

## $\sigma$ 2P,O-hybrid ligands: Synthesis of the first 4-hydroxy-1,3-benzazaphospholes by ortho-lithiation of m-amidophenyl diethyl phosphates

Aluri B., Shah K., Gupta N., Fomina O., Yakhvarov D., Ghalib M., Jones P., Schulzke C., Heinicke J.  
Kazan Federal University, 420008, Kremlevskaya 18, Kazan, Russia

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### Abstract

Copyright © 2014 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim. The m-phosphorylanilides **2** are available from anilides **1** by the Atherton-Todd reaction; the selective ortho-lithiation of the o'-methyl-protected phosphorylpivalanilide **2b** with tBuLi proceeded in high yield in the presence of ClSiMe<sub>3</sub>. The ortho-lithiation is followed by rapid 1,3-migration of the PO<sub>3</sub>Et<sub>2</sub> group to yield the phosphonoanilide cis/trans-**3b**. This compound mainly reacts with excess LiAlH<sub>4</sub> by reductive cyclization to form the 4-hydroxy-1H-1,3-benzazaphosphole **6**. The lithiation of the o'-unprotected phosphorylpivalanilide **2a** with LDA was unselective and led to **3a** and **4a** in low yields, whereas additional ortho-lithiation of the benzoyl group occurred for the lithiation of the o'-protected phosphonobenzanilide **2c** with tBuLi/LDA to give **7** in rather low yield. The reduction of crude **7** led to (benzylamino)phenol **8** and the 4-hydroxy-1H-1,3-benzazaphosphole **9** as a minor product. The properties, NMR spectroscopy data, and crystal structures of **5b**, **6**, and **8** are reported.

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### Keywords

Amides, Lithiation, Phosphorus heterocycles, Phosphorylation, Rearrangement