590.4376.

Tetronomycin Na Salt. To a stirred and cooled (-100 °C) solution of **4** (40 mg, 0.32 mmol) in THF (4 mL) was added via cannula a cooled (-100 °C) LDA solution prepared from *i*-Pr_2NH (49 μL, 0.34 mmol) and BuLi (1.48 M in hexane, 0.22 mL, 0.33 mmol) in THF (1.5 mL). After 8 min, dry DMPU (77 μL, 0.64 mmol) was introduced, and to the mixture was added a solution of **63** (63 mg, 0.107 mmol) in THF (1.5 mL) over a 2-min period. Additional 1- and 0.5-mL portions of THF were used to transfer all of the aldehyde **63**. After being stirred at -100 to -95 °C for 20 min, the reaction mixture was quenched with saturated NH_4Cl (3 mL) and then allowed to warm to room temperature before addition of AcOEt (10 mL). The layers were separated, and the aqueous layer was extracted with AcOEt (5 mL × 3). The combined organic extracts were washed with water (5 mL × 2) and brine (5 mL), dried, and concentrated. The residue was subjected to chromatography (silica gel, 11 g, 1:3 AcOEt/hexane) to give an aldol adduct (44 mg, 58%), R_f = 0.25 (1:4 AcOEt/hexane), along with recovered aldehyde **63** (5 mg). A solution of the carbinol product in CH_2Cl_2 (3 mL) was added to a stirred suspension of PCC (45 mg) and powdered 4-Å molecular sieves (150 mg) in CH_2Cl_2 (1 mL). After 20 min, Et_2O (10 mL) was added, and the whole was filtered through a Florisil column (1 g). Evaporation of the filtrate followed by chromatography of the residue (silica gel, 6 g, 1:4 AcOEt/hexane) gave **64** (18.1 mg, 26% from **63**) as an oil: R_f = 0.35 (1:4 AcOEt/hexane). Since this compound is unstable, it was used for the subsequent reaction immediately after ^1H NMR measurement: ^1H NMR (270 MHz) δ 0.58 (6 H, q, *J* = 8.0 Hz), 0.70 (3 H, d, *J* = 6.6 Hz), 0.95 (9 H, t, *J* = 8.0 Hz), 1.00 (3 H, d, *J* = 6.6 Hz), 1.11 (3 H, d, *J* = 6.3 Hz), 1.13 (3 H, d, *J* = 7.6 Hz), 3.05 (1 H, d, *J* = 9.8 Hz), 3.32 (1 H, qd, *J* = 6.3, 4.8 Hz), 3.36 (3 H, s), 3.57 (1 H, m), 3.66 (1 H, q, *J* = 7.6 Hz), 3.90 (3 H, s), 4.08 (2 H, s), 5.14 and 5.15 (each 1 H, d, *J* = 2.7 Hz), 5.43 (1 H, d, *J* = 10.3 Hz).

Treatment of **64** (18 mg, 0.025 mmol) in MeCN (3 mL) with 5% HF (0.15 mL) for 5 min followed by extractive workup with AcOEt (saturated $NaHCO_3$ washing) gave the desilylation product (12.7 mg): R_f = 0.15 (1:4 AcOEt/hexane). It was dissolved in dry DMSO (2 mL) containing LiCl (13 mg, 0.3 mmol), and the solution was stirred at room temperature for 3 d. The mixture was treated with saturated $NaHCO_3$ (5 mL) with stirring for 30 min before extraction with CH_2Cl_2 (5 mL × 4). The combined extracts were dried (Na_2SO_4), and the solvent was evaporated in vacuo. The residual oil was subjected to chromatography (silica gel, 4 g, 2:3 AcOEt/hexane) to give tetronomycin Na salt (5.5 mg, 36% from **64**) as an oil: R_f = 0.32 (2:3 AcOEt/hexane); $[\alpha]^{25}_D$ +140° (*c* 0.648, MeOH). This material was crystallized from *i*-Pr_2O/Et_2O as fine needles: mp 187-189 °C. Natural tetronomycin Na salt recrystallized from the same solvent showed mp 187-189 °C (lit.[1] mp 107-110 °C): $[\alpha]^{28}_D$ +147° (*c* 0.696, MeOH) [lit.[1] $[\alpha]^{28}_D$ +122.5° (*c* 0.8, MeOH)]; IR (KBr) 3328, 1745, 1605, 1438, 966 cm^{-1}; ^1H NMR (270 MHz) δ 0.53 (3 H, d, *J* = 6.6 Hz, Me-16), 0.93 (3 H, d, *J* = 6.4 Hz, Me-27), 1.00 (3 H, d, *J* = 7.1 Hz, Me-6), 2.34 (1 H, m, H-22), 2.50 (1 H, qd, *J* = 10.6, 4.5 Hz, H-12), 3.26 (1 H, d, *J* = 9.8 Hz, H-15), 3.33 (1 H, qd, *J* = 6.4, 2.2 Hz, H-27), 3.38 (3 H, s, OMe), 3.76-3.98 (3 H, m, H-6, CH-14 and H-19), 4.10-4.21 (2 H, m, H-23 and H-26), 4.28 (1 H, d, *J* = 11.2 Hz, CH-14), 4.39 (1 H, br, OH), 4.74 (1 H, d, *J* = 1.5 Hz, CH-4), 5.15 (1 H, d, *J* = 10.6 Hz, H-13), 5.22 (1 H, d, *J* = 1.5 Hz, CH-4), 5.48 (1 H, dd, *J* = 15.2, 9.4 Hz, H-20), 6.15 (1 H, ddd, *J* = 15.2, 11.0, 4.1 Hz, H-21); MS *m/e* 608 (M^+), 470, 469, 442, 441 (base peak); HRMS calcd for $C_{34}H_{49}O_8Na$ 608.3324, found 608,3307.

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Supplementary Material Available: ^1H NMR spectra of all title compounds (57 pages). This material is contained in many 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.

The Structure and Reactivity of 1,2,3,3-Tetrakis(4-(dimethylamino)pyridinium-1-yl)cyclopropene

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Received November 21, 1991

The X-ray single crystal structure of 1,2,3,3-tetrakis(4-(dimethylamino)pyridinium-1-yl)cyclopropene, **1**, is presented together with some reactions of **1**. Both triphenylphosphine and 1-methylimidazole react with **1** to form the ring-opened products, (*Z*)-1-(triphenylphosphonio)-1,2,3,3-tetrakis(4-(dimethylamino)pyridinium-1-yl)allylide (**6**), and the isomeric (*E*)- and (*Z*)-1-(3-methylimidazolium-1-yl)-1,2,3,3-tetrakis(4-(dimethylamino)-pyridinium-1-yl)allylides (**7**), respectively. Cyclic voltammetry shows that **6** oxidizes to its corresponding allyl radical at 1.3 V vs SCE; the isomers of **7** oxidize at 0.48 and 0.61 V. The pK_a's of the conjugate acids of **6** and **7** are -1 and 3.0, respectively. Reaction of **1** with potassium nitrite gave an unexpected product, 1,1,2-tris(4-(dimethylamino)pyridinium-1-yl)ethylene. The reactivity of **1** was compared to some analogous systems, 2-phenyl-1,3,3-tris(4-(dimethylamino)pyridinium-1-yl)cyclopropene (**12**) and 2-phenyl-1,3,3-tris(3-methylimidazolium-1-yl)cyclopropene (**13**). The phenyl substituent significantly alters the reactivity of **12** and **13**, such that both compounds do not form ring-opened products when treated with strong nucleophiles.

In earlier papers,[1,2] we reported the reaction of tetrachlorocyclopropene with 4-(dimethylamino)pyridine (DMAP) to give 1,2,3,3-tetrakis(4-(dimethylamino)-pyridinium-1-yl)cyclopropene tetrachloride (**1**) and the further reaction with DMAP to give the highly stabilized allylic anion, 1,1,2,3,3-pentakis(4-(dimethylamino)-pyridinium-1-yl)allylide tetrachloride, **3** (Scheme I). In this paper we report the X-ray single-crystal structure of **1** and the preparation and properties of new compounds formed from **1** with other nucleophiles. The general reactivity of **1** was explored further by comparing it with similar highly charged cyclopropenyl systems.

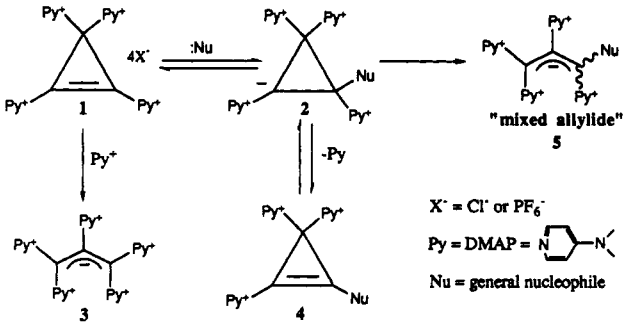
Structure of 1. The structure of **1** (PF_6^- salt) has been determined by X-ray crystallography. An ORTEP diagram not including the four PF_6^- gegenions is shown in Figure

(1) Waterman, K. C.; Streitwieser, A., Jr. *J. Am. Chem. Soc.* **1984**, *106*, 3874.

(2) Waterman, K. C.; Speer, D. V.; Streitwieser, A., Jr.; Look, G. C.; Nguyen, K. O.; Stack, J. G. *J. Org. Chem.* **1988**, *53*, 583-588.

0022-3263/92/1957-2902$03.00/0

Scheme I



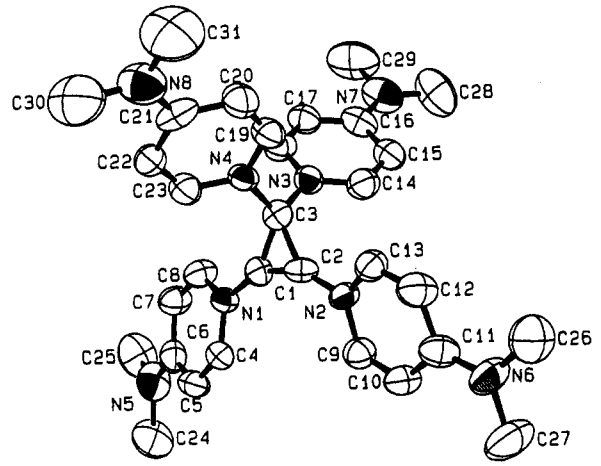


Figure 1. ORTEP drawing of 1.

Table I. Selected Bond Lengths (Figure 1)

bond	length, Å (ESD)	bond	length, Å (ESD)
N1–C1	1.373 (12)	N5–N6	1.325 (9)
N2–C2	1.374 (8)	N6–C11	1.312 (8)
N3–C3	1.470 (7)	N7–C16	1.343 (10)
N4–C3	1.479 (6)	N8–C21	1.357 (8)
C1–C2	1.295 (14)	C1–C3	1.455 (10)
C2–C3	1.468 (8)		

1. Figure 1 is not a representation of the unit cell. While the overall unit cell has C_2 symmetry, the individual molecules with their gegenions do not.

The two DMAP moieties that are bound to the vinyl carbons are nearly coplanar with the cyclopropene double bond, as are the phenyl rings in 1,2,3-triphenylcyclopropene[3] and 1,2-diphenyl-3-nitrocyclopropene.[4] As expected, the vinyl–DMAP bonds are shorter than the methylene–DMAP bonds (1.37 Å vs 1.47 Å; see Table I). The methylene–DMAP bonds are essentially the same as those in related compounds.[3,5,6] The vinyl–DMAP bonds are shorter than the normal C—N single bond length of 1.47 Å. All of these bond lengths are between a normal C—N single bond length of 1.47 Å and a C=N double bond length of 1.27 Å. The dimethylamino groups are virtually planar and coplanar with the pyridinium rings. All of these structural features indicate significant conjugation of the dimethylamino groups. The cyclopropene double-bond length is comparable to that found in cyclopropene (1.300 Å)[7] and 1,2,3-triphenylcyclopropene (1.293 Å).[3] The C—C single bond lengths of the ring (average 1.462 Å) are significantly shorter than in cyclopropene itself (1.515 Å)[7] and in 1,2,3-triphenylcyclopropene (average 1.516 Å),[3] but only slightly shorter than 1,2-diphenyl-3-nitrocyclopropene (1.483 Å).[4] It is well-known that π-acceptor substituents on the cyclopropene ring shorten these ring bond lengths[3,4,8] apparently by interaction of the π-orbital on C1 of the substituent with the Walsh-e_A-orbital of the cyclopropene ring. The expected slight lengthening of the distal (C=C) bond is not observed in these compounds. One effect unique to the pyridinium systems is the through-space electrostatic effect of the positively charged rings, but insufficient data exists at this time to allow an accurate assessment of these effects. Full details of the crystal structure are available as supplementary material.

Table II. Reactions of Nucleophiles with 1 (Gegenion = Cl^- or PF_6^-)

nucleophile	product 3	product 5
Ph_3P		√
CN^-		√
methylimidazole		√
4-(decylmethylamino)pyridine, 9		√
SCN^-		√
N_3^-	√	
$PhSO_2^-$	√	
$(MeO)_3P$	√	
$(Me_2N)_2C{=}S$	√	
4-alkylpyridine	√	
4-alkoxypyridine	√	
NO_2^-	√[a]	

[a] Product 8 was also isolated.

Results and Discussion

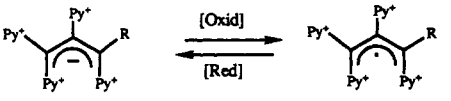
The reaction of 1 with different types of pyridines has been studied extensively. The reaction with DMAP was rapid at 0 °C in chloroform and gave in high yield the deep-red 1,1,2,3,3-pentakis(4-(dimethylamino)pyridinium-1-yl)allylide tetrachloride, 3, undoubtedly via a cyclopropyl anion intermediate, 2, as shown in Scheme I. These reactions have been carried out in methanol and acetonitrile (after exchange of gegenions to $4PF_6^-$) with essentially the same results.

A mixed allylide was also obtained with cyanide ion[2] as the nucleophile in methanol and acetonitrile. Compounds of types 3 and 5 (Nu = CN) are extraordinarily stable compounds. They are stable to bench-top conditions of air and moisture, although the chloride salts are often deliquescent. The cyano mixed allylide is significantly more stable than the perpyridinium adducts, as evidenced by its pK_a being about 4 units lower and the fact that it does not undergo electrocyclic ring closure to an indolizine, even at high temperature.[2] Table II lists the general nucleophiles that have been allowed to react with 1 to give either 3 or 5.

Reaction of 1 with General Nucleophiles. A number of non-pyridine type nucleophiles have been studied in these reactions. Two general types of behavior have been found. With some nucleophiles the intermediate cyclopropyl anion ring opens to give the corresponding allylide 5 in analogy to the reactions of DMAP and cyanide ion. In the other type of behavior the allylide product does not contain the added nucleophile and only the allylide 3 results, often in good yield. These two types of behavior are summarized in Table II.

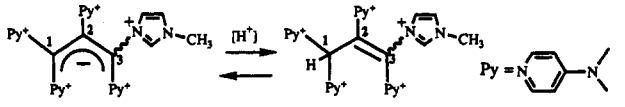
(3) Domnin, I. N.; Kopf, J.; Keyaniyan, S.; De Meijere, A. *Tetrahedron* **1985**, *41*, 5377–5382.
(4) Cheer, C. J.; Berstein, D.; Greenberg, A.; Ping-Chiang, L. *J. Am. Chem. Soc.* **1988**, *110*, 226–230.
(5) Smith, K. A.; Streitwieser, A., Jr. *J. Org. Chem.* **1983**, *48*, 2629–2630.
(6) Waterman, K. C. Ph.D. Dissertation, University of California at Berkeley, 1985.
(7) Kasai, P. H.; Myers, R. J.; Eggers, D. F.; Wiberg, K. B. *J. Chem. Phys.* **1959**, *30*, 512–516.
(8) Allen, F. H. *Tetrahedron* **1982**, *38*, 645.

Scheme II



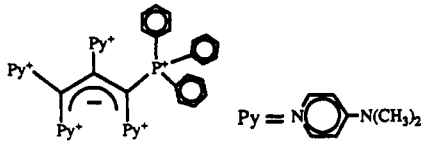
	E^0 (V vs. SCE)	pK_a
1. Py=R=DMAP	0.437	3.2
2. Py=DMAP, R=1-Me-imidazole	0.48, 0.61	3.0
3. Py=DMAP, R=CN	0.722	-0.8
4. Py=DMAP, R=PPh_3	1.3	-1

Scheme III. Protonation of the Mixed Imidazolium Allylides



7

Mixed allylide products were formed with triphenylphosphine and 1-methylimidazole. The product of 1 and triphenylphosphine after several recrystallizations yielded only one isomer of the hexafluorophosphate salt of the 1-(triphenylphosphonio)-1,2,3,3-tetrakis(4-(dimethylamino)pyridinium-1-yl)allylide, **6** (from its ^1H NMR spectrum).

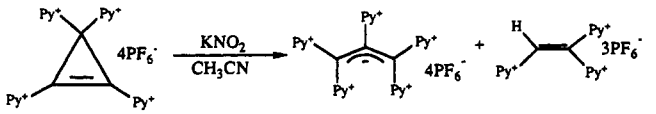


6

The bulk of the triphenylphosphonium group suggests the *Z* isomer shown, which affords less crowding of the phenyl rings. The ^1H NMR spectrum of **6** shows that the α-protons on the C2 pyridinium ring are significantly upfield (7.87 ppm) compared to the analogous C2 α-protons of **3** (8.15 ppm). It is unlikely that the α-protons of the C2 ring would be so affected if **6** were the *E* isomer. The β-protons of the pyridinium rings of **6** are split into four sets of distinct doublets at 6.72, 6.64, 6.33, and 6.11 ppm, which are also upfield of the multiplet of β-protons at 6.72 ppm of **3**. After purification by both ion-exchange and Bio-Gel filtration chromatography, the chloride and tetrafluoroborate salts were also isolated. Cyclic voltammetry of the tetrafluoroborate salt in acetonitrile shows that **6** oxidizes at a relatively high potential of 1.3 V vs SCE. Previously, the highest oxidation potential found was that of the cyano allylide[2] (Scheme II). Apparently, the strongly electron-withdrawing cyano group stabilizes the anion more than the radical. Similarly, **6** is a stabilized ylide in which the phosphorus also stabilizes the anion more than the radical. The pK_a of the conjugate acid of **6** was determined from its ^1H NMR spectra. A 1:1 ratio of **6** and its conjugate acid occurred in 2.1 M D_2SO_4 or 18% D_2SO_4,[9] corresponding to an H_0 value of -1.1,[10] and a pK_a value of approximately -1.

1-Methylimidazole, in which the heterocyclic nitrogen is conjugated to an amino nitrogen in a manner somewhat analogous to DMAP, also reacts with **1** (as either the hexafluorophosphate or chloride salts) to give the *E* and *Z* isomers of 1-(3-methylimidazolium-1-yl)-1,2,3,3-tetrakis(4-(dimethylamino)pyridinium-1-yl)allylide, **7**. These 3-methylimidazolium mixed allylide isomers can be protonated in aqueous solution to give the corresponding propenes (Scheme III).

Scheme IV. Formation of 8



1 3 8

The ylides **7** are deep-red and the propenes are colorless; thus the aqueous pK_a value of 3.0 for the conjugate acid of **7** was determined spectrophotometrically using solutions of **7** in buffers. In 3 M DCl/D_2O solution, protonated **7** gave ^1H NMR peaks corresponding to two different 3-methylimidazolium substituents. If site 3 were protonated, then only one type of 3-methylimidazolium moiety would be present. Therefore, the protonation most likely occurs at site 1, generating the two different conjugate acids of **7** (Scheme III). Earlier work done on the cyano mixed allylide[1,2,6] also showed that the *E* and *Z* isomers are formed as a result of protonation at site 1.

Weak nucleophiles such as fluoride, and even excess chloride ion in methanol, gave faint orange solutions (even though chloride is frequently used as the gegenion; the color is due to small amounts of **3**). Benzenesulfinate and azide ions gave incomplete reactions at room temperature (unreacted **1** by NMR). When the reaction mixtures were heated or when a complexing agent such as 18-crown-6 or 15-crown-5 was used to increase the nucleophilicity of the anion, the yield of **3** increased to about 70% (based on **1**). Incomplete reactions also resulted with the nucleophiles trimethyl phosphite and 1,1,3,3-tetramethyl-2-thiourea. After purification by Bio-Gel filtration chromatography, the only products obtained were **3** and **1**.

Additional nucleophiles studied include phenoxide, hydroxide, triethylamine, cyanate, thiocyanate, and nitrite but only two gave definitive results. Reaction of thiocyanate appeared to give an unstable mixed allylide. When the red product was desalted, the salt that was removed contained no thiocyanate (ferric ion test), indicating that all of the thiocyanate was incorporated into the red product. However, the ^1H NMR spectrum of the red product was not interpretable, and attempts to crystallize this material led to decomposition. The reaction of **1** (PF_6^- salt) with KNO_2 in acetonitrile was unique in that it gave **3** and an unexpected product, 1,1,2-tris(4-(dimethylamino)pyridinium-1-yl)ethylene, **8**, in about a 1:1 mixture (Scheme IV). The structure of **8** was assigned from NMR and analytical data. Although the two compounds crystallize simultaneously, the deep ruby red plates of **3** could be separated by hand from the pale orange prisms of **8**. When dissolved in D_2O, the vinyl proton of **8** undergoes deuterium exchange overnight, with the peak at 7.66 ppm disappearing. This indicates that the vinyl proton of **8** is fairly acidic. Moreover, after 1 week, no decomposition was noted in the ^1H NMR spectrum, an indication that the intermediate vinyl anion is relatively stable in water.

The source of **8** has not been established. The reaction was first noted with the 18-crown-6 complex of KNO_2 in acetonitrile. Later it was found that the 18-crown-6 was not necessary despite the low solubility of KNO_2 in acetonitrile. Traces of water in the reaction mixture gave somewhat more **8** and less **3** and some water is always present because of the hygroscopic nature of these salts; thus water is undoubtedly the source of the vinyl proton and may be involved in the decomposition itself. When the same reaction was performed in methanol, the only

(9) The conversion from molarity to percent sulfuric acid was taken from Weast, R.; Astle, M. J. In *CRC Handbook of Chemistry and Physics*, 61st ed.; CRC Press: Boca Raton, FL, 1981; p D-271.

(10) Rochester, C. H. *Acidity Functions*; Academic Press: London, 1970; Chapter 2.

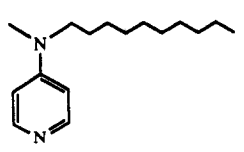
observed products were 3 and DMAP·HCl. A reaction mechanism is only speculative at this point, but the reaction may be analogous to the formation of 1,2-dichloropropenoic acid from the hydrolysis of 1,2-dichlorocyclopropenone.[11]

Reaction of 1 with Pyridines. The several 4-alkylpyridines studied (alkyl = Me, *n*-Pr, and *t*-Bu)[6] have comparable pK_a's[12] and reacted with 1 to give 3 in high yield in both protic and aprotic solvents. The 4-alkylpyridines were recovered unchanged. For example, the reaction of 1 (PF_6^- salt) with 1 equiv of 4-*tert*-butylpyridine in dry acetonitrile gave a 75% yield of 3 (based on 1). This implies that one-quarter of 1 decomposed completely and that the four DMAP units released then reacted completely with the remainder of 1 to give 3. No mixed allylide type product (e.g., 5 with Nu = 4-*tert*-butylpyridine) was seen in these reactions. The fate of the three ring carbons has not yet been determined.

The pK_a of 4-alkoxypyridines is similar to that of the 4-alkylpyridines,[12,13] and two were explored as nucleophiles in the reaction of 1. 4-(Cyclohexyloxy)pyridine and 4-methoxypyridine gave complex product mixtures indicative of γ-pyridone intermediates. Accordingly, these systems were not studied further.

It is evident that elimination of DMAP occurs when some nucleophiles add to the cyclopropene ring of 1 (Scheme I). These results suggest that such equilibria should also complicate the addition of 4-aminopyridines to 1. The mixed cyclopropene species in Scheme I, where the nucleophile is another 4-aminopyridine, should have essentially the same reactivity as 1. Therefore it should be possible to isolate an allylide resulting from further attack of the nucleophile on the mixed cyclopropene. Such an allylide would have three DMAP substituents and two positions occupied by the nucleophilic group. For each possible addition–elimination equilibrium any free DMAP in solution competes with the added nucleophile. If these equilibria are fast in comparison to the ring-opening step, then there will be scrambling of the groups on the cyclopropene unit and many different allylides would be isolated. In the limit of fast addition–elimination equilibria and slow ring opening, a statistical mixture would result. If the ring opening is fast compared to elimination, good yields of simple, single-addition mixed allylides would be obtained.

Reaction of 4-(Decylmethylamino)pyridine with 1. In order to test this scrambling hypothesis, some method was necessary to isolate minor products from the reaction mixture. With gel permeation chromatography[14] such a separation is possible, although the various products must be sufficiently different in size from one another to be discriminated. The nucleophile 4-(decylmethylamino)-pyridine, 9, was chosen because its nucleophilic properties are similar to DMAP, but the solvation and size of the resultant mixed allylides should be grossly different. The



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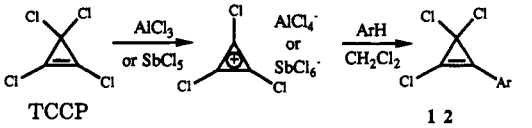
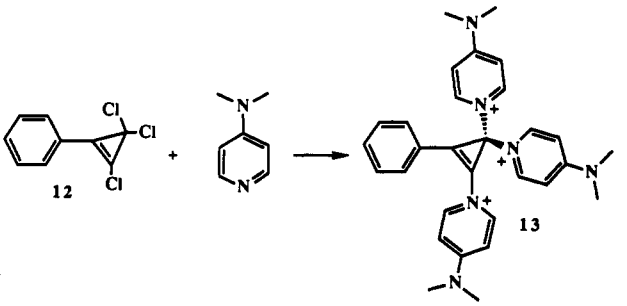
Scheme V. Synthesis of 12



TCCP 12

Scheme VI. Formation of 13



12 13

reaction product from acetonitrile was subjected to gel permeation chromatography to give the singly-substituted mixed allylide 10 as indicated by NMR spectroscopy. The last compound to elute from the column showed an NMR spectrum consistent with a double-addition allylide product, 11. The resonances between 1.7 and 1.2 ppm integrated to 32 protons, and those between 3.26 and 3.1 ppm integrated to 24 protons. There was significant broadening in the two most downfield resonances, probably as a result of slow rotation about the two most downfield resonances, probably as a result of slow rotation about the two decylmethyl groups. The isolation of these products from the addition of an aminopyridine to 1 demonstrates that even with very nucleophilic pyridines, some scrambling occurs of the substituents on the cyclopropene. In previous studies of reactions involving mixed 4-aminopyridines, such multiply-substituted products were undoubtedly formed to small extents but escaped detection by the analytical methods used.

General Reactivity of Related Pyridinium Systems. (1) 2-Phenyl-1,3,3-tris(4-(dimethylamino)pyridinium-1-yl)cyclopropene. In order to increase our general understanding of the densely charged pyridinium systems, the nucleophilic reactivity of a related system, 2-phenyl-1,3,3-trichlorocyclopropene,[11,15,16] 12, was also explored. The synthesis is straightforward, and 12 was obtained in 65% yield from the Friedel–Crafts alkylation of benzene with trichlorocyclopropenium cation (Scheme V). Compound 12 was allowed to react with DMAP in chloroform. The ^{1}H NMR spectrum of the resulting brown solution showed a complex mixture of products. Since the desired multiple-addition product 13 was not formed cleanly isolation of products was not attempted. Nevertheless, it was clear that the reaction is much slower than the corresponding reaction with tetrachlorocyclopropene.

Our work to date has shown that an increase in solvent polarity leads to the formation of products arising from further substitution on the cyclopropene ring. After 2 days in acetonitrile, the reaction of DMAP with 12 formed a large amount of crystalline material. The ^{1}H NMR spectrum of the isolated solid shows signals from two distinct types of DMAP groups, integrating 2:1, as well as resonances from one phenyl ring. Furthermore, ^{13}C NMR data show six different types of quaternary carbon atoms. These data are consistent with the structure shown for compound 13, 2-phenyl-1,3,3-tris(4-(dimethylamino)-

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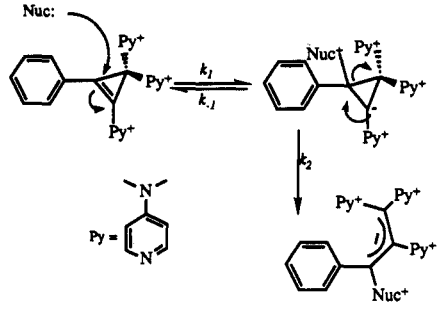
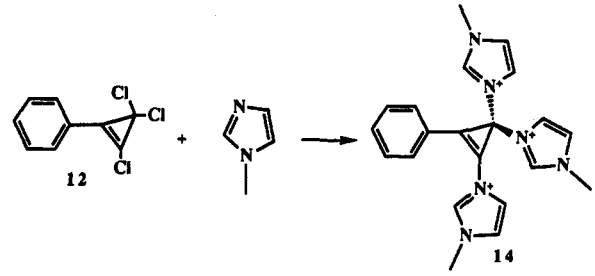
Scheme VII. Nucleophilic Addition to 13



Scheme VIII. Formation of 14



pyridinium-1-yl)cyclopropene (Scheme VI).

The possibility that the structure was the other possible isomer, 3-phenyl-1,2,3-tris(4-(dimethylamino)pyridinium-1-yl)cyclopropene, was rejected on the basis of the ^{13}C NMR data. If the phenyl group were on C3 of the cyclopropene ring, the ^{13}C NMR spectrum would show signals from five quaternary carbons, instead of the six observed. The trichloride salt of 13 is hygroscopic and deliquescent. The tris(hexafluorophosphate) salt, prepared by precipitating 13 from water with $NaPF_6$, is a stable white crystalline solid. This salt was used in all subsequent reactions.

Reactions of Nucleophiles with 13. If the reactivity of 13 were similar to that of 1, the reaction to yield open chain allylides would be straightforward at this point. This has not proved to be the case. Just as the reaction to form the substituted cyclopropene was sluggish in comparison to the corresponding reaction to form 1, the rate of the subsequent ring-opening step was also observed to be dramatically retarded. The reaction of DMAP with 13 $(PF_6^-)_3$ in CD_3CN was followed by NMR spectroscopy. After 15 min at room temperature no discernible reaction had taken place. (The corresponding reaction of DMAP with 1 is completed within 1 min.) After 3 days, some starting material was still evident, and the consumed material slowly began to precipitate from solution as a dark brown, gelatinous solid. The different reactivity (Scheme VII) of the phenyl-substituted system is surprising in view of the fact that the incipient cyclopropyl anion should be nearly as stable as that formed upon the addition of nucleophiles to 1.

The competition of ring opening vs elimination of the intermediate cyclopropyl anion clearly depends strongly on the electronic nature of the substituents. For pyridine itself ring opening can occur after two or three pyridinium groups have added to tetrachlorocyclopropene. The alkylpyridinium-substituted cyclopropyl anion opens only after the third pyridine has added. Cyclopropenes substituted with 4-aminopyridinium groups open only after the fifth addition has occurred, and even then the elimination process competes with the ring-opening process. Only when the cyclopropyl anion is extremely stabilized, as in the case of the addition of cyanide ion to 1,[2] does the ring opening appear to proceed without competing elimination.

(2) 2-Phenyl-1,3,3-tris(3-methylimidazolium-1-yl)-cyclopropene. Although imidazoles are less basic than DMAP, they react readily with tetrachlorocyclopropene. Thus, 12 was allowed to react with 1-methylimidazole in acetonitrile to give high yields of 2-phenyl-1,3,3-tris(3-methylimidazolium-1-yl)cyclopropene, 14 (Scheme VIII). The white product precipitated from the reaction mixture and was purified by recrystallization of the $(PF_6^-)_3$ salt. The structure was confirmed by the presence of four quarternary signals in the ^{13}C NMR spectrum. Unfortunately, the reactivity of 14 mirrors that of 13; the reaction with nucleophiles is slow, and ring opening to isolable monomeric products did not occur.

This large difference in reactivity between the phenyl-substituted derivatives of 1 and 1 itself is quite surprising, especially in view of the fact that the formation of 13 and 14 requires successive addition–elimination reactions. Although the phenylcyclopropenes 13 and 14 are the first compounds of their type, they do not appear to undergo the reaction for which they were prepared, namely, nucleophilic addition followed by anionic cyclopropyl ring opening. No phenyl-substituted allylide products have been isolated to date. The effect of substituents upon the addition of nucleophiles and upon the relative rates of ring opening and elimination are not well understood at present. If the hypothesis that ring opening can only occur from an electron-deficient cyclopropene is true, different phenylcyclopropenes must be synthesized if allylides are to be produced.

Conclusion

The incipient cyclopropyl anion of 1 has several reaction pathways available (Scheme I). The first is trivial: elimination of the nucleophile and regeneration of the reactants. In the second equilibrium, elimination of DMAP generates a new mixed cyclopropene 4. The eliminated DMAP reacts with remaining 1 in solution to form 3. In the decomposition reactions of 1 with weak nucleophiles and with 4-alkylpyridines, the major product identified is always 3. The third pathway, ring opening, is thought to be an irreversible process and produces the desired mixed allylide 5. The ring opening of 2 is extremely selective and limited to reactants that meet two criteria: (1) at the onset it must be strongly nucleophilic to attack the double bond of 1; (2) at the end it must be as electron withdrawing as DMAP to stabilize the allyl anion product 5. Non-pyridine nucleophiles that satisfy these requirements include cyanide ion, triphenylphosphine, and 1-methylimidazole.

The electron-deficient double bond in 1 is prone to nucleophilic attack, due to its two electron-withdrawing pyridinium substituents. The sluggish reactivities of 12 (and 13), however, probably arise from conjugation and electron donation from the phenyl group to the double bond. Because of the enhanced stability of the double bonds of 12 and 13, they are more resistant to nucleophilic attack.

Experimental Section

General. General experimental procedures, spectroscopy, and materials are as described in our previous work.[2,17]

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. Voltammagrams were recorded on a Houston Instruments Model 200 *xy* recorder. Working electrodes used for oxidations were either a Pt disk or a glassy carbon disk, with a Pt coil counter electrode and either a Ag/AgCl saturated KCl or a saturated calomel reference electrode. A hanging mercury drop

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electrode (HMDE) was used for reductions. Aqueous samples were run at a concentration of about 10 mM in 0.1 M KCl as a supporting electrolyte. Samples run in acetonitrile used either tetrabutylammonium tetrafluoroborate or tetrabutylammonium hexafluorophosphate at 0.5 M, and a silver wire pseudoreference electrode, with potentials referenced to ferrocene as an internal standard.

Low-pressure gel filtration chromatography was performed using a peristaltic pump (Bio-Rad Econo-Column Pump) and a 5-cm-diameter 20-cm-long column packed with Bio-Rad Bio-Gel P-2 poly(acrylamide) (−400 mesh or 200–400 mesh) beads. The typical flow rate was 80–150 mL/h depending upon mesh size, and the eluant was 0.1 M KCl. Fractions were either collected manually or with a Buchler Fractomette Alpha 200. Freeze-drying was carried out using a Virtis Freezemobile 12SL. The advantage of this type of system is that it is largely automated and can be left unattended. One-gram quantities could routinely be separated in one 24-h run.

Colorless single crystals of 1,2,3,3-tetrakis(4-(dimethylamino)pyridinium-1-yl)cyclopropene tetrakis(hexafluorophosphate), **1**,[2] suitable for X-ray analysis were grown by slow evaporation from acetone/water (Table SIII, supplementary material). Preliminary cell constants and space-group analysis 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 (9 0 $\bar{4}$, 6 2 8, 2 8 $\bar{4}$) every 1 h and by checking three orientation standards (9 0 $\bar{4}$, 6 2 8, 2 8 $\bar{4}$) every 200 reflections. Reorientation was necessary three times: after 200, 1800, and 5800 reflections.[18] A total of 6373 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. A total of 3173 reflections were rejected, 266 were systematic absences, and 2907 reflections were rejected as "unobserved" ($I < 3\sigma(I)$). The two lowest angle reflections (0,1,1) and (1,1,0) were also rejected from the data set leaving 3198 unique observed reflections. Data collected during the first 6 h were corrected for a 3.9% rise in intensity. No further "decay" was noted for the duration of data collection (93 h). The structure was solved by direct methods (MULTAN), which revealed the position of the four phosphorus atoms. The remaining non-hydrogen atoms were found by an alternating series of full-matrix least-squares refinement and ΔF map techniques. One water molecule was found and included at half occupancy without the corresponding hydrogens. Hydrogen atoms were included in the structure at their calculated positions with d(C–H) = 0.95 Å and with an isotropic thermal parameter 1.25 times the equivalent isotropic thermal parameter of the carbon to which they are attached. The final cycle of least-squares refinement yielded $R = 7.66\%$, $R_w = 9.58\%$, and GOF = 3.53. The majority of residual electron density was located around the four PF_6^- gegenions, two of which showed a high degree of thermal motion.

Reaction of 1 with 4-*tert*-Butylpyridine in Acetonitrile. To a solution of 0.445 g (0.403 mmol) of **1** (PF_6^-) in 20 mL of dry acetonitrile was added a solution of 0.085 g (0.629 mmol, 1.6 equiv) of 4-*tert*-butylpyridine in 5 mL of dry acetonitrile. Within a few minutes the solution was clear red. The mixture was warmed to reflux for 1 h, cooled to room temperature, and stirred overnight. Solvent was removed by rotary evaporation to give a deep-red sticky solid, which was further dried under high vacuum (4 μm). The solid was dissolved in 7 mL of acetone and 30 mL of ether was added, resulting in a red oil. The red oil was triturated with two 10-mL portions of ether to give a red powder. ^{1}H NMR showed pure **3**,[2] with no 4-*tert*-butylpyridine; yield 0.338 g (0.272 mmol), 67%, not including NMR and analysis samples. Anal. Calcd for $C_{38}H_{50}N_{10}F_{24}P_4 \cdot H_2O$: C, 36.67; H, 4.21; N, 11.25; P, 9.95. Found: C, 36.97; H, 3.94; N, 11.22; P, 9.89.

(*Z*)-1-(Triphenylphosphonio)-1,2,3,3-tetrakis(4-(dimethylamino)pyridinium-1-yl)allylide Tetrakis(hexafluorophosphate) (6). To a stirring solution of 0.81 g (0.731 mmol) of **1** in 20 mL of freshly distilled acetonitrile was added 0.21 g (0.804 mmol) of triphenylphosphine (PPh_3). The solution turned deep-red within 15 s and was stirred overnight under a N_2 atmosphere (atm). After removal of the solvent by rotary evaporation, the crude red solid was triturated with diethyl ether. The solid was dissolved in a minimal amount of acetone, and water was added until a precipitate formed. A minimal amount of acetone was then added until the solution became clear again. Chilling for 2 days at 0 °C to yielded 0.50 g (50%) of orange needles, mp 198–201 °C dec: ^{1}H NMR (300 MHz, CD_3CN) δ 7.87 (d, 2, J = 7.7 Hz), 7.74 (m, 6), 7.61 (m, 15), 6.72 (d, 2, J = 7.8 Hz), 6.64 (d, 2, J = 7.9 Hz), 6.33 (d, 2, J = 7.8 Hz), 6.11 (d, 2, J = 7.8 Hz), 3.16 (s, 6), 3.09 (s, 6), 3.04 (s, 6), 3.00 (s, 6); ^{13}C {^{1}H} NMR (75.8 MHz, CD_3CN) δ 156.98, 156.96, 156.91, 156.1, 148.2, 145.7, 145.4, 144.0, 143.0, 140.9, 135.6, 135.5, 135.4, 135.0, 134.83, 134.78, 134.71, 131.2, 131.1, 131.0, 130.97, 122.5, 121.3, 110.2, 109.5, 109.4, 109.0, 41.3, 41.1, 41.03, 40.95; UV–vis (CH_3CN, 1.18×10^{-5} M) 366 (4.40), 298 (4.90). Anal. Calcd for $C_{49}H_{55}N_8P_5F_{24} \cdot H_2O$: C, 42.34; H, 4.13; N, 8.06. Found: C, 42.53; H, 3.83; N, 7.72.

Equilibrium Determination of 6. To 0.5 mL of CD_3CN was added 7.4 mg (5.34×10^{-3} mmol) of **6**. After a ^{1}H NMR spectrum was taken, 50 μL of concd D_2SO_4 (98% w/w) was added to the NMR sample. A spectrum was taken after each 50-μL addition of concd D_2SO_4. Protonation of **6** occurred fully after 150 μL of acid was added; equilibrium between **6** and its conjugate acid was established after 75 μL of acid was in the solution. The concentration of D_2SO_4 was 2.1 M at equilibrium, and the pK_a value was determined:[9,10] ^{1}H NMR (300 MHz, CD_3CN) δ 7.86 (m, 2 H), 7.74 (m, 6 H), 7.60 (m, 15 H), 6.73 (d, J = 7.4 Hz, 2 H), 6.63 (d, J = 7.6 Hz, 2 H), 6.32 (d, J = 7.5 Hz, 2 H), 6.10 (d, J = 7.5 Hz, 2 H), 3.16 (s, 6 H), 3.09 (s, 6 H), 3.05 (s, 6 H), 3.01 (s, 6 H); conjugate acid ^{1}H NMR (300 MHz, CD_3CN) δ 7.87 (m, 2 H), 7.80 (d, J = 7.8 Hz, 2 H), 7.66 (m, 15 H), 7.54 (d, J = 7.4 Hz, 1 H), 7.46 (d, J = 7.8 Hz, 1 H), 6.79 (d, J = 7.9 Hz, 4 H), 6.54 (d, J = 7.8 Hz, 2 H), 6.32 (d, J = 7.7 Hz, 2 H), 3.14 (s, 12 H), 3.11 (s, 6 H), 3.04 (s, 6 H).

(*E*)- and (*Z*)-1-(3-Methylimidazolium-1-yl)-1,2,3,3-tetrakis(4-(dimethylamino)pyridinium-1-yl)allylide Tetrakis(hexafluorophosphate) (7a). To a solution of 0.54 g (0.493 mmol) of **1** in 20 mL of acetonitrile was added 0.05 g (0.543 mmol) of 1-methylimidazole. The solution underwent an immediate color change from clear to dark-red and was stirred under a N_2 atm overnight. After the solvent was removed by rotary evaporation, the crude red solid was triturated with diethyl ether. The reddish solid was dissolved in a minimal amount of acetonitrile, and water was added until a precipitate formed. A minimal amount of acetonitrile was again added until the solution became clear. After this procedure was repeated twice, the solution was chilled at 0 °C overnight to afford 0.35 g (59%) of a bright red solid: ^{1}H NMR (300 MHz, CD_3CN) δ 8.59 (s, 1), 8.43 (q, 1, J = 5.1, 9.7 Hz), 8.09 (t, 2, J = 8.1 Hz), 7.75 (m, 6), 7.32 (m, 1), 7.27 (m, 1), 7.19 (t, 1, J = 1.8 Hz), 7.09 (q, 1, J = 3.6, 5.4 Hz), 6.71 (m, 8), 3.77 (s, 3), 3.15 (dd, 24, J = 2.0, 7.8 Hz). Anal. Calcd for $C_{35}H_{46}N_{10}P_4F_{24} \cdot 2H_2O$: C, 34.38; H, 4.12; N, 11.46; P, 10.13. Found: C, 34.76; H, 4.06; N, 11.17; P, 10.27.

(*E*)- and (*Z*)-1-(3-Methylimidazolium-1-yl)-1,2,3,3-tetrakis(4-(dimethylamino)pyridinium-1-yl)allylide Tetrachloride (7b). To 0.95 g (1.30 mmol) of **1** were added 0.12 g (1.44 mmol) of 1-methylimidazole and 15 mL of distilled acetonitrile. A minimal amount of methanol (2 mL) was added to give a homogeneous dark-red solution, which was stirred overnight under a N_2 atm. The solvent was removed by rotary evaporation, and the crude red solid was triturated with diethyl ether and dried overnight under vacuum to give 0.65 g (62%) of a dark-red powdery solid: ^{1}H NMR (300 MHz, D_2O, internal CH_3CN standard) δ 8.12 (d, 2, J = 7.52 Hz), 7.81 (m, 7), 7.48 (m, 1), 7.40 (d, 1, J = 2.0 Hz), 7.23 (t, 1, J = 2.5 Hz), 6.64 (m, 8), 3.73 (s, 3), 3.63 (t, 3, J = 1.1 Hz), 3.01 (q, 24, J = 5.8, 10.0 Hz); ^{13}C {^{1}H} NMR (125.7 MHz, CD_3OD) δ 157.0, 156.9, 145.7, 145.5, 145.3, 145.0, 144.8, 143.02, 142.97, 109.9, 109.7, 109.52, 109.48, 108.2, 100.0, 40.9, 40.8, 40.6, 40.2, 37.0; UV–vis (H_2O, 6.46×10^{-5} M) 430 (4.09), 294 (4.76). Anal. Calcd for $C_{35}H_{46}N_{10}Cl_4 \cdot 5H_2O$: C, 50.12; H, 6.78; N, 16.70. Found: C, 50.05; H, 7.18; N, 16.72.

Determination of the pK_a of 7b. Seven buffer solutions were prepared by using HPLC-grade water to form stock solutions of 0.20 M HOAc, 0.20 M NaOAc, 0.10 M HCl, and 0.10 M potassium hydrogen phthalate (KHP). A two-point calibration was done on the pH meter using standard buffer solutions of pH 1.00 and

(18) Diffraction data for the crystal structure was collected by Dr. Fred Hollander, director of the UCB X-ray facility.

pH 7.00 (Fisher Scientific) to determine the following buffer pH values for the seven solutions: 2.57 (50.0 mL of KHP + 35.0 mL of HCl), 2.72 (50.0 mL of KHP + 29.0 mL of HCl), 3.26 (50.0 mL of KHP + 15.0 mL of HCl), 3.41 (50.0 mL of KHP + 10.0 mL of HCl), 4.02 (18.0 mL of NaOAc + 82.0 mL of HOAc), 4.63 (55.0 mL of NaOAc + 45.0 mL of HOAc), and 5.02 (70.0 mL of NaOAc + 30.0 mL of HOAc). By use of the seven buffer solutions and standard buffer pH solutions of 1.00, 2.00, and 3.00, and 7.00, dilute solutions of 7 of known concentrations were prepared, and the absorptions at 430 nm were measured. The pK_a's for the six pH solutions of 2.00, 2.57, 2.72, 3.00, 3.26, and 3.41 were determined to be 2.77, 2.79, 2.99, 2.81, 3.28, 3.10, in order of increasing pH. This results in an average pK_a value of 3.0 ± 0.2.

Reaction of 1 with Trimethyl Phosphite or 1,1,3,3-Tetramethyl-2-thiourea. To solutions of about 0.7 mmol of trimethyl phosphite or 1,1,3,3-tetramethyl-2-thiourea in 25 mL of acetonitrile was added about 0.4 mmol of 1. The solutions immediately became orange or red and were stirred at rt under a N_2 atm for 9–12 h. The solvent was removed by rotary evaporation, giving an orange or red solid which was then dissolved in minimal acetonitrile for ion exchange with Amberlyst A-21 resin to the chloride salt. After removal of water by lyophilization, the solid was chromatographed on Bio-Gel P-2 extra-fine grade poly(acrylamide) beads. Fractions were collected, freeze-dried, and desalted with methanol, but ^1H NMR spectra of the fractions showed only unreacted 1 and 3.

Reaction of 1 with KSCN. A 50-mL round-bottomed flask was charged with a solution of 0.309 g (0.394 mmol) of 1 (Cl^- salt) in 15 mL of methanol. A solution of 0.060 g (0.617 mmol, 1.6 equiv) of KSCN in 5 mL of methanol was added slowly. About half way through the addition the solution became orange and then red. The mixture was stirred at room temperature for 24 h. Solvent was removed at room temperature by rotary evaporation, giving a bright red solid. The red solid was treated with a 2-propanol/methanol solution (2/1) and filtered to remove the insoluble white solid. The white solid gave no color change when treated with a solution of $FeCl_3$ (not KSCN). The red solid gave the following: ^1H NMR (250 MHz, D_2O) δ 8.33 (d), 8.20 (d), 8.00 (d), 7.90 (m), 7.80 (d) (DMAP·HCl), 7.70 (d), 6.88 (d), 6.83 (d), 6.80 (m), 6.65 (d) (DMAP·HCl), 3.36 (s), 3.34 (s), 3.30 (s), 3.20 (s), 3.16 (s), 3.15 (s), 3.10 (s), 3.08 (s), 3.07 (s), 3.05 (s), 3.02 (s), 3.01 (s), 2.99 (s), 2.96 (s), (DMAP·HCl). Attempts to crystallize this material lead to decomposition.

1,1,2-Tris(4-(dimethylamino)pyridinium-1-yl)ethylene Tris(hexafluorophosphate) (8a). To a solution of 0.521 g (0.472 mmol) of 1 (PF_6^-) in 20 mL of acetonitrile was added a suspension of 0.062 g (0.729 mmol, 1.5 equiv) of KNO_2 in 10 mL of acetonitrile. The mixture quickly became dark brown and then deep-red. Solvent was removed by rotary evaporation, giving a deep-red solid. The sample was dissolved in 20 mL of acetone and filtered to remove inorganic salts. The acetone solution was diluted with 40 mL of methanol and allowed to stand. Two types of crystals grew: deep-red plates and orange prisms. The crystals were separated by hand. ^1H NMR of the red plates showed pure 3.[2] The orange prisms gave the following: ^1H NMR (250 MHz, CD_3CN) δ 7.98 (d, J = 8.0 Hz, 2 H), 7.77 (d, J = 8.1 Hz, 2 H), 7.65 (d, J = 8.0 Hz, 2 H), 7.47 (s, 1 H), 7.04 (d, J = 8.0 Hz, 2 H), 6.98 (d, J = 8.1 Hz, 2 H), 6.92 (d, J = 8.0 Hz, 2 H), 3.33 (s, 6 H), 3.31 (s, 6 H), 3.26 (s, 6 H); ^{13}C NMR (50.78 (MHz, CD_3CN, decoupled) δ 158.51, 158.31, 157.55, 140.62, 140.42, 133.50, 124.19, 110.74, 109.73, 109.58, 41.69, 41.64, 41.30. A DEPT experiment revealed the carbon at 133.50 to be quaternary, and the carbon at 124.19 to be a CH. The carbons at 41 were all CH_3's. Anal. Calcd for $C_{20}H_{31}N_6P_3F_{18}·H_2O$: C, 29.71; H, 4.11; N, 10.40; P, 11.49. Found: C, 30.02; H, 4.21; N, 10.24; P, 11.12.

1,1,2-Tris(4-(dimethylamino)pyridinium-1-yl)ethylene Trichloride (8b). To a mixture of 0.397 g (4.66 mmol) of potassium nitrite in 50 mL of acetonitrile was added 0.949 g (0.859 mmol) of 1 (hexafluorophosphate salt). Upon addition of the latter, the reaction mixture immediately turned dark-red. After chilling overnight at 0 °C, the reaction mixture was decanted to remove the insoluble potassium nitrite and dried by rotary evaporation to afford a dark-red solid. The solid was dissolved in a minimal amount of acetonitrile for ion exchange with Amberlyst A-21 resin to the chloride salt. After removal of water by lyophilization, the solid was chromatographed on Bio-Gel P-2 extra-fine poly(acrylamide) beads to separate 3 from 8. Fractions corresponding to the ethylene were collected, combined, and lyophilized to remove the water. The remaining red solid was then dissolved in a minimal amount of methanol, and the liquid was filtered through a pipet with a plug of glass wool. After rotary evaporation, the solid was dissolved in two drops of water, to which was added 0.50 mL of acetonitrile. This solution, after chilling at 0 °C overnight, yielded 0.087 g (20%) of small red crystals: ^1H NMR (200 MHz, D_2O, CH_3CN internal standard) δ 7.98 (d, J = 7.7 Hz, 2 H), 7.87 (d, J = 8.0 Hz, 2 H), 7.72 (d, J = 7.8 Hz, 2 H), 7.66 (s, 1 H), 6.97 (d, J = 6.1 Hz, 2 H), 6.92 (d, J = 6.2 Hz, 2 H), 6.82 (d, J = 6.1 Hz, 2 H), 3.23 (s, 6 H), 3.22 (s, 6 H), 3.16 (s, 6 H). Anal. Calcd for $C_{20}H_{31}N_6Cl_3·2H_2O$: C, 48.25; H, 7.08; N, 16.88. Found: C, 47.90; H, 7.20; N, 16.69.

4-(Methylamino)pyridine.[19] 4-Bromopyridine hydrochloride (Aldrich Chemical) (3.98 g, 20.5 mmol) was placed in a 300-mL Paar reactor constructed of Monel alloy. Aqueous 40% methylamine (140 mL) was cooled to 0 °C and poured directly into the Paar reactor. The mixture was heated and stirred at 175 °C (375 psi) for 8 h. The reaction mixture was allowed to cool and extracted 4 × 100 mL with chloroform. The chloroform extracts were combined and dried over K_2CO_3. The solvent was removed in vacuo leaving slightly yellow 4-(methylamino)pyridine (1.940 g, 17.9 mmol, 87.5% yield). The melting point of the crude material was 123–126 °C. The crude material was purified by sublimation giving 1.887 g of white crystalline 4-(methylamino)pyridine, mp 125–126 °C (lit.[19] mp 124.5–126 °C). With 4-chloropyridine hydrochloride the yield was reduced slightly to 80%.

4-(Decylmethylamino)pyridine (9). 4-(Methylamino)pyridine (20 mmol) was dissolved in 10 mL of dry dimethylsulfoxide (DMSO) and added dropwise via syringe to a suspension of NaH (22 mmol) in 10 mL of DMSO under argon. The mixture was stirred for 90 min until H_2 evolution was no longer evident. Decyl bromide (20 mmol) was added via syringe pump (3 h for the complete addition) to the vigorously stirred solution. The reaction mixture was stirred for an additional 12 h. Aqueous 10% KOH (25 mL) was carefully added to the reaction mixture. The resulting suspension was extracted 4 × 50 mL with petroleum ether (50–60 °C boiling range). The petroleum ether extracts were washed with aqueous KOH solution to remove residual DMSO. The petroleum ether extracts were dried over K_2CO_3, and the solvent was removed by rotary evaporation, leaving a yellow oil. Distillation under high vacuum yielded a colorless oil in 83.4% yield: ^1H NMR ($CDCl_3$) δ 8.19 (dd, 2 H, J_1 = 5.0 Hz, J_2 = 1.6 Hz), 6.45 (dd, 2 H, J_1 = 5.0 Hz, J_2 = 1.6 Hz), 3.30 (bt, 2 H, J = 7.5 Hz), 2.93 (s, 3 H), 1.56 (bm, 2 H), 1.27 (bs, 14 H), 0.88 (bt, J = 6.3 Hz, 3 H); ^{13}C NMR ($CDCl_3$) δ 153.1, 149.6, 106.19, 51.32, 37.24, 31.72, 29.44, 29.39, 29.31, 29.15, 26.84, 26.51, 22.53, 13.97. Anal. Calcd for $C_{16}H_{28}N_2$: 77.36; H, 11.36; N, 11.28. Found: C, 77.59; H, 11.26; N, 11.41.

Reaction of 9 with 1. A solution of 9 (52 mg, 0.2 mmol) in 10 mL of CH_3CN was added all at once to a solution of 1 ($4PF_6^-$) (224 mg, 0.2 mmol) in 25 mL of CH_3CN. The flask was stoppered and allowed to stand for 48 h. The solvent was removed, and the resulting red solid was ion exchanged to the chloride salt using a column of Amberlyst A-21 resin and 50% aqueous acetonitrile as eluant. The solvent mixture was removed in vacuo, and the red solid was chromatographed on Bio-Gel P-2 (40- × 2.5-cm column, 20 mL/h flow rate). Three distinct bands formed during the elution. It was unclear whether the final band was composed of more than one product. The fractions were collected, freeze-dried, and desalted with methanol. Preliminary product determination was made by ^1H NMR spectroscopy. Fraction 1 contained 3 exclusively. Fractions 2 and 3 were chromatographed again. Fraction 2, containing compound 10, gave only one band on repeated chromatography. Fraction 3, containing compound 11, was found to be contaminated with a small quantity of 10 and was rechromatographed. Compounds 10 and 11 were converted to their PF_6^- salts by treating them with aqueous solutions of $NaPF_6$ and isolating the precipitates by filtration. The orange solids were washed with ether containing 1% triethylamine in order to remove any unreacted base, followed by pure ether, and

(19) Wilbaut, J. P.; Broekman, F. W. *Recl. Trav. Chim. Pays-Bas* **1961**, *80*, 309–312.

were dried in vacuo. Compound **10** was isolated as a light orange solid (92 mg, 0.07 mmol) in 34% yield from this procedure. Anal. Calcd for $C_{47}H_{68}N_{10}P_4F_{24}$: C, 41.72; H, 5.07; N, 10.35; P, 9.16. Found: C, 41.45; H, 4.69; N, 10.33; P, 8.94. Attempted recrystallization of this material from acetone/water failed. Compound **11** was isolated in 9% yield (0.018 mmol, 27 mg) from this procedure but did not meet analysis. Anal. Calcd for $C_{56}H_{86}N_{10}P_4F_{24}$: C, 45.47; H, 5.86; N, 9.47; P, 8.38. Found: C, 46.01; H, 6.22; N, 9.21; P, 8.02.

1-Phenyl-2,3,3-trichlorocyclopropene (12).[14,15] Into a 100-mL round-bottomed flask were placed 2.667 g (20.0 mmol) of $AlCl_3$ and 3.796 g (21.3 mmol) of TCCP (see refs 2, 3). The mixture was spot warmed with a heat gun under a stream of dry nitrogen. The resulting reddish-purple solid was pumped on under high vacuum (10 μm) for 10 min to remove unreacted TCCP. To the solid was added 50 mL of dichloromethane and a magnetic stir bar. The mixture became dark green upon stirring. A solution of 1.448 g (18.5 mmol) of dry benzene in 50 mL of dichloromethane was added slowly. Evolution of HCl was noted after about half of the benzene solution was added. The homogeneous dark purple mixture was stirred for 30 min and was then thrown onto 100 mL of ice and water. The dichloromethane layer was extracted with three 100-mL portions of water and dried over $MgSO_4$. Dichloromethane was removed by rotary evaporation to give an amber oil. The oil was taken into 10 mL of petroleum ether and placed in a freezer. Crystals were collected and washed with cold petroleum ether (save washes). The crystals were recrystallized from 8 mL of petroleum ether: yield 0.173 g, 3.7%; mp 40–43 °C (lit.[14,15] mp 37–39 °C). A better method for purifying the product was found. The crude oil was transferred to a sublimation apparatus and frozen with a ice/methanol bath and then evacuated. The solid was then sublimed at 40 °C (yield 60%): ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.73 (m, 2 H), 7.55 (m, 3 H); ^{13}C NMR (50.8 MHz, decoupled, $CDCl_3$) δ 132.0, 129.8, 129.3, 128.0, 121.5, 121.2, 59.3.

2-Phenyl-1,3,3-tris(4-(dimethylamino)pyridinium-1-yl)-cyclopropene Trichloride (13). A solution of 2-phenyl-1,3,3-trichlorocyclopropene, **12** (2.19 g, 10 mmol), in 10 mL of acetonitrile and a solution of DMAP (5.00 g, 40.9 mmol) dissolved in 75 mL of acetonitrile were mixed and placed in a 125-mL stoppered Erlenmeyer flask. The mixture became warm and gradually darkened. After 30 min a white, crystalline solid began to be deposited on the sides of the flask. The mixture was allowed to stand for 24 h. The dark brown mixture was filtered rapidly through a medium porosity fritted disk to yield 2-phenyl-1,1,3-tris(4-(dimethylamino)pyridinium-1-yl)cyclopropene trichloride (4.24 g, 7.24 mmol, 72%) as off-white, blocky, extremely hygroscopic crystals: ^{1}H NMR (400 MHz, D_2O) δ 8.36 (d, 2 H, J = 8.0 Hz), 8.09 (d, 4 H, J = 8.0 Hz), 7.79 (dd, 2 H, J_1 = 7.6 Hz, J_2 = 1.5 Hz), 7.54 (m, 3 H), 7.09 (d, 2 H, J = 8.0 Hz), 6.87 (d, 4 H, J = 8.1 Hz), 3.29 (s, 6 H), 3.14 (s, 12 H); ^{13}C NMR (100 MHz, D_2O) methyl δ 41.20, 40.51; methine δ 139.52, 138.69, 133.60, 130.93, 130.41, 109.58, 109.00; quat δ 157.35, 157.29, 119.98, 112.79, 104.56, 68.31. The material isolated in this manner was free from impurities (by NMR) but was very hygroscopic. The tris(hexafluophosphate), prepared as an analytical sample, was precipitated from the trichloride in water with $NaPF_6$, filtered, and recrystallized from acetone/water to give highly refractive transparent prisms. The crystals were dried in vacuo at 100 °C for 24 h prior to analysis. During this time the crystals became white and opaque: ^{1}H NMR (400 MHz, CD_3CN) δ 8.27 (d, 2 H, J = 8.1 Hz), 7.99 (d, 4 H, J = 8.1 Hz), 7.86 (d, 2 H, J = 6.9 Hz), 7.69 (m, 3 H), 7.10 (d, 2 H, J = 8.1 Hz), 6.92 (d, 4 H, J = 8.1 Hz), 3.38 (s, 6 H), 3.24 (s, 12 H); ^{13}C NMR (100 MHz, CD_3CN) methyl δ 42.02, 41.28; methine δ 140.66, 139.71, 134.36, 131.83, 131.10, 109.94, 109.66; quat δ 158.15, 157.95, 120.78, 113.65, 105.38, 69.15. Anal. Calcd for $C_{30}H_{35}N_6P_3F_{18}$: C, 39.40; H, 3.86; N, 9.19. Found: C, 39.55; H, 4.13; N, 8.97.

2-Phenyl-1,3,3-tris(3-methylimidazolium-1-yl)cyclopropene Trichloride (14). 1-Methylimidazole (2.62 g, 32 mmol) in 5 mL of acetonitrile was added dropwise to a swirled solution of 2-phenyl-1,3,3-trichlorocyclopropene (1.73 g, 7.9 mmol) in 50 mL of acetonitrile. The solution became warm and turned green. Almost immediately, crystalline solid began to be deposited on the sides of the flask. The mixture was allowed to stand for 24 h. The mixture was filtered to yield 3.2 g of hygroscopic white solid. ^{1}H NMR of the solid revealed that it contained **14** and some other unidentified compound. The solid was ion exchanged to the PF_6^- salt and recrystallized from acetone/water by slow evaporation. Highly refractive needles formed upon standing. The crystalline material was collected by filtration and dried in vacuo to yield pure **14** (1.62 g, 2.04 mmol, 26%). Upon drying the crystals became opaque: ^{1}H NMR (400 MHz, CD_3CN) δ 9.25 (s, 1 H), 8.70 (s, 2 H), 8.01 (t, 1 H, J = 2.0 Hz), 7.93 (d, 2 H, J = 7.0 Hz), 7.73 (m, 4 H), 7.61 (t, 2 H, J = 2.0 Hz), 7.55 (t, 2 H, J = 2.0 Hz), 4.04 (s, 3 H), 3.88 (s, 6 H); ^{13}C NMR (100 MHz, CD_3CN) δ 139.36, 137.84, 135.37, 132.71, 131.13, 126.91, 126.56, 123.90, 122.16, 119.45, 108.44, 106.94, 38.18, 37.62. Anal. Calcd for $C_{21}H_{23}N_6P_3F_{18}$: C, 31.75; H, 2.92; N, 10.58. Found: C, 32.11; H, 2.68; N, 10.53.

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Supplementary Material Available: X-ray data for **1** (10 pages). Ordering information is given on any current masthead page.