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Catalyst-Free Syntheses of [2]Rotaxanes Utilizing a Pentacoordinated Hydrosilane as an End-Capping Agent

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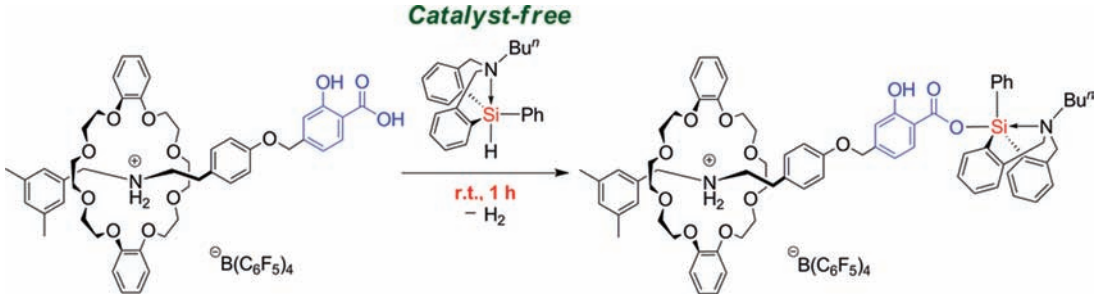
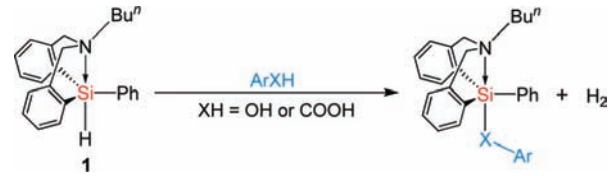
ABSTRACT



A pentacoordinated hydrosilane activated by an intramolecular nitrogen−silicon dative bond was utilized as an end-capping agent for catalyst-free syntheses of [2]rotaxanes. The end-capping reaction of a pseudo[2]rotaxane bearing a salicylic acid terminus with the pentacoordinated hydrosilane readily proceeded at room temperature to produce the corresponding silyl-capped [2]rotaxane.

Extensive efforts have been devoted to developing efficient syntheses of mechanically interlocked molecules by utilizing a variety of synthetic methods.[1] Among them, the reactions featuring high chemoselectivity and broad functionality tolerance, such as the Huisgen 1,3-dipolar cycloaddition[2] and olefin metathesis,[3] have been successfully applied to the construction of various interlocked architectures, promoting rapid progress in this field. To date, most of the reactions employed in the syntheses of interlocked molecules involve the use of catalysts or activating agents. In view of simplifying purification procedures as well as atom economy, a new synthetic method that demands no such additive is still desired. Here, we report the efficient syntheses of [2]rotaxanes that can be performed without loading any catalyst and activating agent.

Scheme 1. Catalyst-Free Reactions of **1** with Oxygen Nucleophiles



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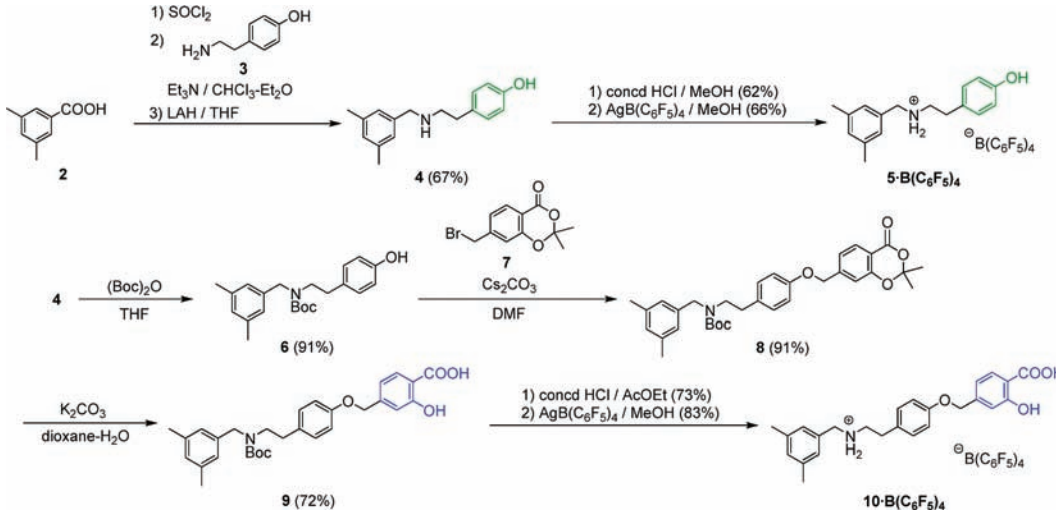
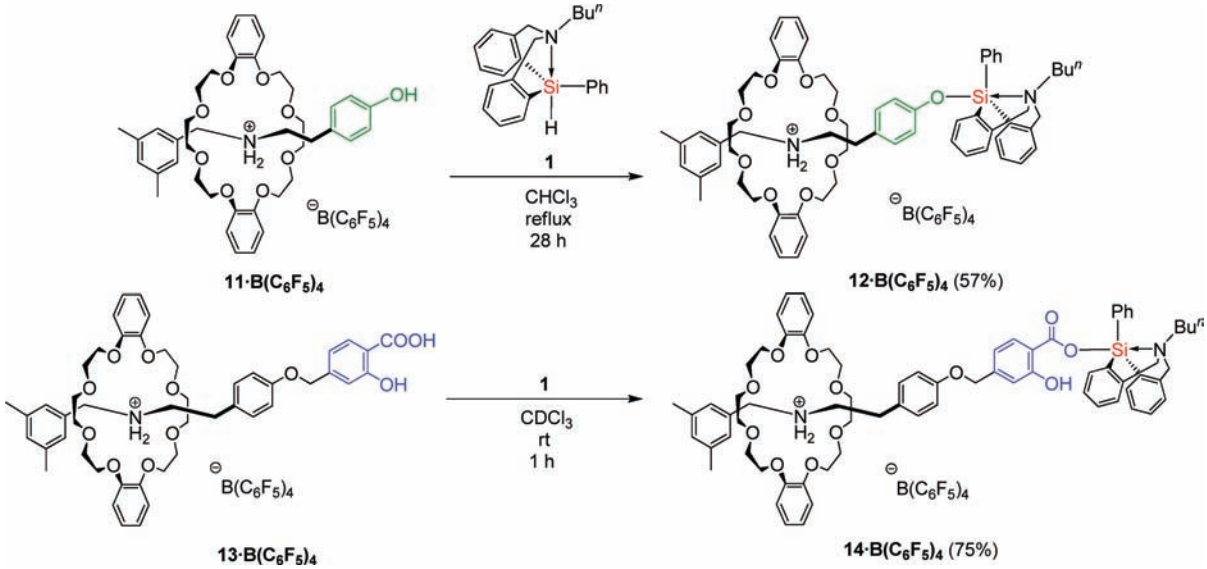
Scheme 2. Synthesis of Axle Molecules



Highly coordinated hydrosilanes[4] bearing an intramolecular dative bond between silicon and donor (nitrogen or oxygen) atoms exhibit high reactivity toward nucleophiles.[5] Recently, we have demonstrated that the neutral pentacoordinated hydrosilane **1**[6a] smoothly reacts with phenol and benzoic acid derivatives in the absence of any catalyst and activating agent to produce the corresponding silyl ether and silyl benzoates, respectively, with evolution of hydrogen as the sole side product (Scheme 1).[6b] We also reported that the reaction of **1** with benzoic acid derivatives, especially salicylic acid, is much faster than that with phenol.[6b] This type of reaction involving **1** is expected to be useful for the syntheses of interlocked molecules under additive-free conditions. To probe the utility of the reaction between **1** and oxygen nucleophiles, it was applied to the end-capping step for [2]rotaxane syntheses.

As axle molecules, we prepared two kinds of ammonium salts **5·B(C_6F_5)$_4$** and **10·B(C_6F_5)$_4$** bearing a phenol and a salicylic acid terminus, respectively (Scheme 2). Preparation of **5·B(C_6F_5)$_4$** began with 3,5-dimethylbenzoic acid (**2**), which was converted via a chlorination−amination−reduction sequence to amine **4**. Treatment of **4** with hydrochloric acid followed by anion exchange to tetrakis(pentafluorophenyl)borate afforded **5·B(C_6F_5)$_4$** in moderate yield. The axle **10·B(C_6F_5)$_4$** was synthesized from the Boc-protected amine **6**, which was easily obtained from **4**. Introduction of a salicylic acid moiety was accomplished via arylmethylation of **6** with bromide **7**[7] to give **8** in excellent yield. After removal of the acetonide moiety of **8** under basic conditions, deprotection of the Boc group with hydrochloric acid followed by anion exchange afforded the ammonium salt **10·B(C_6F_5)$_4$**.

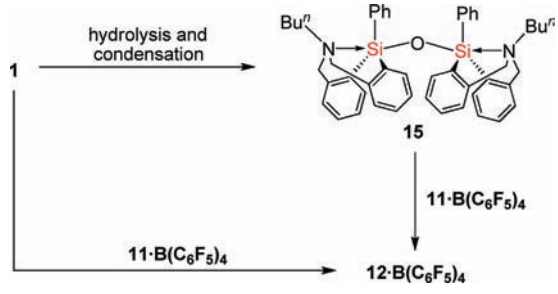
Scheme 3. Synthesis of [2]Rotaxanes **12·B(C_6F_5)$_4$** and **14·B(C_6F_5)$_4$** Utilizing Pentacoordinated Hydrosilane **1** as End-Capping Agent



With two types of axle molecules in hand, the synthesis of rotaxanes utilizing **1** as an end-capping agent was examined (Scheme 3). Solutions of pseudo[2]rotaxanes **11·B(C_6F_5)$_4$** and **13·B(C_6F_5)$_4$** were prepared by treatment of the corresponding axle molecules with dibenzo-24-crown-8 (DB24C8) in chloroform. Slow addition of **11·B(C_6F_5)$_4$** to an equimolar amount of **1** in chloroform over 4 h under reflux conditions, followed by continual refluxing for 24 h, afforded the corresponding [2]rotaxane **12·B(C_6F_5)$_4$** with a silyl ether terminus. This rotaxane was formed in 78% yield, as estimated by ^{1}H NMR, and isolated as a colorless solid in 57% yield. In contrast with the reaction of **11·B(C_6F_5)$_4$** that required heating, the end-capping of pseudorotaxane **13·B(C_6F_5)$_4$** bearing a salicylic acid terminus with **1** proceeded much faster under milder conditions. The reaction of 2 molar equiv of **1** with **13·B(C_6F_5)$_4$** in chloroform was completed within 1 h at room temperature, yielding [2]rotaxane **14·B(C_6F_5)$_4$** with a silyl salicylate terminus in 75% isolated yield. In neither case was addition of any catalyst or activating agent necessary, which is due to the high electrophilicity of the silicon atom in **1** enhanced by the intramolecular coordination. Although both **12·B(C_6F_5)$_4$** and **14·B(C_6F_5)$_4$** have a pentacoordinated silicon atom, these [2]rotaxanes were found to be stable in wet chloroform at room temperature for 2 days.

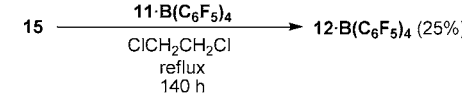
The difference in the reactivity of **1** toward **11·B(C_6F_5)$_4$** and **13·B(C_6F_5)$_4$** is consistent with our previous observation;[6b] the reaction of **1** with phenol took 13 h under reflux conditions in chloroform, while that with salicylic acid was completed within 10 min at room temperature. Interestingly, monitoring of the reaction progress by ^{1}H NMR spectroscopy during these rotaxane syntheses indicated that the formation mechanisms of **12·B(C_6F_5)$_4$** and **14·B(C_6F_5)$_4$** are different. In the case of the synthesis of **12·B(C_6F_5)$_4$**, the rotaxane was formed only in ca. 30% yield just after the addition of **11·B(C_6F_5)$_4$** to **1**. At that moment, no unreacted **1** was observed in the ^{1}H NMR spectrum, and instead, a considerable amount of disiloxane **15** was detected, which was presumably generated by the hydrolysis of **1** followed by dehydrative condensation (Scheme 4). After further heating

Scheme 4. Mechanism for the Formation of [2]Rotaxane **12·B(C_6F_5)$_4$** under Heated Conditions



of the reaction mixture, the amount of **12·B(C_6F_5)$_4$** was gradually increased along with the decrease of **11·B(C_6F_5)$_4$** and **15**, and the yield of **12·B(C_6F_5)$_4$** finally reached 78% after heating for 24 h. This result indicates that disiloxane **15** also acts as an end-capping agent, although the reactivity of **15** is much lower than that for **1** (Scheme 4). Involvement of **15** in the formation of **12·B(C_6F_5)$_4$** was confirmed by the following control experiment: treatment of **15** with **11·B(C_6F_5)$_4$** in 1,2-dichloroethane under reflux conditions afforded **12·B(C_6F_5)$_4$** (Scheme 5).

Scheme 5. Synthesis of **12·B(C_6F_5)$_4$** from Disiloxane **15**



In sharp contrast, monitoring of the reaction between **1** and **13·B(C_6F_5)$_4$** by ^{1}H NMR spectroscopy revealed that the resonances due to [2]rotaxane **14·B(C_6F_5)$_4$** immediately appeared upon mixing both compounds at room temperature. This observation confirms that the end-capping to form **14·B(C_6F_5)$_4$** is achieved directly by the reaction between **1** and **13·B(C_6F_5)$_4$**. The reaction rate of **1** with **13·B(C_6F_5)$_4$** is comparable to that of **1** with salicylic acid, indicating that the existence of the interlocked moiety does not significantly affect the reactivity of the salicylic acid functionality in **13·B(C_6F_5)$_4$**. It is worth noting that this rapid end-capping reaction can be performed at room temperature under additive-free conditions. Recently, a rotaxane synthesis utilizing copper-free 1,3-dipolar cycloaddition between an azide and a strained bicyclic alkene has been reported.[8] However, this reaction requires heating and longer reaction time.

In summary, the efficient end-capping syntheses of [2]rotaxanes have been achieved by utilizing the high reactivity of a pentacoordinated hydrosilane toward oxygen nucleo-

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philes such as phenol and salicylic acid. This end-capping procedure requires no catalyst and activating agent. Furthermore, the end-capping involving a salicylic acid functionality enabled a quick synthesis of a [2]rotaxane at room temperature. This procedure, which is performable under mild and additive-free conditions, is expected to serve as a promising tool for constructing a wide range of interlocked structures.

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Supporting Information Available: Experimental procedures for the preparation of **4**−**10**, disiloxane **15**, and rotaxanes **12**·$B(C_6F_5)_4$ and **14**·$B(C_6F_5)_4$. This material is available free of charge via the Internet at http://pubs.acs.org.

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