Electronic Supplementary Material (ESI) for Dalton Transactions

Electronic Supplementary Information

to

Bis(triphenyl-λ^5-phosphanylidene)ammonium fluoride: A reactive fluoride source to access the hypervalent silicates $[Me_nSiF_{5-n}]^-$ (n = 0-3)

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Contents

S1. Synthesis of [PNP][BF_4]

The synthesis of [PNP][BF_4] was performed following a published general procedure.[1] A hot concentrated aqueous solution of Na[BF_4] (50.0 g, 455 mmol) was added to a stirred solution of [PNP]Cl (10.0 g, 17 mmol) in 200 ml of water. The reaction mixture was cooled to 0 °C for 1 h and the precipitated product was isolated by filtration, washed with cold water, and dried at 100 °C in vacuum. The product remained as colorless solid (8.9 g, 14 mmol, 82 %).

IR (diamond, cm^{-1}): $\tilde{\nu}$ = 440 (vw), 459 (vw), 494 (vs), 525 (vs), 532 (s), 547 (s), 576 (m), 619 (vw), 684 (sh), 690 (vs), 722 (vs), 745 (m), 763 (w), 8799 (w), 846 (vw), 865 (vw), 942 (vw), 995 (ws), 1023 (sh), 1035 (sh), 1047 (vs, br, [BF_4]$^-$), 1091 (m), 1113 (m), 1168 (vw), 1185 (w), 1260 (s, br), 1285 (sh), 1316 (sh), 1435 (m), 1483 (w), 1589 (vw), 3058 (vw). Raman (40 mW, 1000 scans, cm^{-1}): $\tilde{\nu}$ = 130 (vs), 140 (sh), 193 (vw), 233 (w), 248 (w), 267 (vw), 286 (vw), 617 (w), 666 (m), 1003 (s), 1027 (m), 1111 (w), 1167 (vw), 1187 (vw), 1576 (w), 1589 (s), 3059 (s). ^1H NMR (400.17 MHz, CD_2Cl_2, 298 K): δ = 7.47 (m, *m*-H, [PNP]$^+$), 7.49 (m, *o*-H, [PNP]$^+$), 7.66 (m, *p*-H, [PNP]$^+$); ^{11}B (128.39 MHz, CD_2Cl_2, 298 K): δ = -1.2 (quint, [BF_4]$^-$); ^{19}F NMR (376.53 MHz, CD_3CN, 298 K) δ = -153.5 (sbr, [$^{10}BF_4$]$^-$), -154.5 (q, [$^{11}BF_4$]$^-$); $^{31}P\{^1H\}$ NMR (161.99 MHz, CD_2Cl_2, 298 K) δ = 21.0 (s).

It has to be noted that the synthesis of [PNP][BF_4] from [PNP]Cl and Ag[BF_4] in CH_2Cl_2 solution without details has been described previously.[2]

S2. Characterization of new compounds

Actual spectra for all new compounds are presented in this section.

S2.1. Characterization of (PNP)F

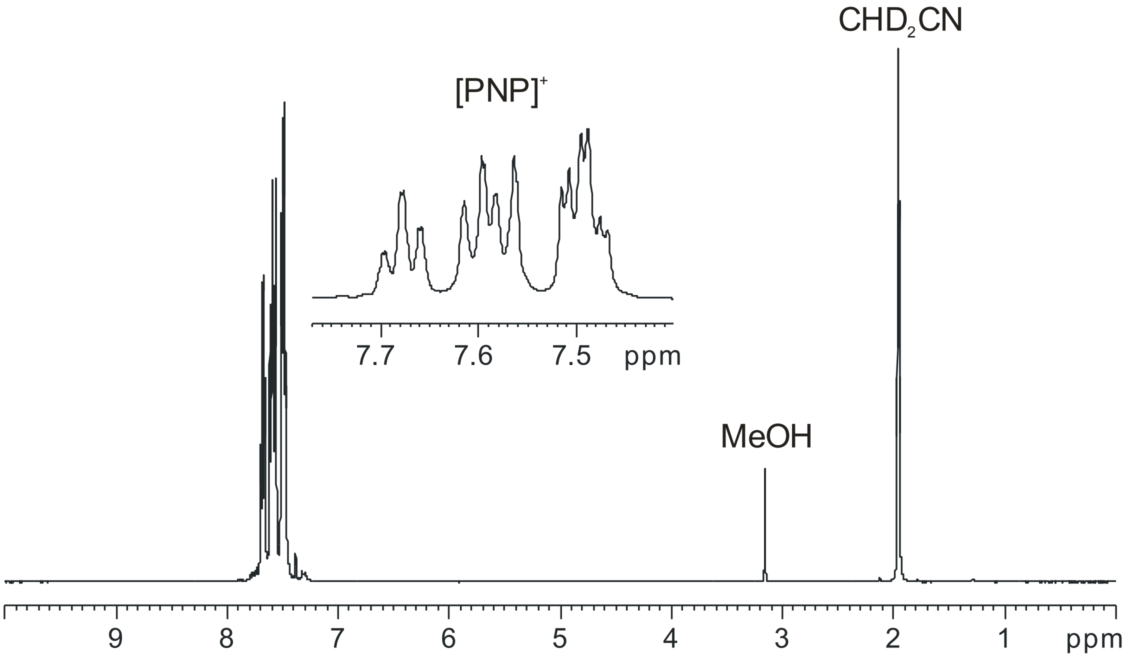


Fig. S1. ^{1}H-NMR-spectrum (400.17 MHz) of (PNP)F in CD_3CN at 25 °C.

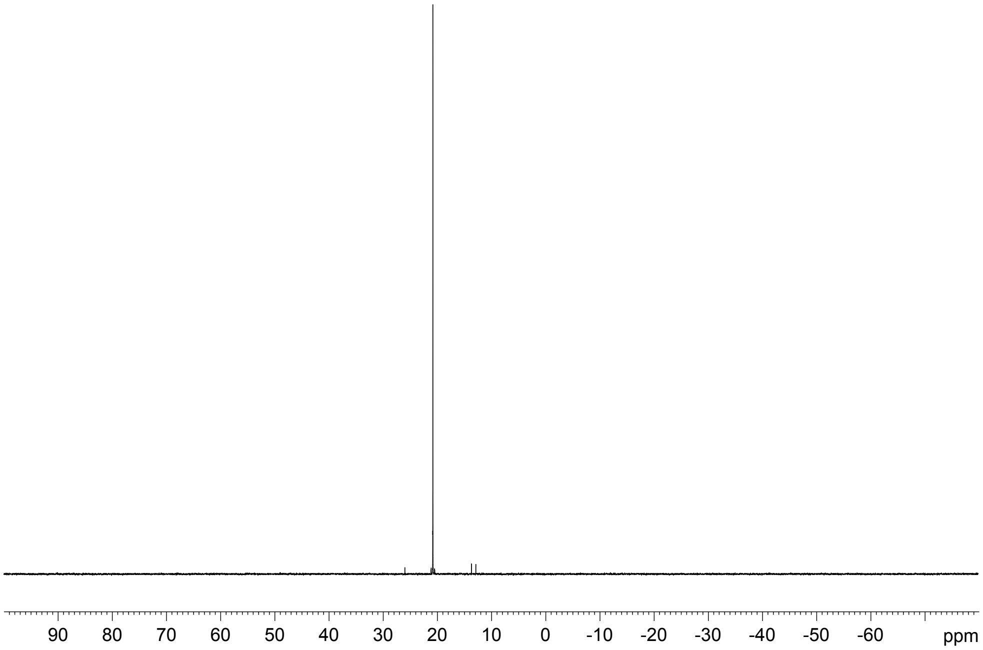


Fig. S2. $^{31}P\{^1H\}$-NMR-spectrum (161.99 MHz) of (PNP)F in CD_3CN at 25 °C.

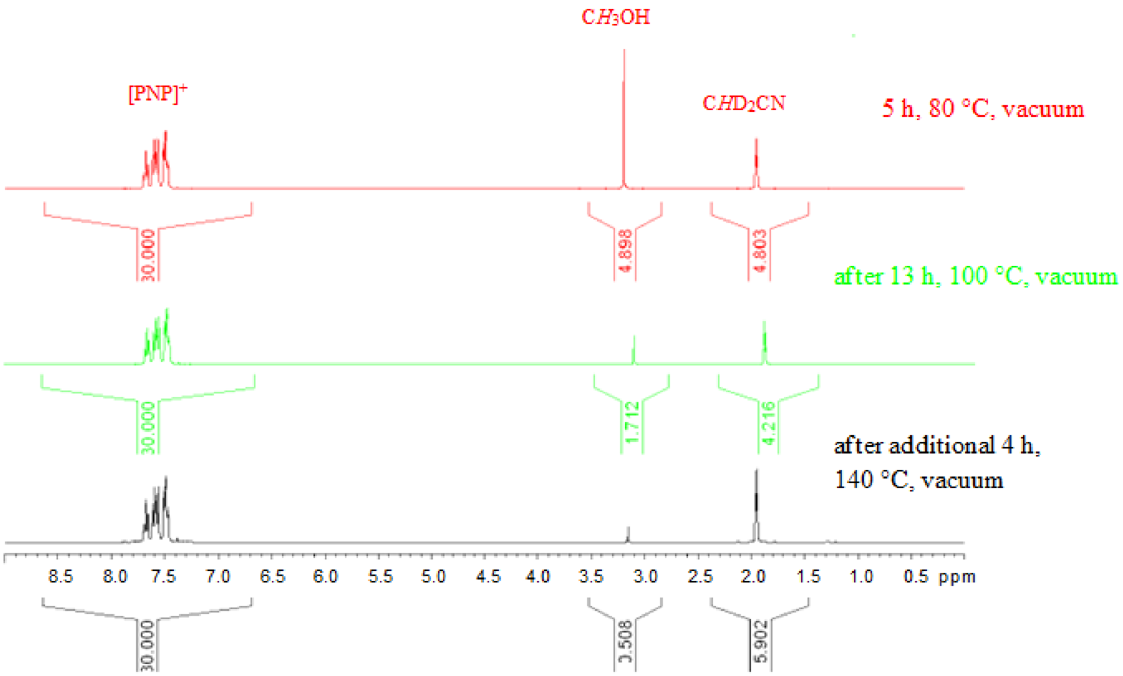


Fig. S3. ^{1}H-NMR-spectra (400.17 MHz) of (PNP)F in CD_3CN at 25 °C. A) Product dried 5 h at 80 °C at 10^{-3} mbar; B) product dried additional 13 h at 100 °C at 10^{-3} mbar; C) product dried additional 4 h at 140 °C at 10^{-3} mbar.

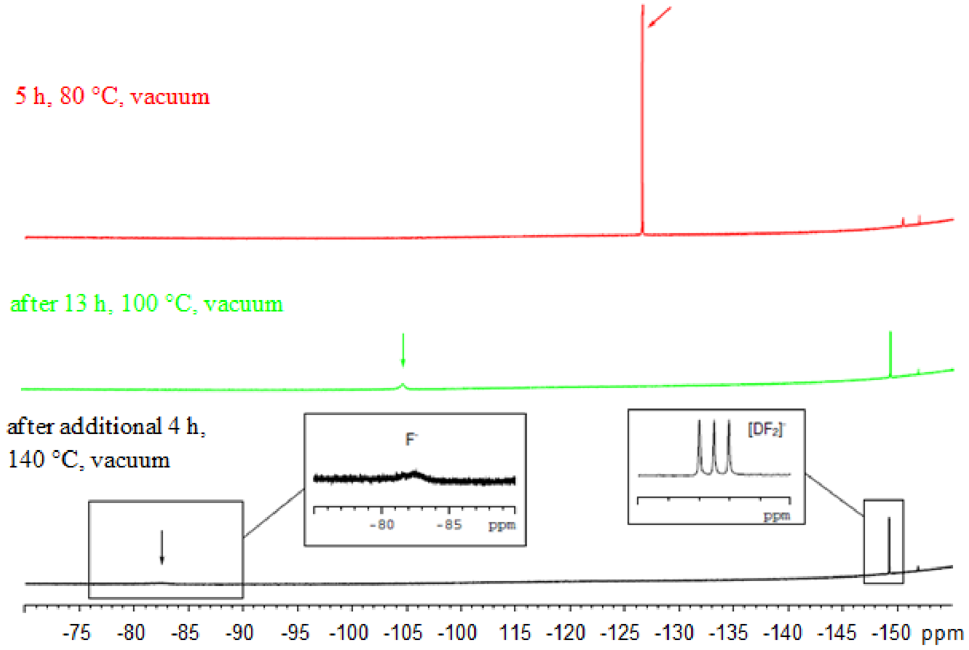


Fig. S4. ^{19}F-NMR-spectra (376.54 MHz) of (PNP)F in CD_3CN at 25 °C. A) Product dried 5 h at 80 °C at 10^{-3} mbar; B) product dried additional 13 h at 100 °C at 10^{-3} mbar; C) product dried additional 4 h at 140 °C at 10^{-3} mbar. Note that the ^{19}F chemical shift of "naked" F^- and its rate of reaction with CD_3CN are strongly dependent on the concentration of residual traces of methanol. A detailed discussion of the solvent dependency of ^{19}F NMR chemical shifts can be found in the literature.[3]

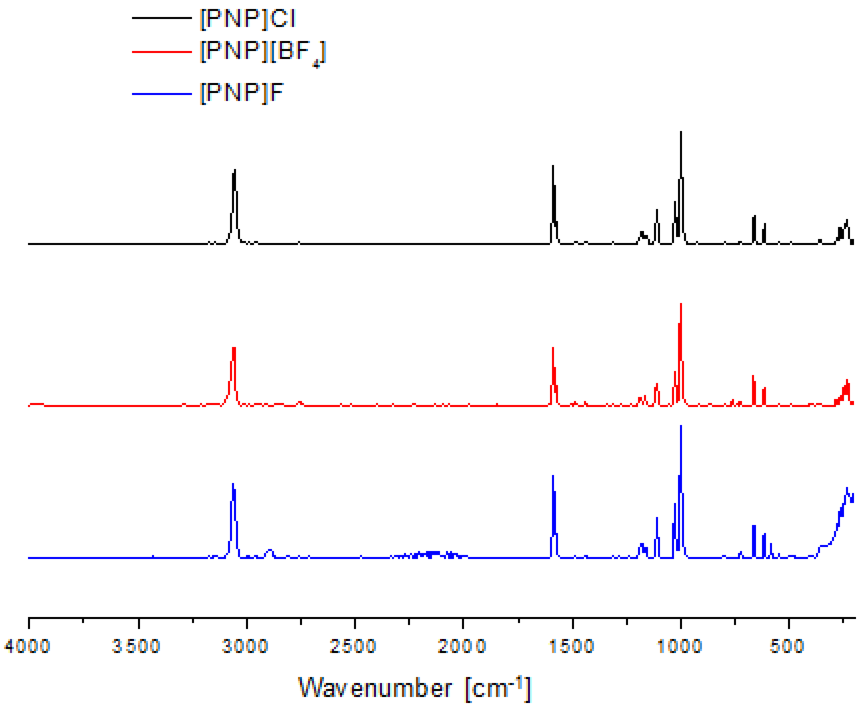


Fig. S5. FT-Raman spectra of [PNP]Cl (black), [PNP][BF$_4$] (red) und (PNP)F (blue)

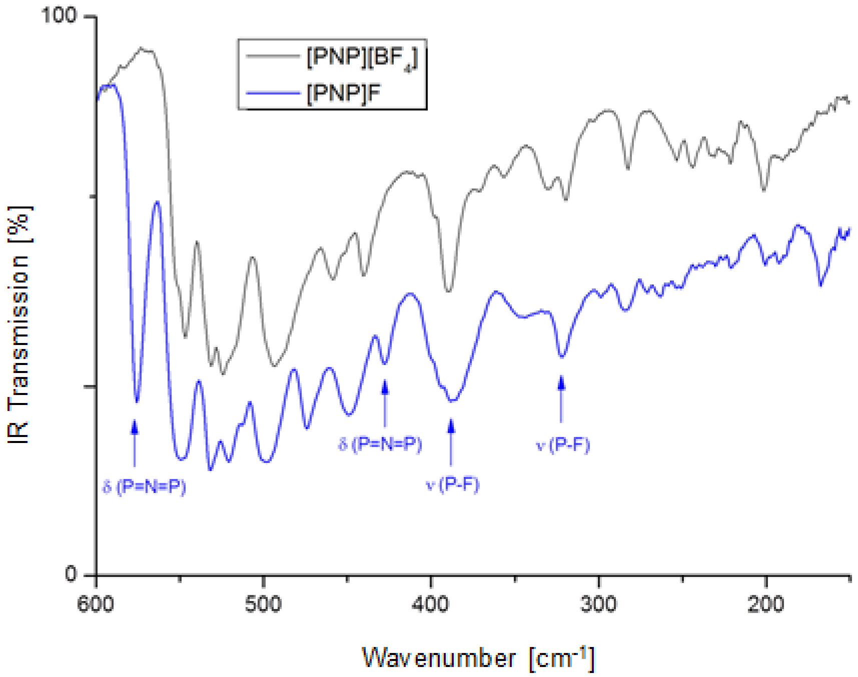


Fig. S6. FIR spectra of [PNP][BF$_4$] (black) and (PNP)F (blue). The MIR region is presented in the actual paper.

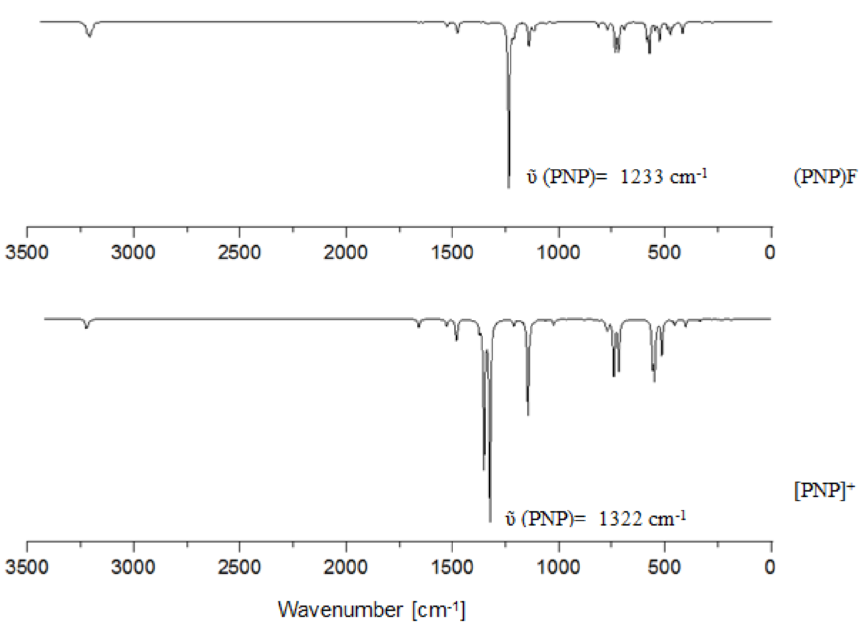


Fig. S7. Calculated (PBE0/def2-TZVPP) IR spectra of $[PNP]^+$ and (PNP)F. The spectra are very similar with the exception of the position of the P=N=P stretching vibration, which is significantly shifted to higher wave numbers in (PNP)F.

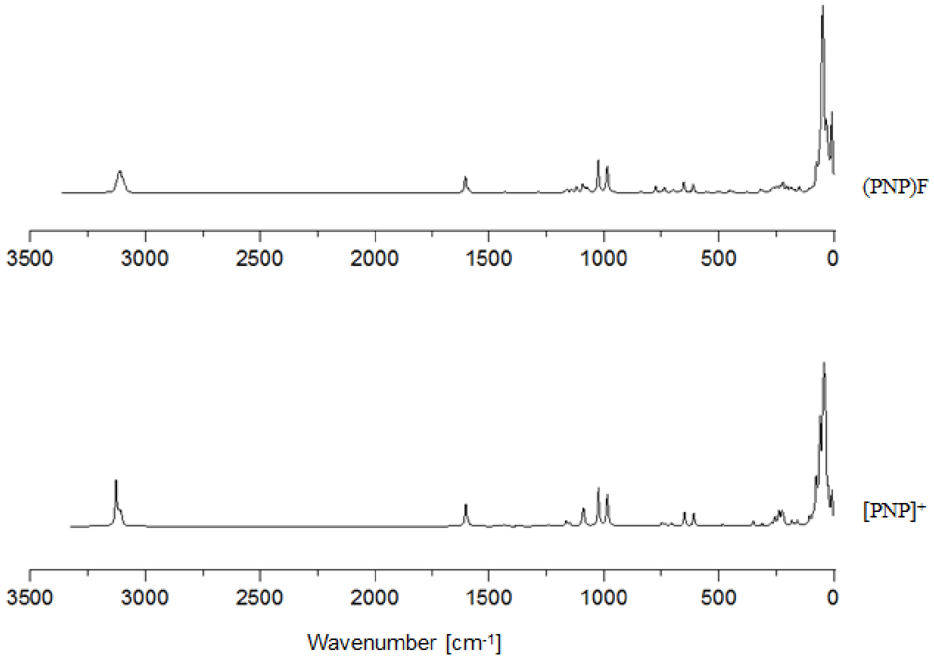


Fig. S8. Calculated (PBE0/def2-TZVPP) Raman spectra of $[PNP]^+$ and (PNP)F. The spectra are very similar. Therefore it cannot expected to distinguish $[PNP]^+$ and (PNP)F by Raman spectroscopy.

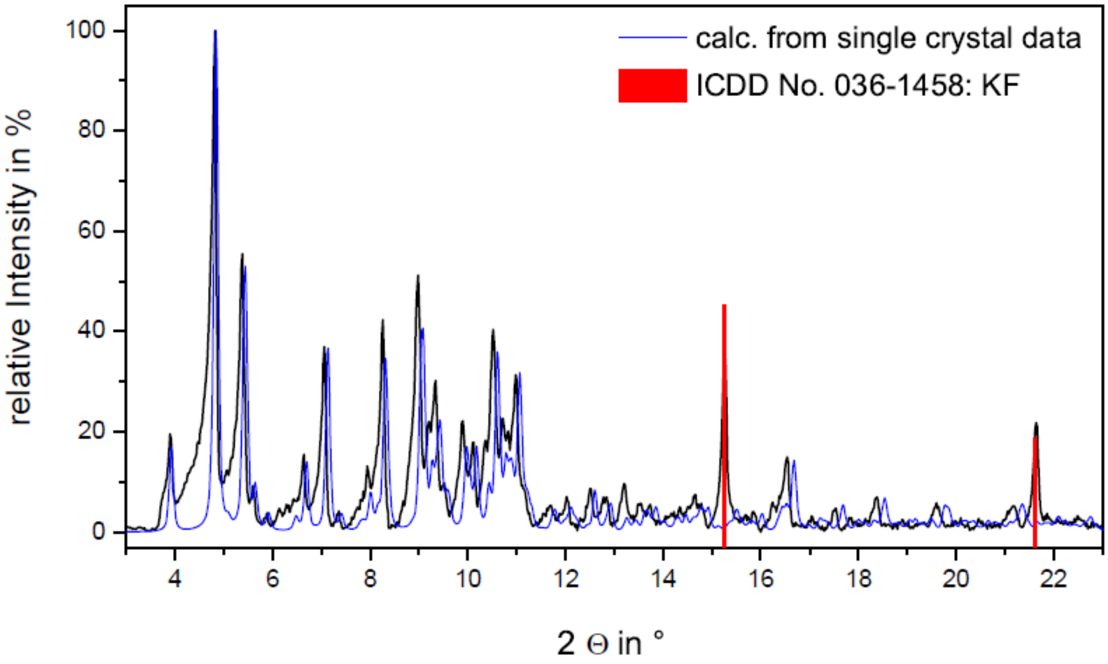


Fig. S9. Experimental (black) and from single crystal data calculated powder diffractogram of (PNP)F. The diffractogram contains traces of potassium fluoride.

S2.2. Solubility of (PNP)F in different solvents

Completely methanol-free (PNP)F is very reactive and at ambient temperature attacks acetonitrile (see Figs. S3 and S4). Thus propionitrile and 1,2-difluorobenzene were tested for solubility and resistance. (PNP)F is soluble in both solvents, but at ambient temperature partial decomposition of the $[PNP]^+$ cation occurs. *N*-diphenylphosphin-triphenylphosphazene and triphenylphosphinimine (Fig. S10) were identified as decomposition products.[4]

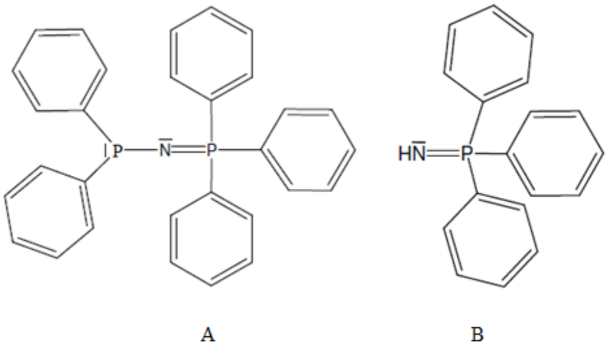


Fig. S10. *N*-diphenylphosphin-triphenylphosphazene (A) and triphenylphosphinimine (B)

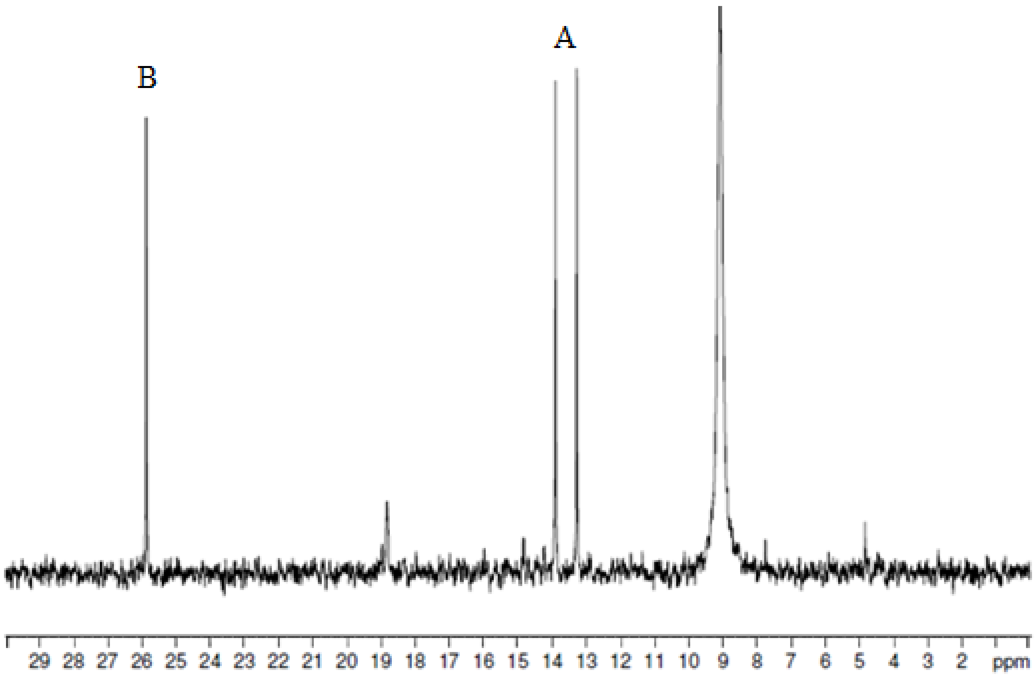


Fig. S11. $^{31}P\{^{1}H\}$-NMR-spectrum (161.99 MHz) of (PNP)F in 1,2-DFB at 25 °C (A = *N*-diphenylphosphin-triphenylphosphazene, B = triphenylphosphinimine, as shown in Fig. S10).

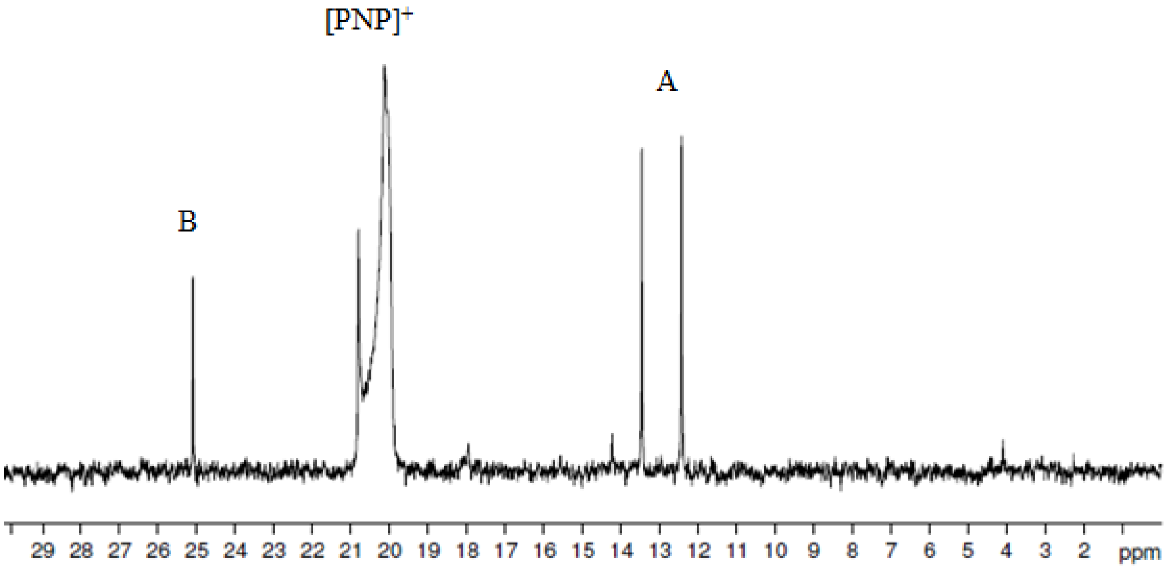


Fig. S12. $^{31}P\{^{1}H\}$-NMR-spectrum (161.99 MHz) of (PNP)F in propionitrile (PFA-NMR-tube insert) at 25 °C (A = *N*-diphenylphosphin-triphenylphosphazene, B = triphenylphosphinimine, as shown in Fig. S10).

S2.3. Characterization of [PNP][Me_3SiF_2]

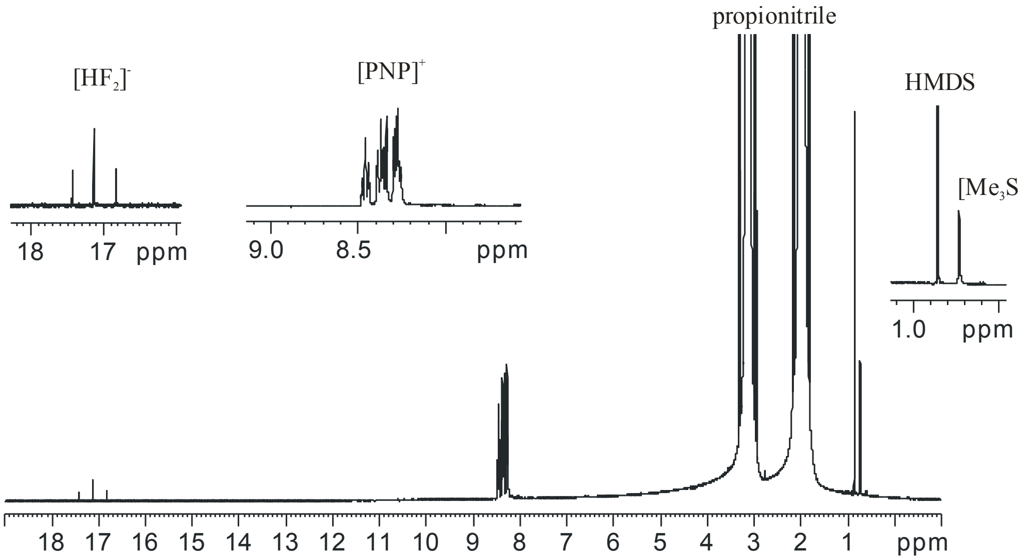


Fig. S13. ^{1}H NMR spectrum (400.17 MHz) of [PNP][Me_3SiF_2] in propionitrile at 298 K. The formation of hexamethyldisiloxane and [HF_2]$^-$ indicates partial hydrolysis of the anion by traces of water in the solvent propionitrile.

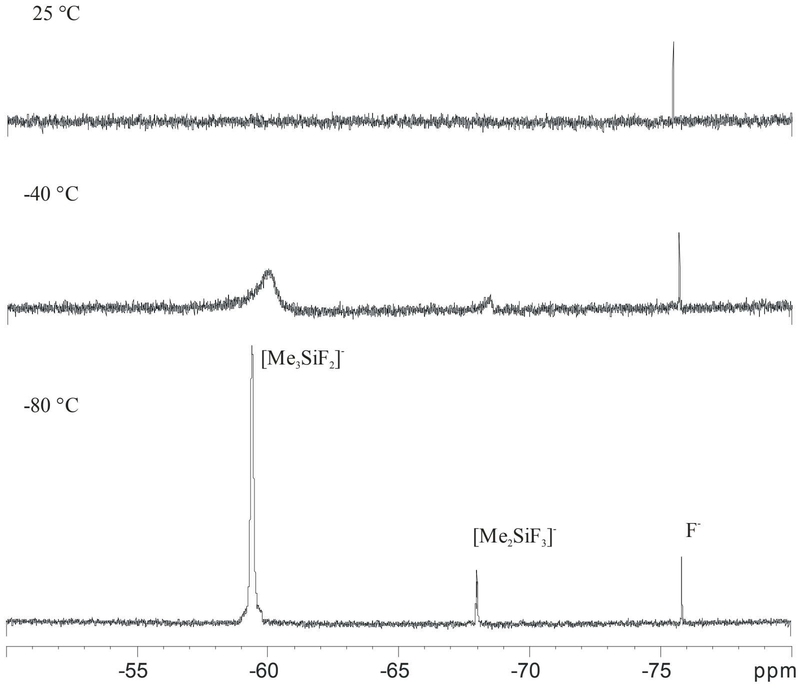


Fig. S14. Selected region of the ^{19}F NMR spectrum (376.54 MHz) of [PNP][Me_3SiF_2] in propionitrile at varying temperatures. At -80 °C a minor resonance for [Me_2SiF_3]$^-$ becomes visible. The origin of this signal (either a product of an exchange process or a Me_2SiF_2 impurity in the Me_3SiF starting material) remains unclear.

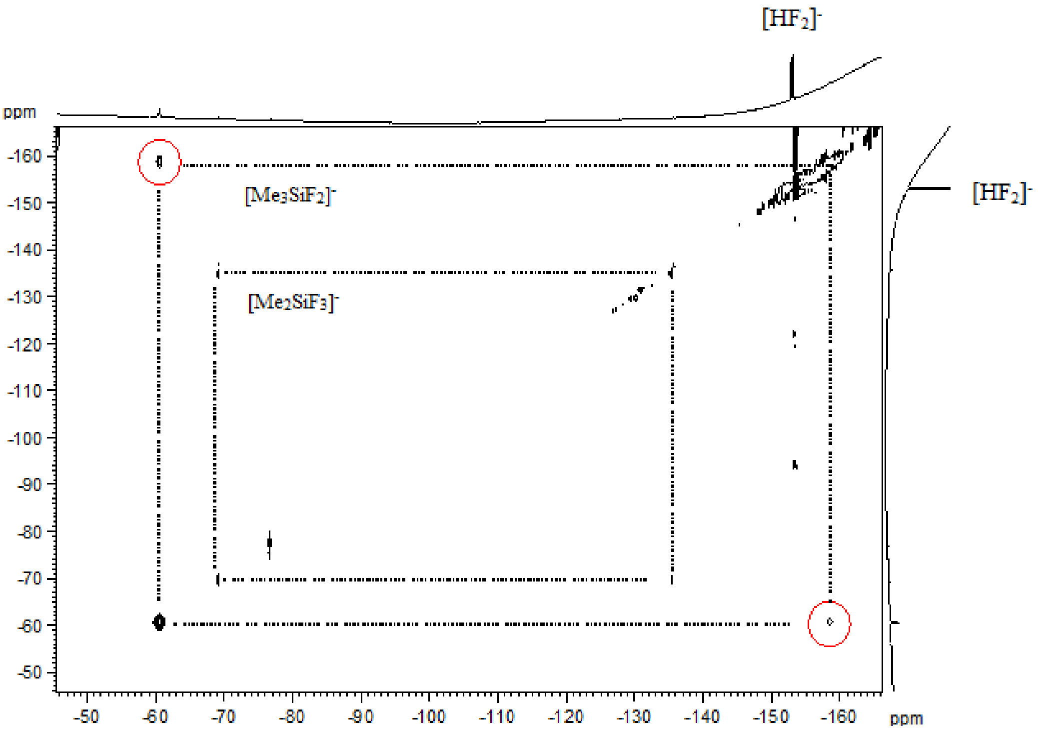


Fig. S15. $^{19}F,^{19}F$-EXSY spectrum (376.54 MHz, mixing time: 0.1 s.) of $[PNP][Me_3SiF_2]$ in propionitrile at -60 °C. The cross peaks demonstrate intramolecular chemical exchange between fluorine atoms in axial and equatorial position in the anions. The lack of cross peaks between signals of different fluorinated compounds shows that intermolecular exchange of fluorine atoms plays only a minor role, if any at all, at this temperature.

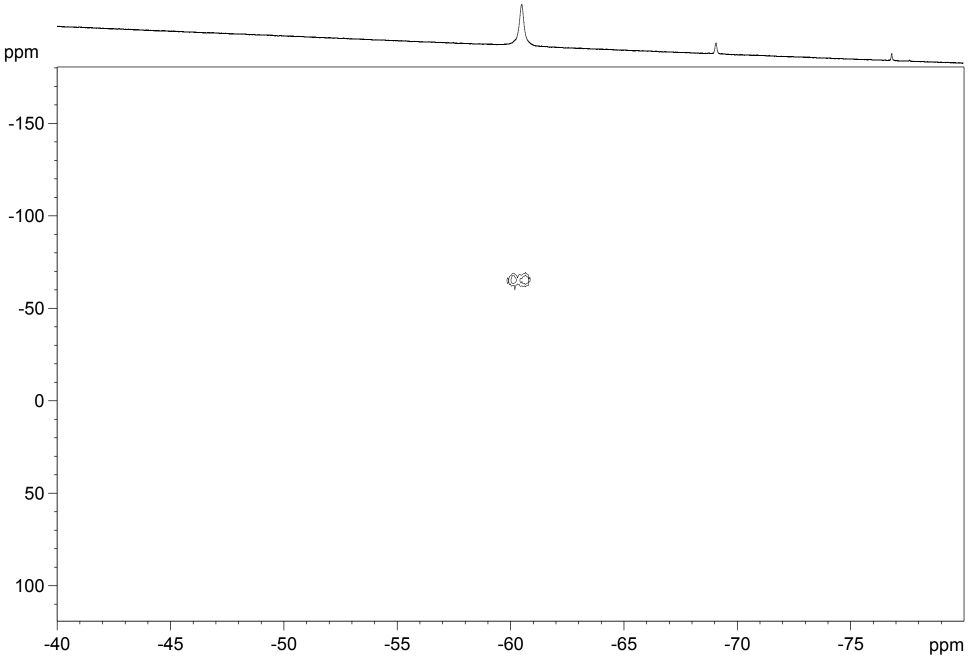


Fig. S16. $^{19}F,^{29}Si$-HMBC spectrum (376.54 MHz, optimized for 250 Hz) of $[PNP][Me_3SiF_2]$ in propionitrile at -70 °C.

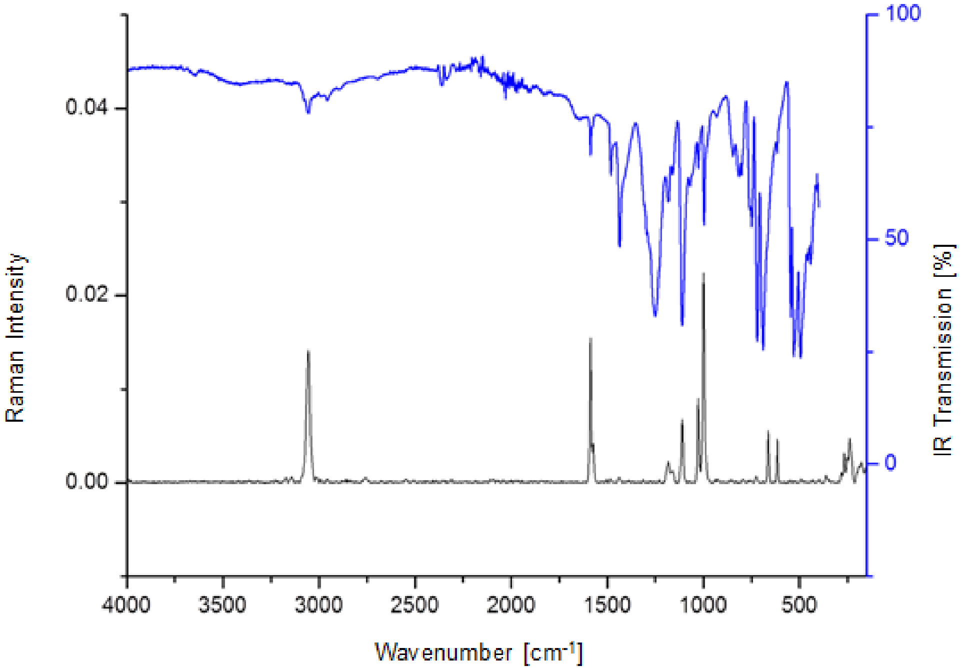


Fig. S17. IR (blue, top) and Raman (black, bottom) spectra of [PNP][Me_3SiF_2]

S2.4. Characterization of [PNP][Me_2SiF_3]

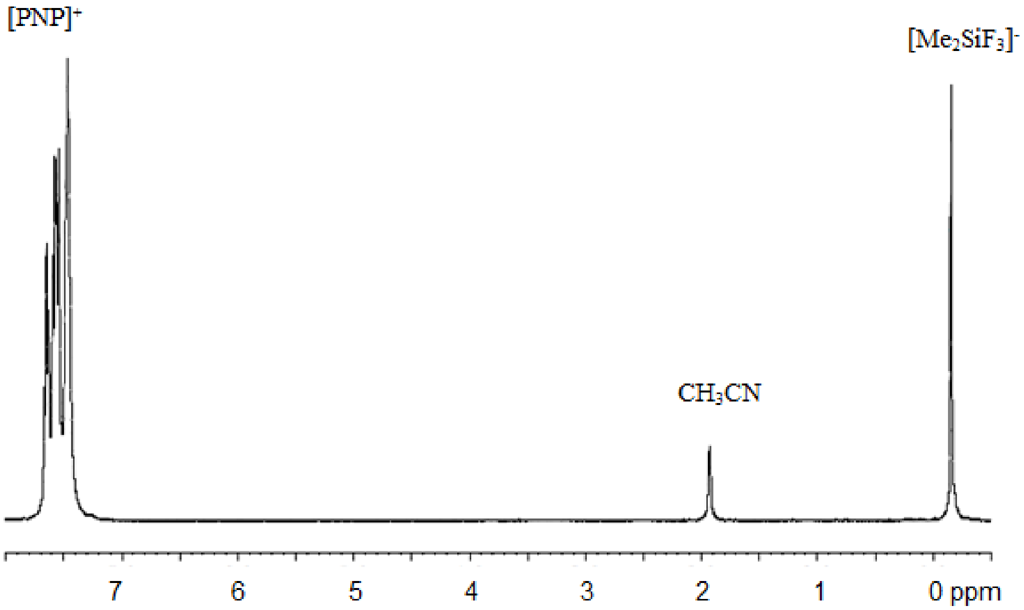


Fig. S18. ^{1}H NMR spectrum (400.17 MHz) of [PNP][Me_2SiF_3] in acetonitrile at 298 K.

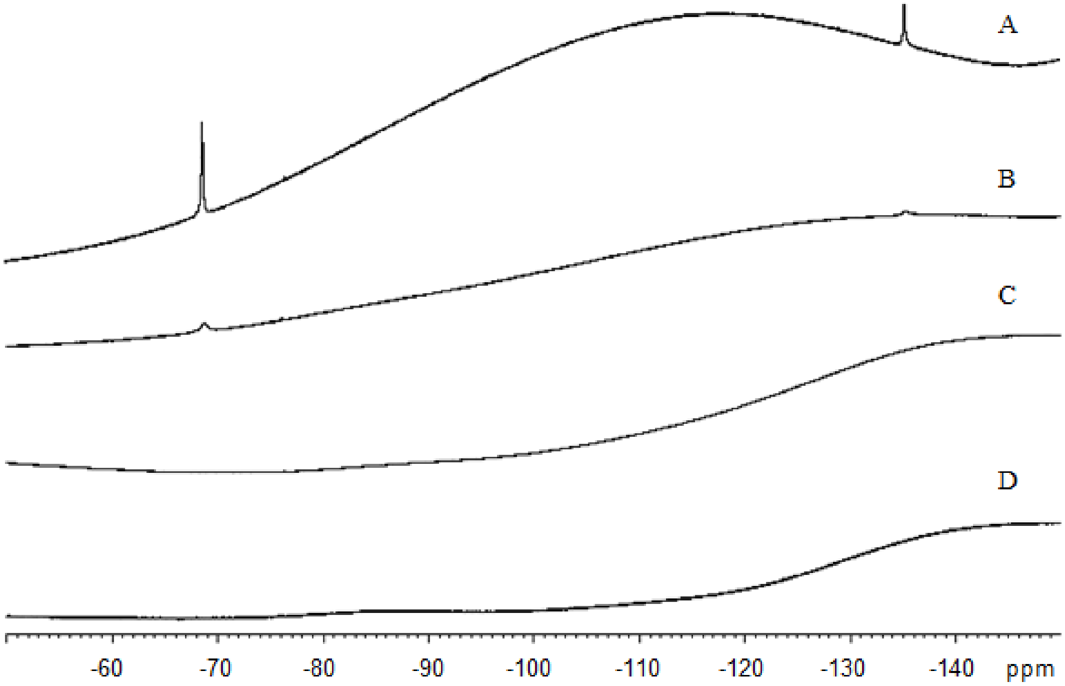


Fig. S19. ^{19}F NMR spectra (376.54 MHz) of [PNP][Me_2SiF_3] in propionitrile. A) at 203 K; B) at 233 K; C) at 263 K; D) at 298 K.

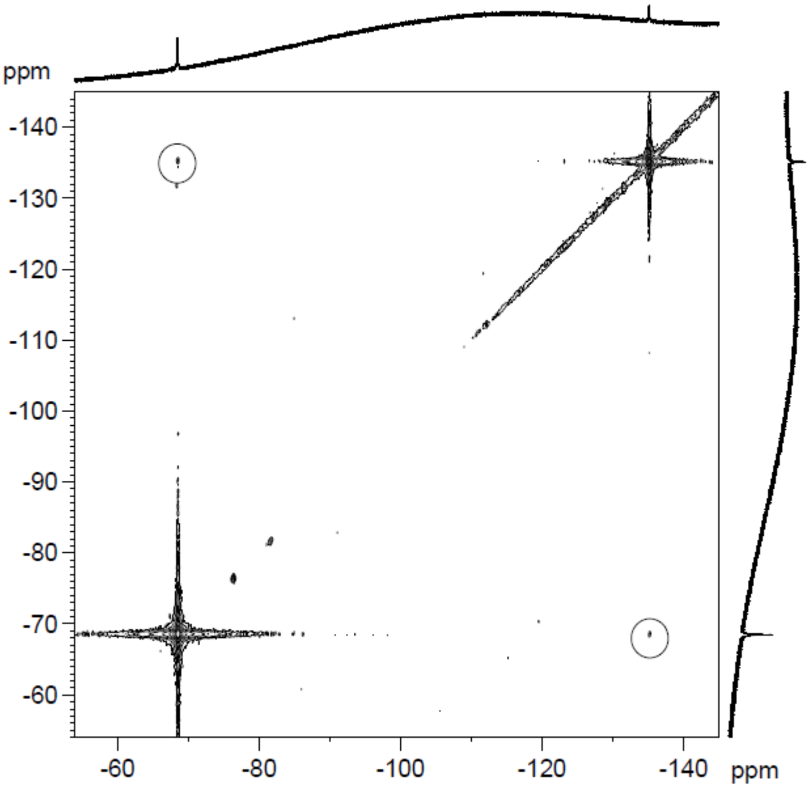


Fig. S20. ^{19}F,^{19}F COSY spectrum (376.54 MHz) of [PNP][Me_2SiF_3] in propionitrile at 193 K.

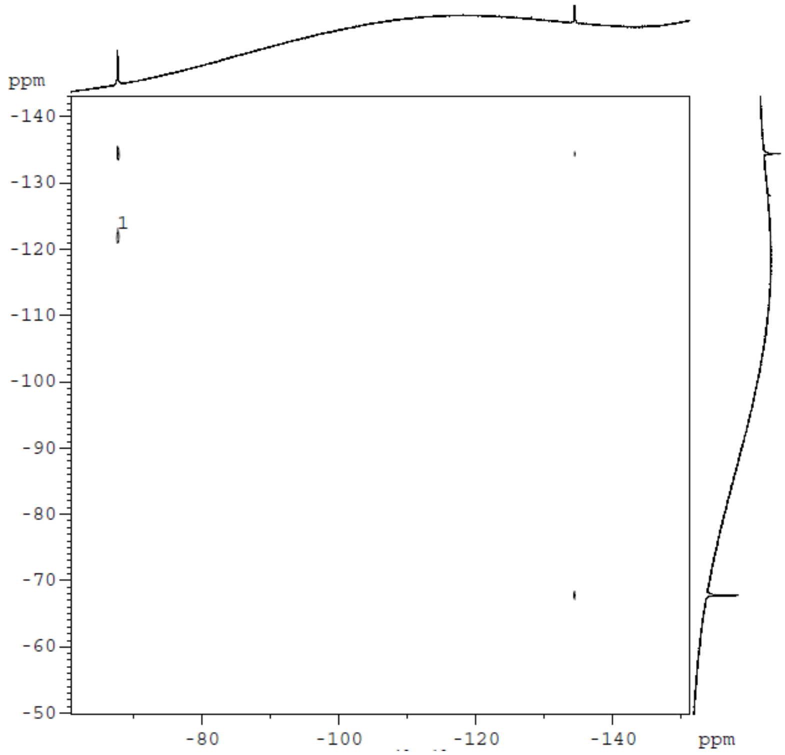


Fig. S21. Double quantum filtered $^{19}F,^{19}F$ COSY spectrum (376.54 MHz) of [PNP][Me_2SiF_3] in propionitrile at 193 K. (1: artifact of unknown origin).

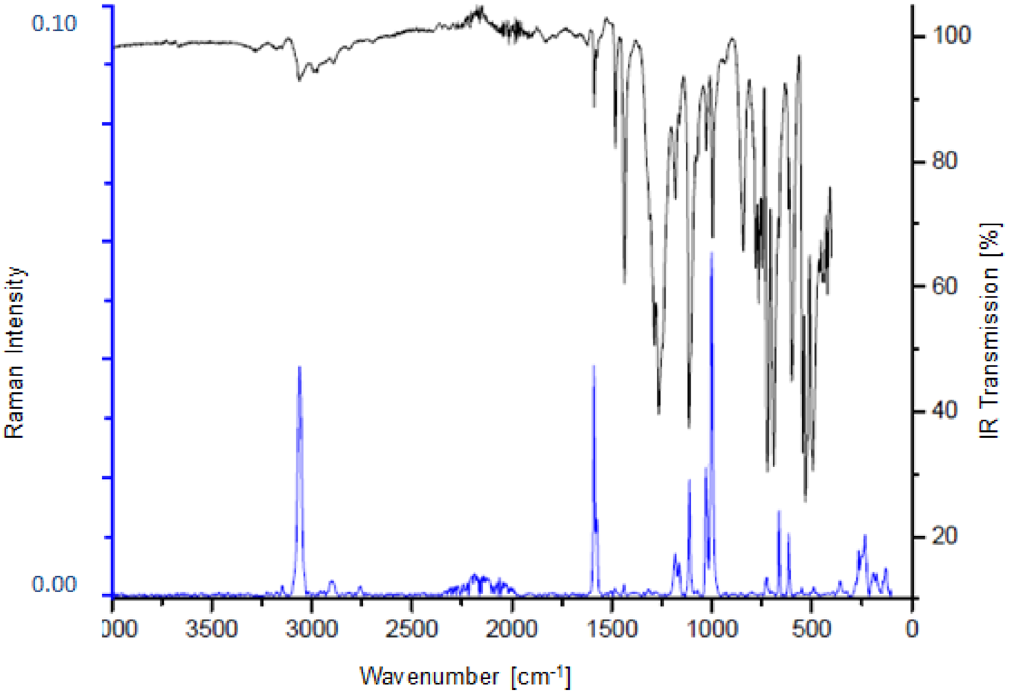


Fig. S22. IR (blue, top) and Raman (black, bottom) spectra of [PNP][Me_2SiF_3]

S2.5. Characterization of [PNP][MeSiF$_4$]

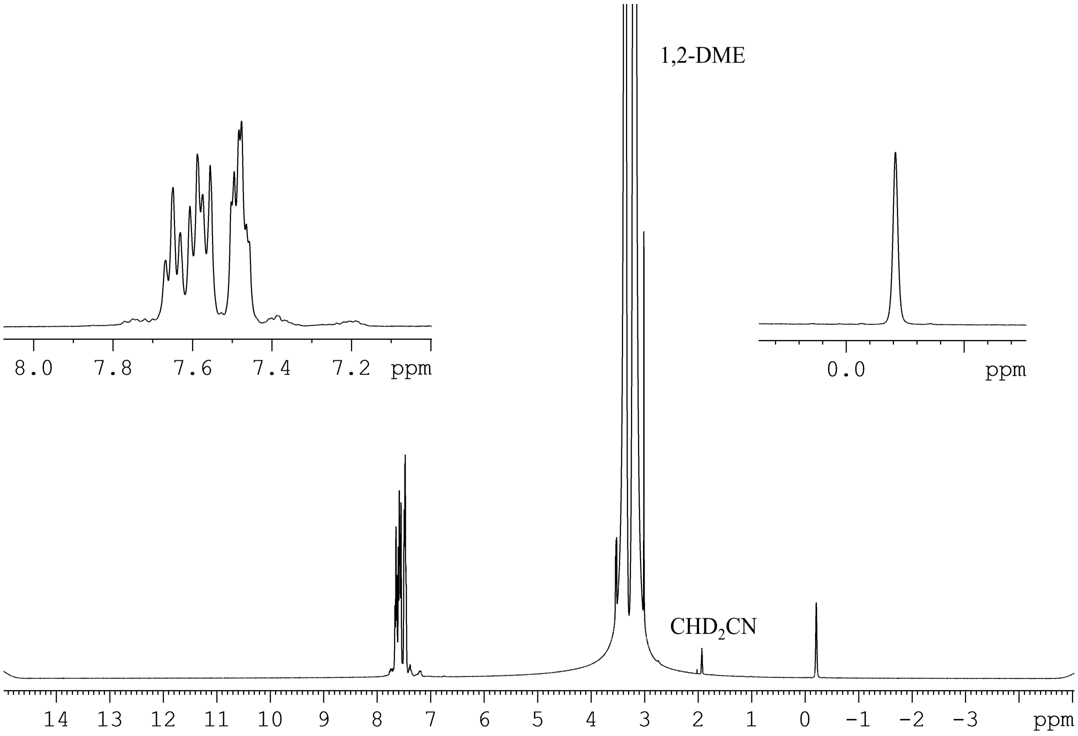


Fig. S23. ^{1}H NMR spectrum (400.17 MHz) of [PNP][MeSiF$_4$] in DME/CD$_3$CN at 223 K.

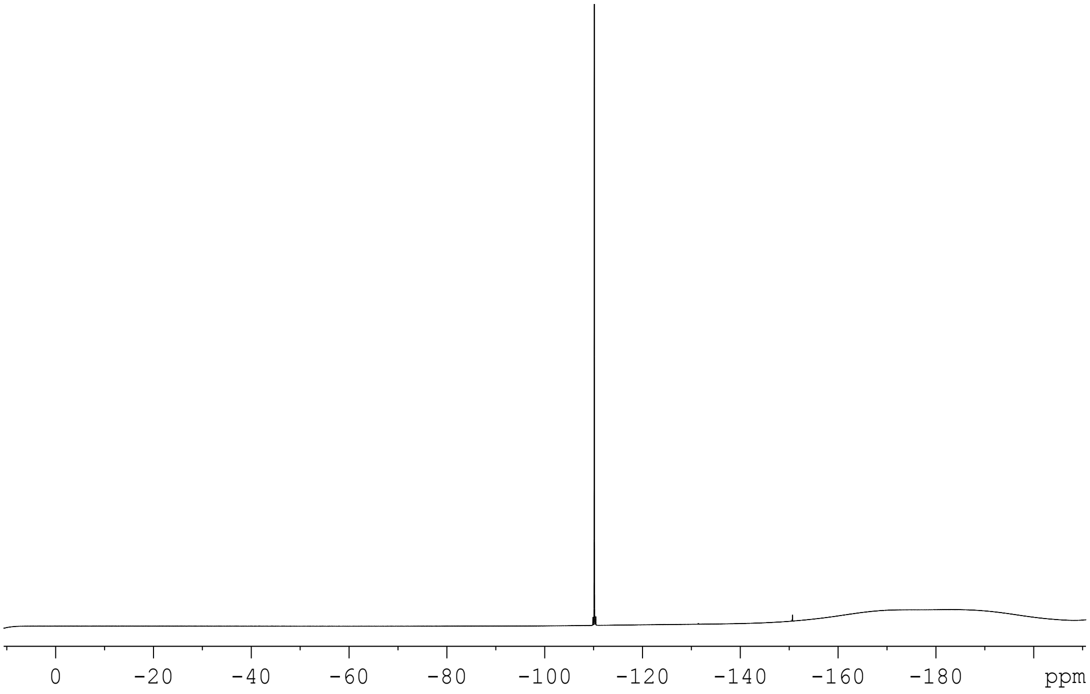


Fig. S24. ^{19}F NMR spectra (376.54 MHz) of [PNP][MeSiF$_4$] in DME/CD$_3$CN at 223 K.

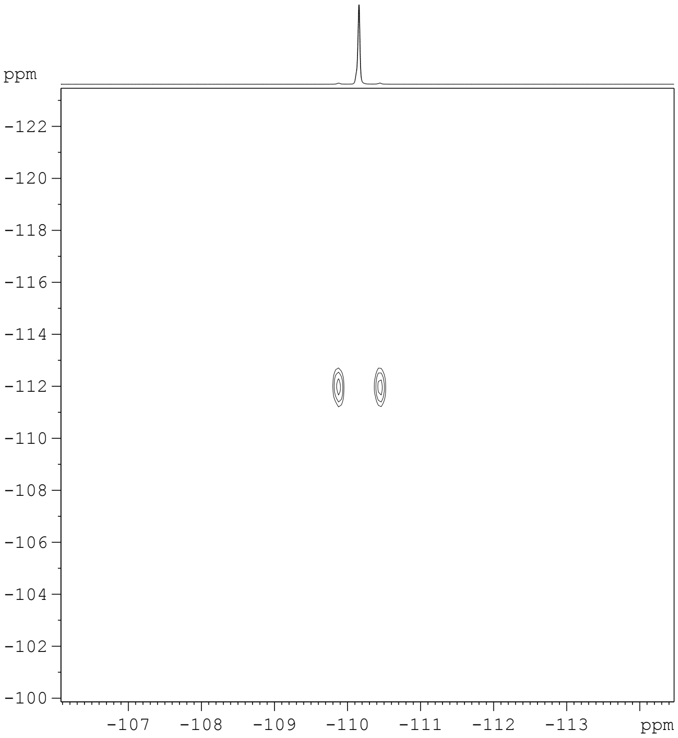


Fig. S25. ^{19}F,^{29}Si-HMBC (376.54 MHz, optimized for 210 Hz) of [PNP][MeSiF$_4$] in DME/CD$_3$CN at 223 K.

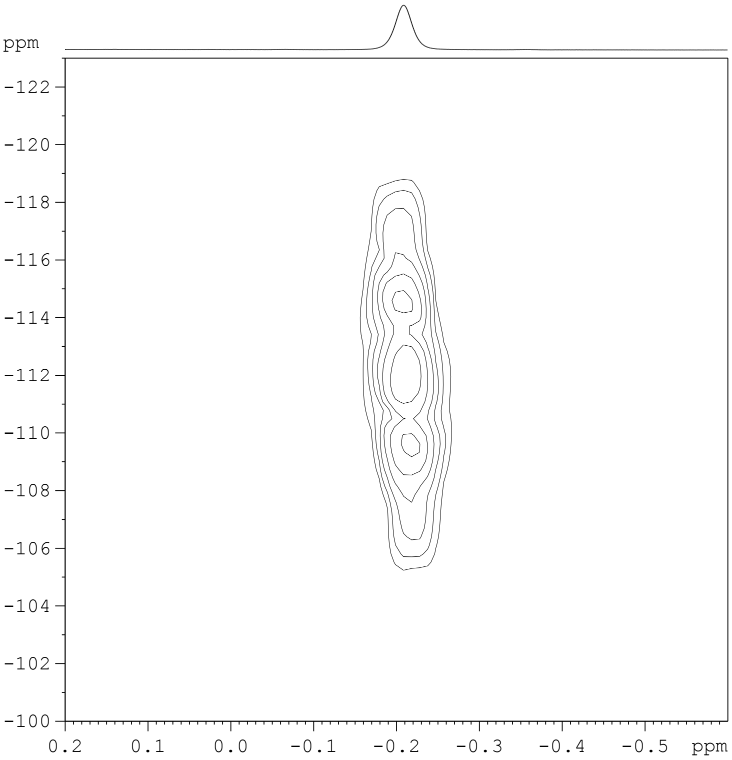


Fig. S26. ^{1}H,^{29}Si-HMBC (400.17 MHz, optimized for 10 Hz) of [PNP][MeSiF$_4$] in DME/CD$_3$CN at 223 K. The cross peak shows a quintet splitting in the ^{29}Si-dimension due to the $^{1}J_{F-Si}$-coupling.

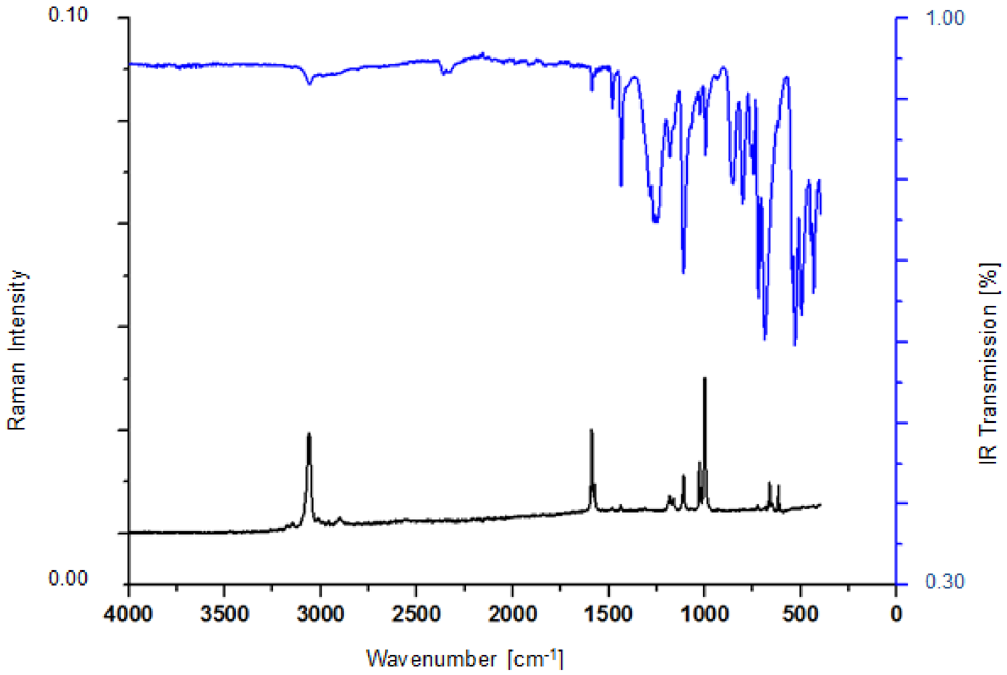


Fig. S27. IR (blue, top) and Raman (black, bottom) spectra of [PNP][$MeSiF_4$]

S2.6. Characterization of [PNP][SiF_5]

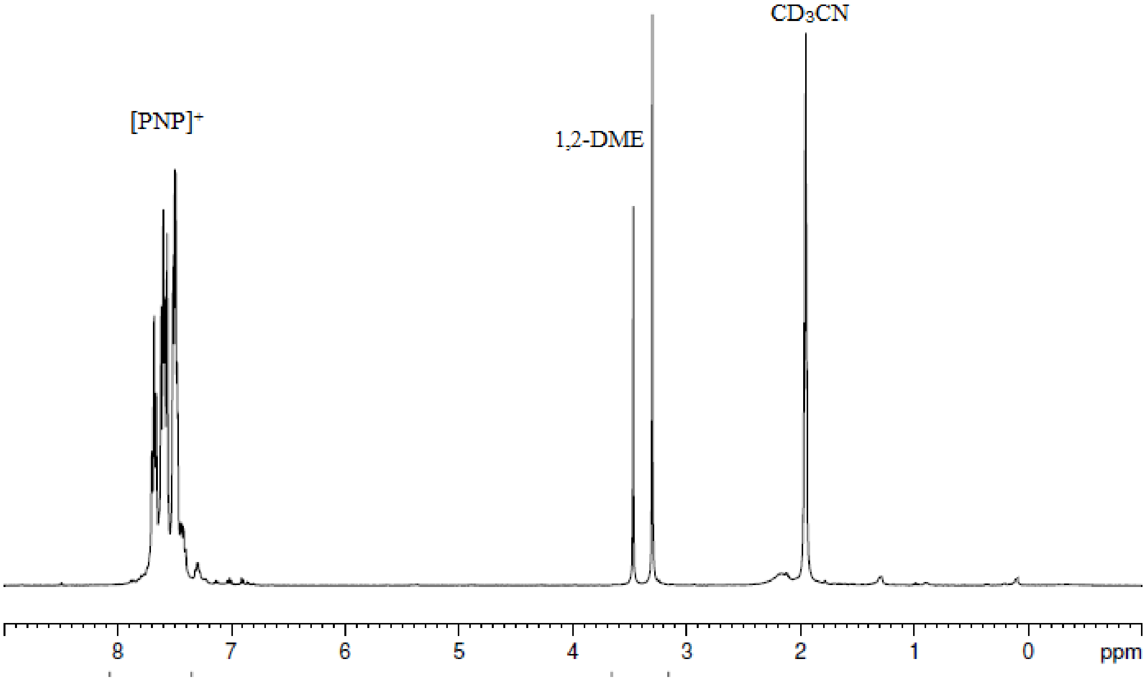


Fig. S28. ^{1}H NMR spectrum (400.17 MHz) of [PNP][SiF_5] in acetonitrile at 298 K.

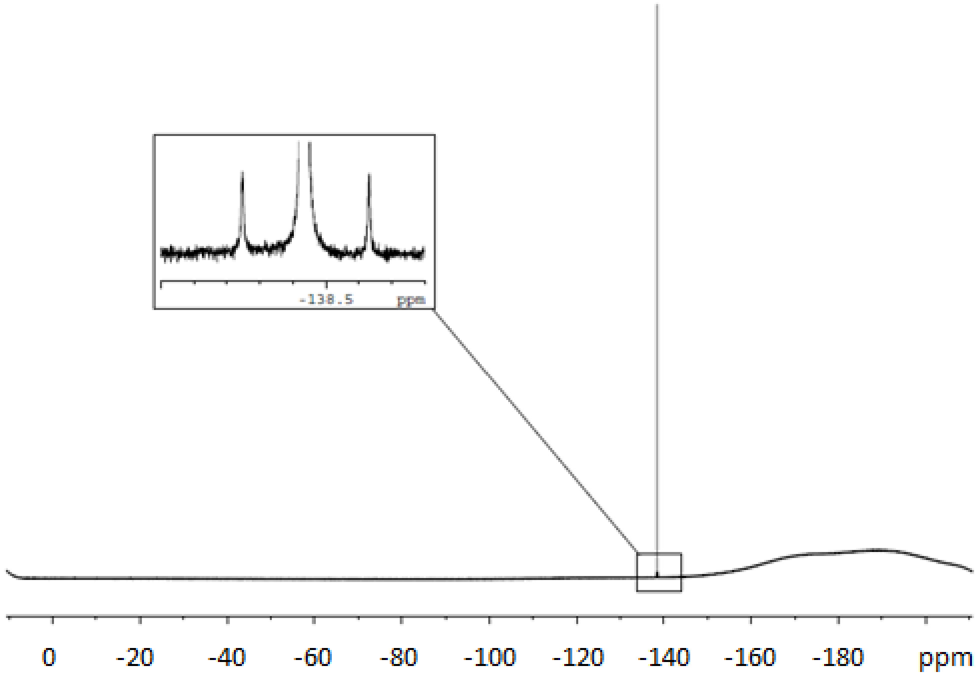


Fig. S29. ^{19}F NMR-spectrum (376.54 MHz) of [PNP][SiF_5] in CD_3CN at 25 °C.

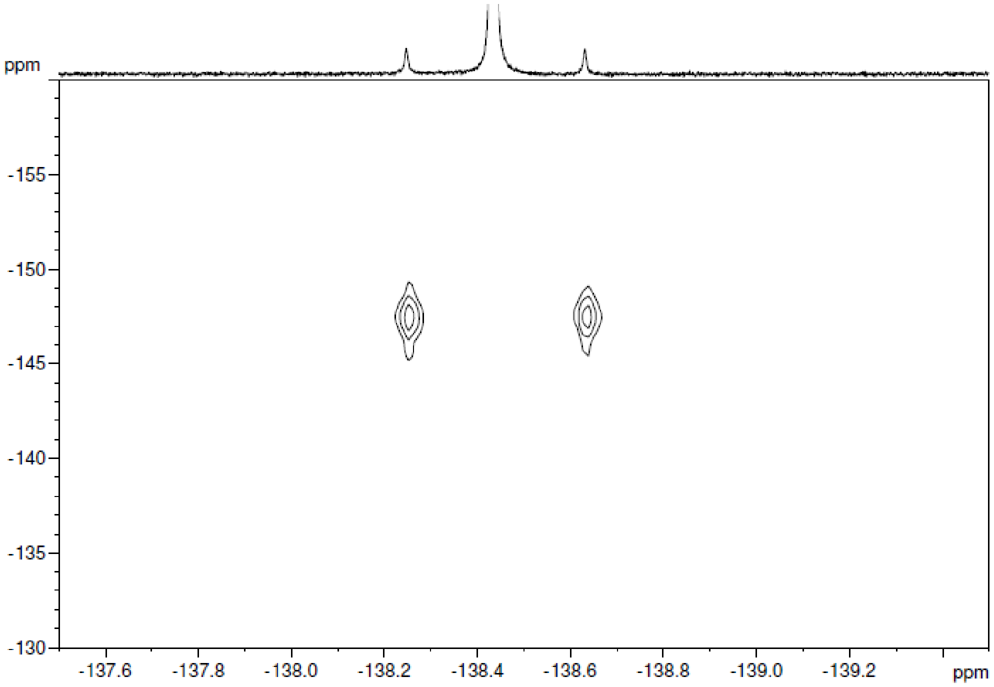


Fig. S30. ^{19}F,^{29}Si-HMBC spectrum (376.54 MHz, optimized for 145 Hz) of [PNP][SiF_5] in acetonitrile at 25 °C.

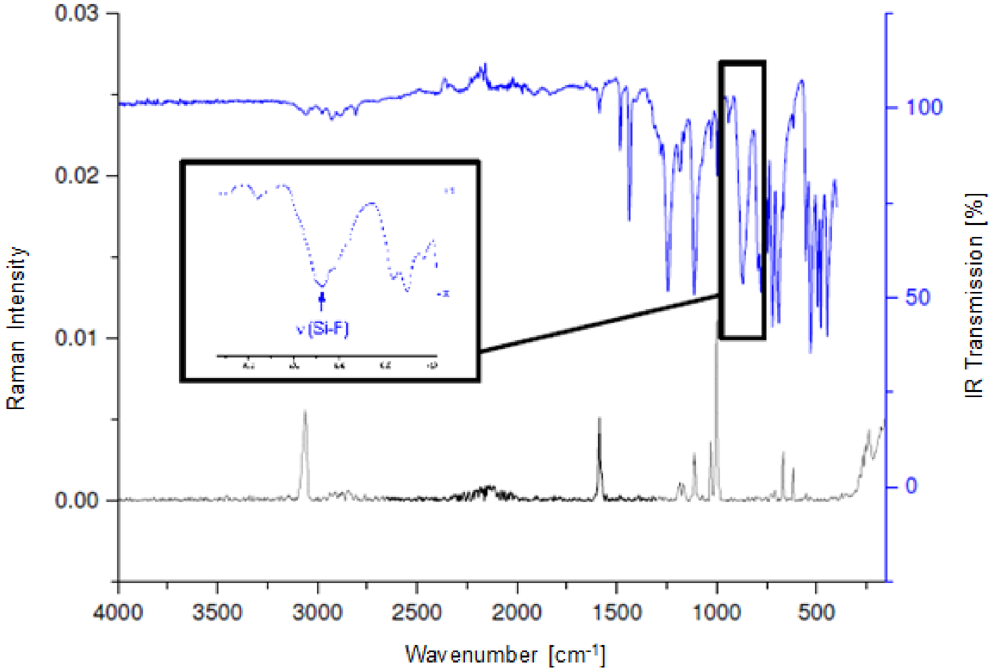


Fig. S31. IR (blue, top) and Raman (black, bottom) spectra of [PNP][SiF_5]

S3. DFT Calculations

DFT (PBE0 functional) calculations were performed with the def2-TZVPP basis sets as implemented in the program TURBOMOLE.[5] Frequency calculations were calculated analytically with the AOFORCE module at the same level.[6] The calculated structure is a true minimum on the energy hyper surface as shown by the absence of imaginary frequencies. The graphical representation of the structure was prepared with the program ChemCraft.[7]

S3.1. Total energies (incl. ZPE), symmetries, and coordinates for all calculated compounds

[PNP]$^+$: -2125.2093077, C_1

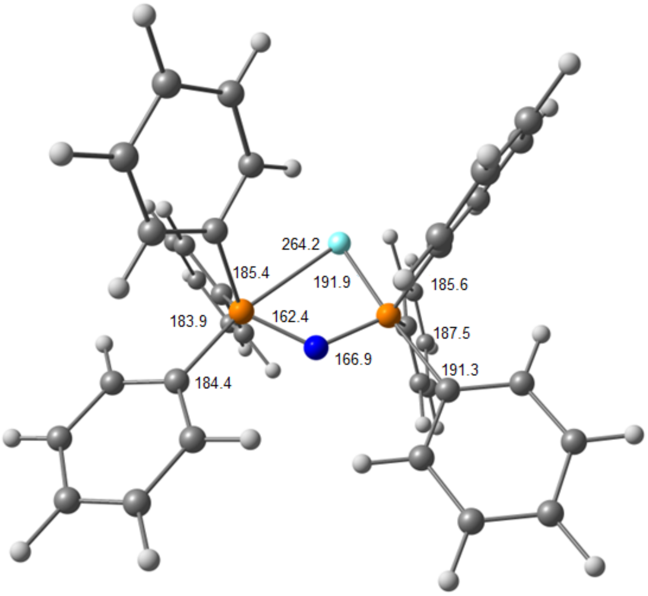
P	-0.2838834	1.4699352	-0.3016210
P	0.0273620	-1.5260719	-0.0606605
N	-0.3892268	-0.0851492	-0.5537793
C	-1.5345112	2.2588673	-1.3292052
C	-2.5321698	1.4871342	-1.9179869
H	-2.5337204	0.4144533	-1.7711619
C	-3.5099395	2.0928739	-2.6931172
H	-4.2839854	1.4894800	-3.1507303
C	-3.4935565	3.4661406	-2.8832087
H	-4.2559358	3.9375323	-3.4910258

C	-2.4974918	4.2386300	-2.3002951
H	-2.4801601	5.3101580	-2.4544233
C	-1.5193877	3.6392256	-1.5255140
H	-0.7406959	4.2493892	-1.0835936
C	1.3203279	2.1365550	-0.7778957
C	2.0572377	1.4686542	-1.7542051
H	1.6876193	0.5374038	-2.1643406
C	3.2600336	1.9936505	-2.1972258
H	3.8301699	1.4691313	-2.9536604
C	3.7318694	3.1887705	-1.6733480
H	4.6725413	3.5977114	-2.0207934
C	3.0017024	3.8598035	-0.7030590
H	3.3707505	4.7905584	-0.2909285
C	1.7990028	3.3377241	-0.2540346
H	1.2418439	3.8626279	0.5125049
C	-0.5928559	1.9804056	1.4003161
C	-1.8667744	2.3886946	1.7907597
H	-2.6587385	2.4757982	1.0568416
C	-2.1215932	2.6971394	3.1180925
H	-3.1119174	3.0194482	3.4144073
C	-1.1089281	2.6021012	4.0605768
H	-1.3083156	2.8497304	5.0958934
C	0.1632711	2.1991346	3.6774611
H	0.9567516	2.1351507	4.4116390
C	0.4226474	1.8881154	2.3532558
H	1.4208260	1.5871717	2.0575655
C	-0.3016930	-2.6657355	-1.4154248
C	-0.5884155	-2.1672842	-2.6829636
H	-0.6306126	-1.0966623	-2.8381508
C	-0.8245084	-3.0411467	-3.7339790
H	-1.0479877	-2.6500743	-4.7186898
C	-0.7766265	-4.4104777	-3.5227523
H	-0.9633793	-5.0916277	-4.3437492
C	-0.4944110	-4.9112192	-2.2584254
H	-0.4632516	-5.9805609	-2.0915198
C	-0.2576958	-4.0435880	-1.2061434
H	-0.0476447	-4.4445085	-0.2217933
C	-0.9356858	-2.0675137	1.3616968
C	-2.2013972	-1.5196882	1.5600694
H	-2.5597732	-0.7395595	0.9001044
C	-2.9981357	-1.9700420	2.5995591
H	-3.9796495	-1.5387052	2.7512637
C	-2.5396905	-2.9716484	3.4428913
H	-3.1641987	-3.3231558	4.2549151
C	-1.2810605	-3.5222869	3.2495675
H	-0.9205845	-4.3012443	3.9097386
C	-0.4785198	-3.0731339	2.2132795
H	0.5080403	-3.5001455	2.0783105
C	1.7687584	-1.7033455	0.3735831
C	2.2219554	-1.2919635	1.6280346
H	1.5172900	-0.9430379	2.3736593

C	3.5721334	-1.3462475	1.9311274
H	3.9182400	-1.0343095	2.9086654
C	4.4785298	-1.8098862	0.9869991
H	5.5333312	-1.8563233	1.2280998
C	4.0340482	-2.2227205	-0.2600119
H	4.7391254	-2.5929591	-0.9936498
C	2.6833203	-2.1713603	-0.5682606
H	2.3399798	-2.5059175	-1.5395507

(PNP)F: -2225.1748296, C_1

P	-0.1856082	1.3303823	0.1475536
P	0.1624506	-1.5672539	-0.0641343
F	0.7203607	0.6480629	1.5289076
N	-0.3944828	-0.1562620	-0.4905528
C	-1.0912959	2.2241719	-1.2593132
C	-1.8103354	1.5727509	-2.2562486
H	-1.8554076	0.4919376	-2.2389946
C	-2.4760427	2.2821964	-3.2500547
H	-3.0300862	1.7473147	-4.0136126
C	-2.4361331	3.6666410	-3.2642721
H	-2.9521945	4.2227763	-4.0382132
C	-1.7275882	4.3356319	-2.2743132
H	-1.6881072	5.4189565	-2.2720884
C	-1.0676697	3.6199473	-1.2891883
H	-0.5185132	4.1643398	-0.5275607
C	1.3750170	2.2342449	-0.2009070
C	1.9583392	2.0536901	-1.4515408
H	1.4706864	1.4178701	-2.1814162
C	3.1536598	2.6789519	-1.7705339
H	3.6032908	2.5145676	-2.7426872
C	3.7633170	3.5236902	-0.8543964
H	4.6893290	4.0260083	-1.1080740
C	3.1795302	3.7224751	0.3878989
H	3.6472388	4.3828798	1.1088725
C	2.0018377	3.0678407	0.7193546
H	1.5728183	3.2113406	1.7020643
C	-1.3633155	1.9526304	1.4306353
C	-2.7239999	2.0029650	1.1285869
H	-3.0651203	1.7268230	0.1392466
C	-3.6531028	2.4019773	2.0775631
H	-4.7062963	2.4153398	1.8229415
C	-3.2341523	2.7998217	3.3379578
H	-3.9566101	3.1310347	4.0747308
C	-1.8834290	2.7658800	3.6492301
H	-1.5442790	3.0675231	4.6333597
C	-0.9599881	2.3244658	2.7133640
H	0.0802604	2.2425902	2.9906994
C	-0.6014509	-2.7608016	-1.1969108
C	-0.9103034	-2.3522945	-2.4928569
H	-0.7145691	-1.3280154	-2.7829191



C	-1.4679325	-3.2466038	-3.3931444
H	-1.7060537	-2.9194660	-4.3980782
C	-1.7250444	-4.5543224	-3.0064845
H	-2.1661733	-5.2513532	-3.7089534
C	-1.4225794	-4.9661038	-1.7170104
H	-1.6290651	-5.9836980	-1.4081997
C	-0.8614945	-4.0742815	-0.8151566
H	-0.6379548	-4.4012081	0.1929923
C	-0.2793219	-2.1489764	1.5930095
C	-1.4813056	-1.7090391	2.1418795
H	-2.0863194	-0.9905981	1.6024902
C	-1.8894584	-2.1702226	3.3821985
H	-2.8207823	-1.8154882	3.8064586
C	-1.1022018	-3.0737670	4.0828439
H	-1.4213090	-3.4309258	5.0547256
C	0.0965809	-3.5132641	3.5421373
H	0.7176002	-4.2119206	4.0897569
C	0.5092147	-3.0521898	2.3001133
H	1.4524350	-3.3892389	1.8874073
C	1.9534915	-1.8336857	-0.2441608
C	2.8502704	-1.2187345	0.6328266
H	2.4725655	-0.5911545	1.4285394
C	4.2142309	-1.3920719	0.4664182
H	4.9003533	-0.9069965	1.1500918
C	4.7017049	-2.1733420	-0.5721174
H	5.7698976	-2.3036324	-0.6990485
C	3.8184494	-2.7843834	-1.4476050
H	4.1906275	-3.3954253	-2.2610592
C	2.4508211	-2.6178850	-1.2841279
H	1.7706991	-3.1051139	-1.9709209

OCF$_2$: -312.8351501, C_{2v}

C	0.0000000	0.0000000	-0.0932283
O	0.0000000	0.0000000	-1.2619268
F	1.0578709	0.0000000	0.6775776
F	-1.0578709	0.0000000	0.6775776

SiF$_4$: -688.8243395, T_d

Si	0.0000000	0.0000000	0.0000000
F	-0.9012670	0.9012670	0.9012670
F	0.9012670	-0.9012670	0.9012670
F	-0.9012670	-0.9012670	-0.9012670
F	0.9012670	0.9012670	-0.9012670

MeSiF$_3$: -628.8238882, C_{3v}

Si	0.0000000	0.0000000	0.8374258
F	0.7331490	-1.2698514	1.4223132
F	0.7331490	1.2698514	1.4223132
F	-1.4662980	0.0000000	1.4223132

C	0.0000000	0.0000000	-0.9898155
H	1.0218652	0.0000000	-1.3715166
H	-0.5109326	-0.8849613	-1.3715166
H	-0.5109326	0.8849613	-1.3715166

Me$_2$SiF$_2$: -568.8145589, C_{2v}

F	0.0000000	1.2737659	1.6054817
Si	0.0000000	0.0000000	0.6435653
C	1.5666414	0.0000000	-0.3308233
F	0.0000000	-1.2737659	1.6054817
C	-1.5666414	0.0000000	-0.3308233
H	1.6320058	0.8843485	-0.9676270
H	2.4289446	0.0000000	0.3388129
H	1.6320058	-0.8843485	-0.9676270
H	-1.6320058	0.8843485	-0.9676270
H	-1.6320058	-0.8843485	-0.9676270
H	-2.4289446	0.0000000	0.3388129

Me$_3$SiF: -508.8018588, C_{3v}

Si	0.0000000	0.0000000	0.4280838
F	0.0000000	0.0000000	2.0415066
C	-0.8897116	1.5410256	-0.1192961
C	-0.8897116	-1.5410256	-0.1192961
C	1.7794231	0.0000000	-0.1192961
H	1.8538732	0.0000000	-1.2093179
H	2.3029408	0.8831921	0.2527086
H	2.3029408	-0.8831921	0.2527086
H	-0.9269366	-1.6055013	-1.2093179
H	-0.3866036	-2.4360013	0.2527086
H	-1.9163372	-1.5528092	0.2527086
H	-0.9269366	1.6055013	-1.2093179
H	-1.9163372	1.5528092	0.2527086
H	-0.3866036	2.4360013	0.2527086

Me$_4$Si: -448.7897452, T_d

Si	0.0000000	0.0000000	0.0000000
C	-1.0841093	1.0841093	1.0841093
C	1.0841093	-1.0841093	1.0841093
C	1.0841093	1.0841093	-1.0841093
C	-1.0841093	-1.0841093	-1.0841093
H	1.7279081	0.4801139	-1.7279081
H	0.4801139	1.7279081	-1.7279081
H	1.7279081	1.7279081	-0.4801139
H	-1.7279081	-1.7279081	-0.4801139
H	-1.7279081	-0.4801139	-1.7279081
H	-0.4801139	-1.7279081	-1.7279081
H	-1.7279081	0.4801139	1.7279081
H	-0.4801139	1.7279081	1.7279081
H	-1.7279081	1.7279081	0.4801139
H	1.7279081	-1.7279081	0.4801139

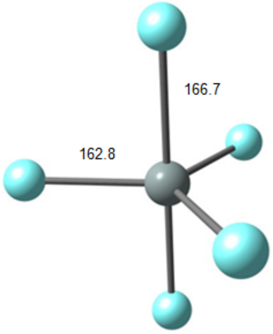
H	1.7279081	-0.4801139	1.7279081
H	0.4801139	-1.7279081	1.7279081

$[OCF_3]^-$: -412.7069236, C_{3v}

C	0.0000000	0.0000000	0.1450160
O	0.0000000	0.0000000	1.3590240
F	-0.6324554	1.0954449	-0.5013467
F	-0.6324554	-1.0954449	-0.5013467
F	1.2649108	0.0000000	-0.5013467

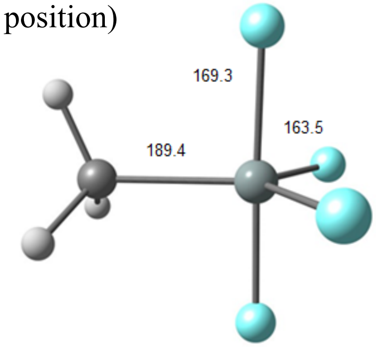
$[SiF_5]^-$: -788.7297226, D_{3h}

Si	0.0000000	0.0000000	0.0000000
F	-0.8141718	-1.4101870	0.0000000
F	0.0000000	0.0000000	-1.6668405
F	-0.8141718	1.4101870	0.0000000
F	1.6283437	0.0000000	0.0000000
F	0.0000000	0.0000000	1.6668405



$[MeSiF_4]^-$: -728.7094072, C_s (isomer I, methyl group in equatorial position)

Si	0.7744651	0.0208669	0.0000000
C	-1.1202625	0.0059004	0.0000000
F	0.7833840	-1.6742044	0.0000000
F	1.6279725	0.0104114	-1.3951863
F	1.6279725	0.0104114	1.3951863
F	0.8232774	1.7127315	0.0000000
H	-1.5609951	1.0030982	0.0000000
H	-1.4779070	-0.5446076	0.8750140
H	-1.4779070	-0.5446076	-0.8750140

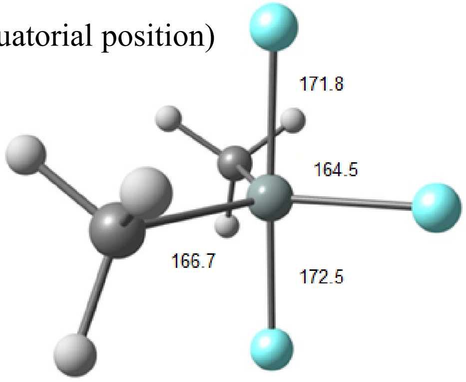


$[MeSiF_4]^-$: -728.7034822, C_s (isomer II, methyl group in axial position)

Si	0.0001098	-0.7897520	0.0000000
F	-0.8268912	-0.8244754	-1.4278666
C	0.0006699	1.1357033	0.0000000
F	-0.8268912	-0.8244754	1.4278666
F	1.6505261	-0.8242132	0.0000000
F	0.0015265	-2.4634389	0.0000000
H	0.5109212	1.5306476	0.8843987
H	-1.0208924	1.5293565	0.0000000
H	0.5109212	1.5306476	-0.8843987

$[Me_2SiF_3]^-$: -668.6866766, C_s (isomer I, two methyl groups in equatorial position)

Si	0.5456054	0.0668191	0.0000000
C	-0.3542660	-0.0062666	-1.6744408
F	0.6400772	-1.6552584	0.0000000
F	2.1896238	0.1272706	0.0000000
C	-0.3542660	-0.0062666	1.6744408
F	0.5107947	1.7849042	0.0000000
H	-0.6385148	0.9753447	-2.0562188



H	-1.2472485	-0.6330577	-1.5908585
H	0.2969787	-0.4978882	-2.4041242
H	0.2969787	-0.4978882	2.4041242
H	-1.2472485	-0.6330577	1.5908585
H	-0.6385148	0.9753447	2.0562188

[Me$_2$SiF$_3$]$^-$: -668.6765103, D_{3h}, (isomer II, two methyl groups in axial positions)

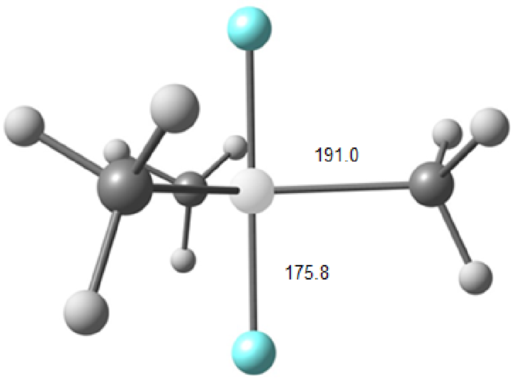
Si	0.0000000	0.0000000	0.0000000
F	0.8384297	1.4522029	0.0000000
C	0.0000000	0.0000000	-1.9295820
F	0.8384297	-1.4522029	0.0000000
F	-1.6768595	0.0000000	0.0000000
C	0.0000000	0.0000000	1.9295820
H	-0.5108207	-0.8847674	-2.3236094
H	1.0216414	0.0000000	-2.3236094
H	-0.5108207	0.8847674	-2.3236094
H	-0.5108207	-0.8847674	2.3236094
H	-0.5108207	0.8847674	2.3236094
H	1.0216414	0.0000000	2.3236094

[Me$_2$SiF$_3$]$^-$: -668.6778599, C_1 (isomer III, one methyl group in axial position, one methyl group in equatorial position)

Si	0.6213097	-0.4658080	0.0788623
C	-1.2412198	-0.8486206	-0.1159309
F	0.9360820	-2.1365687	0.1491920
F	1.5611361	-0.4160753	-1.2878749
F	1.2578395	-0.3505472	1.6074567
C	0.4540577	1.4753762	0.0194017
H	-1.8749293	0.0395512	-0.1761081
H	-1.5773016	-1.4657832	0.7227737
H	-1.3904542	-1.4467827	-1.0203435
H	0.0122063	1.8058493	-0.9283472
H	1.4272786	1.9691943	0.1191122
H	-0.1860050	1.8402145	0.8318060

[Me$_3$SiF$_2$]$^-$: -608.6634142, C_s (isomer I, two fluorine atoms in axial position)

Si	-0.0018025	-0.0554733	0.0000000
C	-1.9090830	0.0508107	0.0000000
F	0.0562746	1.7017685	0.0000000
C	0.9550793	-0.0478514	1.6527008
C	0.9550793	-0.0478514	-1.6527008
F	-0.0630246	-1.8047345	0.0000000
H	-2.3937424	-0.9271000	0.0000000
H	-2.2442798	0.6164320	-0.8754301
H	-2.2442798	0.6164320	0.8754301
H	1.8984307	0.4933740	1.5285422
H	1.1639238	-1.0500119	2.0312157
H	0.3825349	0.5054215	2.4043457
H	1.8984307	0.4933740	-1.5285422



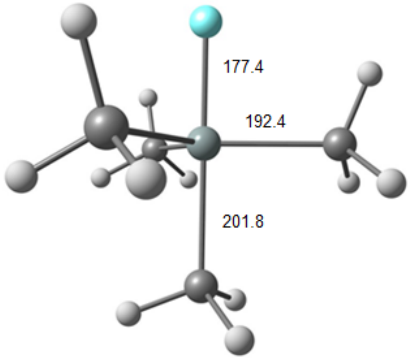
H	0.3825349	0.5054215	-2.4043457
H	1.1639238	-1.0500119	-2.0312157

[Me$_3$SiF$_2$]$^-$: -608.6524375, C_s (isomer II, one fluorine atom in axial position, one fluorine atom in equatorial position)

C	0.5232885	-0.5205389	1.6550842
Si	-0.4401448	-0.4203833	0.0000000
F	-0.5341661	-2.1536313	0.0000000
C	-0.5215163	1.5545173	0.0000000
C	0.5232885	-0.5205389	-1.6550842
F	-2.1088718	-0.4346467	0.0000000
H	1.2775577	-1.3113952	1.6264125
H	-0.1905060	-0.7980552	2.4395665
H	0.9942598	0.4205074	1.9512830
H	-0.1905060	-0.7980552	-2.4395665
H	1.2775577	-1.3113952	-1.6264125
H	0.9942598	0.4205074	-1.9512830
H	0.4872734	1.9896052	0.0000000
H	-1.0458873	1.9417512	-0.8831567
H	-1.0458873	1.9417512	0.8831567

[Me$_4$SiF]$^-$: -548.6278501, C_{3v} (isomer I, fluorine atom in axial position)

Si	0.0000000	0.0000000	0.4178481
C	-0.9619506	-1.6661473	0.4360134
C	0.0000000	0.0000000	-1.6004441
C	-0.9619506	1.6661473	0.4360134
C	1.9239011	0.0000000	0.4360134
F	0.0000000	0.0000000	2.1917294
H	-1.1708111	-2.0279043	1.4444110
H	-0.3916195	-2.4318179	-0.1019894
H	-1.9102063	-1.5550614	-0.1019894
H	0.5095376	0.8825451	-2.0128235
H	-1.0190753	0.0000000	-2.0128235
H	0.5095376	-0.8825451	-2.0128235
H	-0.3916195	2.4318179	-0.1019894
H	-1.1708111	2.0279043	1.4444110
H	-1.9102063	1.5550614	-0.1019894
H	2.3018258	0.8767565	-0.1019894
H	2.3018258	-0.8767565	-0.1019894
H	2.3416221	0.0000000	1.4444110



[Me$_4$SiF]$^-$: -548.6190374, C_s (isomer II, fluorine atom in equatorial position)

C	-0.7063205	0.0392111	1.6182121
Si	0.3534000	-0.0198005	0.0000000
C	0.6289171	1.9490663	0.0000000
C	0.4092541	-2.0071764	0.0000000
C	-0.7063205	0.0392111	-1.6182121
F	2.0549656	-0.1136834	0.0000000
H	-1.2862059	0.9624726	1.7124505
H	-0.0190615	0.0051896	2.4736286

H	-1.3804128	-0.8171119	1.7172629
H	0.9354384	-2.3956489	-0.8813008
H	-0.5998595	-2.4407843	0.0000000
H	0.9354384	-2.3956489	0.8813008
H	-0.0190615	0.0051896	-2.4736286
H	-1.2862059	0.9624726	-1.7124505
H	-1.3804128	-0.8171119	-1.7172629
H	-0.3251814	2.4923991	0.0000000
H	1.1958144	2.2758771	0.8811794
H	1.1958144	2.2758771	-0.8811794

S.3.2 Total energies incl. ZPE of the different stereo isomers of the anions $[Me_nSiF_{5-n}]^-$ (n = 1-4)

Table S1: Calculated total energies ($E + ZPE$; PBE0/def2-TZVPP level) and of the different stereo isomers of the anions $[Me_nSiF_{5-n}]^-$ (n = 1-4). The last column shows the energy differences between the different stereo isomers.

		$Me_{ax.}$	$Me_{eq.}$	$E + ZPE$ (in Hartree)	$E + ZPE$ (in kJ mol^{-1})	ΔE (kJ mol^{-1})
$[MeSiF_4]^-$	isomer I	-	1	-728.7094072	-1913226.49	0.0
	isomer II	1	-	-728.7034822	-1913210.934	15.6
$[Me_2SiF_3]^-$	isomer I	-	2	-668.6866766	-1755636.816	0.0
	isomer II	2	-	-668.6765103	-1755610.124	26.7
	isomer III	1	1	-668.6778599	-1755613.668	23.1
$[Me_3SiF_2]^-$	isomer I	-	3	-608.6634142	-1598045.745	0.0
	isomer II	1	2	-608.6524375	-1598016.926	28.8
	isomer III	2	1		[a]	
$[Me_4SiF]^-$	isomer I	3	1	-548.6278501	-1440422.377	0.0
	isomer II	2	2	-548.6190374	-1440399.239	23.1

[a] Structure optimization of the potential isomer III with two both fluorine atoms in equatorial position led to the structure of isomer I. Therefore no minima of isomer III could be localized on the potential energy surface.

S.3.3 Calculated Fluoride Ion Affinities (*FIA*) of the neutral silanes Me_nSiF_{4-n} (n = 0-4)

The *FIA* of the silanes Me_nSiF_{4-n} (n = 0-4) was calculated by using the isodesmic approach developed by Christe et al..[8] The gas-phase reaction enthalpy ΔH_r(eq. S1) of the silanes with $[OCF_3]^-$ to the $[Me_nSiF_{5-n}]^-$ anions (n = 0-4) and OCF_2 was calculated on the PBE0/def2-TZVPP level (eq. S1). The *FIA* of OCF_2 is experimentally known to be 209 kJ·mol^{-1} (eq. S2).[8] Addition of equations S1 and S2 gives the *FIA*s to the neutral silanes Me_nSiF_{4-n} (n = 0-4).

$Me_nSiF_{4-n} + [OCF_3]^- \rightarrow [Me_nSiF_{5-n}]^- + OCF_2$ ΔH_r(eq. S1) eq. S1

$OCF_2 + F \rightarrow [OCF_3]^-$ $FIA = 209\ \mathrm{kJ{\cdot}mol^{-1}}$ eq. S2

$Me_nSiF_{4-n} + F^- \rightarrow [Me_nSiF_{5-n}]^-$ ΔH_r(eq. S3) = eq. S3 (eq. S1 + eq. S2)

$$\Delta H_r(\text{eq. S1}) - 209\ \mathrm{kJ{\cdot}mol^{-1}} = -FIA\ (Me_nSiF_{4-n})$$

Table S2: Calculated gas phase reaction enthalpies ΔH_r (0 K; PBE0/def2-TZVPP level) according to equation S1 and the calculated *FIA* by using the experimental *FIA* of OCF_2 (209 $kJ\cdot mol^{-1}$)[8].

	ΔH_r (eq. S1) in $kJ\cdot mol^{-1}$	*FIA* in $kJ\cdot mol^{-1}$
SiF_4	-88.2	297.2 (*307.7*)[a]
$MeSiF_3$	-36.1	245.1
Me_2SiF_2	-0.9	209.9
Me_3SiF	26.8	182.2
Me_4Si	88.4	120.6

[a] Calculated at MP2/PDZ level of theory in ref. [8].

S.3.4. Thermodynamic estimations

The thermodynamics for the reaction of (PNP)F with the silanes Me_nSiF_{4-n} were estimated to explain the failure of the synthesis of $[PNP][Me_4SiF]$. The reaction enthalpy ΔH_r in the condensed was calculated according to the Born-Fajans-Haber cycle in Fig. S.32. According to spectroscopic and crystal structure data (PNP)F cannot be described as either a purely ionic or covalent compound. Therefore only rough thresholds were estimated for this reactions by either assuming purely ionic or purely covalent (PNP)F. It is evident from the calculated values in Table S.3 that the reaction of Me_4Si with (PNP)F is much less favored due to its much lower *FIA*.

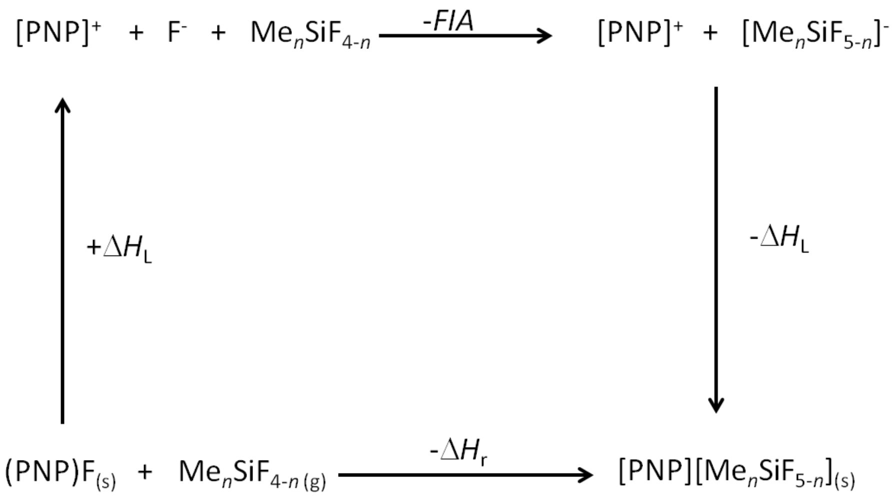


Fig. S32. Born-Fajans-Haber cycle for the reaction of (PNP)F with the silanes Me_nSiF_{4-n}.

Table S3: Estimated thermodynamics for the reactions according to Fig. S.30. Enthalpies are given in kJ mol^{-1}.

	ΔH_L[a]	ΔH_r (ionic [PNP]F)[b]	ΔH_r (covalent [PNP]F)[c]
SiF_4	-88.2	-236	≥ -147
$MeSiF_3$	-36.1	-182	≥ -93
Me_2SiF_2	-0.9	-146	≥ -57
Me_3SiF	26.8	-117	≥ -28
Me_4Si	88.4	-54	≥ +35

[a] The lattice enthalpies were calculated by a volume-based approach.[9] The volumes were taken from the experimental crystal structures.

[b] The reaction enthalpy in condensed phase was calculated assuming purely ionic [PNP]F. A lattice enthalpy of 366 kJ mol^{-1} was used in these estimations. The lattice enthalpy was estimated based on the experimental volume.

[c] The reaction enthalpy in condensed phase was calculated assuming covalent (PNP)F. A *FIA* of 455 kJ mol^{-1} (PBE0/def2-TZVPP) was used in these estimations. The sublimation enthalpy of (PNP)F is unknown and was neglected.

The reaction enthalpies in the solid state were estimated based on either purely ionic or covalent (PNP)F. Both estimations give only a rough limit. If ionic [PNP]F is assumed then covalent interactions would be ignored, which should increase the lattice enthalpy of [PNP]F. Estimations based on covalent (PNP)F neglect the unknown sublimation enthalpy of (PNP)F. Therefore the actual reactions have to be less favored. This is in good agreement with the experimental findings. Obviously, the reaction of (PNP)F with Me_4Si is endothermic and thus cannot be observed. In addition, these estimations show that a covalent description of (PNP)F is in better agreement with the experimental observations than an ionic description.

S4. Crystal structure data

S.4.1. Representations of the asymmetric unit of the crystals structures of the [PNP]silicates

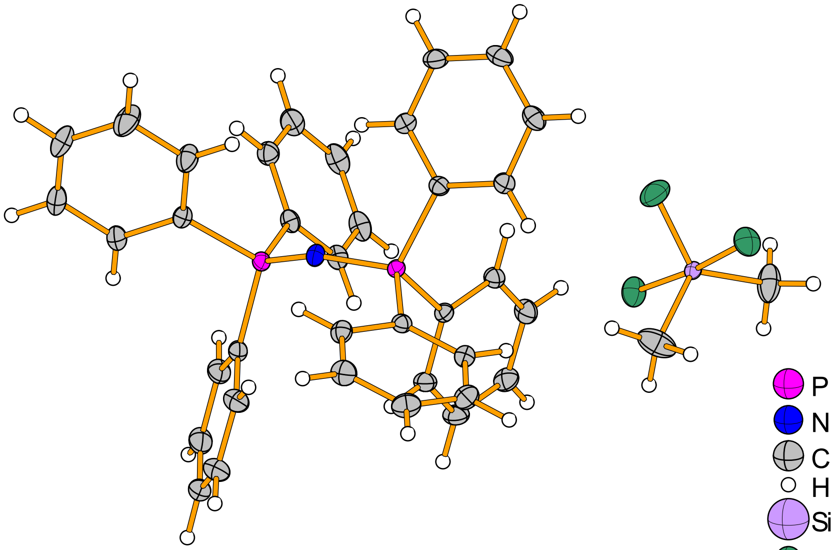


Fig. S33. Part of the crystal structure of [PNP][Me_2SiF_3]. Ellipsoids are drawn at 50% probability and hydrogen atoms are drawn with arbitrary radii.

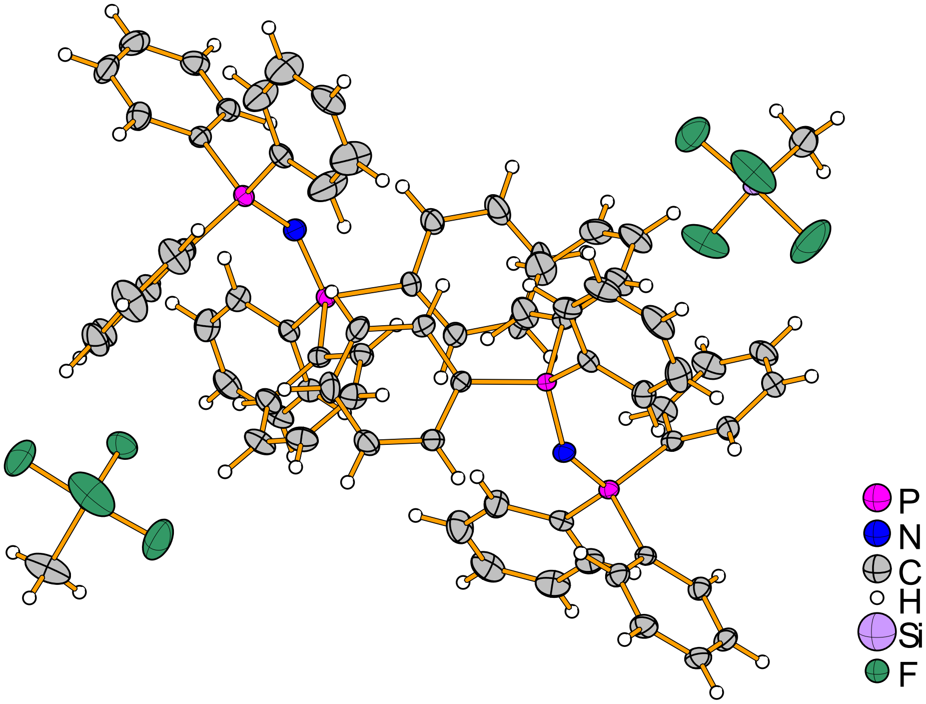


Fig. S34. Part of the crystal structure of [PNP][$MeSiF_4$]. Ellipsoids are drawn at 50% probability and hydrogen atoms are drawn with arbitrary radii. The asymmetric unit contains two cations and two anions.

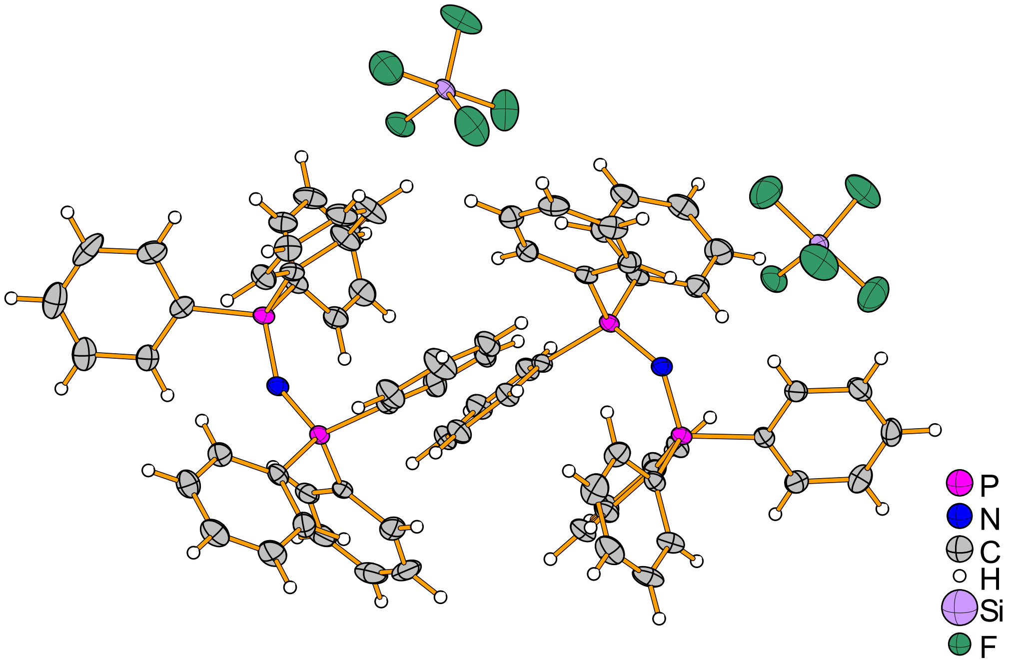


Fig. S35. Part of the crystal structure of [PNP][SiF_5]. Ellipsoids are drawn at 50% probability and hydrogen atoms are drawn with arbitrary radii. The asymmetric unit contains two cations and two anions.

S.4.2. Additional crystal structure data

In this section five additional crystal structures are reported. These data were obtained in the course of the investigation of the [PNP]F, but are not essential to the understanding of the main paper. Table S1 summarizes the crystallographic parameters for these structures. The single-crystal X-ray structure determinations were carried out on a Bruker APEX-II diffractometer equipped with a CCD area detector diffractometer using Mo-Ka (0.71073 Å) radiation. The crystals were mounted onto a cryo loop using fluorinated oil and frozen in the cold nitrogen stream of the goniometer. The structures were solved by direct methods (SHELXS).[10] Subsequent least-squares refinement on F^2 (SHELXL 97-2) located the positions of the remaining atoms in the electron density maps. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were placed in calculated positions using a riding model and were refined isotropically in blocks. The data were corrected for absorption (semi-empirical from equivalents). Graphical representations of the structures were prepared with the program DIAMOND.[11]

Table S3. Crystallographic parameters for $[PNP][SiF_5]\bullet{}^1/_2OEt_{2,}$ $[PNP]_2[SiF_6]\bullet6(MeOH)$, $[PNP][HF_2/Cl]\bullet3(MeOH)$, $[PNP][HF_2/Cl]\bullet{}^1/_4(CH_3CN)$, and $[PNP][HF_2/Cl]\bullet2(CH_3CN)$

	[PNP] $[SiF_5]\bullet{}^1/_2OEt_2$	**$[PNP]_2$ $[SiF_6]\bullet6(MeOH)$**	**[PNP] $[HF_2/Cl]\bullet3(MeOH)$**	**[PNP] $[HF_2/Cl]\bullet{}^1/_4(CH_3CN)$**	**[PNP] $[HF_2/Cl]\bullet2(CH_3CN)$**
CCDC number	954026	937496	955394	955393	955395
Formula	$C_{38}H_{35}F_5NO_{0.50}P_2Si$	$C_{78}H_{84}F_6N_2O_6P_4Si$	$C_{39}H_{42}Cl_{0.08}F_{1.85}NO_3P_2$	$C_{146}H_{125}Cl_{0.32}F_{7.36}N_5P_8$	$C_{40}H_{36}Cl_{0.40}F_{1.20}N_3P_2$
M	698.70	1411.44	672.51	2348.50	657.64
Crystal system	Triclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/c$	C2/c	$P2_1/c$	$P2_1/n$
a/pm	1172.34(2)	1113.1(2)	3917.2(8)	2684.9(5)	1625.60(3)
b/pm	1176.02(2)	1213.9(2)	905.78(18)	1745.7(4)	1399.32(3)
c/pm	1413.30(2)	2669.6(5)	2354.6(5)	2623.9(5)	1682.26(3)
α /°	68.9697(8)	90	90	90	90
β /°	69.5406(8)	91.74(3)°	121.67(3)	91.13(3)	112.9540(10)
γ /°	70.8268(8)	90	90	90	90
U/nm^3	1.65746(5)	3.6054(12)	7.111(2)	12.296(4)	3.52369(12)
T/K	100(2)	123(2)	123(2)	123(2)	173(2)
Z	2	2	8	4	4
μ(Mo-K$_\alpha$)/mm^{-1}	0.227	0.191	0.175	0.186	0.192
No. of data collected	47991	28032	43058	121162	35516
No. of unique data	14259	8259	8028	27831	8912
R_{int}	0.0268	0.0494	0.0550	0.0613	0.0327
R_1, wR_2 (I>2σ(I))^a	0.0428, 0.1089	0.0516, 0.1117	0.0448, 0.0954	0.0537, 0.1316	0.0527, 0.1205
R_1, wR_2 (all data)	0.0576, 0.1179	0.0641, 0.1190	0.0703, 0.1080	0.0911, 0.1494	0.0857, 0.1385

^{a} $R_1 = \sum||F_o|-|F_c|| / \sum|F_o|$, $wR_2 = (\sum[w(F_o^2-F_c^2)^2]/\sum[wF_o^4])^{1/2}$

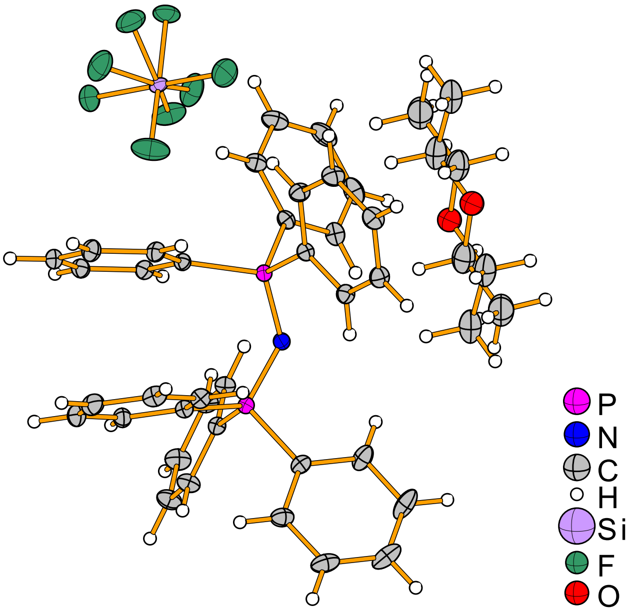


Fig. S36. Part of the crystal structure of $[PNP][SiF_5]\bullet{}^1/_2OEt_2$. Ellipsoids are drawn at 50% probability and hydrogen atoms are drawn with arbitrary radii. Single crystals suitable for X-ray diffraction were obtained from CH_3CN/OEt_2 solution. The asymmetric unit contains a half disordered molecule of diethyl ether. The $[SiF_5]^-$ anion is disordered as well, which is quite common for this anion. An ordered structure of $[PNP][SiF_5]$ was obtained by crystallization from CH_3CN/*t*-BuOMe and is reported in the main paper.

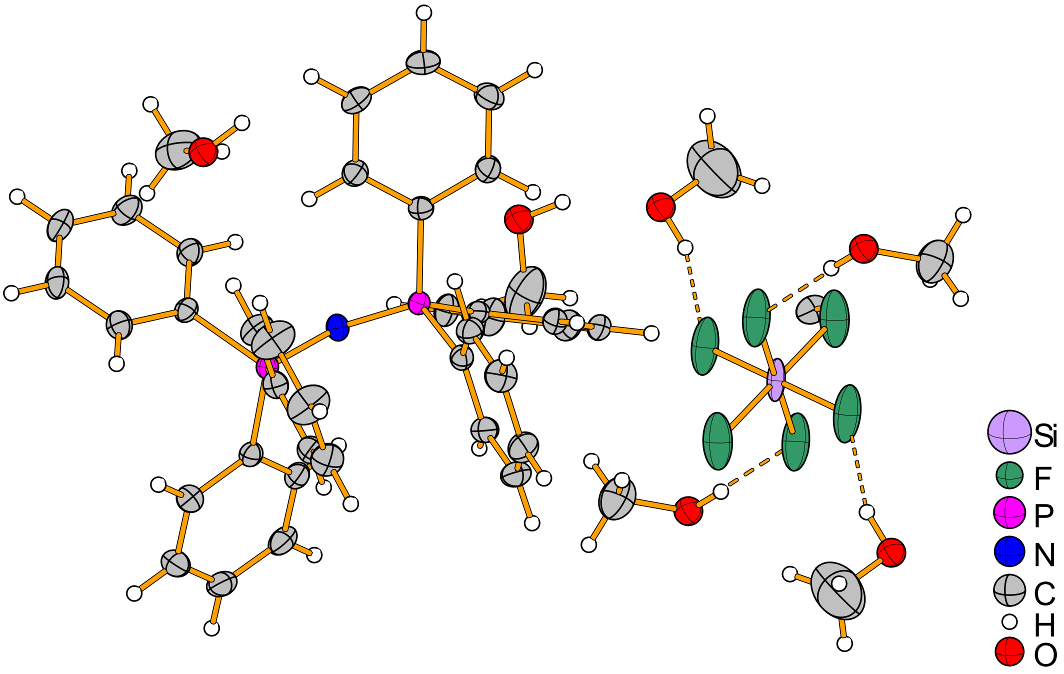


Fig. S37. Part of the crystal structure of $[PNP]_2[SiF_6]\bullet6(MeOH)$. Ellipsoids are drawn at 50% probability and hydrogen atoms are drawn with arbitrary radii. Single crystals suitable for X-ray diffraction were obtained from $MeOH/OEt_2$ solution. The product was obtained from a failed attempt to prepare [PNP]F using AgF as fluoride source.

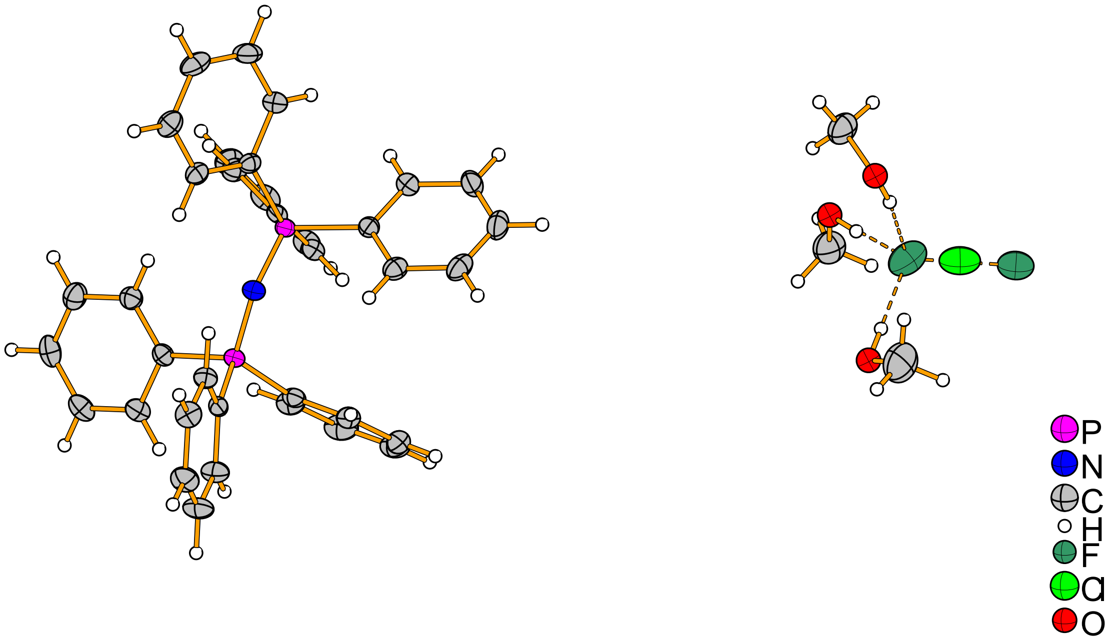


Fig. S38. Part of the crystal structure of [PNP][HF_2/Cl]•3(MeOH). Ellipsoids are drawn at 50% probability and hydrogen atoms are drawn with arbitrary radii. Single crystals suitable for X-ray diffraction were obtained from MeOH/OEt_2 solution. The product was obtained from a failed attempt to prepare [PNP]F using AgF as fluoride source. The anion position is occupied by $[HF_2]^-$ (85 %) and chloride (15 %).

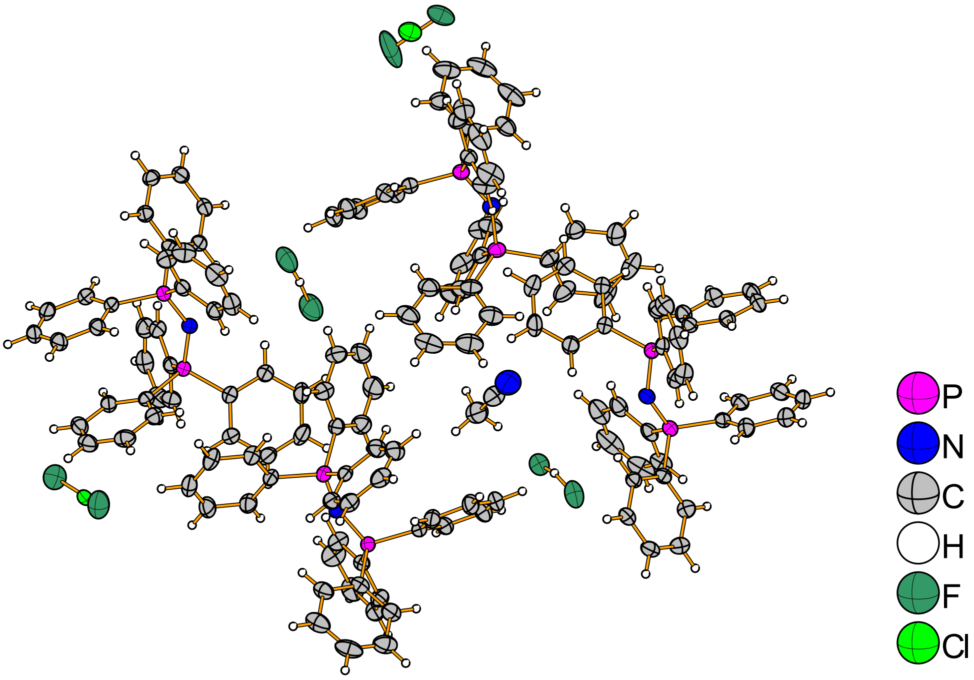


Fig. S39. Part of the crystal structure of [PNP][HF_2/Cl]•$^1/_4$(CH_3CN). Ellipsoids are drawn at 50% probability and hydrogen atoms are drawn with arbitrary radii. Single crystals suitable for X-ray diffraction were obtained from CH_3CN/OEt_2 solution. The product was obtained from a failed attempt to prepare [PNP]F using AgF as fluoride source. Part of the anion position are mixed occupied by $[HF_2]^-$ and chloride.

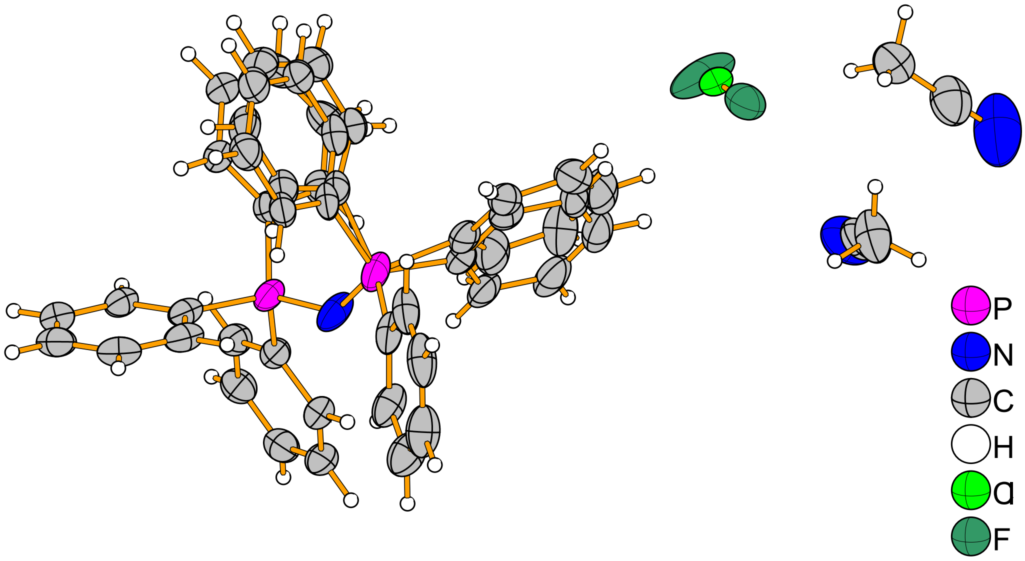


Fig. S40. Part of the crystal structure of [PNP][HF_2/Cl]•2(CH_3CN). Ellipsoids are drawn at 50% probability and hydrogen atoms are drawn with arbitrary radii. Single crystals suitable for X-ray diffraction were obtained from H_3CCN/OEt_2 solution. The product was obtained from a failed attempt to prepare [PNP]F using AgF as fluoride source. The anion position is occupied by $[HF_2]^-$ (60 %) and chloride (40 %), which leads to a related disorder of two phenyl rings over two position.

S5. References

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