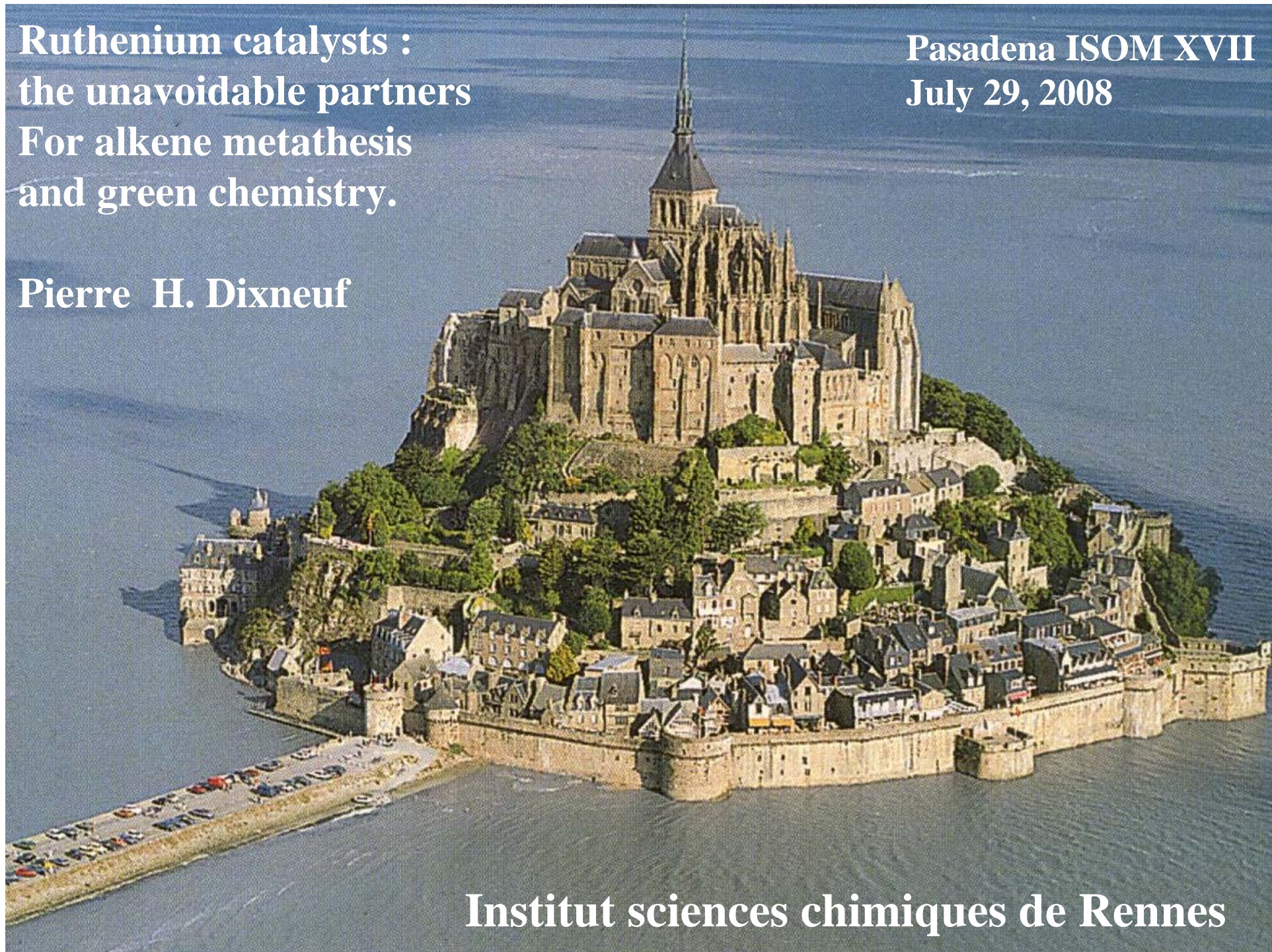


**Ruthenium catalysts :  
the unavoidable partners  
For alkene metathesis  
and green chemistry.**

**Pierre H. Dixneuf**

**Pasadena ISOM XVII  
July 29, 2008**



**Institut sciences chimiques de Rennes**



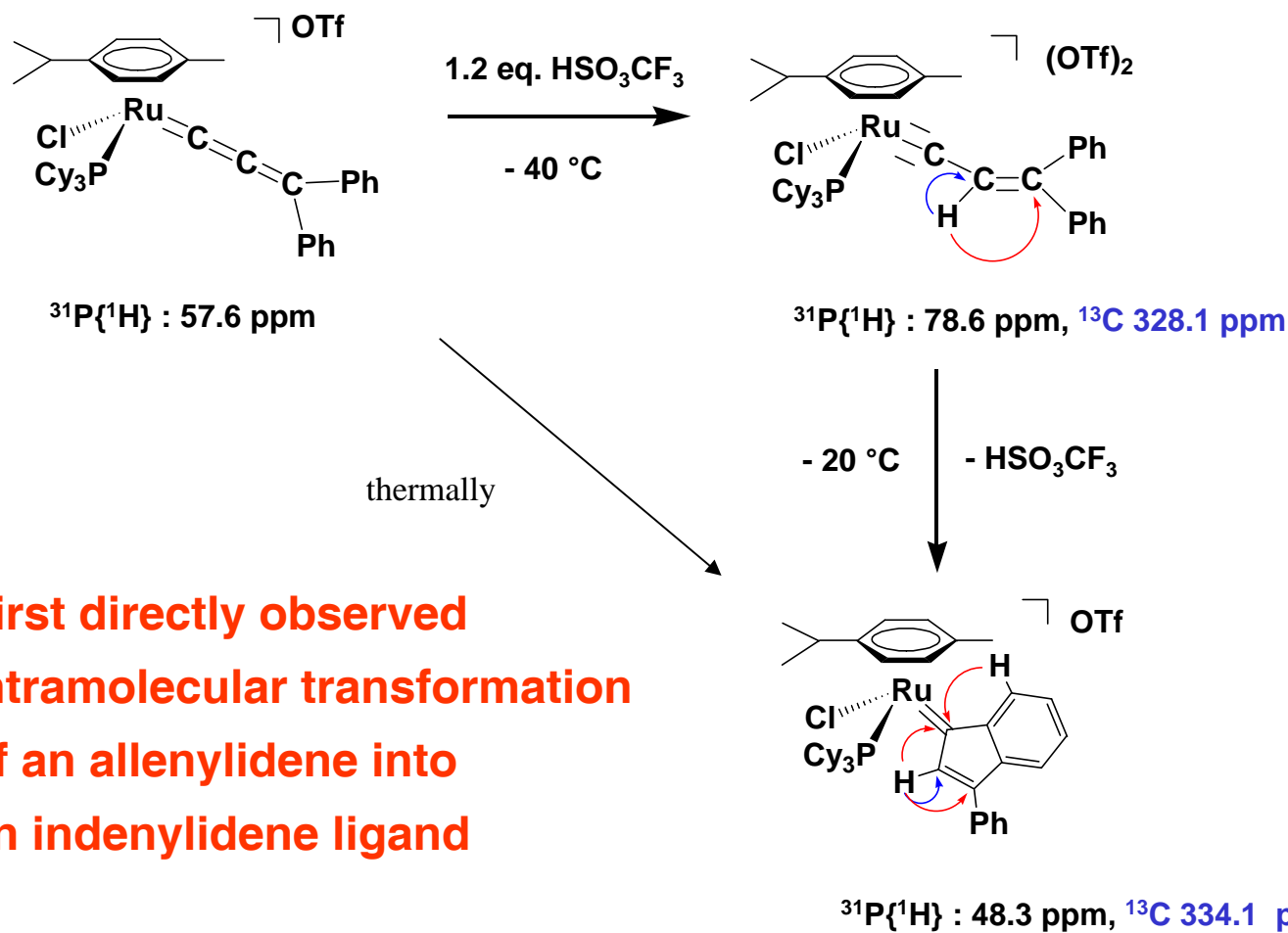
# ruthenium catalysts in alkene metathesis

## Rennes contribution

- . the ionic catalysts from arene-ruthenium allenylidene to indenylidene initiators
- . new OM initiators on Ru site action
  - Styrene
  - propargyl derivatives
- . metathesis in ionic liquids
- . ethenolysis of methyloleate
- . Alkene metathesis inhibitors



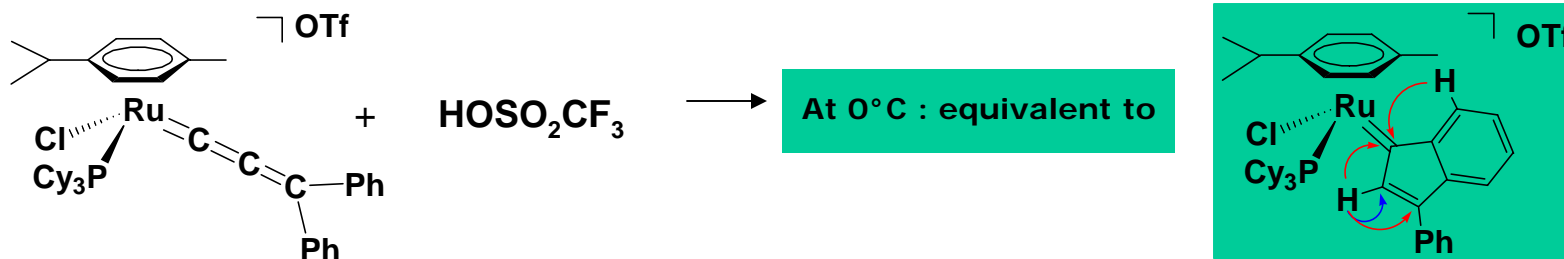
## Low Temperature NMR Study : Formation of Alkenylcarbyne and Indenylidene Species



**First directly observed  
Intramolecular transformation  
of an allenylidene into  
an indenylidene ligand**



## Cyclooctene polymerisation with various ruthenium-allenylidene derivatives



[cyclooctene]/[Ru] = 10.000 (5 eq. Acid)

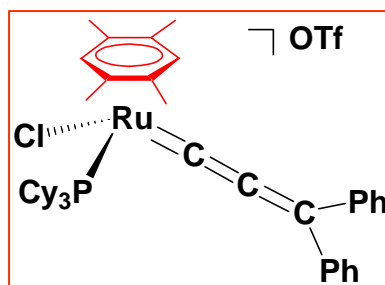
5 min r. t. 97 %  $M_n = 387 \times 10^3$ , PDI = 1.5

TOF = 116.400 mol/h

[cyclooctene]/[Ru] = 100.000 (100 eq. Acid)

5 min r. t. 88 %  $M_n = 857 \times 10^3$ , PDI = 1.4

TOF = 1.096.000 mol/h



5 min r. t. 92 %  $M_n = 286 \times 10^3$

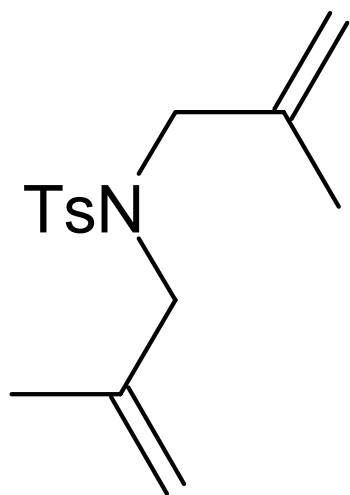
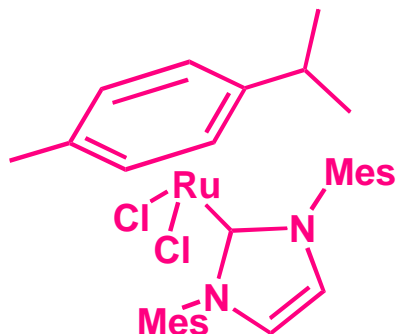
PDI = 1.6 TOF = 110.000 mol/h

[cyclooctene]/[Ru] = 10.000 (5 eq. Acid)

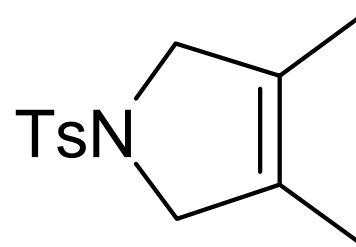
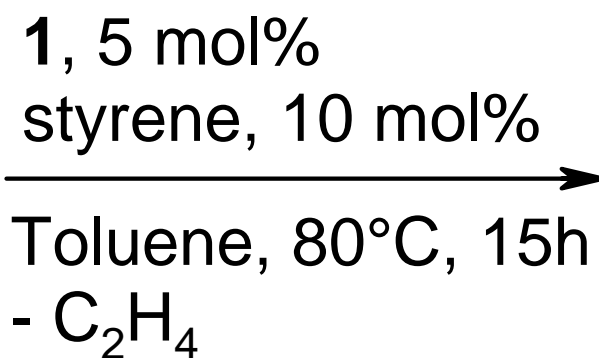


# Styrene as initiator for alkene metathesis

In reactions difficult to perform =  
formation of tetrasubstituted alkenes

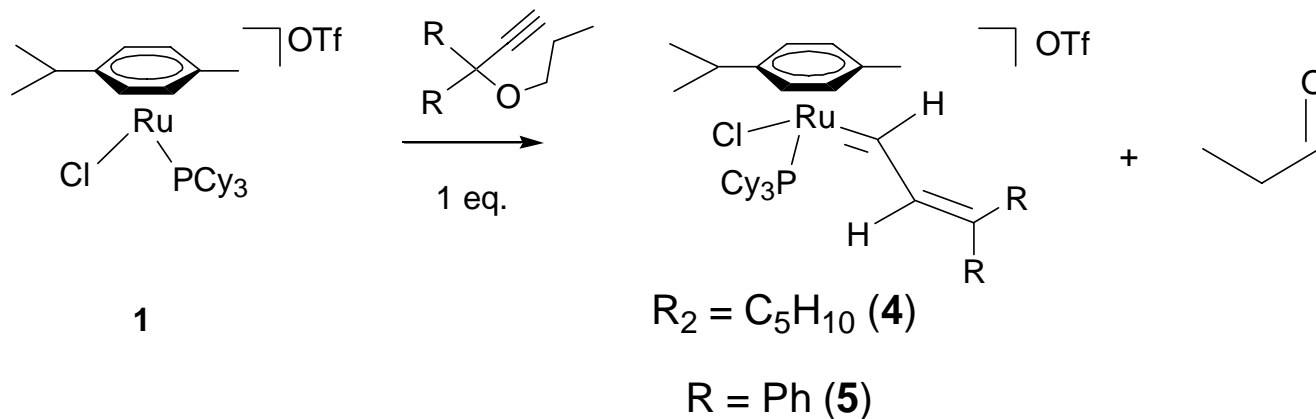


5



C= 70%

6



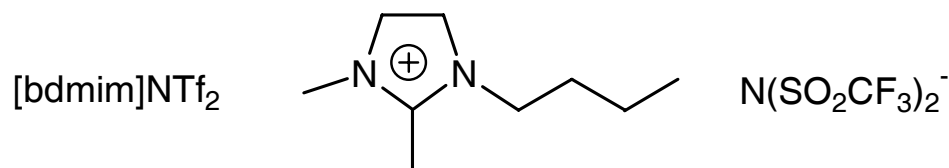
	<b>catalyst</b>	<b>substrate</b>	<b>product</b>		<b>Conversion(%)</b>	<b>TOF(h<sup>-1</sup>)</b>
<b>4</b>				1 h	99	49.50
<b>4</b>				15 min	99	198
<b>5</b>				15 min	95	190
<b>4</b>				4 h	99	12.37

**2 % mol catalyst at room temperature.**



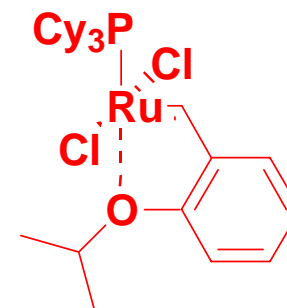
# Ethenolysis of methyl oleate In room temperature ionic liquids

5 mol % catalyst, 20°C, 10 bar, 2 h  
methyl oleate : 0.5 M in [bdmim]NTf<sub>2</sub>



extraction of reaction products with heptane. The catalyst is insoluble in heptane.

	Conv %	1-decene	9-decenoate
1 <sup>st</sup> run	95	95	95
2 <sup>nd</sup>	95	95	95
3 <sup>rd</sup>	85	85	85



only traces of self metathesis



# Enyne metathesis versus cyclopropanation

