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REACTIONS OF PHOSPHORUS FLUORIDES AND ORTHO-CARBORANE DITERTIARY AMINOPHOSPHINES

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Fluorophosphine bidentate ligands containing *o*-carborane as backbone can be prepared by the reaction of the lithium-*o*-carboranes and PF_2X derivatives to give only two species: the unsymmetrical $(C_6H_5)_2P[B_{10}H_{10}C_2]PF_2$ and the cyclic $FP[B_{10}H_{10}C_2]_2PF$, both in low yield. However, exchange of F and NMe_2 groups by use of PF_5 or PF_3 provides a facile way to produce several new fluorophosphines.

Phosphorus pentafluoride forms solid adducts with the *o*-phosphino derivatives $(C_6H_5)_2P[B_{10}H_{10}C_2]P(NMe_2)_2$, $(Me_2N)_2P[B_{10}H_{10}C_2]P(NMe_2)_2$ and $(C_6H_5)_2P[B_{10}H_{10}C_2]H$. All the adducts contain a phosphorus-phosphorus bond as evidenced from i.r., NMR and stoichiometry. The stability of the adducts reflects the strength of the P-P bond formed upon complexation. When suspensions or solutions of the adducts are heated they exchange F and NMe_2 groups and no redox occurs. The products $(C_6H_5)_2P[B_{10}H_{10}C_2]P(F)NMe_2$(I) and $Me_2N(F)P[B_{10}H_{10}C_2]P(F)NMe_2$(II) react further with PF_5 giving $(C_6H_5)_2P[B_{10}H_{10}C_2]PF_2$(III) and $F_2P[B_{10}H_{10}C_2]PF_2$(IV).

The precursors also react with phosphorus trifluoride to produce only (I) and $(Me_2N)_2P[B_{10}H_{10}C_2]P(F)NMe_2$(V) regardless of the reaction conditions. All the products I-V have been identified by ^1H, ^{19}F, and ^{31}P NMR and i.r. spectroscopy, mass spectrometry, and elemental analysis. The NMR spectra of the novel (IV) have been analysed as $X_2AA^1X_2^1$ spin system.

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FLUOROSULFATES OF GROUP(IV) ELEMENTS

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Synthesis of binary and ternary fluorosulfates of tin and germanium by metal oxidation in a $HSO_3F/S_2O_6F_2$ mixture is investigated. Attempts to obtain $Ge(SO_3F)_4$ resulted in the formation of $GeF_2(SO_3F)_2$. Instead $Ge(SO_3F)_4$ has been stabilized by the formation of $M_2[Ge(SO_3F)_6]$ (where M = Cs or ClO_2) complexes. In the tin system simple alternative routes to the previously known $Sn(SO_3F)_4$ and $M_2[Sn(SO_3F)_6]$ are found. In addition a new compound of the composition $Cs[Sn(SO_3F)_5]$ is formed and identified by the Mossbauer spectrum as a novel structural type with an oligomeric anion. Structural conclusions are based on vibrational spectra (Raman and IR), ^{119}Sn Mossbauer spectra and solution studies in HSO_3F via conductivity and NMR (^{19}F and ^{119}Sn) measurements. Attempted synthesis of $Sn(II)Sn(IV)(SO_3F)_6$ was not successful.