Massive Electrostatic Effects on Heteropolar C–C Disconnections: Transforming a Phenyl Anion into a Potent Leaving Group

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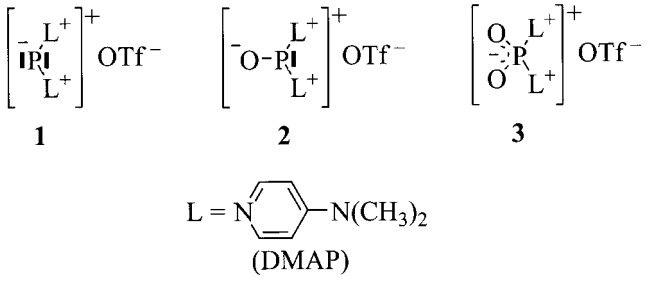
The SASAPOS protocol – a general reaction sequence which allows the complete exchange of various neutral ligands X in organic, elementorganic, and inorganic systems by cationic ligands L^+ – has been applied to a small variety of pentafluoro benzene derivatives C_6F_5–E (E = –C(O)H, –C(N–Ph)H, $–PCl_2$/$–P(L^+)_2$, –H) yielding the ion clusters $C_6(L^+)_5$–E $(F_3CSO_3^-)_5$. The reaction conditions required to observe a heteropolar C–C or C–P disconnection, with a highly stabilized pentakisonio-substituted phenyl anion as the key intermediate, are specified. When E = H, the latter compound also figures as the key intermediate during H/D exchange under basic conditions.

Introduction

In previous work we have demonstrated that mono-cationic leaving groups based on P^I, P^{III}, and P^V such as **1**–**3** (cf. Scheme 1) are excellent nucleofuges in various S_N reactions.[1]



Scheme 1. Monocationic leaving groups **1**–**3**.

Evidently strong electrostatic stabilization of the lone pairs of the nucleofuge is responsible for the performance of **1**–**3** as leaving groups. We concluded that, in principle, many cationically substituted fragments could function as novel nucleofuges; their performance should increase with increasing positive charge.

In a revealing experiment we have recently verified these expectations (Scheme 2).[2]

The resonance contributor **5/B** – although certainly of minor importance in the ground state of **5** – has been explicitly included in Scheme 2 to indicate, in principle, an electronic analogy to nucleophilic carbenes of the Arduengo type.

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Such an extremely facile decarboxylation of an aryl carboxylate is unprecedented. It must be due to massive electrostatic stabilization of the $C(sp^2)$ lone pair in **5** by the five cationic ligands. Below we report on our investigations in which this phenomenon is further analyzed.

Results and Discussion

Recently we introduced the SASAPOS (**s**elf-**a**ctivated **s**ilyl-**a**ssisted **p**oly**o**nio-**s**ubstitution) protocol as a general reaction sequence which allows one to exchange completely various neutral ligands X in organic, elementorganic, and inorganic systems T with diverse cationic ligands $–L^+$[1–11] according to Scheme 3.

We have applied this protocol to a small variety of pentafluoro benzene derivatives C_6F_5–R (**7**–**9**), with R representing several key electrofuges.[12,13]

The results obtained when "sasaposing" pentafluoro benzaldehyde **7** and the corresponding phenyl imine **8**[12] are summarized in Scheme 4.

When the aldehyde **7** was subjected to the SASAPOS protocol only the pentakisonio-substituted benzene derivative **6** was isolated in high yield (74%). The latter salt was independently synthesized by "sasaposing" pentafluoro benzene.[7] Thus the fluorine/onio exchange in **7** is closely connected to a deformylation, an unusual C–C disconnection with aromatics. This process is most likely to occur after the completion of the SASAPOS cascade, but deformylation after partial ligand exchange cannot be strictly ruled out. By contrast, the starting aldehyde **7** is thermally stable at least up to its boiling point of 165 °C. As indicated in Scheme 4, two main mechanistic variations of this deformylation are feasible. Path A would involve direct thermal fragmentation of the cationically substituted aldehyde

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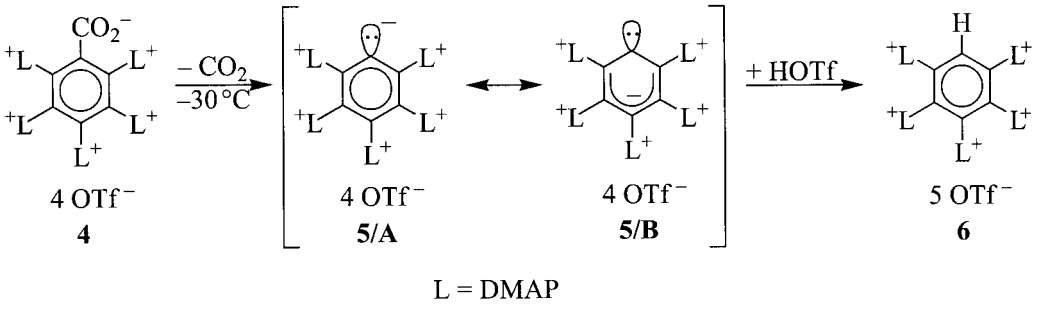
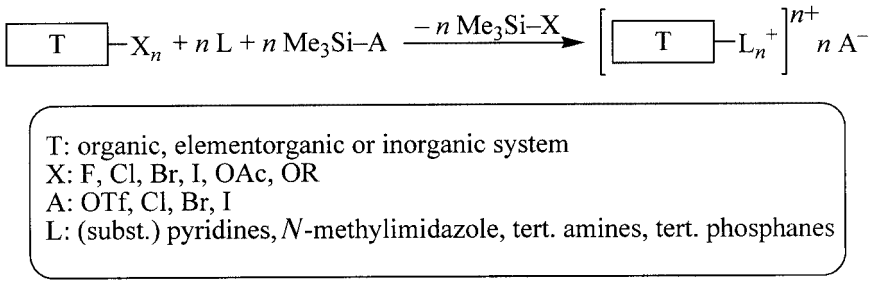


Scheme 2. Electrostatically activated decarboxylation of **4** involving the percationically substituted leaving group **5**.



Scheme 3. The general SASAPOS protocol.

10 to the observed product **6**. However, according to Path B (cf. Scheme 4) the deformylation could be facilitated by the addition of L to the highly electrophilic carbonyl function in **10** and the expulsion of the corresponding formylonio system **14** as an electrofuge. We have synthesized the latter compound in previous work.[4] Above 80 °C, it decomposes into L, HOTf, and CO. In any case, both of these mechanistic variations of the deformylation process would profit from the pronounced tendency of **5** to act as a "carbanionic" leaving group.

By remarkable contrast the analogous SASAPOS sequence with the *N*-phenylimine **8** yielded the corresponding peronio-substituted system **12** as a stable salt in nearly quantitative yield. A heterolytic C–C disconnection between the benzene ring and the imidoyl function was thus, somewhat surprisingly, not observed. This is probably due to the sterically enforced *E* configuration of imine **12**. The well-known[14] stereoelectronics of nitrilium ion-forming fragmentations require an *E* relationship between the N lone pair in **12** and the leaving group **5**, which is not realizable in the congested ion cluster **12**.[7]

The attempt to generate the elusive aldehyde **10** by acid-catalyzed hydrolysis of its Schiff base **12** yielded its hydrate **13** in high yield. This behavior is expected for an aldehyde with a potent electron-withdrawing group, but to the best of our knowledge it has never been reported for an aromatic aldehyde.

In order to generate aldehyde **10** from its hydrate **13** by dehydration, the latter was treated at room temperature with molecular sieves (4 Å) in acetonitrile. This operation resulted in the exclusive formation of the pentakisonio-substituted benzene derivative **6**. Under the catalytic influence of the zeolitic material, a heteropolar C–C disconnection took place, with **5** as nucleofuge and formic acid or formiate as the electrofuge.

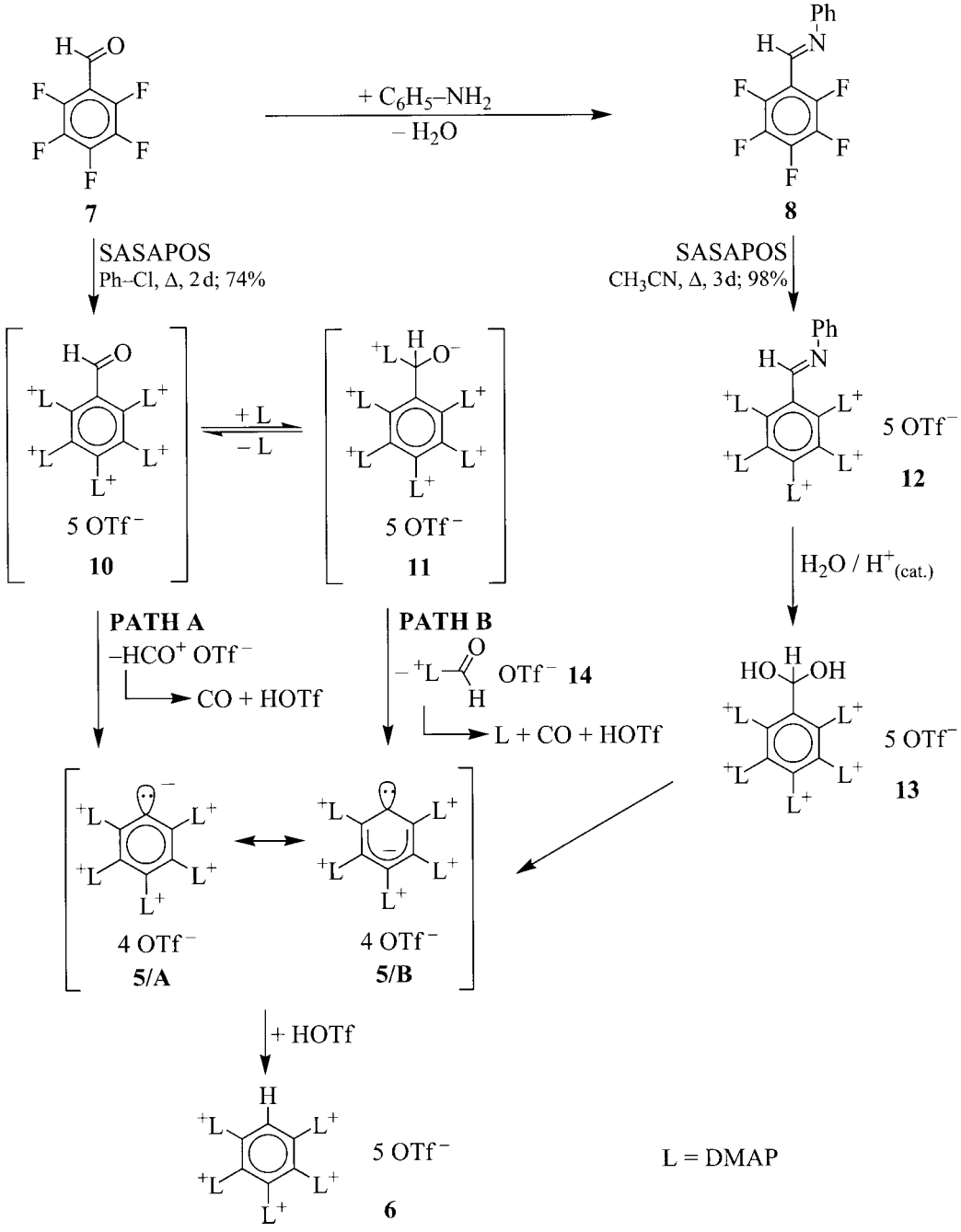
The pentakisonio-substituted system **6** was also produced in excellent yield (96%) and purity when dichloro pentafluorophenyl phosphane **9**[13] was subjected to the SASAPOS protocol. Here the substitution cascade on the aromatic ring was achieved already at room temperature and led to completion within minutes. Obviously, the dichloro phosphanyl substituent in **9** is a much better activator for a SASAPOS cascade than organic acceptor functions, like formyl or imidoyl functions in **7** or **8**. A rationale is given in Scheme 5.

From our experience with SASAPOS cascades on phosphorus polyhalides[15] we conclude that **15** should be formed in a rapid first step. This conclusion was confirmed by ^{1}H-NMR-monitoring.

The bisonio phosphanyl substituent in **15** represents a novel, very powerful acceptor function which very effectively triggers a rapid SASAPOS cascade at the aromatic ring yielding the heptacationically substituted system **16**. After completion of the latter process, further nucleophilic attack of L at the phosphorus center in **16** yields an (inseparable) mixture of nucleofuge **5** and trisonio phosphane **17**.[15] Hydrolysis of this mixture yields pure **6** in high yield.

The results summarized in Scheme 4 and Scheme 5 underline that a phenyl anion is massively stabilized by five cationic substituents, thereby transforming it into a powerful nucleofuge. This led us to expect that **5** might by accessible by simple deprotonation of **6**.

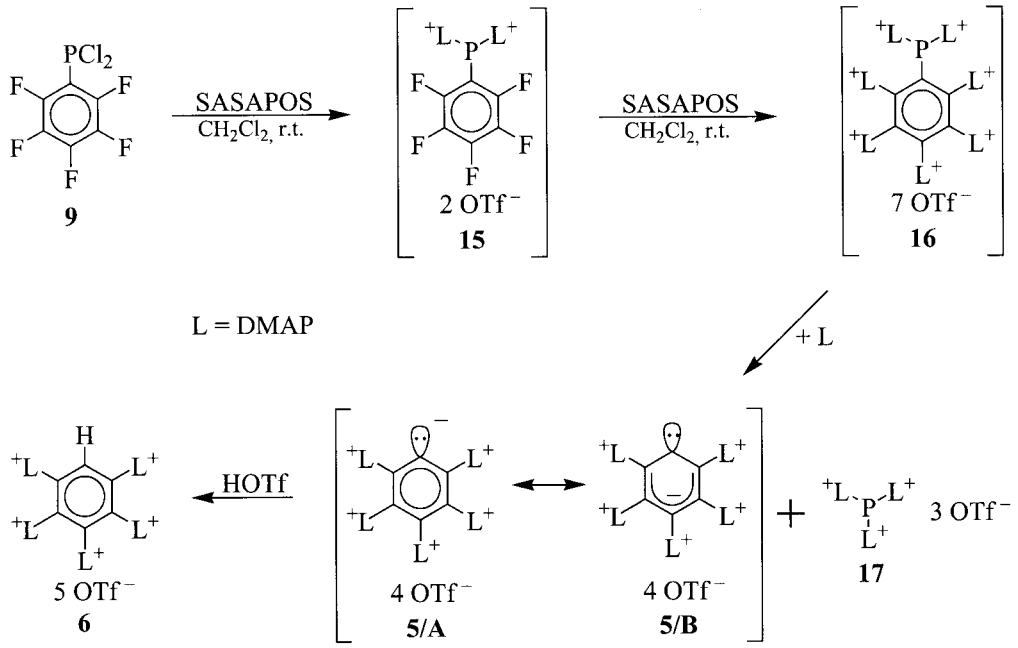
Therefore, benzene derivative **6** was treated in acetonitrile solution with KO*t*Bu or alternatively as suspension in THF with *n*-butyllithium. The resulting salt-like products (e.g. mixtures of **5** and alkali triflate) were isolated by filtration



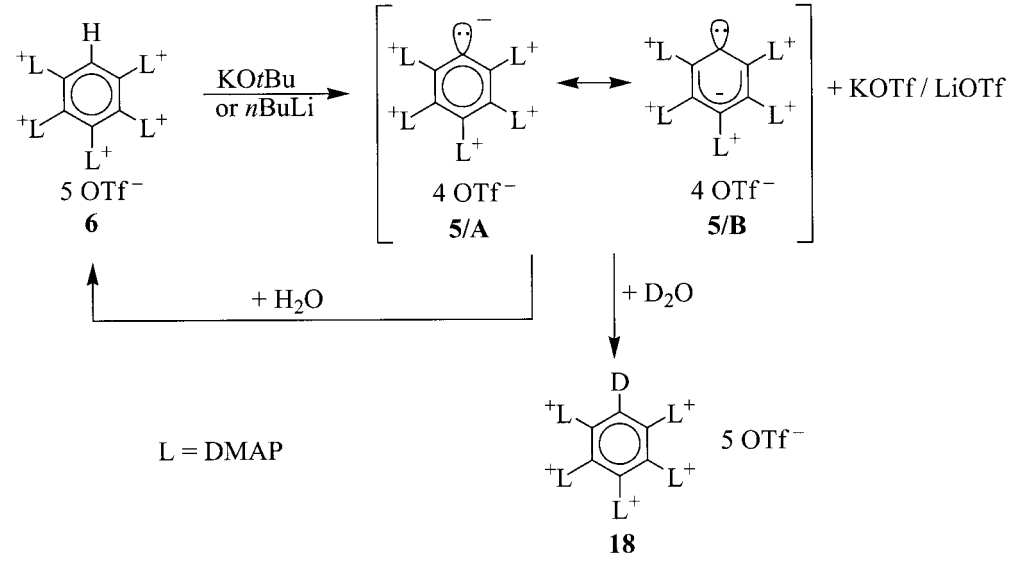
Scheme 4. SASAPOS cascades of pentafluoro benzaldehyde **7** and phenyl imine **8**.

(in the case of the acetonitrile solutions, after addition of diethyl ether) and characterized by NMR spectroscopy and FAB-MS after trapping by addition of either H_2O or D_2O according to Scheme 6. In contrast to the addition of water, which regenerated **6**, the trapping with D_2O yielded the corresponding deutero benzene derivative **18**, which we independently synthesized in previous work.[2]

Besides some minor signals corresponding to decomposition products (formed by exchange of DMAP by OH^- during the trapping reactions; cf. ref. 7) of **6**, or **18**, the ^{1}H- and ^{13}C-NMR spectra of **5** recorded in nitromethane containing H_2O or D_2O were identical to those of independently synthesized **6** or **18**. The difference between the NMR spectra of **6** and **18** is the absence of the signal at 8.6 ppm (which corresponds to the benzene proton in **6**) in the ^{1}H NMR spectrum of **18**, and the low intensity and broadening of the resonance at δ = 132 ppm (which corresponds to the hydrogen-substituted carbon atom in **6**) in the ^{13}C NMR spectrum of **18**. The H/D exchange according to Scheme 6 was further confirmed by FAB-MS. The peaks of the sample triggered with D_2O appear at exactly one *m*/*z* unit higher than in the corresponding spectrum recorded in the presence of water (see experimental section for detailed interpretation).



Scheme 5. SASAPOS protocol applied to dichloro pentafluorophenyl phosphane **9**.



Scheme 6. Deprotonation of benzene derivative **6** and subsequent trapping reactions.

Conclusions

The above results provide a detailed insight into the leaving group potential of the percationically substituted phenyl anion derivative **5**, which we have invoked in previous work.[2] By transforming pentafluoro benzaldehyde **7** into phenyl imine **8** followed by SASAPOS and hydrolysis we have specified the reaction conditions for C–C disconnections via **5** (e.g. room temperature). The same mild conditions are required for the C–P disconnection observed during the SASAPOS cascade of dichloro pentafluorophenyl phosphane **9**. Based on these results we now conclude that the pentakisonio phenyl moiety may also figure as a strong acceptor substituent, introducing the massive electrostatic effects of the pentacationic ligand into a broad variety of systems. Corresponding experiments are under way.

Experimental Section

General Remarks: All reactions were carried out under N_2 atmosphere in dry solvents.

Pentakis[(4-dimethylamino)-1-pyridinio]benzene Pentakis(trifluoromethanesulfonate) (6) from 7: Pentafluoro benzaldehyde **7** (208 mg, 1.06 mmol) was added to a solution of DMAP (907 mg, 7.42 mmol) and Me_3SiOTf (1.15 mL, 6.36 mmol) in chlorobenzene (25 mL). The reaction mixture was stirred under reflux for 2 d; the formation of a light brown precipitate occurred after 3 h. The pre-

cipitate was filtered, washed with CH_2Cl_2 (5 × 5 mL), and dried in high vacuum to yield 1.12 g (74.1%) of **6** as a light brown powder. ^{1}H NMR (400 MHz, CD_3CN): δ = 3.18 (s, 6 H, CH_3), 3.20 (s, 12 H, CH_3), 3.24 (s, 12 H, CH_3), 6.87 (d, ^3J(H,H) = 8.06 Hz, 2 H, H3/5 DMAP), 6.89 (d, $^3J_{H,H}$ = 8.05 Hz, 4 H, H3/5 DMAP), 7.00 (d, $^3J_{H,H}$ = 8.30 Hz, 4 H, H3/5 DMAP), 8.02 (d, $^3J_{H,H}$ = 8.06 Hz, 4 H, H2/6 DMAP), 8.06 (d, $^3J_{H,H}$ = 8.05 Hz, 2 H, H2/6 DMAP), 8.12 (d, $^3J_{H,H}$ = 8.06 Hz, 4 H, H2/6 DMAP), 8.65 (s, 1 H, benzene) ppm. ^{13}C NMR (100 MHz, CD_3CN): δ = 41.37 (s, CH_3), 41.42 (s, CH_3), 109.81 (s, C3/5 DMAP), 110.54 (s, C3/5 *p*-DMAP), 110.63 (s, C3/5 DMAP), 121.81 (q, $|^1J_{C,F}|$ = 319.9 Hz, CF_3), 132.84 (s, C6 benzene), 137.94 (s, C1/5 benzene), 138.31 (s, C3 benzene), 140.99 (s, C2/6 DMAP), 141.43 (s, C2/6 DMAP), 142.38 (s, C2/4 benzene), 157.42 (s, C4 *p*-DMAP), 157.45 (s, C4 DMAP), 157.80 (s, C4 DMAP) ppm. FAB-MS (NBA): *m*/*z* = 1279 [M – OTf]$^+$, 1129 [M – HOTf – OTf]$^+$, 1009 [M + H – DMAP – 2OTf]$^+$. $C_{46}H_{51}F_{15}N_{10}O_{15}S_5$ (1429.24) + 2H_2O: calcd. C 37.71, H 3.78, N 9.56, S 10.94; found C 37.44, H 3.60, N 9.43, S 11.30.

Pentakis[(4-dimethylamino)-1-pyridinio]benzene Pentakis(trifluoromethanesulfonate) (6) from 9: Dichloro pentafluorophenyl phosphane **9** (0.10 mL, 1.15 mmol) was added to a solution of DMAP (1.26 g, 10.3 mmol) and Me_3SiOTf (1.66 mL, 9.20 mmol) in CH_2Cl_2 (25 mL) whereupon the color of the solution changed from colorless via yellow to dark red during 2 minutes. The separation of a red precipitate started after 10 min. Water (1 mL) was added after additional 12 h of stirring, during which the red color of the suspension disappeared. The yellow oil resulting from full removal of the solvent was stirred in CH_2Cl_2 (50 mL) overnight. The formed precipitate was filtered, washed with CH_2Cl_2 (5 × 5 mL), and dried in high vacuum to yield 1.58 g (96.4%) of **6** as a colorless powder. See data above.

Pentakis[(4-dimethylamino)-1-pyridinio]benzene Pentakis(trifluoromethanesulfonate) (6) from 13: Molecular sieves (4 Å) (ca. 1.0 g) were added to a solution of **13** (1.23 g, 0.83 mmol) in CH_3CN (20 mL). After 20 d, the solvent was reduced to a minimum after removal of the molecular sieve, and CH_2Cl_2 (20 mL) was added. The resulting precipitate was filtered, washed with CH_2Cl_2 (5 × 5 mL), and dried in high vacuum to yield 795 mg (67.0%) of **6** as a light red powder. See data above.

Pentakis[(4-dimethylamino)-1-pyridinio]benzaldehyd-phenylimine Pentakis(trifluoromethanesulfonate) (12): DMAP (1.60 g, 13.0 mmol) and Me_3SiOTf (1.76 mL, 9.78 mmol) were added to a solution of pentafluoro benzaldehyde phenylimine **8** (442 mg, 1.63 mmol) in CH_3CN (20 mL). The reaction mixture was stirred with heating under reflux conditions for 3 d. The solvent was fully removed in high vacuum and CH_2Cl_2 (25 mL) was added. The resulting precipitate was filtered, washed with CH_2Cl_2 (5 × 5 mL), and dried in high vacuum to yield 2.45 g (98.0%) of **12** as a light yellow powder. ^{1}H NMR (400 MHz, CD_3NO_2): δ = 3.28 (s, 6 H, CH_3), 3.29 (s, 12 H, CH_3), 3.35 (s, 12 H, CH_3), 6.90 (m, 2 H, phenyl), 7.00 (m, 1 H, phenyl), 7.01 (d, $^3J_{H,H}$ = 7.93 Hz, 2 H, H3/5 DMAP), 7.02 (d, $^3J_{H,H}$ = 8.06 Hz, 4 H, H3/5 DMAP), 7.13 (d, $^3J_{H,H}$ = 8.06 Hz, 4 H, H3/5 DMAP), 7.32 (m, 2 H, phenyl), 8.23 (d, $^3J_{H,H}$ = 8.06 Hz, 2 H, H2/6 DMAP), 8.29 (d, $^3J_{H,H}$ = 8.06 Hz, 4 H, H2/6 DMAP), 8.39 (d, $^3J_{H,H}$ = 8.06 Hz, 4 H, H2/6 DMAP) ppm. ^{13}C NMR (100 MHz, CD_3NO_2): δ = 41.34 (s, CH_3), 41.42 (s, CH_3), 41.45 (s, CH_3), 109.89 (s, C3/5 DMAP), 110.54 (s, C3/5 DMAP), 110.64 (s, C3/5 *p*-DMAP), 122.05 (q, $|^1J_{C,F}|$ = 320.0 Hz, CF_3), 122.42 (s, C2/6 C_6H_5), 130.44 (s, C4 C_6H_5), 130.74 (s, C3/5 C_6H_5), 137.93 (s, C1/4 benzene), 139.10 (s, C1/4 benzene), 140.56 (s, C2/3/5/6 benzene), 141.41 (s, C2/6 *p*-DMAP), 141.58 (s, C2/6 DMAP), 142.07 (s, C2/3/5/6 benzene), 142.73 (s, C2/6 DMAP), 150.06 (s, CH imine), 150.18 (s, C1 C_6H_5), 157.66 (s, C4 DMAP), 158.13 (s, C4 DMAP) ppm. FAB-MS (NBA): *m*/*z* = 1382 [M – OTf]$^+$, 1232 [M – HOTf – OTf]$^+$. $C_{53}H_{56}F_{15}N_{11}O_{15}S_5$ (1532.37) + 2H_2O: calcd. C 40.59, H 3.86, N 9.82, S 10.22; found C 40.85, H 3.77, N 9.57, S 10.10.

Pentakis[(4-dimethylamino)-1-pyridinio]benzaldehyd-hydrate Pentakis(trifluoromethanesulfonate) (13): Me_3SiOTf (0.40 mL, 2.21 mmol) and H_2O (2 mL) were added to a suspension of **12** (3.38 g, 2.21 mmol) in CH_3CN (30 mL). The solvent was fully removed in high vacuum after 2 d, and CH_2Cl_2 (40 mL) was added. The resulting precipitate was recrystallized from CH_3CN/diethylether, filtered, washed with diethyl ether (5 × 5 mL), and dried in high vacuum to yield 2.36 g (73.0%) of **13** as a light brown powder. ^{1}H NMR (400 MHz, CD_3NO_2): δ = 3.28 (s, 6 H, CH_3), 3.29 (s, 12 H, CH_3), 3.37 (s, 12 H, CH_3), 7.01 (d, $^3J_{H,H}$ = 8.18 Hz, 2 H, H3/5 DMAP), 7.01 (d, $^3J_{H,H}$ = 7.93 Hz, 4 H, H3/5 DMAP), 7.04 (s, 2 H, OH), 7.11 (d, $^3J_{H,H}$ = 7.93 Hz, 4 H, H3/5 DMAP), 8.13 (d, $^3J_{H,H}$ = 7.93 Hz, 2 H, H2/6 DMAP), 8.21 (d, $^3J_{H,H}$ = 7.93 Hz, 4 H, H2/6 DMAP), 8.31 (d, $^3J_{H,H}$ = 7.93 Hz, 4 H, H2/6 DMAP), 9.73 (s, 1 H, $C(OH)_2$ H) ppm. ^{13}C NMR (100 MHz, CD_3NO_2): δ = 41.43 (s, CH_3), 41.48 (s, CH_3), 41.52 (s, CH_3), 110.07 (s, C3/5 DMAP), 110.70 (s, C3/5 DMAP), 110.81 (s, C3/5 *p*-DMAP), 121.82 (q, $|^1J_{C,F}|$ = 319.0 Hz, CF_3), 134.81 (s, C1/4 benzene), 140.98 (s, C2/6 *p*-DMAP), 141.37 (s, C2/6 DMAP), 141.69 (s, C2/3/5/6 benzene), 141.87 (s, C2/3/5/6 benzene), 142.09 (s, C2/6 DMAP), 143.29 (s, C1/4 benzene), 157.66 (s, C4 DMAP), 158.16 (s, C4 DMAP), 185.29 [s, $C(OH)_2$ H] ppm.

Trapping Reactions of 5

Deprotonation with KO*t*Bu: a stoichiometric amount of KO*t*Bu was added to a solution of **6** in acetonitrile (20 mL). Diethyl ether (70 mL) was added to the red-brown reaction mixture after 30 min. The resulting precipitate was filtered, washed with diethyl ether (5 × 5 mL), and dried in high vacuum to yield 64% of a pale yellow powder.

Deprotonation with *n*BuLi: a stoichiometric amount of *n*BuLi (1.6 M in hexane) was added to a suspension of **6** in THF (20 mL) at –78 °C. The green-brown reaction mixture was warmed to room temperature after 30 min. After 1 h of additional stirring, the precipitate was filtered, washed with THF (5 × 5 mL), and dried in high vacuum to yield 71% of a pale yellow powder.

^{1}H NMR (400 MHz, CD_3NO_2/H_2O): δ = 3.18 (s, 6 H, CH_3), 3.20 (s, 12 H, CH_3), 3.24 (s, 12 H, CH_3), 6.87 (d, $^3J_{H,H}$ = 8.21 Hz, 2 H, H3/5 DMAP), 6.90 (d, $^3J_{H,H}$ = 7.78 Hz, 4 H, H3/5 DMAP), 6.99 (d, $^3J_{H,H}$ = 7.70 Hz, 4 H, H3/5 DMAP), 8.01 (d, $^3J_{H,H}$ = 7.70 Hz, 4 H, H2/6 DMAP), 8.05 (d, $^3J_{H,H}$ = 7.69 Hz, 2 H, H2/6 DMAP), 8.12 (d, $^3J_{H,H}$ = 8.25 Hz, 4 H, H2/6 DMAP), 8.64 (s, 1 H, benzene) ppm. ^{13}C NMR (100 MHz, CD_3NO_2/H_2O): δ = 41.36 (s, CH_3), 41.43 (s, CH_3), 109.80 (s, C3/5 DMAP), 110.56 (s, C3/5 *p*-DMAP), 110.65 (s, C3/5 DMAP), 121.86 (q, $|^1J_{C,F}|$ = 319.7 Hz, CF_3), 132.86 (s, C6 benzene), 137.93 (s, C1/5 benzene), 138.29 (s, C3 benzene), 140.96 (s, C2/6 DMAP), 141.42 (s, C2/6 DMAP), 142.37 (s, C2/4 benzene), 157.40 (s, C4 *p*-DMAP), 157.45 (s, C4 DMAP), 157.80 (s, C4 DMAP) ppm. ^{1}H NMR (400 MHz, CD_3NO_2/D_2O): δ = 3.18 (s, 6 H, CH_3), 3.20 (s, 12 H, CH_3), 3.24 (s, 12 H, CH_3), 6.87 (d, $^3J_{H,H}$ = 8.23 Hz, 2 H, H3/5 DMAP), 6.89 (d, $^3J_{H,H}$ = 8.06 Hz, 4 H, H3/5 DMAP), 7.00 (d, $^3J_{H,H}$ = 8.24 Hz, 4 H, H3/5 DMAP), 8.00 (d, $^3J_{H,H}$ = 8.24 Hz, 4 H, H2/6 DMAP), 8.04 (d, $^3J_{H,H}$ = 7.94 Hz, 2 H, H2/6 DMAP), 8.11 (d, $^3J_{H,H}$ = 8.24 Hz, 4 H, H2/6 DMAP) ppm. ^{13}C NMR (100 MHz, CD_3NO_2/D_2O): δ = 41.34 (s, CH_3), 41.42 (s, CH_3), 109.79 (s, C3/5 DMAP), 110.54 (s, C3/5 *p*-DMAP), 110.64 (s, C3/5 DMAP), 121.77 (q, $|^1J_{C,F}|$ = 319.9 Hz, CF_3), 132 (mb, C6 benzene), 137.90 (s, C1/5 benzene), 138.25 (s,

C3 benzene), 140.93 (s, C2/6 DMAP), 141.39 (s, C2/6 DMAP), 142.30 (s, C2/4 benzene), 157.39 (s, C4 *p*-DMAP), 157.43 (s, C4 DMAP), 157.77 (s, C4 DMAP) ppm. FAB-MS (NBA/H_2O): *m*/*z* = 1279 [M – OTf]$^+$, 1129 [M – HOTf – OTf]$^+$, 1009 [M + H – DMAP – 2OTf]$^+$. FAB-MS (NBA/D_2O): *m*/*z* = 1280 [M – OTf]$^+$, 1130 [M – HOTf – OTf]$^+$, 1010 [M + H – DMAP – 2OTf]$^+$.

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[16] For further details on the electrostatic activation of SASAPOS cascades by cationic substituents see refs.[9,10].

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