

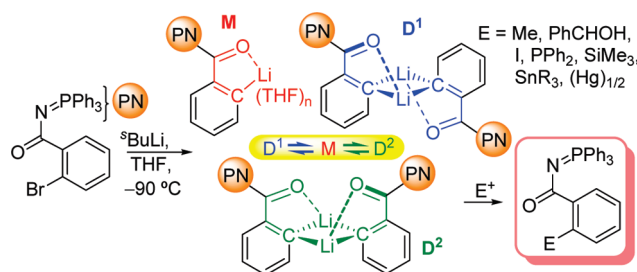
Synthesis, Structure, and Reactivity of *N*-Benzoyl Iminophosphoranes *Ortho* Lithiated at the Benzoyl Group

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Ortho lithiation of *N*-benzamido-*P,P,P*-triaryliminophosphoranes through deprotonation with alkylolithium bases was achieved with *ortho*-C=O and *ortho*-P=N chemoselectivity. However, the synthetic scope of these processes was rather limited. *Ortho*-lithiated *N*-benzamido-*P,P,P*-triphenyliminophosphorane **8** was efficiently prepared via lithium/halogen exchange of the corresponding *ortho*-brominated precursor with *s*-BuLi in THF at $-90\text{ }^{\circ}\text{C}$. The reaction of **8** with a variety of electrophiles provides an easy and mild method for the regioselective synthesis of *ortho*-modified iminophosphoranes via C–C (alkylation and hydroxyalkylation) and C–X (X = I, Si, P, Sn, and Hg) bond-forming reactions. NMR characterization of **8** in THF solution showed that **8** exists as an equilibrium mixture of one monomer and two dimers. The Li atoms of these species become members of five-membered rings through chelation by the *ortho*-metalated carbon and the carbonyl oxygen. The dimers differ in the relative orientation of the two chelates with respect to the plane defined by the C_2Li_2 core. The equilibrium between all species is established by splitting the dimers into monomers and subsequent recombination with formation of a different dimer.

Introduction

Selective *ortho* lithiation of aryl rings bearing heteroatom-containing functional groups is a powerful synthetic strategy in organic and organometallic synthesis.¹ From the organic chemistry point of view, the method gives access to *ortho* derivatives with excellent regiocontrol through reactions of the carbanions with a great variety of electrophiles (Scheme 1,

compounds **4**).² On the other hand, the lithiated species may act as bidentate ligands that can be used in the preparation of

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