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X-ray and multinuclear NMR study of the mixed aggregate $[(Ph_2P(O)N(CH_2Ph)CH_3)\cdot LiOC_6H_2\text{-}2,6\text{-}\{C(CH_3)_3\}_2\text{-}4\text{-}CH_3)\cdot C_7H_8]_2$: a model for the directed metalation of phosphinamides ☆

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Abstract

The addition of $LiBu^n$ to a toluene solution of $Ph_2P(O)N(CH_2Ph)CH_3$ **1** and 2,6-di-*tert*-butyl-4-methylphenol **5** leads to the formation of the mixed dimer $[(Ph_2P(O)N(CH_2Ph)CH_3)\cdot LiOC_6H_2\text{-}2,6\text{-}\{C(CH_3)_3\}_2\text{-}4\text{-}CH_3)\cdot C_7H_8]_2$ **6**. The single crystal X-ray structure shows that two lithium aryloxide moieties dimerize giving rise to a Li_2O_2 core in which each lithium atom is additionally coordinated to a phosphinamide **1** ligand. The multinuclear magnetic resonance study (^1H, ^7Li, ^{13}C, ^{31}P) indicates that the solid-state structure is preserved in toluene solution. Complex **6** may be considered as a model for the pre-complexation step preceding the metalation of phosphinamides by an organolithium base.
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Keywords: Phosphinamides; Phenolate; X-ray; Multinuclear magnetic resonance; ^{31}P; ^7Li coupling; CIPE

1. Introduction

Directed deprotonation of organic compounds by organolithium bases and subsequent addition of an electrophile represents a very efficient strategy for the regio- and stereoselective functionalization of a great variety of substrates [1]. The mechanism of the lithiation step has been interpreted in two ways. In one hypothesis, substrate and base forms a complex through lithium coordination to the lone pairs of the directing group. This complexation brings the carbanion moiety in close proximity (complex-induced proximity effect, CIPE) [2] to the acidic hydrogen, thus facilitating the metalation. The alternative explanation assigns to the directing group the role of stabilizing the transition state for the deprotonation rather than that of pre-complexation, so that the transfer of a particular hydrogen to the base is kinetically enhanced [3].

In the course of our studies on the synthetic applications of *N*-alkyl-*N*-benzyldiarylphosphinamides we have reported that their lithiation in THF at −90 °C in the presence of HMPA (hexamethylphosphoramide) or DMPU (*NN*′-dimethylpropyleneurea), followed by addition of an electrophile afforded tetrahydrobenzo[*c*][1,2]aza-1λ^5-phospholes **2** with very high regio- and stereocontrol (Scheme 1) [4]. These dearomatized products arise from an anionic cyclization reaction involving a benzylic anion. In absence of coordinating solvents, products **3** and **4** derived from the electrophilic quench of *ortho* and benzylic anions, respectively, were also obtained [5]. NMR monitoring of the dearomatization reaction revealed the formation of a pre-lithiation

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