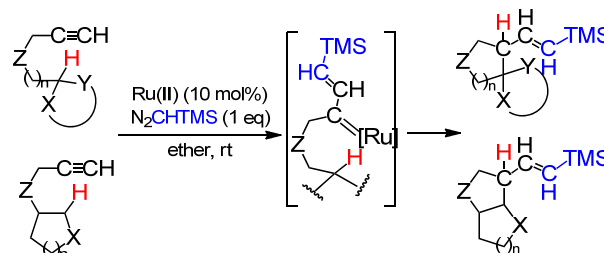


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We have recently developed a novel tandem Ru-catalyzed carbene addition to terminal alkynes/insertion of Csp^3 -H bonds in alkynyl acetals, ethers and amines under mild conditions.¹ This cascade provides an efficient approach to form complex spiro and fused bicyclic structures in 1,5- and 1,6-hydride shift/cyclization sequences from vinylcarbene Ru intermediates.



Ru-Catalyzed 1,5 and 1,6-Hydride Shift/Cyclization

Entry	Substrate	Product	Yield(%) ^a
1			80
2			25
3			61 ^b
4			40 ^b
5			53 ^b
6			79
7			48
8			85

1,6-Hydride Shift

9			90 ^b
10			61

1,5-Fused Bicycles

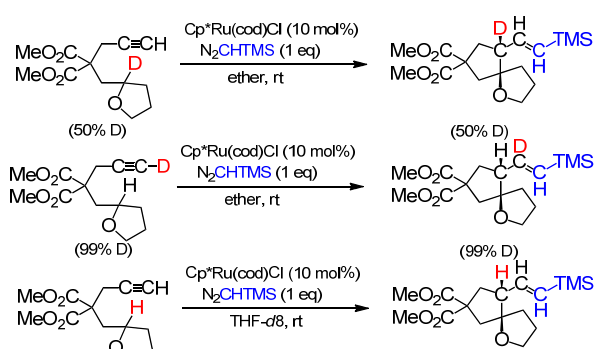
11			87 ^b
12			61

Conditions: ^aether, rt; ^bdioxane, 60 °C.

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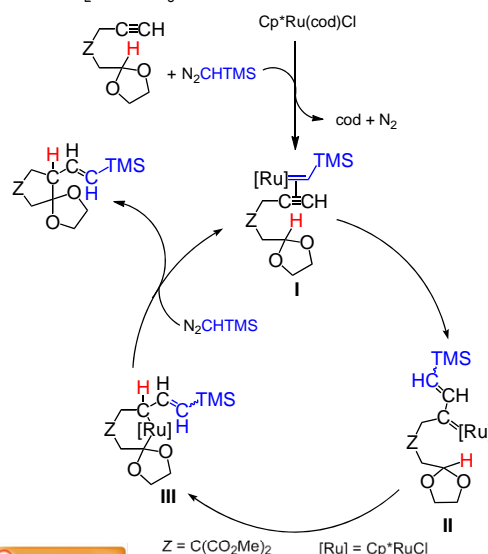
References: ¹ Cambeiro, F.; López, S.; Varela, J. A.; Saá, C. *Angew. Chem. Int. Ed.* 2012, 51, 723-727.

Labelling Studies



Mechanistic Proposal

The catalytic transformation of alkynyl derivatives with (trimethylsilyl)diazomethane in the presence of $Cp^*RuCl(COD)$ could be understood supposing the initial formation of ruthenium carbene species **I**. Oxidative coupling to give a metallacyclobutene followed by opening of this species would lead to the ruthenium vinyl carbene **II**. The electrophilic Ru carbene could induce a 1,5-hydride shift that would lead to the formation of a transient oxonium ion, which would in turn interact with the nucleophilic ruthenium to afford the metallacycle **III**. Final reductive elimination would give rise to the spiro compound with recovery of the catalytic Ru(II) species in the presence of $N_2CHSiMe_3$.



Z = $C(CO_2Me)_2$ [Ru] = Cp^*RuCl