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Efficient synthesis of [2]- and higher order rotaxanes via the transition metal-catalyzed hydrosilylation of alkyne

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Abstract—A novel end-capping method of pseudorotaxanes via the hydrosilylation of the alkyne of the axle terminal was developed. $RuHCl(CO)(PPh_3)_3$ and $RhCl(CO)(PPh_3)_3$ complexes catalyzed the hydrosilylation reactions of the alkyne moiety of several pseudorotaxanes at ambient temperature to give the corresponding [2]- and higher order rotaxanes in high yields with excellent regio- and stereoselectivity.

Several molecular recognition motifs have been applied to rotaxane synthesis so far. In particular, the combination of *sec*-ammonium salt and crown ethers have been extensively studied in rotaxane synthesis because of their structural diversity and the high stability of the crown ether–ammonium salt complex.[1] Since the interaction between crown ether and ammonium salt is depressed by the action of the base, a limited variety of reactions can be applied to the synthesis of this type of rotaxane. Therefore, the exploration of novel synthetic methods is always essential to synthesize various functionalized rotaxanes. We focused our attention on the application of transition-metal catalyzed reactions to rotaxane synthesis because they proceed under mild conditions with high functional group tolerance. The Suzuki-coupling reaction provides an effective synthesis of rotaxanes such as cyclodextrin-based rotaxanes.[2] Some rotaxanes and catenanes were synthesized via metathesis reaction using ruthenium complexes.[3] We have recently reported an efficient end-cap exchange of [2]rotaxanes via Pd-catalyzed allylic alkylation.[4] Meanwhile, transition metal-catalyzed hydrosilylation of alkynes quantitatively affords vinylsilanes with high regio- and stereoselectivity.[5] The reaction proceeds smoothly with high functional group tolerance at low temperatures in non-polar solvents without any additive, suggesting that it could be an effective end-capping reaction of pseudorotaxane. Since various reactions of vinylsilanes such as acylation, Hiyama coupling, and rearrangement reactions via epoxide are known, special interest can be placed in the introduction of the vinylsilane moiety to rotaxanes in the light of the synthesis of functionalized rotaxanes. Here, we wish to report a novel end-capping method of pseudorotaxanes via the transition metal-catalyzed hydrosilylation of the alkyne moiety at the axle terminal.

First, hydrosilylation of pseudorotaxane complex **1**·DB24C8 with excess dimethylphenylsilane was carried out in the presence of 5 mol % of $RuHCl(CO)(PPh_3)_3$[6] (Chart 1). However, no corresponding [2]rotaxane **2** was obtained at all. Since we have already observed that DB24C8 acts as a bulky group to strongly depress the reactivity of the functional groups on the axle,[4] it could

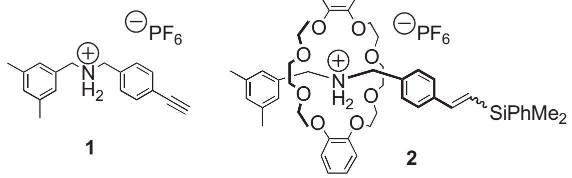

Chart 1.

Keywords: Rotaxane; Hydrosilylation; Alkyne; Transition metal-catalyst.

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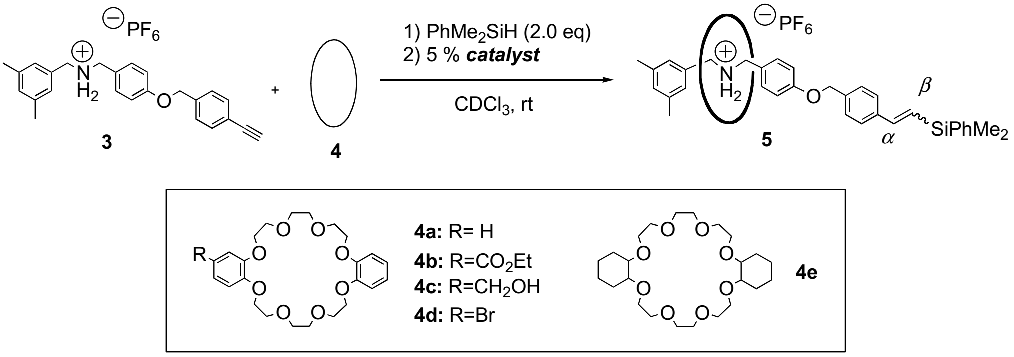


Scheme 1.

Table 1. Synthesis of rotaxane **5** by transition metal-catalyzed hydrosilylation[a]

Entry	Catalyst	Wheel	Rotaxane (%)[b]	β-*trans*/β-*cis*/α[c]
1	$H_2PtCl_6 \cdot nH_2O$	**4a**	**5a** (18)	93:2:5
2	$RuHCl(CO)(PPh_3)_3$	**4a**	**5a** (84)	98:2:0
3	$RhCl(PPh_3)_3$	**4a**	**5a** (77)	97:0:3
4	$RuHCl(CO)(PPh_3)_3$	**4b**	**5b** (88)	98:2:0
5	$RuHCl(CO)(PPh_3)_3$	**4c**	**5c** (86)	96:4:0
6	$RuHCl(CO)(PPh_3)_3$	**4d**	**5d** (81)	99:1:0
7	$RuHCl(CO)(PPh_3)_3$	**4e**	**5e** (80)	93:3:0

[a] Initial concentration; [**3**] = 167 mM. Reactions were carried out at ambient temperature for 6 h in $CDCl_3$.

[b] Isolated yield.

[c] Estimated by ^1H NMR.

be deduced that the short distance between the alkyne and the crown ether moieties prevents hydrosilylation. Therefore, we designed and synthesized a new axle **3** with a longer spacer between the ammonium and the alkyne moieties.

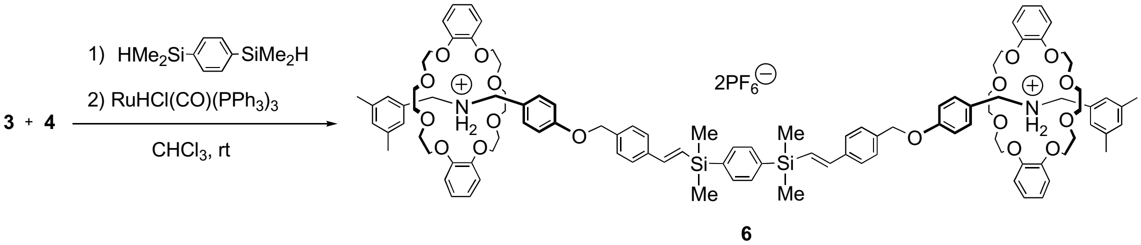
The end-capping of pseudorotaxane **3**·DB24C8 with dimethylphenylsilane was carried out in the presence of 5 mol % catalyst in $CDCl_3$ at ambient temperature (Scheme 1). The results are summarized in Table 1. While $H_2PtCl_6 \cdot nH_2O$ was ineffective for this system (entry 1), $RuHCl(CO)(PPh_3)_3$ and Wilkinson's catalyst $RhCl(PPh_3)_3$ effectively catalyzed the end-capping reaction.

In every case, β-*trans* vinylsilane was formed with high regio- and stereoselectivity. When **3** was used as axle, [2]rotaxane **5a** with β-*trans* vinylsilane end-cap was obtained in 84% and 77% yield, respectively (entries 2 and 3). Ozawa and co-workers reported β-*trans* selective hydrosilylation of phenylacetylene with dimethylphenylsilane when $RuHCl(CO)(PPh_3)_3$ was used as catalyst.[7] Ojima and Faller reported that a neutral rhodium complex catalyzed hyrosilylation with high β-*cis* selectivity, while a cationic rhodium complex catalyzed hydrosilylation with high β-*trans* selectivity.[8,9] Therefore, the stereoselectivity observed in entry 3 is for the cationic rhodium complex. It can be deduced that the ammonium group transformed Wilkinson's catalyst to a cationic complex due to the hydrogen-bonding between the ammonium group and the chloride anion, and the low coordination ability of PF_6.

When OTf salt was used as axle, [2]rotaxane **5a** with OTf counterion was obtained with high β-*trans* selectivity. The counter anion did not affect the regio- and stereochemistry of hydrosilylation.

The preparation of functionalized rotaxanes was examined using crown ethers bearing various functional groups via $RuHCl(CO)(PPh_3)_3$-catalyzed hydrosilylation (entries 4–7). Rotaxanes **5b–d** with ester, alcohol, and halide moieties on the wheel were obtained in high yields (81–88%) (entries 4–6). When dicyclohexano-24-crown-8 (DC24C8) **4e** was used instead of DB24C8, the corresponding rotaxane **5e** was obtained in 80% yield (entry 7). These results clearly demonstrate that $RuHCl(CO)(PPh_3)_3$-catalyzed hydrosilylation is one of the most versatile pseudorotaxane end-capping methods due to the efficiency of the reaction, the high regio- and stereoselectivity, and the high functional group tolerance.

Further, to assess the application of this end-capping method, the preparation of [3]rotaxane was investigated.



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Scheme 2.

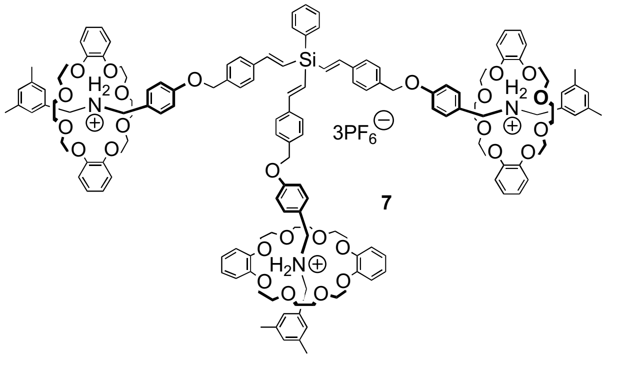

Chart 2.

Thus, a catalytic amount of $RuHCl(CO)(PPh_3)_3$ was added to a mixture of **3**·DB24C8 and a half equivalent of 1,4-bis(dimethylsilyl)benzene in $CDCl_3$ at ambient temperature to give the corresponding [3]rotaxane **6** in 62% yield with high β-*trans* (*trans*/*cis* = 98/2) selectivity (Scheme 2). [4]Rotaxane **7** was also obtained in 50% yield using phenylsilane as the hydrosilylation reagent (Chart 2). These results indicate that the hydrosilylation method can also be applied to the synthesis of higher interlocked compounds bearing various functional groups.

In summary, we have demonstrated that the transition metal-catalyzed hydrosilylation of alkyne can be an efficient end-capping method of pseudorotaxanes having alkyne moiety at the axle terminal. The reaction proceeded smoothly at ambient temperature to give the corresponding [2]- and higher order rotaxanes in high yields and excellent regio- and stereoselectivities. Studies of the reactions of the resulting rotaxanes to obtain functional rotaxanes are in progress.

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Supplementary data

Supplementary material available: Spectroscopic data for [2]rotaxanes **5** and [3]rotaxane **6**. Supplementary data associated with this article can be found, in the online version at doi:10.1016/j.tetlet.2005.03.186.

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