Tetrakis(pentafluorophenyl)borate: a New Anion for Silylium Cations in the Condensed Phase

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Reaction in benzene of silyl hydrides (R_3Si-H) with triphenylmethyl tetrakis(pentafluorophenyl)borate produces silyl cations with reduced coordination to the anion.

The challenge in producing silylium ions (R_3Si^+) in the condensed phase is in foiling interactions with any conceivable nucleophilic partner. Interaction with the anion (A^-) can produce ion pairs or neutral covalent species (R_3Si-A); interaction with the solvent (S) can produce in the extreme a complex in which the charge is no longer on silicon (R_3Si-S^+). We report herein new formulations of solvent and anion that produce the freest silylium ions to date.

In the past, we have used polar solvents of low nucleophilicity in attempts to generate silylium ions, including dichloromethane, sulfolane and acetonitrile.[1] Although ionic materials are formed, particularly in dilute solution, the relatively high field ^{29}Si chemical shifts suggest significant interactions with solvent, as is the case to a lesser extent with stannylium ions (R_3Sn^+).[2] We have now been able to prepare silylium borates in hydrocarbon solvents such as benzene. As even these aromatics may serve as weak π donors, we also have dispensed with the solvent entirely. We report herein the first ^{29}Si chemical shifts of solid silylium ions, using cross polarization and magic-angle spinning (CPMAS) methods.

Anions used in the past have included perchlorate, trifluoromethanesulfonate, halides and azide,[1] with varying degrees of ionicity. We reported briefly on a silyl tetraphenylborate in acetonitrile,[1] but its precursor, triphenylmethyl tetraphenylborate,[3] was not stable in sulfolane or dichloromethane and results were limited. We now report results with the tetrakis(pentafluorophenyl)borate anion ($TPFPB^-$). Multiple substitution with fluorine atoms renders the anion much more stable than tetraphenylborate.[4]

Reaction of Ph_3C^+ $TPFPB^-$ with hydridosilanes (R_3SiH) normally leads in those cases we report herein to nearly quantitative conversion to triphenylmethane and silylium salts of this anion. We usually carry the reaction out in benzene, but it also may be carried out in excess silane as the solvent. In either case, the solvent may be removed to yield a stable solid, which may be examined directly, redissolved in benzene to reconstitute the same material or dissolved in a new solvent. Residual triphenylmethane may be removed by washing the solid with hexane. Results for a variety of substituents are presented in Table 1.

Table 1 ^{29}Si chemical shifts for R_3Si–X

R	Solvent	δ (X = H)	δ (X = TPFPB)	Δδ
Me	C_6D_6	~17.5	83.6	101.1
	None[a]		84.8	
Et	C_6D_6	0.2	92.3	92.1
	C_6H_5Me	0.3	81.8	81.5
	Sulfolane	0.3	58.4	58.1
	MeCN	6.0	36.7	30.7
	None[a]	0.2	94.3	94.1
Pr^i	C_6D_6	12.0	107.5	95.5
	None[a]		107.6	
Me_3Si	C_6D_6	~117.4	111.1	228.5

[a] Spectrum recorded in the solid state with cross polarization and magic-angle spinning.

^{29}Si chemical shifts move downfield (more positive) with a decrease in coordination. The key spectral parameter that automatically takes substituent effects into consideration is the difference between the chemical shift of the neutral, tetracoordinate starting hydride and that of the product of hydride removal (Δδ in Table 1). For alkyl ligands, from methyl to isopropyl, the shift is 90–100 ppm downfield in benzene. These values indicate reduced coordination to anion or solvent. The smaller values for R = Et and Pr^i compared with Me may indicate agostic interactions of the alkyl groups possessing β-hydrogens. When the ligand R is trimethylsilyl, the shift is 228.5 ppm. This value is in accord with a substantially free silylium ion. Calculations have been carried out only for Me_3Si^+, with values of Δδ suggested variously to be 242,[5] 341[6] or 373[7] for the gas phase.

Increased coordination with solvent is seen in the triethylsilylium series for benzene to toluene to sulfolane to acetonitrile. It is clear from these observations that complexation is not an either/or proposition; it comes in varying degrees. When benzene is the solvent, there appears to be little association between solvent and solute, as the values are essentially the same as those obtained in the solid state. The latter preparations used excess silane (no benzene was present) as the original solvent, which was removed by evaporation and washing with hexane. Strong coordination has been observed with ethers[8] and acetonitrile.[9]

If there is coordination with the anion through any of the fluorine atoms, one would expect changes in the NMR spectral parameters between Ph_3C^+ $TPFPB^-$ and silylium$^+$ $TPFPB^-$, but there is none. The ^{19}F chemical shifts respectively for the *ortho, meta* and *para* fluorines of the trityl salt are −166.5, −132.3 and −162.5 and of the triethylsilylium salt are −166.8, −132.3 and −162.8, which are experimentally identical. By this criterion there is no difference between Ph_3C^+ and Et_3Si^+ in coordination of C^+ or Si^+ with fluorine on the anion, although residual coordination could be spread over the 20 fluorines. The ^{11}B chemical shift and linewidth also provide information about cation–anion interactions, as the quadrupolar boron atom is very sensitive to deviations from tetrahedrality. The chemical shift is identically −20.0 in both cases, and the narrow linewidth likewise is the same (22 Hz).

These results support the description of these silyl species as having reduced nucleophilic interactions with solvent and anion. In the case of the trimethylsilyl substituent, the NMR data support a nearly free cationic structure. Reaction of the solution of $(Me_3Si)_3SiTPFBP$ with diisobutylaluminium hydride (DIBALH) reformed the starting material $(Me_3Si)_3SiH$, confirming the persistence of the overall skeleton. Careful theoretical studies are still required to determine the sensitivity of the calculated ^{29}Si shift to small deviations from planarity, to weak external coordination and to agostic interactions.

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