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Alkene and enyne metathesis reactions on allylic and propargylic amines

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Abstract—Treatment of *cis*-4,5-diaminocyclohexene derivatives bearing allyl or propargyl groups on the nitrogen atoms, with first or second generation Grubbs metathesis catalysts, results in initiation of metathesis cascades which include ring-opening of the unstrained cyclohexene ring. This contrasts with the previous work on the analogous cyclohexene ethers where metathesis reactions occurred exclusively between the side-chains and no ring-opening of the cyclohexene unit was observed.

Over the last decade, first[1] and second[2] generation Grubbs' catalysts **1** and **2** (and related complexes[3]) have found many applications in organic synthesis as they very efficiently initiate the various alkene[4] and enyne[5] metatheses of organic compounds and are tolerant of many functional groups, moisture and air. We have previously reported the use of catalyst **1** for the ring-opening metathesis polymerization (ROMP) of norbornene derivatives leading to synthetic polymers bearing biologically relevant functional groups.[6] We have also used both catalysts **1** and **2** to convert readily available norbornene ethers into highly functionalized polycyclic oxygenated heterocycles through a cascade of up to eight consecutive alkene and enyne metatheses involving both ring-closing metathesis (RCM) and ring-opening metathesis (ROM) events.[7] Recently, we have shown that similar metathesis cascades can be conducted on 4,5-diallyloxy (or propargyloxy) derivatives of cyclohexene, but that the unstrained, disubstituted alkene unit within the cyclohexene ring never participates in these metathesis cascades.[8] In this Letter, we report the synthesis and metathesis of the related *N*,*N*′-bis-tosyl-4,5-diallylamino (or propargylamino) derivatives of cyclohexene and demonstrate that the cyclohexene unit of these compounds can participate in metathesis cascade sequences, leading to 2,2′-bis-(tetrahydropyridine) derivatives.[9]

Amino groups are one of the few functional groups which are known to cause difficulties for ruthenium-based metathesis catalysts as they can coordinate to the transition metal and deactivate it. A number of methodologies have been developed to allow nitrogen-containing substrates to be used with catalysts **1** and **2**,[10] including the addition of Lewis acids to coordinate to the amine,[11] the use of ammonium salts[12] and the use of amines bearing strongly electron-withdrawing sulfonamide-based protecting groups.[13]

We chose the latter strategy because of its generality and widespread use, so our initial metathesis target was diallyl amine **5**; which was prepared from the known *cis*-4,5-diaminocyclohexene[14] **3** (itself prepared in four steps from commercially available cyclohexene 4,5-dicarboxylic anhydride) via *N*,*N*′-bis-tosyl derivative **4** as shown in Scheme 1. Treatment of compound **5** with first generation Grubbs' catalyst **1** (5 mol%) in dichloromethane at room temperature for 20 h resulted in quantitative formation of 6,8-fused bicycle **6**[15] through a single RCM event,[16] a result which is exactly analogous to that previously reported for the analogous oxygen-containing derivative: *cis*-4,5-bis-allyloxycyclohexene.[8] However, treatment of compound **5** with second generation Grubbs' catalyst **2** (5 mol%) under identical reaction conditions resulted in the formation of a mixture of 6,8-fused bicycle **6**, and 2,2′-bis-(tetrahydropyridine) **7**. Formation of the latter compound requires that the disubstituted alkene within the unstrained cyclohexene group participates in a RCM–ROM–RCM cascade.

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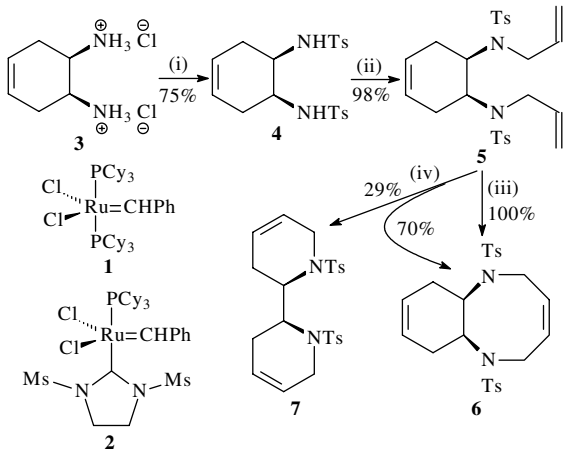


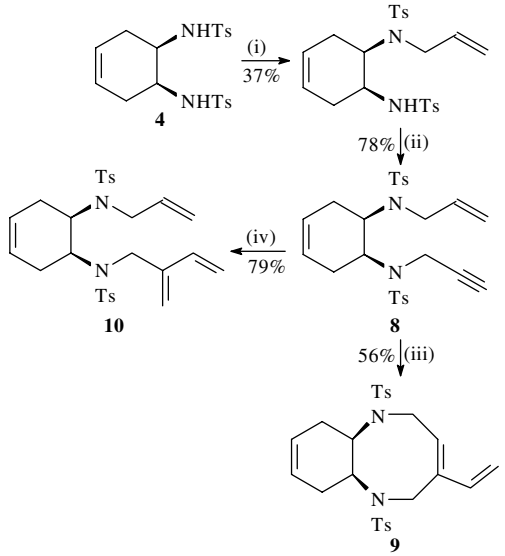
Scheme 1. Reagents and conditions: (i) TsCl (2.2 equiv)/Et_3N (4.0 equiv), CH_2Cl_2, N_2; (ii) NaH (3.0 equiv)/allyl-Br (5.0 equiv), DMF, N_2; (iii) compound **1** (5 mol%), CH_2Cl_2, N_2, rt; (iv) compound **2** (5 mol%), CH_2Cl_2, N_2, rt.

Compound **7** was the minor product (29%) under these conditions and we were not able to find conditions which favoured the formation of this product.[15] In particular, conducting the reactions with catalysts **1** or **2** under an ethene atmosphere[17] (to form methylidene ruthenium complexes[18] in situ) only reduced the yield of both products; catalyst **1** forming compound **6** in an 83% yield under these conditions, whilst catalyst **2** gave compound **6** in just a 21% yield and compound **7** in a 9% yield.

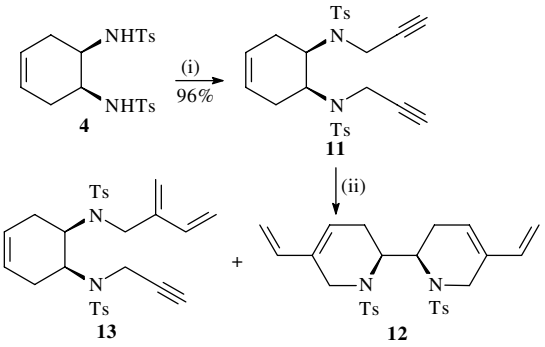
To allow enyne metatheses of cyclohexene diamine derivatives to be investigated, *N*-allyl-*N*′-propargyl derivative **8** was prepared from compound **4** in two steps as shown in Scheme 2. When compound **8** was treated with first generation Grubbs' catalyst **1** (10 mol%) at 35 °C in dichloromethane under an inert atmosphere, the product of a ring-closing enyne metathesis process, 6,8-fused diene **9** was isolated as the only product in a modest 56% yield.[15] However, when this reaction was carried out under an ethene atmosphere, the only isolated product was compound **10** resulting from enyne cross-metathesis between the terminal alkyne and ethene.

Since the cyclohexene unit of substrate **5** had shown a propensity to be involved in enyne metathesis cascades even when an alternative metathesis route was available, the metathesis of bis-propargylamine **11** was also investigated. Compound **11** was prepared by propargylation of compound **4** (Scheme 3) and treated with either catalyst **1** or **2**. When these reactions were conducted under an inert atmosphere, no reaction occurred. However, by conducting the reactions under an ethene atmosphere, the enyne metathesis cascade was facilitated and a mixture of bis-(tetrahydropyridine) **12** and mono-alkyne **13** was isolated.[15] The highest yield of compound **13** was obtained using catalyst **1** (10 mol%) in dichloromethane at room temperature. Under these conditions, compound **13** was obtained in a 63% yield, along with 16% of compound **12** and 20% of recovered starting material **11**. The highest yield of compound **12** (22%) was obtained using catalyst **2** (10 mol%) in toluene at 60 °C, and under these conditions compound **13** (59%) and starting material **11** (18%) were also isolated. Compound **13** is formed by an enyne cross-metathesis between one of the alkyne units of substrate **11** and ethene. Interestingly, no evidence for the formation of the corresponding bis-diene resulting from enyne metathesis at both alkynes was ever obtained from these reactions. The formation of compound **12** demonstrates that a cyclohexene unit can be involved in metathesis cascades using both first and second generation Grubbs catalysts.

The results obtained with compound **11** are in marked contrast to the metathesis of the analogous oxygen-containing derivative: *cis*-4,5-bis-propargyloxy-cyclohexene which was inert to catalyst **1**, but which reacted in the presence of catalyst **2** and ethene to give a mixture of three products.[8] Two of these products were the dienes



Scheme 2. Reagents and conditions: (i) NaH (1.2 equiv)/allyl-Br (1.0 equiv), DMF, N_2; (ii) NaH (3.0 equiv)/propargyl-Br (3.0 equiv), DMF, N_2; (iii) compound **1** (10 mol%), CH_2Cl_2, N_2, 35 °C; (iv) compound **1** (10 mol%), CH_2Cl_2, $H_2C{=}CH_2$, 35 °C.

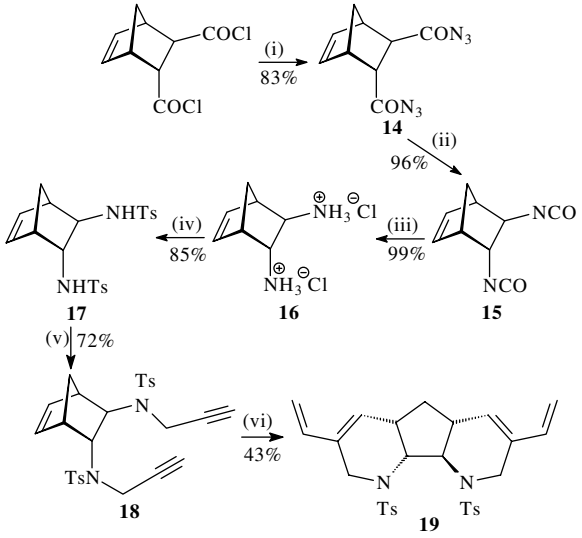


Scheme 3. Reagents and conditions: (i) NaH (3.0 equiv)/propargyl-Br (5.0 equiv), DMF, N_2; (ii) compound **1** (10 mol%), CH_2Cl_2, $H_2C{=}CH_2$, rt (**12**, 16%; **13**, 63%) or **2** (10 mol%), toluene, $H_2C{=}CH_2$, 60 °C (**12**, 22%; **13**, 59%).

formed by cross-metathesis (CM) between ethene and one or both of the alkynes. The third product was a 6,8-fused triene formed by a CM–RCM(enyne)–CM metathesis process. The cyclohexene unit was not involved in any of these processes.

Finally, we extended this chemistry to enyne metathesis of 2,3-diaminonorborn-5-ene derivatives. Initially, we planned to investigate the *endo*-cis-isomer by analogy with our previous work on norbornene ethers.[7] However, whilst we were able to prepare *N*,*N*′-ditosyl-*endo*-*cis*-2,3-diaminonorborn-5-ene from the known *endo*-*cis*-2,3-diaminonorborn-5-ene[19] without difficulty, all attempts to bis-propargylate the *N*,*N*′-ditosyl-derivative gave an inseparable mixture of mono and di-propargylated material. The difficulty in accomplishing this alkylation is presumably due to both nitrogen atoms being in the sterically more hindered *endo*-position of the norbornene unit and bearing large tosyl groups. To overcome this problem, the synthesis of the corresponding *trans*-2,3-diaminonorborn-5-ene derivative was undertaken. The parent *trans*-2,3-diaminonorborn-5-ene **16** had not previously been reported, but we were able to access it from commercially available *trans*-norborn-5-ene-2,3-dicarbonyl chloride by a double Curtius rearrangement as shown in Scheme 4. Thus, treatment of *trans*-norborn-5-ene-2,3-dicarbonyl chloride with sodium azide gave bis-acylazide **14**, which underwent a double Curtius rearrangement in refluxing toluene to give norborn-5-ene-*trans*-2,3-diisocyanate **15**. Acidic hydrolysis of bis-isocyanate **15** gave diamine **16** as its dihydrochloride salt. Bis-tosylation of diamine **16** gave *N*,*N*′-ditosyl-derivative **17**, which, unlike the *endo*-cis-diastereomer, was readily bis-propargylated under standard conditions to give enyne metathesis precursor **18**.

Treatment of compound **18** with first generation Grubbs' catalyst **1** in the presence of ethene resulted in the formation of tricyclic bis-diene **19** in a 43% yield as the only isolated compound.[15] Compound **19** could in principle be formed by two different routes. An initial CM between ethene and one of the terminal alkynes (probably the *exo*-propargylamino group) could initiate an RCM–ROM–RCM(enyne)–CM cascade leading to compound **19** in a single sequence. Alternatively, if the initial reaction occurs between ethene and the strained norbornene unit, this would establish a cyclopentane bearing two vinyl groups and two propargylamino groups, each of which could separately undergo an RCM(enyne) followed by quenching of the conjugated ruthenium alkylidene with ethene to give compound **19**. It was not possible to increase the yield of compound **19** above 43% using catalyst **1**, and the use of catalyst **2** (even at 60 °C in toluene under an ethene atmosphere) failed to give any isolable product.[20]



Scheme 4. Reagents and conditions: (i) NaN_3, THF/H_2O, −10–25 °C; (ii) toluene, reflux; (iii) 6 N HCl, reflux; (iv) TsCl (2.0 equiv)/Et_3N (4.0 equiv), CH_2Cl_2, N_2; (v) NaH (3.0 equiv)/propargyl-Br (5.0 equiv), DMF, N_2; (vi) compound **1** (5 mol%), CH_2Cl_2, $H_2C{=}CH_2$, rt.

In conclusion, we have demonstrated that in marked contrast to the corresponding allyl and propargyl ethers, 4,5-diaminocyclohexene derivatives do undergo metathesis reactions involving ring-opening of the cyclohexene unit leading to mono- and bis-tetrahydropyridines. In addition, a suitably substituted norbornene derivative was found to undergo a cascade of enyne metatheses, leading to a tricyclic bis-diene.

Acknowledgements

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