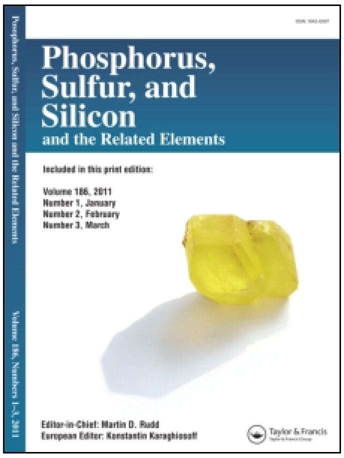

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Sterically Hindered Pentacoordinated Phosphorus and Silicon Compounds

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STERICALLY HINDERED PENTACOORDINATED PHOSPHORUS AND SILICON COMPOUNDS

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Abstract The synthesis and X-ray structures of the first examples of five-coordinated acyclic derivatives of phosphorus and silicon incorporating the bulky substituents, the 1-naphthyl and t-butyl groups, are reported. Increases in bond distances induced by steric and electronic interactions are apparent for these compounds. The results are related to proposed intermediates which model these derivatives in nucleophilic substitution reactions suggesting the importance of steric control.

INTRODUCTION

The present work concentrates on five-coordinated derivatives of phosphorus and silicon, containing bulky acyclic ligands. We report the synthesis of $Ph(\underline{1}\text{-}Np)_2PF_2$ 1, Ph_3PF_2 2, $[Ph_2(\underline{1}\text{-}Np)SiF_2][S(NMe_2)_3]$ 3, $[PhMeSiF_3][N(\underline{n}\text{-}Bu)_4]$ 4, and 18-crown-6 potassium salts of $[\underline{t}BuSiF_4]^-$ 5, $[\underline{t}\text{-}BuPhSiF_3]^-$ 6, $[\underline{t}\text{-}Bu_2SiF_3]^-$ 7, and $[(\underline{1}\text{-}Np)PhSiF_3]^-$ 8. Single crystal X-ray structures of 1-4, 6, and the 18-crown-6 potassium salt of $[xyl_2SiF_3]^-$ 9 are presented. Previously, structural characterization of pentacoordinated derivatives of phosphorus and silicon possessing only acyclic ligands have been confined to small groups in general, although $(C_6F_5)_3PF_2$ is an exception.[1] For example, the series Me_nPF_{5-n} (0 → 3),[1] Cl_nPF_{5-n} (n = 0 → 5),[2] Ph_nSiF_{5-n} (n = 0 → 2)[3] and HPF_4,[1] $(C_6F_5)_3PF_2$[1] and $(NMe_2)_3PF_2$[1] have been studied.

As the steric bulk is progressively increased around the central phosphorus or silicon atom, changes in bond parameters and even the basic geometry may be expected. Since pentacoordinated derivatives serve as models for proposed transition states in a variety of nucleophilic substitution reactions for these elements,[4,5] it is important to obtain structural information on isolatable examples of five-coordinated species which approximate the transition state composition as closely as possible.

It is noted that in the alkaline hydrolysis of chiral phosphonium salts R R' R'' R''' P^+, reaction which proceeds with predominant inversion of configuration, changes over to predominant retention as the size of one of the acyclic substituents (R) increases from phenyl to 1-naphthyl.[6] A similar study on the alkaline hydrolysis of sterically crowded phosphonium salts $R_1R_2R_3R_4P^+$ shows that the best departing group, the benzyl group, loses out in being displaced as the steric crowding around phosphorus is increased.[7] For Ph(1-Np)(1-NpMe)$(CH_2Ph)P^+$, hydrolysis results in only 21% toluene but a 59% yield of 2-methylnaphthalene.

Related studies[8] on the stereochemical behavior of 1-NpPhSi(F)OMen reacting with alkyl lithiums show a high degree of retention of configuration in all cases, but a changeover to predominant loss of O-menthyl instead of fluorine as the steric size of the attacking nucleophile is increased from MeLi to neopentyl Li.

Our projected studies have as a goal to model reactions such as these to ascertain the degree to which steric factors control the stereochemical outcome.

SYNTHESIS

The fluorophosphoranes, Ph_3PF_2 and Ph(1-Np)$_2$PF$_2$, were synthesized in reasonable yield (∿ 50%) from the reaction of the corresponding phosphines Ph_3P and (1-Np)$_2$PPh with dimethylamino sulfur trifluoride, NMe_2SF_3,[9] in ether at room temperature.

The fluorosilicate $[PhMeSiF_3][N(n\text{-}Bu)_4]$ was synthesized by the addition of ($\underline{n}$-Bu)$_4$NF•3H$_2$O to PhMeSiF$_2$ in methylene chloride solution. The $\underline{1}$-naphthyl derivative [Ph$_2$($\underline{1}$-Np)SiF$_2$][S(NMe$_2$)$_3$] resulted from the reaction of Ph$_2$($\underline{1}$-Np)SiNMe$_2$ with SF$_4$ in ether solution. The 18-crown-6 salts, $\underline{5}$-$\underline{8}$, resulted from treatment of the precursor fluorosilanes with the latter ether and K^+F^-.

STRUCTURAL

The X-ray studies showed trigonal bipyramids with the fluorine atoms located, as expected, in axial positions. Examination of the bond parameter data for sterically hindered compounds relative to non-sterically hindered derivatives leads to the following conclusions: (1) the bond length increases for axial bonds parallel those for equatorial bonds of the same type, suggesting a general loosening of the entire structure; (2) for the less sterically hindered phosphoranes, PCl_nF_{5-n}, the rate of increase of the equatorial bond is about one-third that found for the axial bond when comparing bond lengths to the same type of ligand; (3) the sum of axial and equatorial bond angle deviations from the ideal values of 180° and 120°, respectively, show an increase that parallels the build-up in steric bulk around the central atom, at least in the case of the silicon series so far studied. Insufficient data is available on phosphorus on this point so far.

These results imply that the course of nucleophilic substitution reactions concerned with reactants having large steric effects which would suffer an increase in steric hindrance as the transition state configuration is approached, may readily be altered. Accordingly, a steric basis giving underlying mechanistic control implied by the transition state modeling studies reported here, agrees in general with the observed reaction sequences cited earlier that appear to follow a steric course.

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