Rotaxane Synthesized by End-capping via Hydroruthenation of Axle Terminal Acetylene and Its Derivation to η^3-Allylruthenium Complex-containing Rotaxane

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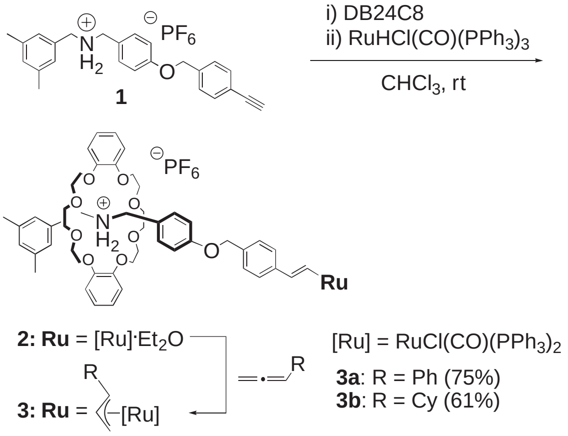
The hydroruthenation of pseudorotaxane **1**·DB24C8 having an alkyne moiety at the axle terminal with $RuHCl(CO)(PPh_3)_3$ gave [2]rotaxane **2** with an alkenylruthenium complex moiety in a good yield. The carbometalation of allenes with **2** resulted in the formation of the corresponding [2]rotaxanes **3** with η^3-allylruthenium complex moieties in good yields.

Recently, rotaxanes with active catalytic sites have been receiving much attention because the cooperation of their components is the basic feature of the biomimetic catalyst.[1] Rowan and Nolte have developed the first [2]rotaxane catalyst that mimics the DNA λ-exonuclease.[1a] We have reported [2]rotaxane catalysts for asymmetric benzoin condensation mimicking a Vitamin B_1-catalyzed system.[1b] These findings clearly suggest the potential usefulness of a rotaxane catalyst for the development of a unique and sophisticated catalyst system. However, the introduction of a catalytic site into rotaxanes still represents a challenging task, although various synthetic methods of rotaxanes have been developed so far.[2]

Recently, we have reported the synthesis of vinylsilane-terminated [2]rotaxanes by $RuHCl(CO)(PPh_3)_3$-catalyzed hydrosilylation of alkyne moieties of the axle components.[3] The reaction proceeds via the alkenylruthenium species, $Ru(CH{=}CHR)Cl(CO)(PPh_3)_2$,[4] which is the important intermediate in various organic transformations.[5] Meanwhile, the η^3-allylruthenium complex, which can be synthesized via the carbometalation of the alkenylruthenium complex with allenes,[5e] has been reported to react as an ambiphilic allylation reagent,[6] a catalyst for cyclization reactions,[7] and a precursor of various ruthenium complexes.[8] Thus, rotaxanes possessing alkenyl- or η^3-allylruthenium complex moieties can be regarded as useful intermediates for the construction of rotaxane catalysts and functionalized rotaxanes. In this report, the efficient end-capping synthesis of ruthenium complex-functionalized [2]rotaxanes and its derivation to rotaxanes bearing η^3-allylruthenium complex moieties will be described.

The pair of *sec*-ammonium salt axle and dibenzo-24-crown-8 (DB24C8) wheel is one of the most effective combinations for the construction of rotaxanes.[2] The authors chose ammonium salt **1** with a terminal alkyne group as the axle component. Since the reactivity of functional groups on the axle is strongly suppressed due to the steric hindrance of DB24C8 when the axle is surrounded by the wheel,[3,9] an axle component with a long spacer between the ammonium and alkyne moieties was designed and synthesized (Scheme 1).



Scheme 1.

The addition of 1.2 equiv. of DB24C8 to a suspension of **1** in $CHCl_3$ at ambient temperature resulted in the dissolution of **1** to give a clear colorless solution. The formation of pseudorotaxane (**1**·DB24C8) was confirmed by the characteristic change of ^1H NMR spectrum similar to that observed in related systems.[10] By the addition of 1.0 equiv. of $RuHCl(CO)(PPh_3)_3$ to the solution of **1**·DB24C8, the ruthenium complex was completely dissolved within 30 min. The initial clear colorless solution turned to clear reddish orange as the reaction progressed, indicating the formation of alkenylruthenium complex **2** through the hydrometalation of the axle terminal alkyne moiety. The purity of **2** isolated by the repeated precipitation in Et_2O reached 95% by ^1H NMR (yield 96%). [2]Rotaxane **2** was characterized by ^1H NMR and IR spectra. In Figure 1a, benzylic protons of the ammonium group (H_e and H_d) appeared at 4.48–4.37 ppm with complex coupling, which is characteristic of crown ether–ammonium salt type rotaxanes.[2,10] Vinyl protons (H_a and H_b) were observed at 8.49 and 5.61 ppm with coupling constant $J = 13.2$ Hz, which coincides with that of corresponding vinylruthenium complexes.[11]

The reactivity of the alkenylruthenium complex moiety of **2** was examined to characterize it as the "reactive" rotaxane and to finally confirm the structure of **2** by deriving it to a stable product. Two allenes were chosen as reactants. The reaction was conducted by mixing phenylallene with freshly prepared **2** at ambient temperature. The reaction proceeded smoothly within 2 h to give the corresponding η^3-allylruthenium complex-containing [2]rotaxane **3a**[12] in 75% yield by purification with preparative HPLC (eluent: $CHCl_3$). When less reactive cyclohexylallene[5e] was used, similar ruthenium complex-containing [2]rotaxane **3b** was obtained in 61% yield. These results clearly indicate that **2** is a useful reactive [2]rotaxane for further functionalization. It should be noted that no degradation of rotaxane structure, like dethreading of the axle component during the insertion of allene into the Ru-complex moiety of **2**, occurred, confirming that the Ru complex moiety is sufficiently bulky as end-cap.

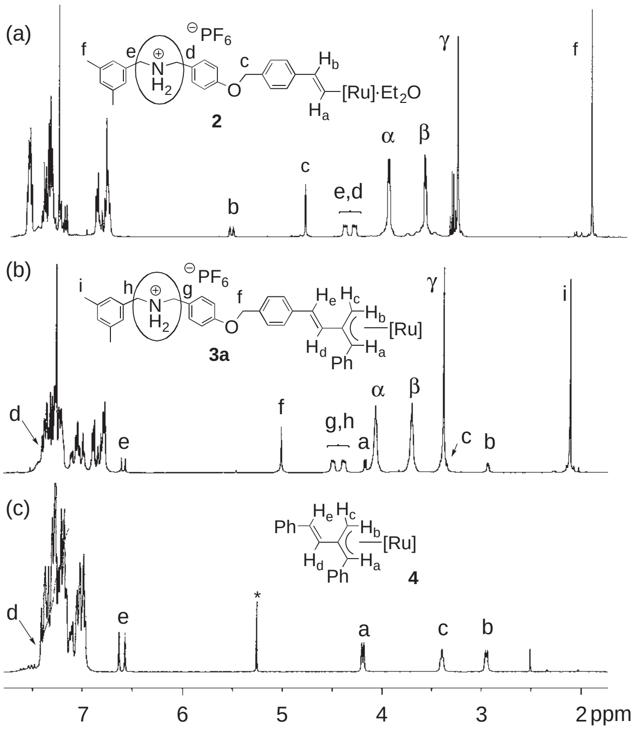


Figure 1. Partial ^{1}H NMR spectra of (a) rotaxane **2**, (b) rotaxane **3a**, and (c) ruthenium complex **4** in $CDCl_3$. Asterisk (*) denotes the signal of the residual solvent. [Ru] = $RuCl(CO)(PPh_3)_2$.

The structure of [2]rotaxane **3** was characterized by ^{1}H NMR and IR spectra and elemental analyses. Benzylic protons of the ammonium group (H_g and H_h) were observed at 4.51–4.38 ppm with complex coupling similarly to the case of **2**. Vinylic and allylic protons ($H_{a\text{–}e}$) were observed as reported for a similar (2-alkeyl-η^3-allyl)ruthenium complex.[8] The crystal of **3** was stable under air at ambient temperature, indicating that **3** can be easily handled for further reaction. Meanwhile, **3** was confirmed to decompose above 50 °C in chloroform probably because of the formation of a highly reactive cationic complex at that temperature.[13]

In conclusion, alkenylruthenium complex-terminated [2]-rotaxane was prepared in a high yield and derived to corresponding [2]rotaxanes carrying η^3-allylruthenium complex moieties by reaction with allenes. The potential reactivity of **2** as demonstrated in the present paper points to the likelihood of various functionalizations of rotaxane. Further study of these [2]rotaxane ruthenium complexes is under progress.

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12 **3a**: Yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40–6.78 (m, 57H), 6.59 (d, 1H, $J = 15.6$ Hz), 5.01 (s, 2H), 4.51–4.48 (m, 2H), 4.41–4.38 (m, 2H), 4.18 (d, 1H, $J = 6.4$ Hz), 4.07 (brs, 8H), 3.71 (brs, 8H), 3.40 (brs, 9H), 2.95 (d, 1H, $J = 4.9$ Hz), 2.13 (s, 6H) IR (NaCl) 1931, 1541, 1506, 1456, 1435, 1252, 1123, 841, 746, 696, 557, 519 cm^{-1}. Anal. Calcd for $C_{96}H_{97}ClF_6NO_{10}P_3Ru\cdot(CHCl_3)_{0.75}$: C, 62.55; H, 5.30; N, 0.75%. Found: C, 62.58; H, 5.44; N, 0.83%.

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