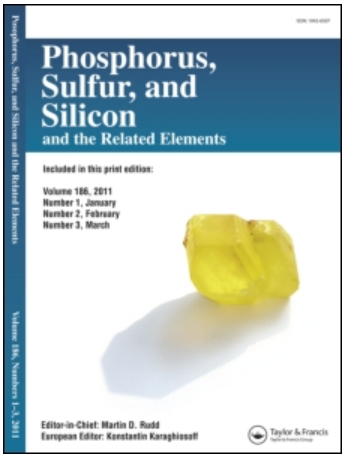

Phosphorus, Sulfur, and Silicon and the Related Elements

Publication details, including instructions for authors and subscription information:
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To cite this Article Nakamoto, Masaaki , Kojima, Satoshi and Akiba, Kin-Ya(1999) 'Spirophosphoranide (10-P-4) with Hexafluoro-2-Phenyl-2 - Propanol: X-Ray Structure, Stereomutation and Substitution', Phosphorus, Sulfur, and Silicon and the Related Elements, 147: 1, 277
To link to this Article: DOI: 10.1080/10426509908053619
URL: http://dx.doi.org/10.1080/10426509908053619

Phosphorus, Sulfur and Silicon, 1999, Vol. 147, pp. 277-277
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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).

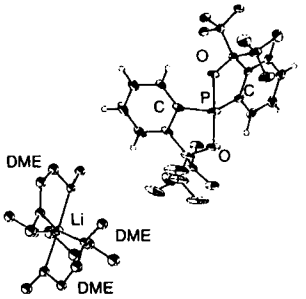
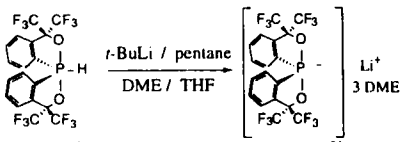


Figure 1. ORTEP drawing of Lithium Phosphoranide **2-Li**

Scheme 1



1 $\delta(^{31}P) = -45.5$ **2-Li** $\delta(^{31}P) = 44$

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 kcal mol^{-1} for **1'**, while $\Delta G^{\ddagger}$ = 18.6 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).