

NMR, PGSE Diffusion, and X-ray Diffraction Studies of Lithium and Potassium Salts Derived from Diphenylphosphino(*o*-cyanophenyl)aniline and Their Crown Ether Complexes

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¹H, ³¹P, and ⁷Li pulsed-gradient spin-echo (PGSE) diffusion and variable-temperature NMR results for THF solutions of the lithium and potassium salts derived from diphenylphosphino(*o*-cyanophenyl)aniline are reported and compared to the solid-state results obtained via X-ray diffraction studies. The solution results favor mononuclear salts, sometimes strongly ion paired, whereas the solid-state data reveal dinuclear species. The structures of the products from reactions of these salts with crown ethers are determined via PGSE and ¹H Overhauser NMR methods.

Introduction

The chemistry of compounds containing P–N bonds continues to attract considerable attention, with applications in increasingly diverse fields.^{1,2} Primary and secondary aminophosphines are especially interesting because the NH acidic hydrogen is easily removed, yielding anions, with a negative charge residing on the P–N unit.³ The P–N bond in the anion is shorter than the normal P–N single bonds observed in aminophosphines but longer than the P=N double bond moieties found in phosphazenes,^{4,7d} suggesting that the bond is intermediate between the two. The facile deprotonation of the N–H bond to afford the corresponding iminophosphorane anion leads to questions with respect

to the distribution of the negative charge.^{5,6} Cleavage of iminophosphoranes can also provide phosphinoamides.⁷

A number of interesting “PN” salts have been studied (Chart 1). X-ray diffraction studies for the lithium salt [$\{\text{Li}(\text{PPh}_2\text{NPh})(\text{Et}_2\text{O})_2\}_2$] (**1**)⁸ reveal a dinuclear structure with the two N and two Li centers forming a four-membered ring. The phosphorus lone pair appears oriented toward the lithium ion, hinting at the presence of a P \cdots Li bond, although this interaction is not observed in solution. Interestingly, the structure of the lithium salt $[\text{Li}(\text{PPh}_2\text{NPPh}_2)(\text{THF})_3]$ (**2**) was found to be monomeric with the lithium cation interacting with both the P and N centers.⁹ For LiPPh_2 (**3**), it has been suggested that polymeric chainlike structures exist in a THF solution.¹⁰ However, using ⁷Li pulsed-gradient spin-echo (PGSE) diffusion NMR spectroscopy, we have recently reported that the structure is monomeric with the Li cation solvated as $\text{Li}(\text{THF})_4^+$.¹¹ The lithium salts **4–8** have been prepared by treatment of the corresponding aminophosphines with *n*-BuLi in diethyl ether or THF. Both $[\{\text{LiPPh}_2\text{N}$

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