCCO_2Me$, 17040-15-2; (±)-3-keto-9-methyl-Δ^4-octahydronaphthalene, 40573-28-2; (±)-*trans*-2-carbomethoxy-3-keto-9-methyl-Δ^4-octahydronaphthalene, 112042-29-2; Δ^4-cholestenone, 601-57-0.

Pyridiniumcarbons: Perpyridinium Derivatives of Cyclopropene and Allyl Anion

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The structure and reactivity of the first pyridiniumcarbons, compounds in which every available position is substituted by an *N*-pyridinium cation group, are discussed. Tetrakis(4-(dimethylamino)pyridinium-1-yl)-cyclopropene (**1**) and pentakis(4-(dimethylamino)pyridinium-1-yl)allylid (**2**) were prepared by reaction of tetrachlorocyclopropene with 4-(dimethylamino)pyridine, DMAP. Compound **2** was prepared from **1** by further reaction with DMAP; **1** was found to react with cyanide ion to give (*E*)-1-cyano-1,2,3,3-tetrakis(4-(dimethylamino)pyridinium-1-yl)allylid (**4**). The one isomer formed is a thermodynamic product in that protonation followed by deprotonation gives only **4**. Protonation occurs γ to the nitrile giving both (*E*)- and (*Z*)-propene isomers. Both **1** and **2** produce a 1,2,3-tripyridinium-1-ylindolizine (**6**) on heating. The pK_a's of the conjugate acids of **2** and **4** are 3.2 and −0.8, respectively.

In earlier papers,[1,2] we reported the reaction of pyridines with tetrachlorocyclopropene, TCCP,[3] to form indolizines. This reaction was proposed to involve successive nucleophilic additions of the pyridine to the cyclopropene double bond to form cyclopropyl anions, which could eliminate chloride ion and then be further substituted by additional pyridinium groups. With additional pyridinium substitution, the cyclopropyl anion is increasingly stabilized toward chloride elimination, and competing electrocyclic ring opening can occur to the isomeric substituted allyl anion. A further electrocyclic ring closure involving the allyl anion moiety and a pyridinium substituent can then occur to lead to the indolizine product.[4] Electron-donating substituents on the pyridine were proposed to destabilize the intermediate cyclopropyl anion, resulting in a greater degree of pyridinium-1-yl substitution. With 4-(dimethylamino)pyridine, DMAP, a rather basic pyridine, substitution on TCCP occurs to replace all of the chlorines and results in the formation of the cyclopropene, **1**.[5]

(1) Smith, K. A.; Streitwieser, A., Jr. *J. Org. Chem.* **1983**, *48*, 2629–2630.
(2) Smith, K. A.; Waterman, K. C.; Streitwieser, A., Jr. *J. Org. Chem.* **1985**, *50*, 3360–5.
(3) Tobey, S. W.; West, R. *J. Am. Chem. Soc.* **1966**, *88*, 2481; *Tetrahedron Lett.* **1963**, 1179–1182.
(4) Sasaki, T.; Kanematsu, K.; Kakehi, A.; Ito, G. *Tetrahedron* **1972**, *28*, 4947–4958.

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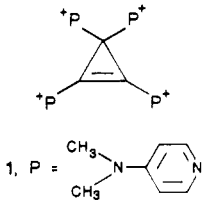
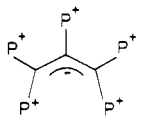


1, P =

This compound represents the first example of a "pyridiniumcarbon", a compound in which all available positions are substituted by *N*-pyridinium groups. Electrocyclic ring opening of 1 occurs only after the addition of another DMAP group. The product of this reaction is another pyridiniumcarbon, **2**.



2, P = DMAP

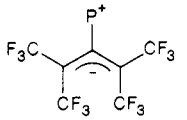
It is convenient to refer to this type of structure as an "allylid" rather than as a simple allyl anion to emphasize the presence of the positive pyridinium moieties. The allylid **2** is air and moisture stable at room temperature, and could be isolated as a red crystalline solid. In this paper, we discuss further the reactions to form these pyridiniumcarbons and explore some of the reactivity of this new class of compounds. We also show how more general compounds having other pyridinium-1-yl groups can be formed.

Results and Discussion

Structures of 1 and 2. Compound **1** was obtained as a white precipitate having a satisfactory analysis for the indicated structure, assuming the presence of 6.5 molecules of water.[6] The chloride ions could be replaced completely by other gegenions, such as AsF_6^-, PF_6^-, or BF_4^-; each shows a one-to-one ratio of two types of *N*-(4-dimethylamino)pyridinium cations. The ^{13}C NMR spectrum shows peaks consistent with two DMAP units, plus absorptions at δ 67.9 and 101.3, corresponding to the alkyl and vinyl cyclopropene carbons, respectively. The shift for the methylene carbon is slightly upfield from the 75.8 ppm shift of bis(4-(dimethylamino)pyridinium-1-yl)methane, prepared from the reaction of DMAP with diiodomethane. The vinylic carbon is shifted considerably from the analogous position of TCCP (122.7 ppm)[7] and of 1,2,3-triphenylcyclopropene (112.5 ppm).[8]

Compound **2** was obtained as dark red hygroscopic needles having a satisfactory analysis. The ^1H NMR spectrum shows three types of DMAP's with a ratio of 1:2:2. The unique DMAP appears downfield from the others. This is consistent with the assigned structure of **2** in that the unique DMAP is attached to the C-2 allyl carbon, which has the least amount of negative charge. The ^{13}C NMR spectrum indicates the presence of three types of DMAP units and two other nonproton coupled carbons at δ 100.0 and 135.2, corresponding to C-1 and C-2 of the allyl anion, respectively. These values are remarkably close to those for (1,1,3,3-tetraphenylallyl)lithium where the chemical shifts for C-1 and C-2 are reported to be 104.8 and 131.3 ppm, respectively.[9] This similarity in the chemical shifts is noteworthy considering the rather large perturbation involved in going from the four phenyl groups in (1,1,3,3-tetraphenylallyl)lithium to the five positively charged pyridiniums of **2**. Note that the NMR spectra require that rotation of the pyridiniums be fast on the NMR time scale, but that of the terminal allylic carbons is slow. The ^1H NMR spectrum of **2** showed no evidence of coalescence up to 90 °C in D_2O.

The visible spectra of **1** and **2** are markedly different. The spectrum of **1** shows no visible absorptions, whereas that of **2** absorbs strongly at λ_{max} = 448 nm. The absorption of **2** suggests an extended conjugated system, but there are no suitable analogies to serve as references. The spectrum of (1,1,3,3-tetraphenylallyl)lithium is shifted to longer wavelength, λ_{max} = 563 nm.[10] Other analogies are pentacyanoallyl anion that has λ_{max} = 393, 412 nm[11] and 1,1,3,3-tetrakis(trifluoromethyl)-2-(4-(dimethylamino)-pyridinium-1-yl)allylid, **3**, that has λ_{max} = 298 nm.[12]



3, P = DMAP

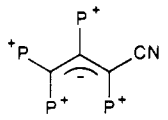
Reactions with Tetrabromocyclopropene, 4-Pyrrolidinopyridine, and 4-(4-Methyl-1-piperidinyl)-pyridine. To better understand the reaction of DMAP with TCCP, some variations of the original reaction were carried out. In an earlier study, we had showed that pyridines react with tetrabromocyclopropane, TBCP,[3] to give products containing more pyridinium-1-yl substituents than with TCCP.[1,2] Bromide is a better leaving group than chloride and gives greater substitution by pyridine relative to the ring opening that leads to indolizines. With DMAP, however, no difference in behavior between TCCP and TBCP was found. The bromide salts of **1** or **2** could be isolated depending on the number of equivalents of DMAP used. The reaction to form **1** was also not sensitive to the substituents on the exocyclic pyridine nitrogen. For example, 4-pyrrolidinopyridine, PPY, and 4-(4-methyl-1-piperidinyl)pyridine, MPP, reacted with TCCP to give products analogous to **1** and **2**. The properties of these pyridinium-1-yl carbons were similar to those of the DMAP derivatives.

One question arising from the proposed mechanism for the formation of **2** from **1** concerns the reversibility of the electrocyclic ring-opening reaction. The reaction of **1** with PPY gave an allylid product whose ^1H NMR showed two types of PPY with an integrated intensity corresponding to one PPY for four DMAP's. Analogously, when the PPY analogue of **1** was treated with DMAP, only one DMAP (two types) compared to four PPY's were observed. The fact that only a single entering pyridine is found shows that the addition reaction and ring opening is not reversible. As expected, in both cases the entering pyridine ends up on a terminal carbon of the allylid; the isomeric *E* and *Z* products are formed in each case in about equal amounts.

Reaction of 1 with Cyanide. Expanding on the idea of nucleophilic addition of **1** followed by electrocyclic ring

(5) Waterman, K. C.; Streitwieser, A., Jr. *J. Am. Chem. Soc.* **1984**, *106*, 3874–5.
(6) The water of hydration indicated in this formula and others in this paper are those that give the best fit to combustion analyses. These compounds are generally hygroscopic, and nonintegral values may represent water picked up during weighing.
(7) Albert, K. H.; Dürr, H. *Org. Magn. Reson.* **1979**, *12*, 687–690.
(8) This sample was prepared by Chia-Chung Chen.
(9) Bauer, H.; Angrick, M.; Rewicki, D. *Org. Magn. Reson.* **1979**, *12*, 624–7.
(10) Streitwieser, A., Jr.; Hammons, J. H.; Ciuffarin, E.; Brauman, J. I. *J. Am. Chem. Soc.* **1967**, *89*, 59–62.
(11) Middleton, M. J.; Little, E. L.; Coffman, D. D.; Engelhardt, V. A. *J. Am. Chem. Soc.* **1958**, *80*, 2795–2806.
(12) Farnham, W. B.; Middleton, W. J.; Fultz, W. C.; Smart, B. E. *J. Am. Chem. Soc.* **1986**, *108*, 3125–7.

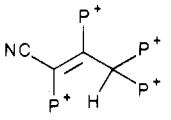
opening to an allylid, 1 was treated with cyanide ion to give the yellow crystalline 4 in high yield. This compound



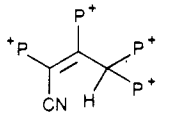
4, P = DMAP

shows a CN IR stretch at 2157 cm^{-1}, corresponding to a slight weakening of this bond compared to the CN stretch for 1,1,2,3,3-pentacyanoallyl anion (2193 cm^{-1}).[13] The UV–vis spectrum of 4 shows an absorption at λ_{max} = 389 nm (log ϵ = 4.36). The ^1H NMR spectrum of 4 shows the presence of only four types of DMAP's and indicates the presence of only one isomer of 4. The chemical shifts for both the α and β DMAP ring protons are grouped such that one coupled doublet in each case is downfield from the other three doublets that are grouped together. In the case of 2, the α DMAP ring protons are similar to those of 4 (one downfield from the other four), whereas the β DMAP ring protons are all grouped together. Since the downfield doublets in each case correspond to the DMAP at C-2, these data suggest that the DMAP at C-2 is in a different chemical environment for 4 than for 2. This result strongly suggests, but clearly does not demand, the *E* configuration shown in 4.

This difference in stereochemical behavior between cyanide ion and pyridines suggests that 4 is a thermodynamic product. The alternative of rapid topomerization of the allylid is not likely for such a hindered system;[14] moreover, rapid rotation about a terminal allylid carbon would result in only three types of DMAPs. On protonation of 4 with D_2SO_4 in D_2O, the ^1H NMR spectrum showed what appears to be an equimolar ratio of the deuteriated versions of the following two protonated species, **5a** and **5b**. When the solution was neutralized,



5a



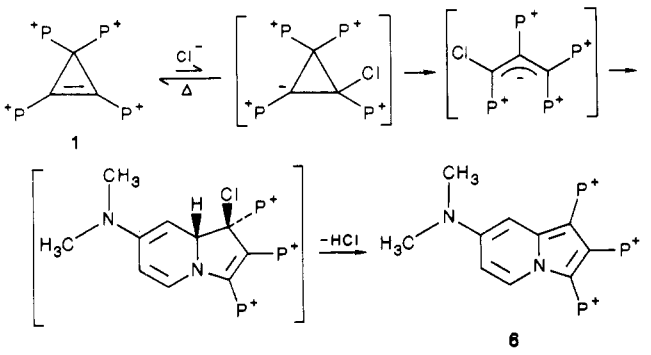
5b

a spectrum identical with the original was obtained. Since both cis and trans protonated products were observed, yet only one isomer was observed in the deprotonated form, 4 must be a thermodynamic product. It is interesting to note that protonation predominates at C-3 rather than α to the nitrile group; however, a small amount of the less stable protonated product is clearly present to account for the cis–trans equilibration.

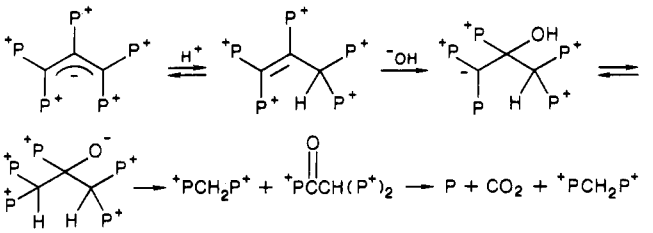
The allylid 4 is remarkably stable at high temperatures. No cyclization or decomposition could be detected after 40 min at 220 °C. As a result, 4 could be dried by heating under a vacuum. When dry, the allylid 4 is yellow, while the hydrated form is red.

Thermal Reactivity of 1 and 2. After 1 was heated under vacuum in the solid phase to 180 °C, some DMAP–HCl sublimed, leaving behind a mixture of products from which, after displacement of the chloride counterions by hexafluorophosphate, an indolizine was isolated. The 1,2,3-tripyridinium-1-yl-substituted indolizine 6 formed probably arose via an initial reversal of chloride

Scheme I



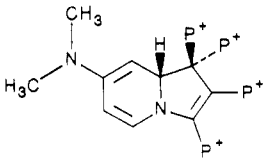
Scheme II



P = DMAP

elimination as shown in Scheme I. Although it is possible that other indolizines were also formed in this reaction, 6 was the dominant product. The preference for formation of 6 compared to other possible indolizines is consistent with the tendency of HCl to eliminate in preference to pyridine in the formation of indolizines on reaction of pyridine with TCCP.[2] In the latter case, the dihydropyridine intermediate appears to show exclusive HCl elimination.

After 2 was heated to 170 °C for 5 min in the solid phase under vacuum, 1 equiv of DMAP–HCl sublimed, leaving behind the pure indolizine 6. In this case, cyclization apparently occurred to give only the dihydroindolizine 7,



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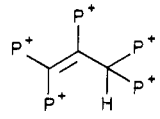
which eliminated DMAP–HCl to give the product. These cyclization reactions of 1 and 2 to the trisubstituted indolizine 6 supports the proposed intermediacy of an allylid in the formation of indolizines by reaction of pyridine with TCCP.[1,2] The formation of 6 from 2 shows that a pyridine itself can act as a leaving group in the cyclization process. Note that 6 is the first example of a 1,2,3-tripyridinium-1-ylindolizine derivative.

On heating a DMSO solution of 2 to reflux, a mixture of about 26% 6, 31% $CH_2(P^+)_2$ (P = DMAP), and 43% DMAP was formed, based on ^1H NMR spectroscopy. These proportions correspond roughly to formation of one DMAP for each 6 formed, and another DMAP for every two $CH_2(P^+)_2$ molecules formed. This stoichiometry suggests the hydrolysis mechanism shown in Scheme II (note that 2 is present as the hexahydrate) in addition to the cyclization.

Acidity of Polypyridinium Compounds. The pyridinium allylid 2 can be protonated in aqueous solution to give the propene 8. Since the ylid 2 is colored and the propene 8 is not, the aqueous pK_a of 8 could be determined spectrophotometrically with 2 as its own indicator. By this

(13) Little, E. L.; Middleton, W. J.; Coffman, D. D.; Engelhardt, V. A.; Sausen, G. N. *J. Am. Chem. Soc.* **1958**, *80*, 2832–2838.

(14) Boche, G.; Martens, D.; Wagner, H. U. *J. Am. Chem. Soc.* **1976**, *98*, 2668–9. Boche, G.; Buckl, K.; Martens, D.; Schneider, D. R. *Tetrahedron Lett.* **1979**, 4967–4970. Thompson, T. B.; Ford, W. T. *J. Am. Chem. Soc.* **1979**, *101*, 5459–5464.



8

method, the pK_a was found to be 3.15 ± 0.11. By comparison, the acidity of 5-pyridinium-1-ylcyclopentadiene is reported to be 10.0,[15] and the acidity of 1,1,3-triphenylpropene is about 26.6.[16] These comparisons demonstrate the high degree of stabilization imparted to the allyl anion system by the pyridinium-1-yl groups of **2**.

The pK_a of the PPY analogue of **8** was determined by the same method to be 3.4 ± 0.1, and similarly, the pK_a of the MPP analogue was found to be 3.6 ± 0.2. These slightly higher values are indicative of the slightly more electron-donating character of the pyrrolidino and methylpiperidino groups, respectively, as compared to the dimethylamino group. The pK_a of the conjugate acid of **4** was determined in aqueous solution to be about −0.8. This makes the conjugate acid of **4** 4 orders of magnitude more acidic than **8** and demonstrates the greater electron-withdrawing power of a nitrile compared to a pyridinium cation. This acidity is the highest reported for an ylid precursor.

Conclusions

Compounds **1** and **2** (and their PPY and MPP analogues) represent the first examples of pyridiniumcarbons, compounds in which all available positions are bound to pyridinium cation groups. These remarkable compounds have a high density of positive charge that gives them unusual properties for organic compounds. In general, these compounds are water soluble and stable in air, although frequently hygroscopic. The formation of **1** and **2** from TCCP and DMAP does not appear to be affected by slight modifications of either substrate. TBCP reacts with DMAP, and TCCP reacts with PPY and MPP in analogous fashion to the reaction of TCCP with DMAP. The reaction to form **2** from **1** was shown to be irreversible by studies on the formation of mixed allylids. This reaction of **1** may be a general reaction with nucleophiles. An additional example is the reaction of **1** with cyanide ion to give the allylid **4**. The allylids are allyl anions stabilized by multiple positive pyridinium moieties; i.e., they are "positively charged allyl anions"! Their stability is further indicated by the relatively high acidities of their conjugate acids; the pK_a's of the pyridinium systems of the type **8** are about 3 and that of the cyano analogue **4** is −0.8.

Experimental Section

General Methods. Materials were obtained from commercial suppliers and used without further purification, unless explicitly indicated otherwise. Reagent grade acetonitrile was distilled from CaH_2 and stored over 4-Å molecular sieves. Dry methanol was prepared by distillation of reagent grade methanol from Mg and was stored over 3-Å sieves. Infrared spectra were determined on a Perkin-Elmer 297 infrared spectrophotometer. UV–vis spectra were determined on either a Cary 118, an IBM, or a Hewlett-Packard 5054 spectrophotometer. ^1H NMR spectra were determined at 180, 200, or 250 MHz on Nicolet FT spectrometers constructed in the University of California, Berkeley (UCB) NMR laboratory. ^{13}C NMR spectra were determined at 45.288 or 50.784 MHz on the above instruments. Chemical shifts are referenced to TMS either directly as an internal standard (indicated), indirectly by the resonance of the solvent, or added standard (indicated) referenced to TMS. The NMR spectral data are recorded as chemical shift in ppm (multiplicity [br, broad; s, singlet; d, doublet; dd, doublet of doublets; t, triplet; q, quartet; m, multiplet], number of protons, and coupling constant in hertz). Elemental analyses were performed by the Microanalytical Laboratory, College of Chemistry, UCB.

1,2,3,3-Tetrakis(4-(dimethylamino)pyridinium-1-yl)-cyclopropene Tetrachloride (1). To a stirred solution of TCCP[3] (0.892 g, 5.0 mmol) in 25 mL of 80% CH_2Cl_2/20% ether at 0 °C was added dropwise DMAP (1.23 g, 10.0 mmol, Reilly) in 20 mL of the same solvent mixture over a 5-min period. DMAP was added until the appearance of a red color (**2**). This color served as a suitable endpoint indicator for the addition of the DMAP solution. After the mixture was stirred for 5 min at 0 °C and at 25 °C for an additional 5 min, the white precipitate was filtered through a fritted disk and washed with fresh solvent (CH_2Cl_2/Et_2O). Multiple precipitations from MeOH solution with acetone yielded 2.38 g of pure product (3.5 mmol, 71%): IR (KBr) 3400 cm^{-1} (br, s), 3050 (m), 2660 (w), 1635 (sharp, vs), 1575 (sharp, s), 1400 (sharp, s), 1345 (s), 1260 (m), 1205 (s), 1130 (br, s); ^1H NMR (D_2O, CH_3COCH_3 standard) δ 8.21 (4, d, J = 7.8), 8.02 (4, d, J = 7.8), 7.07 (4, d, J = 7.8), 6.91 (4, d, J = 7.8), 3.29 (12, s), 3.17 (12, s); ^1H NMR ($CDCl_3$, TMS standard) δ 9.88 (d, 4, J = 7.8), 9.47 (d, 4, J = 7.8), 7.11 (d, 4, J = 7.8), 6.91 (d, 4, J = 7.8), 3.35 (s, 12), 3.24 (s, 12); ^{13}C NMR (D_2O, CH_3CN standard) δ 156.5 (s), 156.3 (s), 138.4 (d, $^1J_{CH}$ = 189.1), 137.4 (d, $^1J_{CH}$ = 185.0), 109.0 (d, $^1J_{CH}$ = 174.0), 108.5 (d, $^1J_{CH}$ = 172.2), 101.3 (s), 67.9 (s), 40.5 (q, $^1J_{CH}$ = 141), 39.8 (q, $^1J_{CH}$ = 140); ^{13}C NMR (CD_3OD) δ 158.72, 158.5, 141.4, 140.3, 110.4, 110.1, 103.5, 70.3, 41.7, 41.0. Anal.[6] ($C_{31}H_{40}N_8Cl_4 \cdot 6.5H_2O$) C, H, N; Cl: calcd 18.14, found 18.68.

1,2,3,3-Tetrakis(4-(dimethylamino)pyridinium-1-yl)-cyclopropene Tetrakis(hexafluoroarsenate). To an aqueous solution of **1** was added an aqueous solution of excess $AgAsF_6$ (Alfa). A precipitate formed immediately. The solution was filtered, and the solid was washed with several portions of water. The product was recovered from the solid by washing with acetone, filtering, and evaporating the filtrate to dryness under vacuum. After redissolving in acetone and precipitating with MeOH, the filtered solid was dried under vacuum to leave a nonhygroscopic, slightly orange solid: ^1H NMR (CD_3COCD_3, TMS standard) δ 8.71 (d, 4, J = 8.0), 8.53 (d, 4, J = 8.0), 7.33 (d, 4, J = 8.0), 7.20 (d, 4, J = 8.0), 3.53 (s, 12), 3.40 (s, 12), 2.07 (s, 6, [acetone]). Anal. ($C_{31}H_{40}N_8As_4F_{24} \cdot CH_3COCH_3$) C, H, N, Cl.

1,2,3,3-Tetrakis(4-(dimethylamino)pyridinium-1-yl)-cyclopropene Tetrakis(hexafluorophosphate). To an aqueous solution of **1** was added excess $NaPF_6$ (Alfa). The precipitated product was washed with H_2O, dissolved in acetone, filtered, and pumped dry under vacuum to give a slightly orange solid: ^1H NMR (CD_3CN) δ 7.98 (d, 4, J = 7.6), 7.82 (d, 4, J = 7.6), 6.96 (d, 4, J = 7.6), 6.83 (d, 4, J = 7.6), 3.25 (s, 12), 3.14 (s, 12); ^{13}C NMR (CD_3COCD_3) δ 157.2, 156.8, 139.8, 138.9, 109.0, 108.6, 103.1, 69.4, 40.6, 39.9. Anal. ($C_{31}H_{40}N_8P_4F_{24} \cdot 1.5CH_3COCH_3$) C, H, N, P. In the absence of acetone: ($C_{31}H_{40}N_8P_4F_{24} \cdot H_2O$) C, H, N, P.

1,2,3,3-Tetrakis(4-(dimethylamino)pyridinium-1-yl)-cyclopropene Tetrakis(tetrafluoroborate). To an aqueous solution of **1** was added excess $AgBF_4$ (Aldrich) in H_2O. The precipitate was filtered, and the filtrate was evaporated to dryness under vacuum. ^1H NMR (D_2O) δ 8.13 (d, 4, J = 7.9), 7.94 (d, 4, J = 7.9), 7.06 (d, 4, J = 7.9), 6.90 (d, 4, J = 7.9), 3.29 (s, 12), 3.17 (s, 12).

1,1,2,3,3-Pentakis(4-(dimethylamino)pyridinium-1-yl)allylid Tetrachloride (2). To a solution of 0.289 g of TCCP[3] (95% by GLC; 1.54 mmol) in 4 mL of dry $CHCl_3$ at 0 °C was added a mixture of 1.031 g of DMAP (8.45 mmol, Reilly) in 10 mL of $CHCl_3$ via syringe under Ar. The red mixture was stirred at 0 °C for 15 min and allowed to warm to room temperature for 5 h. The bright red precipitate was filtered through a fritted disk. The solid was washed with cold $CHCl_3$ and dried under vacuum to give 1.367 g of crude product. Recrystallization from a mixture of 98% CH_3CN and 2% MeOH gave 0.812 g of red hygroscopic needles (59% yield). UV–vis (MeOH, 7.991×10^{-5} M) 450 (4.35), (MeOH, 7.991×10^{-6} M) 450 (4.43); IR (Nujol) 2800 cm^{-1} (br, vs), 1625 (sharp, s), 1545 (ms), 1440 (ms), 1370 (m), 1190 (br); ^1H NMR (CD_3OD, TMS standard) δ 8.81 (2, d, J = 7.66), 8.37 (8, dd, J = 7.94, 7.94), 6.93 (10, m), 3.27 (12, s), 3.23 (18, s); ^1H NMR (D_2O,

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$CHCl_3$ standard) δ 7.90 (2, d, J = 7.5), 7.59 (4, d, J = 7.7), 7.58 (4, d, J = 7.6), 6.40 (10, m), 2.81 (12, s), 2.76 (18, s); ^{13}C NMR (D_2O, CH_3CN standard) δ 156.4, 154.9, 154.8, 142.5, 142.1, 142.0, 139.9, 108.1, 107.6, 106.3, 99.9, 39.6, 39.4, 38.6; ^{13}C NMR (CD_3OD) δ 158.5, 156.9, 145.2, 144.8, 143.0, 135.2, 109.9, 109.8, 109.5, 100.0, 40.9, 40.8, 40.7. Carbon multiplicities were confirmed by a DEPT experiment. Anal. ($C_{38}H_{50}N_{10}Cl_4 \cdot 6H_2O$) C, H, N, Cl.

1,1,2,3,3-Pentakis(4-(dimethylamino)pyridinium-1-yl)allylid Tetrakis(tetrafluoroborate). To an aqueous solution of approximately 0.1 g of **2** in 10 mL of H_2O was added a large excess (greater than 10 equiv) of $NaBF_4$ (Aldrich). After the mixture was stirred for 5 min, an equal volume of acetone was added. Addition of an equal volume of ether produced a precipitate. The solution was filtered with vacuum, and the solid was redissolved in the minimum necessary amount of CH_3CN (approximately 30 mL for 0.1 g of **2**). This solution was filtered, and an equal volume of ether was added to the filtrate, again precipitating a red solid. The solid was recrystallized from CH_3CN/*i*-PrOH: ^1H NMR (D_2O) δ 8.07 (d, 2, J = 7.6), 7.76 (d, 4, J = 7.6), 7.74 (d, 4, J = 6.5), 6.63 (m, 10), 3.05 (s, 12), 3.00 (s, 18). Anal. ($C_{38}H_{50}N_{10}B_4F_{16} \cdot 0.5CH_3CN$) C, H, N, Cl.

Bis(4-(dimethylamino)pyridinium-1-yl)methane Diiodide. To a solution of 1.60 g of DMAP (6.4 mmol, Aldrich) in CH_3CN was added 1.25 mL of CH_2I_2 (1.55 mmol) via a syringe. The solution was refluxed for 2 days, filtered, and washed with cold CH_3CN and CH_2Cl_2. Crystallization from EtOH afforded 2.5 g (30%) of yellow flakes: mp 302.0–302.5 °C; UV–vis (H_2O) 302 (4.69); ^1H NMR (D_2O, CH_3COCH_3 standard) δ 8.01 (d, 4, J = 8.0), 6.78 (d, 4, J = 7.9), 6.12 (s, 2), 2.04 (s, 12); ^1H NMR (DMSO-d_6) δ 8.56 (d, 4, J = 6.9), 7.15 (d, 4, J = 6.9), 6.42 (s, 2), 3.23 (s, 12); ^{13}C NMR (DMSO-d_6) δ 160.3, 145.0, 112.4, 75.8, 44.5. Anal. ($C_{15}H_{22}N_4I_2 \cdot H_2O$) C, H, N; I: calcd 47.90, found 48.41.

1,2,3,3-Tetrakis(4-(dimethylamino)pyridinium-1-yl)cyclopropene Tetrabromide. To a solution of 0.282 g of DMAP (2.3 mmol; Aldrich) in 20 mL of a mixture of 20% ethyl ether and 80% CH_2Cl_2 was added dropwise, at 0 °C under N_2, 0.10 g of TBCP[3] (0.28 mmol) in 10 mL of the same solvent mixture, resulting in the formation of a white precipitate. After the mixture was filtered and washed with the ether/CH_2Cl_2 mixture, successive precipitations from MeOH with acetone gave the cream-white hygroscopic product (0.33 g, 68%): IR (CCl_4) 3500 cm^{-1} (w, br), 1650 (w, sharp), 790 (s, br); ^1H NMR (D_2O) δ 8.19 (d, 4, J = 7.9), 8.00 (d, 4, J = 7.8), 7.06 (d, 4, J = 7.9), 6.90 (d, 4, J = 7.9), 3.28 (s, 12), 3.16 (s, 12). Anal. ($C_{31}H_{40}N_8Br_4 \cdot 4H_2O$) C, H, N; Br: calcd 34.91, found 35.74.

1,1,2,3,3-Pentakis(4-(dimethylamino)pyridinium-1-yl)allylid Tetrabromide. To a solution of 0.493 g of DMAP (4.04 mmol; Aldrich) in 20 mL of $CHCl_3$ at 0 °C was added 0.081 mL of TBCP[3] (0.228 mmol) in 10 mL of $CHCl_3$ via a syringe under N_2, resulting in a gradual color change to red. After 24 h, the solvent was removed under vacuum giving a red solid, which was purified by multiple precipitations from MeOH solution with ether to give 0.48 g of product (0.50 mmol, 75.2%): ^1H NMR (D_2O) δ 8.2 (d, 2), 7.9 (d, 8), 6.7 (d, 10), 3.1 (m, 30).

1,2,3,3-Tetrakis(4-pyrrolidinopyridinium-1-yl)cyclopropene Tetrachloride. A solution of 1.000 g (5.624 mmol) of TCCP in 15 mL of 20% diethyl ether/CH_2Cl_2 was cooled in an ice bath, and while stirring with a glass rod, a solution of 2.951 g (19.91 mmol, 3.5 equiv) of 4-(pyrrolidino)pyridine, PPY (Aldrich; sublimed), in 15 mL of the same solvent mixture was added dropwise, giving the immediate appearance of a red color. To the mixture was added 40 mL of diethyl ether, resulting in a brown precipitate, which was isolated by suction filtration. The brown solid was dissolved in 15 mL of methanol (a minimum amount), and a beige solid (3.034 g, 79%) was precipitated with 400 mL of cold acetone. This precipitation was repeated once more to give 2.203 g (57% yield) of beige solid: ^1H NMR (D_2O) δ 8.12 (d, 4, J = 7.8), 7.94 (d, 4, J = 7.8), 6.90 (d, 4, J = 7.8), 6.74 (d, 4, J = 7.8), 3.60 (m, 8), 3.45 (m, 8), 1.96-1.91 (m, 16). Anal.[6] ($C_{39}H_{48}N_8Cl_4 \cdot 4.5H_2O$) C, H, N, Cl.

1,1,2,3,3-Pentakis(4-pyrrolidinopyridinium-1-yl)allylid Tetrachloride. To a solution of 0.167 g of TCCP[3] (95% by GLC, 3.77 mmol) in a 10 mL mixture of 60% $CHCl_3$ and 40% Et_2O at 0 °C was added 3.35 g of PPY (23.0 mmol; Aldrich; sublimed) in 30 mL of the $CHCl_3$/ether solution via syringe under a N_2 atmosphere. Within 1 min, the reaction mixture turned bright red. The solution was stirred at 0 °C for 10 min and at room temperature for 12 h. The solvent was removed by rotary evaporation followed by high vacuum. The red solid was precipitated three times from *i*-PrOH with ether and recrystallized from MeOH/*i*-PrOH. The red needles were collected over a fritted disk and dried under vacuum, giving 2.48 g of product (72% yield): mp 167 °C dec; UV–vis (H_2O, 2.129×10^{-5} M) 445 (4.20), 298 (4.66); ^1H NMR (D_2O, CH_3COCH_3 standard) δ 8.12 (d, 2, J = 7.5), 7.81 (d, 8, J = 6.6), 6.51 (d, 10, J = 7.0), 3.32 (m, 20), 1.90 (m, 20). Anal. ($C_{48}H_{60}N_{10}Cl_4 \cdot 4H_2O$) C, H, N.

1,1,2,3,3-Pentakis(4-(4-methyl-1-piperidinyl)pyridinium-1-yl)allylid Tetrachloride. A solution of 0.505 g (2.84 mmol) of TCCP in 15 mL of dry $CHCl_3$ was cooled to 0 °C, and a solution of 2.56 g (14.5 mmol, 5.1 equiv) of MPP (Reilly) was slowly added. The solution became amber followed by brown and finally turned a deep red by the end of the addition: ^1H NMR (D_2O) δ 8.09 (d. 2, J = 7.9), 7.82 (m, 8) 6.82 (m, 10), 3.98 (m, 10), 3.05 (m, 10), 1.17 (m, 15), 1.04 (br m, 10), 0.62 (d, 15, J = 5.0); ^{13}C NMR (CD_3OD) δ 157.1, 155.5, 155.4, 145.4, 144.9, 143.4, 134.5, 110.1, 109.9, 109.7, 109.6, 99.9, 79.6, 48.9, 48.7, 48.1, 35.1, 34.9, 34.7, 31.8, 31.6, 31.4, 21.7. Carbon multiplicities were confirmed by a DEPT experiment. The chloride gegenions were exchanged to tetrafluoroborate, and the red solid was recrystallized from hot water, giving deep red blocky crystals, which were collected by suction filtration and dried in a vacuum desicator. These crystals collapsed after a few months: ^1H NMR (CD_3CN) δ 8.24 (d, 2, J = 8.4), 7.86 (d(?), 8, J = 7.3), 6.85 (dd(?), 10, J = 7.3, 6.3), 4.07 (d(?), 10, J = 12.5), 3.15 (m, 10), 2.25 (s(?), 15), 1.82 (d(?), 15, J = 11.7), 1.16 (m, 10), 0.95 (d(?), 15, J = 7.5). Anal. ($C_{58}H_{80}N_{10}B_4F_{16} \cdot 2H_2O$) C, H, N.

1,2,3,3-Tetrakis(4-(dimethylamino)pyridinium-1-yl)-1-(4-pyrrolidinopyridinium-1-yl)allylid Tetrachloride. To a solution of 0.342 g of **1** (0.513 mmol) in MeOH was added 0.160 g of PPY (1.08 mmol; Aldrich) in MeOH. The solvent was removed under vacuum, giving a red, hygroscopic compound. The compound was precipitated two times from *i*-PrOH with acetone and dried under vacuum, giving 0.236 g of product (0.290 mmol, 56.4% yield): mp 160 °C dec; UV–vis (H_2O, 1.52×10^{-5} M) 443 (4.26), 296 (4.69); ^1H NMR (D_2O) δ 8.11 (d, 4, J = 7.77), 7.80 (m, 16), 6.63 (m, 16), 6.49 (m, 4), 3.32 (m, 8), 3.02 (3 s, 48), 1.90 (m, 8).

1-(4-(Dimethylamino)pyridinium-1-yl)-1,2,3,3-tetrakis(4-pyrrolidinopyridinium-1-yl)allylid Tetrachloride. To a solution of 0.132 g of 1,2,3,3-tetrakis(4-pyrrolidinopyridinium-1-yl)cyclopropene (0.171 mmol) in MeOH was added 0.021 g of DMAP (0.172 mmol; Aldrich) in MeOH. The solvent was removed under vacuum, and the red solid was precipitated three times from *i*-PrOH with THF. The compound was washed with acetone and dried under vacuum, giving 0.107 g of product (0.13 mmol, 46% yield): mp 164 °C dec; UV–vis (H_2O, 2.67×10^{-5} M) 445 (4.21), 296 (4.74); ^1H NMR (D_2O, CH_3COCH_3 standard) δ 7.80 (m, 10), 6.70 (m, 10), 3.15 (m, 16), 2.80 (s, 6), 1.70 (m, 16).

(*E*)-1-Cyano-1,2,3,3-tetrakis(4-(dimethylamino)-pyridinium-1-yl)allylid Trichloride (3a). A solution of 0.140 g of KCN (Mallinckrodt, 2.15 mmol) in 10 mL of MeOH and 10 mL of acetonitrile was added slowly to a solution of 1.310 g (1.67 mmol) of **1** in 5 mL of MeOH and 10 mL of acetonitrile at 25 °C. The solution immediately turned deep red. The mixture was stirred for 1 day and then allowed to stand for 1 day. The solution was filtered to remove KCl, and the solvent was removed by rotary evaporation. The dark red solid was dissolved in a minimum volume of hot *i*-PrOH, and more KCl was filtered out. The resulting solution was allowed to crystallize. The bright yellow-orange needle crystals were collected by vacuum filtration and dried under high vacuum to yield 0.824 g (69%) of red-orange, hygroscopic solid, mp >250 °C. An analytical sample was prepared by recrystallization from *tert*-butyl alcohol: UV–vis (H_2O) 389 (4.36); IR (KBr) 2157 cm^{-1}; ^1H NMR (D_2O) δ 8.11 (d, 2, J = 7.4), 7.82 (m, 6), 6.79 (d, 2, J = 7.5), 6.65 (d, 2, J = 7.5), 6.62 (d, 2, J = 7.3), 6.59 (d, 2, J = 7.9), 3.08 (s, 6), 3.05 (s, 6), 3.02 (s, 12); ^{13}C NMR (D_2O, CH_3CN standard) δ 168.6, 156.7, 155.6, 155.2, 144.1, 142.2, 142.0, 140.7, 140.0, 118.9, 108.2, 107.9, 102, 73, 39.9, 39.7, 39.4. Anal.[6] ($C_{32}H_{40}N_9Cl_3 \cdot 3.1H_2O$) C, H, N; Cl: calcd 14.85, found 14.40. A later sample from another preparation was kept for 3 days under vacuum (5 μm). Anal. ($C_{32}H_{40}N_9Cl_3 \cdot 2.5H_2O$) C, H, N.

(*E*)-1-Cyano-1,2,3,3-tetrakis(4-(dimethylamino)-pyridinium-1-yl)allylid Tris(hexafluoroarsenate). A solution

of 0.370 g of $AgAsF_6$ (Alfa; 1.2 mmol) in 20 mL of MeOH was added to a solution of 0.230 g of **4** in 20 mL of MeOH under N_2. A precipitate formed immediately and was removed by vacuum filtration. The filtrate was allowed to crystallize slowly to yield yellow to red crystals: ^1H NMR (CD_3COCD_3) δ 8.51 (d, 2, J = 7.6), 8.23 (d, 2, J = 7.6), 8.15 (d, 4, J = 7.3), 7.11 (d, 2, J = 7.6), 6.94 (d, 2, J = 7.1), 6.92 (d, 2, J = 7.0), 6.88 (d, 2, J = 7.4), 3.32 (s, 6), 3.30 (s, 6), 3.27 (s, 6), 3.24 (s, 6).

(*E*)-1-Cyano-1,2,3,3-tetrakis(4-(dimethylamino)-pyridinium-1-yl)allylid Tris(tetrafluoroborate). A solution of 0.25 g of $AgBF_4$ (Aldrich; 1.3 mmol) in 20 mL of MeOH was added to 0.23 g of **3** in 20 mL of MeOH under N_2. A precipitate formed immediately and was removed by vacuum filtration. The filtrate was allowed to crystallize to yield a yellow solid: ^1H NMR (D_2O) δ 8.10 (d, 2, J = 7.5), 7.80 (m, 6), 6.81 (d, 2, J = 7.1), 6.63 (m, 6), 3.10 (s, 6), 3.08 (s, 6), 3.04 (s, 6).

(*E*)- and (*Z*)-1-Cyano-1,2,3,3-tetrakis(4-(dimethylamino)pyridinium-1-yl)propene trichloride bisulfate: ^1H NMR (D_2O + D_2SO_4) δ 7.91 (d, 2, J = 6.9), 7.90 (d, 4, J = 8.0), 7.63 (d, 2, J = 8.1), 7.60–7.53 (five peaks, 8), 6.92 (d, 2, J = 8.1), 6.75–6.61 (9 peaks, 14), 3.1–3.0 (br m, 48).

1,2,3-Tris(4-(dimethylamino)pyridinium-1-yl)-7-(dimethylamino)indolizine Trichloride (6). From 1. A sublimator containing 0.114 g of **1** (0.150 mmol) was maintained under high vacuum for 20 min and slowly heated to 180 °C. At about 120 °C, the white solid gradually turned red. After 15 min at 180 °C, a white sublimate (DMAP–HCl) was apparent. The red product was then dissolved in MeOH and precipitated with Et_2O. This solid was dissolved in H_2O, and an aqueous solution of excess $NaPF_6$ (Alfa) was added. The green precipitate was filtered and dried in air to give 0.092 g of product (0.10 mmol, 64%). This material was recrystallized from water and acetone: UV–vis (CH_3CN) λ_{max} = 370, 310 nm; ^1H NMR (CD_3CN) δ 7.94 (d, 2, J = 8.0), 7.89 (d, 2, J = 7.9), 7.80 (d, 2, J = 8.0), 7.63 (dd, 1, J = 7.9, 0.5), 6.98 (d, 2, J = 8.0), 6.91 (d, 2, J = 7.9), 6.86 (dd, 1, J = 7.9, 2.6), 6.80 (d, 1, J = 8.0), 6.19 (d, 2, J = 2.4), 3.27 (s, 6), 3.23 (s, 6), 3.17 (s, 6), 3.01 (s, 6).

From 2. A sample of 0.099 g (0.11 mmol) of **2** was placed under a vacuum in a sublimator equipped with a water condenser. The sublimator was heated to 220 °C in an oil bath. Gas evolution was apparent at this point, although no melting was observed. After 10 min, the material in the sublimator changed from bright red to yellow and a white powder (DMAP–HCl, according to ^1H NMR) collected on the cold finger. The sublimator was cooled to room temperature, and the DMAP–HCl was scraped from the cold finger (0.012 g, 0.072 mmol). The yellow unsublimed solid (0.071 g) was crystallized twice from a mixture of 95% CH_3CN and 5% MeOH to give a total of 0.049 g (0.069 mmol, 62%) of product: UV–vis (MeOH, 3.09×10^{-5} M) 356 (4.16); (MeOH, 1.54×10^{-4} M) 364 (4.16); ^1H NMR (CD_3OD, TMS standard) δ 8.41 (d, 2, J = 8.0), 8.38 (d, 2, J = 8.0), 8.32 (d, 2, J = 7.8), 7.89 (d, 1, J = 8.0), 6.95 (dd, 1, J = 7.9, 2.5), 6.9 (m, 6), 6.24 (d, 1, J = 2.5), 3.36 (s, 6), 3.30 (s, 6), 3.25 (s, 6), 3.04 (s, 6). Anal.[6] ($C_{31}H_{39}N_8Cl_3 \cdot 4.75H_2O$) C, H, N, Cl.

1,1,2,3,3-Pentakis(4-(dimethylamino)pyridinium-1-yl)-propene Pentakis(tetrafluoroborate) (8). To a solution of 0.168 g (0.19 mmol) of **2** in 15 mL of *i*-PrOH was added 5 mL of 48% HBF_4 (aqueous, Matheson). A white precipitate formed immediately. After being filtered and washed with *i*-PrOH, the solid was redissolved in 2 mL of water containing one drop of 48% aqueous fluoboric acid. 2-Propanol was added to precipitate the white solid. After the precipitate was dried under vacuum, 0.150 g (0.13 mmol, 72%) of the white solid product was isolated. Crystallization from H_2O/EtOH by evaporation gave large hexagonal crystals, which collapsed to amorphous powders on drying: ^1H NMR (D_2O, CH_3COCH_3 standard) δ 7.86 (d, 4, J = 7.8), 7.83 (d, 2, J = 9.9), 7.68 (d, 4, J = 7.6), 6.93 (d, 2, J = 8.1), 6.86 (d, 4, J = 7.8), 6.80 (d, 4, J = 7.8), 3.13 (s, 24), 3.09 (s, 6). The 3-H is not seen undoubtedly because of exchange for deuterium. Anal. ($C_{38}H_{51}N_{10}B_5F_{20} \cdot 2H_2O$) C, H, N, Cl.

Determination of the pK_a of 8. Three buffers were prepared by using water distilled from $KMnO_4$ to form stock solutions of 0.20 M KCl and 0.20 M (titrated) HCl. An aliquot of 25.0 mL of the KCl solution was placed in each of three flasks and then 26.6, 10.2, and 3.9 mL of the HCl solution were added to the different flasks. With a standard buffer solution of pH 4.01 (Mallinckrodt), a calibrated pH meter was used to determine the following buffer pH values for the three solutions: 1.0, 1.2, and 1.5. By use of the three buffer solutions and the standard buffer, dilute solutions of **2** of known concentrations were prepared, and the absorptions at 442 nm were measured. In addition, the absorption at 442 nm was measured for a known concentration of **2** in neutral solution and in a 1.09 M HCl solution. The pK_a's for each of the four cases were determined to be 3.05, 3.06, 3.20, and 3.28, in order of increasing pH. This results in an average pK_a of 3.15 ± 0.11.

Determination of the Acidity of 5. Extinction coefficients of **4** at λ_{max} = 389 nm were determined at 25 °C in the following titrated sulfuric acid solutions: 0.0 M, log ϵ 4.36; 2.3 M, H_- −0.95,[17] log ϵ 4.12; 8.8 M, H_- −4.89, log ϵ 3.80. By assuming complete protonation in the most strongly acidic solution, these data give a pK_a for **5** of −0.8.

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