Trapping of Transient Thienyllithiums in Halogen Dance Using Zinc Chloride Diamine Complex

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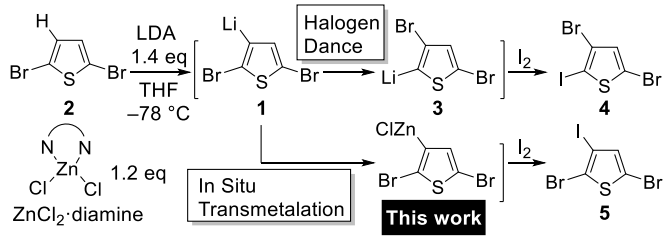
Thienyllithiums bearing a bromo group often undergo halogen dance, the exchange of the lithium atom and the bromo group.[1] The halogen dance of thienyllithium **1** generated from 2,5-dibromothiophene (**2**) proceeded smoothly even at –78 °C to furnish thienyllithium **3**, which then reacts with iodine to afford thiophene **4**. Although the reaction of the first generated thienyllithium **1** provides another constitutional isomer **5**, suppression of the halogen dance has been reported to be difficult.[2] Recently, we also attempted to trap the transient thienyllithium **1** using a flow microreactor; however, selective trapping of thienyllithium **1** could not be realized under the optimized reaction conditions.[3]

We began with the trapping of thienyllithium **1** by in situ transmetalation.[4] Based on the report by Knochel,[5] we treated a mixture of 2,5-dibromothiophene (**2**) and $ZnCl_2$ with LDA at −78 °C, and subsequent addition of iodine provided thiophene **4** and the desired thiophene **5** in 11% and 41% yields, respectively, with a 23% recovery of substrate **2**. These results indicated that $ZnCl_2$ reacted with LDA to provide less basic zinc amide species. Switching to $ZnCl_2$·TMEDA (**6**) exclusively provided the desired thiophene **5** in 95% yield. The product ratio was affected by the alkyl group on the nitrogen atom in the diamine ligand. Thus, $ZnCl_2$·TEEDA (**7**) resulted in the formation of a mixture of thiophene **4** and thiophene **5**. The effects of the diamines on in situ transmetalation, which was observed by in situ IR spectroscopy, and its synthetic application will be also presented.



None	**4** 64%	$ZnCl_2$	**4** 11%
	5 0%		**5** 41%
$ZnCl_2$·TMEDA (**6**)	**4** 1%	$ZnCl_2$·TEEDA (**7**)	**4** 47%
	5 95%		**5** 14%

[1]H NMR yield. [a] Isolated yield.

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