Phenylpentafluorosilicate Anion; ^{19}F Nuclear Magnetic Resonance Evidence

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Summary The existence of the six-co-ordinate phenylpentafluorosilicate anion $[PhSiF_5]^{2-}$ in solution is confirmed by ^{19}F n.m.r. spectroscopy.

In the absence of structural data, compounds of empirical composition M_2RSiF_5 or $(R_4N)_2RSiF_5$[1] may be formulated as double salts, *i.e.* $[R_4N]_2[RSiF_4]F$ containing five-co-ordinate $[RSiF_4]^-$ rather than six-co-ordinate $[RSiF_5]^{2-}$ anions. An earlier attempt to distinguish between $[RSiF_4]^-$ and $[RSiF_5]^{2-}$ anions in solution was unsuccessful because the ^{19}F n.m.r. spectra were dominated by exchange effects,[2] but the problem of verifying the existence of six-co-ordinate silicon species in solution is important in view of the proposal, advanced from time to time,[3,4] that reaction mechanisms of silicon compounds involve six-co-ordinate intermediates.

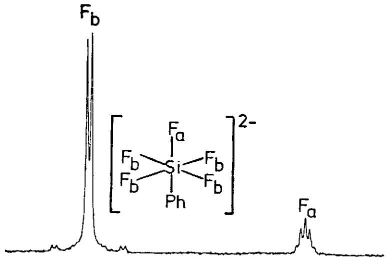

FIGURE. The ^{19}F n.m.r. spectrum of $[Pr_4N]_2[PhSiF_5]$ (0·41 mmol) in dichloromethane (0·5 ml) at −28 °C recorded on a Bruker WH90 spectrometer at 84·66 MHz. Chemical shifts were measured relative to internal C_6F_6 and are reported to high field of $CFCl_3$. F_a, 121·3 p.p.m.; F_b, 114·5 p.p.m.; $J(F_a–F_b)$ 11·0 Hz.

We find that a slight excess of Pr^n_4NF converts all $[PhSiF_4]^-$ into six-co-ordinate $[PhSiF_5]^{2-}$ in dichloromethane solution, as verified by ^{19}F n.m.r. spectroscopy at −28 °C (Figure). Coupling of basal fluorine atoms to ^{29}Si may be seen in the Figure, $J(F_b-^{29}Si)$ 181·8 Hz. Exchange effects in samples of $[PhSiF_5]^{2-}$ are minimized by reducing the concentration of $[PhSiF_4]^-$, $PhSiF_3$, and trace impurities[4] and by lowering the temperature.

Attempts to recrystallize $[Pr^n_4N]_2[PhSiF_5]$ from 1:1 chloroform–ethyl acetate or 1,2-dimethoxyethane resulted in the precipitation of $[Pr^n_4N][PhSiF_4]$ as the least soluble material while the more soluble Pr^n_4NF remained in solution. Samples of $[Pr^n_4N]_2[PhSiF_5]$ in dichloromethane with an excess of F^- and 8—10% HF_2^- decomposed at room temperature within 2 weeks to give C_6H_6, Pr^n_3N, SiF_6^{2-}, and SiF_5^- as the major products.

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