Stable Chlorosilicates

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Synthesis of Chlorosilicates**

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Abstract: *Chlorosilicates represent important intermediates in S_N2 reactions of chlorosilanes. They can be stabilized by the introduction of electron-withdrawing substituents. Salts of various (pentafluoroethyl)chlorosilicates have been isolated and structurally characterized.*

The difference between S_N2 reactions at carbon and at silicon centers is fundamental and well-known. In carbon chemistry, the pentacoordinate geometry always represents a transition state, whereas in silicon chemistry the mechanism of a nucleophilic substitution depends on the nucleophile and the electronic nature of the ancillary ligands (Figure 1).[1] In gas-phase reactions, the pentacoordinate species is mostly a local minimum.

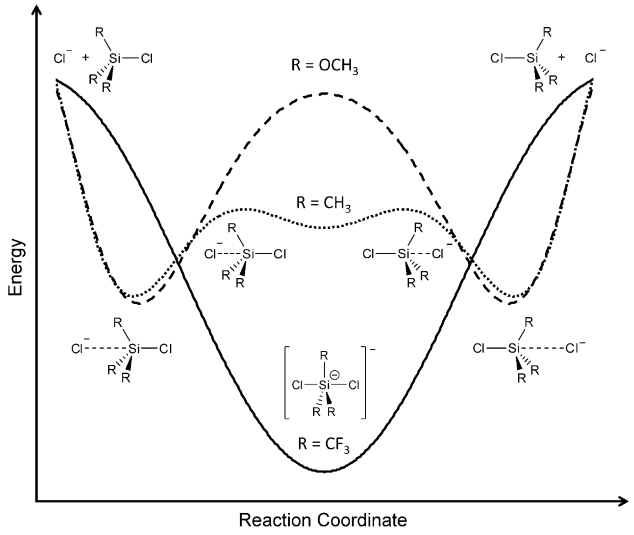

Figure 1. Energy profile for S_N2 reactions of chlorosilanes in the gas phase (compare with Ref. [1]).

However, as the solvation enthalpy of the nucleophile generally exceeds the solvation enthalpy of the pentacoordinate species, the situation may change drastically in solution and the local or global minima characteristic of the gas-phase reaction can become transition states.[2]

Penta- and hexacoordinate fluorosilicates are well-known. The same holds for adducts of chlorosilanes and neutral Lewis bases, which may be envisaged as zwitterions with a silicate motif (Figure 2).[3] However, apart from theoretical investigations,[4] there is little information on anionic chlorosilicates.

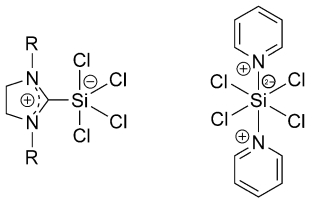

Figure 2. Examples of neutral penta- and hexacoordinate adducts of $SiCl_4$.

Several attempts to synthesize salts of the most simple chlorosilicate $[SiCl_5]^-$ have been reported, but the obtained products lack convincing characterization.[5,6] The pentachlorosilicate was detected in the mass spectrum of $SiCl_4$.[7] Although the formation of a contact ion pair between SiF_4 and CsF is observed under matrix conditions, $SiCl_4$ and CsCl show no reaction.[8] The formation of mixed chlorofluorosilicates from chloride salts and SiF_4, however, has been reported.[9] The reaction of tetrakis(dimethylamino)ethene (TDAE) and $[\{CH_3Cl_2Si\}_2]$ led to the formation of the chlorosilicate $[TDAE][SiCl_2CH_3(SiCl_2CH_3)(SiCl_3)]$ as a minor product.[10] The reaction of Si_2Cl_6 with $[NBu_4]Cl$ yields $[NBu_4]_2[Si_6Cl_{12}\cdot Cl_2]$ at 85 °C. Silyl-substituted chlorosilicates such as $[SiCl_3(SiCl_3)_2]^-$, $[SiCl_4(SiCl_3)_2]^{2-}$, and $[SiCl_2(SiCl_3)_2]^-$ are formed as intermediates in the reaction. Recently, they were isolated at low temperatures and structurally characterized. Solutions from these species at room temperature suffer from spontaneous decomposition.[11]

As electron-withdrawing substituents increase the Lewis acidity of the corresponding silane towards the chloride ion, the preparation and handling of chlorosilicates at room temperature should be possible.

The ^{29}Si NMR spectrum of a solution of [PNP]Cl and $SiCl_4$ in CH_2Cl_2 shows only the resonance for $SiCl_4$ at $\delta = -19.0$ [Eq. (1)].

$$[PNP]Cl + SiCl_4 \xrightarrow[CH_2Cl_2]{//} [PNP][SiCl_5] \qquad (1)$$

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Table 1: Free enthalpy of chloride addition to selected silanes in the gas phase and in CH_2Cl_2 solution ((CPCM)-B3LYP/6-311++G(2d)[14]).

Lewis acid	$\Delta_r G°_{(g)}$ [kJ mol^{-1}]	$\Delta_r G°_{(sol)}$ [kJ mol^{-1}]
$SiCl_4$	−50.9	44.8
$Si(CF_3)Cl_3$	−81.6	21.4
$Si(CF_3)_2Cl_2$	−120.8	−7.9
$Si(CF_3)_3Cl$[15]	−132.4	−10.9
$Si(CF_3)_4$	−133.2	−22.0

As solvation effects could overcompensate the chloride ion affinity (ClIA) in the gas phase, we calculated the chloride ion affinities for various chloro(trifluoromethyl)silanes in CH_2Cl_2 solution as well as in the gas phase (compare Tables 1 and 2).[12] The sum of the solvation enthalpy of the chloride ion and $SiCl_4$ in CH_2Cl_2 solution exceeds the sum of the chloride ion affinity of $SiCl_4$ and the solvation enthalpy of the $[SiCl_5]^-$ ion. An exergonic chloride addition is predicted for chloro(trifluoromethyl)silanes with more than two electron-withdrawing trifluoromethyl groups, even in solution.

Table 2: Calculated solvation enthalphies for selected chlorosilanes and -silicates in CH_2Cl_2 ((CPCM)-B3LYP/6-311++G(2d)[14]).

	ΔG_{solv}		ΔG_{solv}
$SiCl_4$	−3.9	$[SiCl_5]^-$	−170.4
$Si(CF_3)Cl_3$	−7.0	$[Si(CF_3)Cl_4]^-$	−166.2
$Si(CF_3)_2Cl_2$	−7.8	$[Si(CF_3)_2Cl_3]^-$	−157.2
$Si(CF_3)_3Cl$	−12.9	$[Si(CF_3)_3Cl_2]^-$	−153.7
$Si(CF_3)_4$	−0.2	$[Si(CF_3)_4Cl]^-$	−151.2
		Cl^-	−262.2

The thermal stability of trifluoromethylsilanes decreases with an increasing electron deficiency at the silicon center. Thus, tris- and tetrakis(trifluoromethyl)silanes could not be isolated to date, and the considerably more stable pentafluoroethyl derivatives were instead studied.[13,17]

In agreement with the calculation, [PNP]Cl also appears to be inert towards $Si(C_2F_5)Cl_3$ [Eq. (2)].

$$[PNP]Cl + Si(C_2F_5)Cl_3 \xrightarrow[CH_2Cl_2]{//} [PNP][Si(C_2F_5)Cl_4] \qquad (2)$$

However, in the case of $Si(C_2F_5)_2Cl_2$, $Si(C_2F_5)_3Cl$, and $Si(C_2F_5)_4$, the smooth formation of the corresponding chlorosilicates $[Si(C_2F_5)_2Cl_3]^-$, $[Si(C_2F_5)_3Cl_2]^-$ and $[Si(C_2F_5)_4Cl]^-$ was observed [Eqs. (3)–(5)].

The ^{29}Si NMR resonances of the products are in the expected range for pentacoordinate silicon compounds[16] and are deshielded with respect to the fluorosilicate $[Si(C_2F_5)_3F_2]^-$ (cf. Table 3). The same is observed for the ^{19}F NMR resonances of the C_2F_5 group. In all cases, only a single set of signals is observed even at −60 °C.

The molecular structure of $[PNP][Si(C_2F_5)_2Cl_3]$ in the solid state could not be determined. We recently reported, however, the crystal structure of $[Si(NHC)_2Cl_2H][Si(C_2F_5)_2Cl_3]$, which was obtained by the reaction of NHC-$SiCl_4$ and $Si(C_2F_5)_2H_2$.[18] The C_2F_5 groups occupy the axial position.

$$[PNP]Cl + Si(C_2F_5)_2Cl_2 \xrightarrow{CH_2Cl_2} [PNP]^+ \left[Cl_2Si(C_2F_5)_2 \right]^- \qquad (3)$$

$$[PNP]Cl + Si(C_2F_5)_3Cl \xrightarrow{CH_2Cl_2} [PNP]^+ \left[ClSi(C_2F_5)_3 \right]^- \qquad (4)$$

$$[PNP]Cl + Si(C_2F_5)_4 \xrightarrow{CH_2Cl_2} [PNP]^+ \left[Si(C_2F_5)_4 \right]^- \qquad (5)$$

Table 3: NMR data of (pentafluoroethyl)silicates (CH_2Cl_2, RT).

	$\delta^{29}Si$	$\delta^{19}F$, CF_2	$\delta^{19}F$, CF_3
$[PNP][Si(C_2F_5)_2Cl_3]$	−97.2	−118.4	−75.5
$[PNP][Si(C_2F_5)_3Cl_2]$	−94.7	−113.7	−77.7
$[PNP][Si(C_2F_5)_4Cl]$	−96.8	−114.3	−76.8
$[PPh_4][Si(C_2F_5)_3F_2]$[a]	−109.3	−126.9	−83.6

[a] For comparison, see Ref. [17].

$[PNP][Si(C_2F_5)_3Cl_2]$ crystallizes in the monoclinic space group $P2_1/c$.[19] In contrast to $[Si(C_2F_5)_2Cl_3]^-$, the axial positions are occupied by the chlorine atoms (Figure 3). The

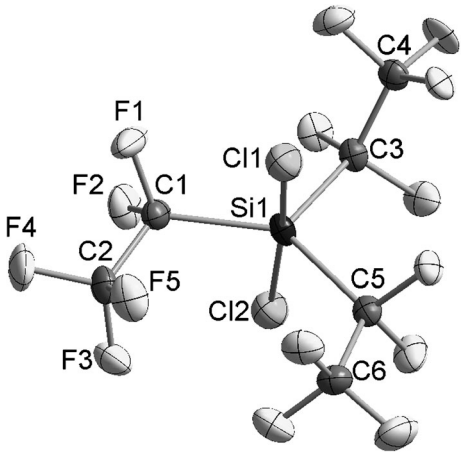

Figure 3. Molecular structure of $[Si(C_2F_5)_3Cl_2]^-$ present in the salt $[PNP][Si(C_2F_5)_3Cl_2]$. Ellipsoids are drawn at the 50% probability level. Two C_2F_5 groups are disordered and only the higher occupied sites are shown here. Selected bond lengths [pm] and angles [°]: Si1–Cl1 218.2(1), Si1–Cl2 217.1(1), Si1–C1 201.4(2), Si1–C3 195.9(2), Si1–C5 200.0(2), C1–F1 137.0(2), C1–F2 136.6(3), C2–F4 132.9(2), C2–F3 133.6(2); Cl1-Si-Cl2 171.8(1), C1-Si1-C3 119.1(1), C3-Si1-C5 102.4(1).

Si-Cl distances of about 218 pm are significantly longer than in $[Si(C_2F_5)_2Cl_3]^-$ (210 pm). The Si-C distances, however, are only slightly shorter ($[Si(C_2F_5)_2Cl_3]^-$: $d(Si\text{-}C)_{av}$ 200.3(1)11 pm, $[Si(C_2F_5)_3Cl_2]^-$: $d(Si\text{-}C)_{av}$ 199.1(2) pm).

$[PNP][Si(C_2F_5)_4Cl]$ crystallizes in the triclinic space group $P\bar{1}$ (Figure 4).[19] The chlorine atom occupies an axial position

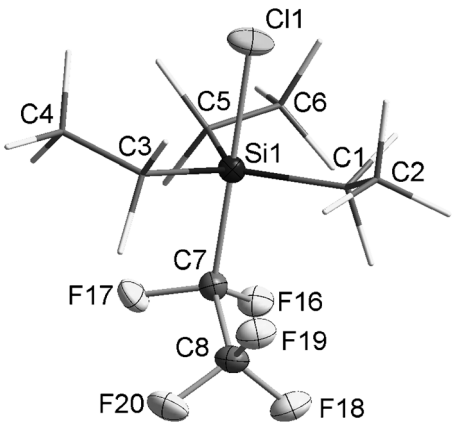

Figure 4. Molecular structure of $[Si(C_2F_5)_4Cl]^-$ present in the salt [PNP][$Si(C_2F_5)_4Cl$]. Ellipsoids are drawn at the 50% probability level. Equatorial C_2F_5 groups are shown as wire and stick models for clarity. Selected bond lengths [pm] and angles [°]: Si1–Cl1 221.8(1), Si1–C1 198.2(2), Si1–C3 198.7(2), Si1–C5 200.4(2), Si1–C7 204.1(2), C7–F16 136.6(3), C7–F17 137.8(2), C8–F18 133.5(3), C8–F19 134.2(3); Cl1-Si1-C7 179.2(1), C1-Si1-C3 123.8(1), C3-Si1-C5 118.6(1), C7-Si1-C1 94.0(1), Cl1-Si1-C1-C2 65.7(2).

with a long Si-Cl distance of 221.8(1) pm. The Si-C distance of the axial C_2F_5 group is about 4 pm longer than those of the equatorial C_2F_5 groups.

In conclusion, we succeeded in the synthesis and characterization of novel chlorosilicates. The preparation of chlorosilicates is not trivial because of the high solvation enthalpy of the chloride ion. Highly Lewis acidic silanes have to be employed to stabilize these common intermediates to an extent where observation and handling at room temperature is possible. This could be realized here by means of electron-withdrawing pentafluoroethyl groups.

Experimental Section

The preparations of $Si(C_2F_5)_2Cl_2$, $Si(C_2F_5)_3Cl$, and $Si(C_2F_5)_4$ are described elsewhere.[20] All other chemicals were obtained from commercial sources and used without further purification. Standard high-vacuum techniques were employed throughout all experiments. Nonvolatile compounds were handled in a dry N_2 atmosphere using Schlenk techniques. IR spectra were recorded with a Bruker Alpha FT-IR spectrometer (Bruker Daltonik GmbH, Bremen, Germany) equipped with a teflon gas cell with KBr windows or an ATR unit with a diamond crystal for liquids and solids. The NMR spectra were recorded on a Bruker Model Avance III 300 spectrometer (^{31}P 121.5 MHz; ^{29}Si 59.6 MHz; ^{19}F 282.4 MHz; ^{13}C 75.5 MHz; ^{1}H 300.1 MHz) with positive shifts being downfield from the external standards (TMS (^{29}Si, ^{1}H), CCl_3F (^{19}F)).

Synthesis of $Si(C_2F_5)(OPh)_3$: A sample of HC_2F_5 (10.1 g, 83.8 mmol) was condensed at −85 °C onto a degassed mixture of 1.6 M *n*-butyllithium in hexane (52.4 mL, 83.8 mmol) and diethyl ether (500 mL). After stirring the mixture for 20 min, a sample of $SiCl(OPh)_3$ (29.0 g, 84.7 mmol) was added and the reaction mixture was allowed to warm up to room temperature. The precipitate was filtered off, and the solvent removed from the filtrate with a rotary evaporator. Distillation of the crude product yielded 25.5 g (59.8 mmol, 71%) of $Si(C_2F_5)(OPh)_3$ as a colorless liquid. b.p. 90 °C (10^{-3} mbar). ^{1}H NMR (neat, RT): $\delta = 6.68$ (m, 2H, *ortho*-H), 6.62 (m, 2H, *meta*-H), 6.50 ppm (m, 1H, *para*-H); $^{13}C\{^{1}H\}$ NMR (neat, RT): $\delta = 151.4$ (s, *ipso*-C), 129.5 (s, *ortho*-C), 123.6 (s, *para*-C), 119.8 (q t, $^{1}J(C,F) = 285$ Hz, $^{2}J(C,F) = 30$ Hz, CF_3), 119.0 (s, *meta*-C), 114.4 ppm (t q, $^{1}J(C,F) = 267$ Hz, $^{2}J(C,F) = 42$ Hz, CF_2); ^{19}F NMR (neat, RT): $\delta = -82.9$ (s, 3F, CF_3), −130.0 ppm (s, 2F, CF_2); ^{29}Si NMR (neat, RT): $\delta = -90.1$ ppm (t, $^{2}J(Si,F) = 39$ Hz).

Synthesis of $Si(C_2F_5)Cl_3$: A mixture of $FeCl_3$ (23 mg, 0.14 mmol, 1.3 mol%), phenylacetylchloride (14.0 g, 90.6 mmol), and $Si(C_2F_5)(OPh)_3$ (5.3 g, 12.3 mmol) was stirred at RT. After 12 h, all the volatiles were removed at reduced pressure. Fractional condensation of the volatile compounds yielded $Si(C_2F_5)Cl_3$ as a colorless liquid (2.0 g, 8.0 mmol, 65%). Vapor pressure 202 mbar (20 °C). $^{13}C\{^{19}F\}$ NMR (neat, RT): $\delta = 118.8$ (s, CF_3), 112.5 ppm (s, CF_2); ^{19}F NMR (neat, RT): $\delta = -81.1$ (s, 3F, CF_3), −128.6 ppm (s, 2F, CF_2); ^{29}Si NMR (neat, RT): $\delta = -12.4$ ppm (t, $^{2}J(Si,F) = 52$ Hz); IR (gas): $\tilde{\nu}$ =1353 (s, νCC), 1224 (vs, νCF_3), 1143 (s, ν$_s$$CF_2$), 1107 (m, ν$_{as}$$CF_2$), 988 (νSiC), 751 (vw, δCF_3), 643 (s, ν$_{as}$SiCl), 603 (w), 560 (w), 510 cm^{-1} (w).

Synthesis of $[PNP][Si(C_2F_5)_2Cl_3]$: A sample of $Si(C_2F_5)_2Cl_2$ (405 mg, 1.2 mmol) was condensed into a solution of [PNP]Cl ([PNP]Cl ≡ μ-nitrido-bis(triphenylphosphorus) chloride) (617 mg, 0.9 mmol) in CH_2Cl_2. Removal of all the volatile compounds yielded $[PNP][Si(C_2F_5)_2Cl_3]$ as a colorless solid (787 mg, 0.9 mmol, 96%). ^{1}H NMR (CD_2Cl_2, RT): $\delta = 7.70$ (m, 6H, *para*-H), 7.55 (m, 12H, *meta*-H), 7.51 ppm (m, 12H, *ortho*-H); ^{19}F NMR (CD_2Cl_2, RT): $\delta = -75.5$ (s, 6F, CF_3), −118.4 ppm (s, 4F, CF_2); $^{13}C\{^{1}H\}$ NMR (CD_2Cl_2, RT): $\delta = 133.6$ (m, *para*-C), 132.0 (m, *meta*-C), 129.3 (m, *ortho*-C), 126.9 ppm (m, $^{1}J(C,P) \approx 107$ Hz); $^{13}C\{^{19}F\}$ NMR (CD_2Cl_2, RT): $\delta = 121.6$ (s, CF_3), 119.5 ppm (s, CF_2); ^{29}Si NMR (CD_2Cl_2, RT): $\delta = -97.2$ ppm (quin, $^{2}J(Si,F) = 45$ Hz); ^{31}P NMR (CD_2Cl_2, RT): $\delta = 21.1$ (s); IR (ATR): $\tilde{\nu}$ =3058 (vw(br), C-H), 1588 (w), 1484 (w), 1437 (m), 1319 (m, νCC), 1301 (m), 1289 (m), 1271 (m), 1198 (s, νCF_3), 1185 (s), 1115 (s), 1095 (s, ν$_s$$CF_2$), 1037 (s, ν$_{as}$$CF_2$), 997 (m), 936 (m, νSiC), 859 (vw), 801 (w), 789 (w), 745 (m), 723 (vs), 690 (vs), 615 (w), 589 (w, δCF_2), 544 (s), 532 (s), 521 (s), 500 (s), 477 (m), 448 (m, νSiCl), 386 cm^{-1} (w).

Synthesis of $[PNP][Si(C_2F_5)_3Cl_2]$: A sample of $Si(C_2F_5)_3Cl$ (1.3 g, 3.0 mmol) was condensed into a solution of [PNP]Cl (1.3 g, 2.2 mmol) in CH_2Cl_2. Removal of all the volatile compounds yielded [PNP][$Si(C_2F_5)_3Cl_2$] as a colorless solid (2.1 g, 2.1 mmol, 95%). ^{1}H NMR (CD_2Cl_2, RT): $\delta = 7.72$ (m, 6H, *para*-H), 7.56 (m, 12H, *meta*-H), 7.49 ppm (m, 12H, *ortho*-H); ^{19}F NMR (CD_2Cl_2, RT): $\delta = -77.7$ (s, 9F, CF_3), −113.8 ppm (s, 6F, CF_2); $^{13}C\{^{1}H\}$ NMR (CD_2Cl_2, RT): $\delta = 133.6$ (m, *para*-C), 132.0 (m, *meta*-C), 129.3 (m, *ortho*-C), 126.9 ppm (m, $^{1}J(C,P) \approx 107$ Hz); $^{13}C\{^{19}F\}$ NMR (CD_2Cl_2, RT): $\delta = 121.3$ (s, CF_3), 118.3 ppm (s, CF_2); ^{29}Si NMR (CD_2Cl_2, RT): $\delta = -94.7$ ppm (sept, $^{2}J(Si,F) = 45$ Hz); ^{31}P NMR (CD_2Cl_2, RT): $\delta = 21.1$ ppm (s); IR (ATR): $\tilde{\nu}$ =3058 (vw, νCH), 1587 (w), 1484 (w), 1437 (m), 1320 (m, νCC), 1300 (m), 1207 (vs, νCF_3), 1183 (s), 1114 (vs), 1085 (m, ν$_s$$CF_2$), 996 (m, νSiC), 959 (m, νSiC), 926 (m, νSiC), 744 (m), 722 (s), 690 (vs), 614 (w), 614 (w, δCF_2), 545 (s), 534 (s), 499 (s), 463 (vs), 424 cm^{-1} (vs).

Synthesis of $[PNP][Si(C_2F_5)_4Cl]$: A sample of $Si(C_2F_5)_4$ (775 mg, 1.5 mmol) was condensed into a solution of [PNP]Cl (632 mg, 1.1 mmol) in CH_2Cl_2. Removal of all the volatile compounds yielded $[PNP][Si(C_2F_5)_4Cl]$ as a colorless solid (1.1 g, 1.0 mmol, 93%). ^{1}H NMR (CD_2Cl_2, RT): $\delta = 7.69$ (m, 6H, *para*-H), 7.55 (m, 12H, *meta*-H), 7.53 ppm (m, 12H, *ortho*-H); ^{19}F NMR (CD_2Cl_2, RT): $\delta = -76.8$ (s, 12F, CF_3), −114.3 ppm (s, 8F, CF_2); $^{13}C\{^{1}H\}$ NMR (CD_2Cl_2, RT): $\delta = 133.6$ (m, *para*-C), 132.0 (m, *meta*-C), 129.3 (m, *ortho*-C), 126.9 ppm (m, $^{1}J(C,P) \approx 107$ Hz); $^{13}C\{^{19}F\}$ NMR (CD_2Cl_2, RT): $\delta = 120.7$ (s, CF_3), 119.5 ppm (s, CF_2); ^{29}Si NMR (CD_2Cl_2, RT): $\delta = -96.8$ ppm (nonet, $^{2}J(Si,F) = 37$ Hz); ^{31}P NMR (CD_2Cl_2, RT): $\delta = 21.1$ ppm (s); IR (ATR): $\tilde{\nu}$ =3059 (vw), 1589 (w), 1484 (w), 1438 (m), 1364 (w), 1322 (m, νCC), 1299 (m), 1270 (m), 1257 (m), 1206 (vs, νCF_3), 1183 (vs, νCF_3), 1112 (vs), 1072 (m, νCF_2), 1058 (m, νCF_2), 1028 (w), 997 (m), 960 (m, νSiC), 942 (m, νSiC), 792 (w), 745 (m), 722 (s),

690 (vs), 616 (w), 614 (w), 591 (w), 544 (s), 533 (s), 498 (s), 465 (vs), 414 (s), 389 cm^{-1} (s).

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[15] Chloride ion affinity is given for $[Si(CF_3)_3Cl_2]^-$ with two axial CF_3 groups. The conformer with two axial chlorine atoms is calculated to be 9.8 kJ mol^{-1} less stable. Details on the relative energy of the conformers of all (trifluoromethyl)chlorosilicates are given in the Supporting Information. The difference in the structure in the crystal of $[PNP][Si(C_2F_5)_3Cl_2]$ might be due to the higher steric demand of the C_2F_5 group.
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[19] Crystals suitable for X-ray diffraction analysis were obtained by slowly cooling a saturated solution of the salt in CH_2Cl_2 at RT. The data for determination of the X-ray structure were collected on an Agilent SuperNova diffractometer with an EOS detector, at 100.0(1) K using MoKα radiation ($\lambda = 71.073$ pm). The structures were solved by direct methods and refined by full-matrix least-squares cycles (program SHELX-97: G. M. Sheldrick, *Acta Crystallogr. Sect. A* **2008**, *64*, 112 – 122). All non-hydrogen atoms were refined anisotropically. Data for [PNP][$Si(C_2F_5)_3Cl_2$]: colorless crystal, $M_r = 994.60$ g mol^{-1}, monoclinic space group $P2_1/c$, $a = 1286.4(1)$, $b = 1799.0(1)$, $c = 1820.6(1)$ pm, $\beta = 97.38(1)°$, $V = 4178.3(1) \times 10^6$ pm^3, $Z = 4$, $\rho_{calcd} = 1.581$ g cm^{-3}, $F(000) = 2008$; 238382 reflections up to $\theta = 30$ collected, 12163 independent reflections, thereof 10908 with $I > 2\sigma(I)$, 626 parameters. Hydrogen atoms refined isotropically, R values: $R_1 = 0.0358$ for reflections with $I > 2\sigma(I)$, $wR_2 = 0.0908$ for all data. Data for [PNP][$Si(C_2F_5)_4Cl$]: colorless crystal, $M_r = 1078.17$ g mol^{-1}, triclinic space group $P\bar{1}$, $a = 1054.8(1)$, $b = 1448.6(1)$, $c = 1456.2(1)$ pm, $\alpha = 84.83(1)$, $\beta = 80.42(1)$, $\gamma = 85.99(1)°$, $V = 2181.7(1) \times 10^6$ pm^3, $Z = 2$, $\rho_{calcd} = 1.641$ g cm^{-3}, $F(000) = 1084$; 95409 reflections up to $\theta = 26$ collected, 8564 independent reflections, thereof 7945 with $I > 2\sigma(I)$, 622 parameters. Hydrogen atoms refined at calculated positions using a riding model, R values: $R_1 = 0.0416$ for reflections with $I > 2\sigma(I)$, $wR_2 = 0.1185$ for all data. CCDC 1006707 and 1006708 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
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