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Spirophosphoranide (10-P-4) with Hexafluoro-2-Phenyl-2-Propanol : X-Ray Structure, Stereomutation and Substitution

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J. C. Martin and I. Granoth reported observation of a stable spirophosphoranide **2-Li**[1]. Here we confirmed the structure of **2-Li** by X-ray analysis and the stereomutational behavior was examined. The X-ray analysis of **2-Li** shows slightly distorted pseudo-trigonal bipyramidal structure with equatorial lone pair electrons.

The apical P-O bond lengths (1.899(2), 1.891(2) Å) are made longer than those of **1** (1.747(1), 1.741(1) Å) and apical-apical bond angle (170.9°) of **2-Li** is reduced by 9.8° (See Figure 1).

Scheme 1

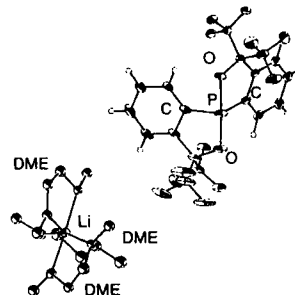
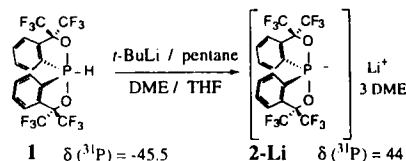


Figure 1. ORTEP drawing of Lithium Phosphoranide **2-Li**

The kinetic measurements for stereomutation of diastereomeric derivatives of the phosphoranide **2'-Li**, in which one of four CF_3 groups is replaced by a CH_3 , were carried out by monitoring by ^{19}F NMR. As compared with corresponding P-H phosphorane **1'**, which is stereochemically stable at room temperature, the phosphoranide **2'-Li** has a relatively rapid stereomutation rate ($\Delta G^\ddagger = 25.6 \text{ kcal mol}^{-1}$ for **1'**, while $\Delta G^\ddagger = 18.6 \text{ kcal mol}^{-1}$ for **2'-Li**). The stereomutational mechanism could be rationalized by the Berry pseudorotation for **1'** and dissociation-association for **2'-Li**. In the case of potassium phosphoranide **2'-K**, the stereomutation was much slower than that of **2'-Li**. It is noted that **2-K** reacted readily with molecular oxygen.

References

- [1] I. Granoth, J.C. Martin; *J. Am. Chem. Soc.*, **100**, 7434 (1978).