I_{18}

LIGAND DISPLACEMENT REACTIONS OF $MF_5.L$ (M = P, As, Sb) STUDIED BY MULTINUCLEAR NMR SPECTROSCOPY

Michael F. A. Dove, Eleanor M. Lloyd Jones* and Jeremy C. P. Sanders
Department of Chemistry, The University, Nottingham NG7 2RD (U.K.)

The pentafluorides of phosphorus, arsenic and antimony are known to form neutral 1:1 complexes with many organic bases (E.L. Muetterties, Advances in the Chemistry of Coordination Compounds, 1961, 513). Such compounds are of interest as possible precursors in the preparation of the hexahalo anions PF_5X^- (P.J. Chevrier and S. Brownstein, J.Inorg.Nucl.Chem., 1980, 42, 1397), AsF_5X^- and SbF_5X^- (M.F.A. Dove, J.C.P. Sanders, E. Lloyd Jones and M.J. Parkin, J.Chem.Soc., Chem.Commun., 1984, 1578). The adducts $MF_5.L$ (M = P, As, Sb; L = MeCN, py, Me_3N) have, therefore, been synthesised in a pure state by direct reaction of the base with the metal pentafluoride in a suitable solvent (such as MeCN, CH_2Cl_2 or $CClF_2CCl_2F$). The adducts were characterised by ^{31}P, ^{75}As, ^{121}Sb and ^{19}F NMR spectroscopy. With the exception of $PF_5.MeCN$, the central nucleus resonances have not previously been studied. Although no ^{75}As ($I = {}^3/2$) or ^{121}Sb ($I = {}^5/2$) resonances could be obtained from the acetonitrile adducts, the central nucleus resonances of the pyridine and trimethylamine adducts showed binomial sextets. Proton decoupling resolved the one bond coupling to ^{14}N (I = 1) in $PF_5.NMe_3$, $PF_5.py$ and $AsF_5.py$.

There is a large contrast between the reactivities of these adducts, which is shown by attempts to displace the base to form MF_5X^- anions. Addition of methanol to $PF_5.L$ and $SbF_5.L$ resulted in the formation of the pentafluoromethoxy anions. $NMe_3H^+PF_5OMe^-$ and $pyH^+SbF_5OMe^-$ were isolated as pure solids and the anions were characterised by NMR, but no ^{121}Sb resonance was obtained from the SbF_5OMe^- anion. SbF_5OMe^- was converted to SbF_5X^- (X = Cl, Br) by reaction with the corresponding acetyl halide. $SbF_5.MeCN$ reacted with $NEt_4{}^+X^-$ (X = Cl, Br, NCS, NCO) to form SbF_5X^-. The previously unobserved SbF_5NCS^- and SbF_5NCO^- anions were shown by ^{14}N NMR to be N-bonded. However, addition of $NEt_4{}^+X^-$ to $PF_5.MeCN$ or $AsF_5.MeCN$ produced a mixture of $MF_6{}^-$ and MF_5X^-. Pyridine and trimethylamine were found to be more difficult to displace. Complete conversion to MF_5X^- was observed only with the antimony adducts. $AsF_5.py$ and $AsF_5.NMe_3$ showed anomalous behaviour since they were air-stable, and inert to substitution of the base.