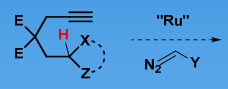
“C-H Bond Functionalization: TandemCatalytic Ru-Carbene Addition/Coupling of sp^3 C-H Bonds in Alkynyl Derivatives”

Fermín Cambeiro, Ana Cajaraville, Susana López and Carlos Saá*
Departamento de Química Orgánica, Facultade de Química,
Universidade de Santiago deCompostela,15782 Santiago de Compostela, SPAIN
Email: fermin.cambeiro@gmail.com

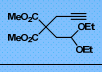
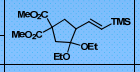
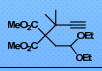
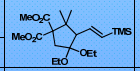
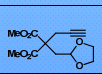
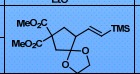
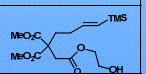
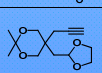
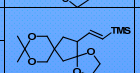
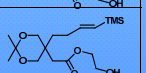
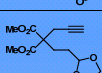
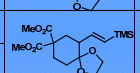
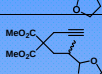
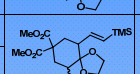
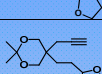
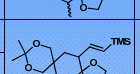
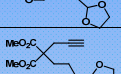
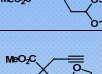
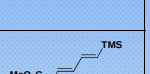
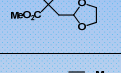
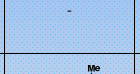
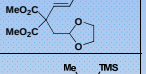
Objective

Exploration of new reactivity of catalytic Ru carbenes, in particular, Csp^3-H functionalization.

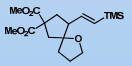
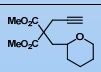
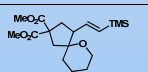
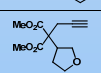
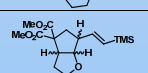
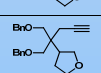
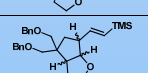
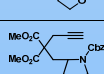
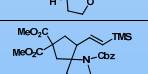


X, Z = C, N, O
Y = TMS, CO_2Et, ...

Alkynyl Acetals

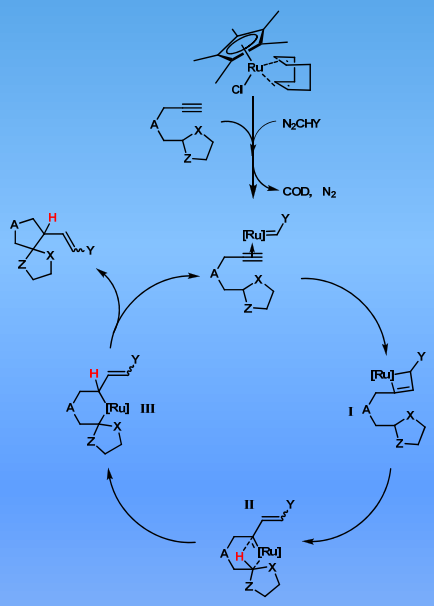
ENTRY	SUBSTRATE	CONDITIONS	YIELD (%)	PRODUCTS	
1		DIOXANE, 60ºC	61		-
		ETHER, r.t.	40		
2		DIOXANE, 60ºC	40		-
		ETHER, r.t.	30		
3		DIOXANE, 60ºC	40/51		
		ETHER, r.t.	80/TRACES		
4		DIOXANE, 60ºC	20/70		
		ETHER, r.t.	21/63		
5		DIOXANE, 60ºC	90		-
		ETHER, r.t.	81		
6		DIOXANE, 60ºC	51		-
		ETHER, r.t.	60		
7		DIOXANE, 60ºC	50		-
		ETHER, r.t.	60		
8		DIOXANE, 60ºC	SM	-	-
		ETHER, r.t.	SM		
9		DIOXANE, r.t.	65	-	
10		ETHER, r.t.	25/11		

Alkynyl Ethers

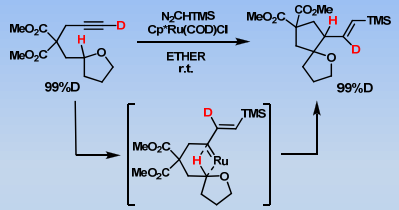
ENTRY	SUBSTRATE	SOLVENT	YIELD (%)	PRODUCT
1		ETHER	79%	
2		ETHER	40%	
3		ETHER	51%	
4		ETHER	78%	
5		ETHER	85%	

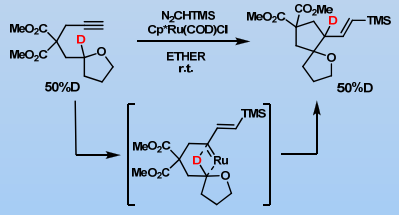
Mechanism

The catalytic transformation of alkynyl acetals/ethers with diazoalkane in the presence of Cp*Ru(COD)Cl can be understood supposing the initial formation of Cp*RuCl(=CHY) as the catalytic species, which first reacts with the terminal triple bond to give the intermediate I, that evolves to the vinylcarbene II. Hydride transfer by Csp^3-H activation gives ruthenacycle III, that after reductive elimination furnishes the bicyclic products.



Labelling Studies





Acknowledgement: This work was supported by the MEC (CTQ2008-06557), *Consolider Ingenio 2010 (CSD2007-00006), and the Xunta de Galicia (2007/XA084 and INCITE08PXIB209024PR). F.C. thanks Xunta de Galicia for a predoctoral contract.*