

Towards Cross-Metathesis of Vinyl Halides

ISOM XVII
Pasadena, CA
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Marc J. A. Johnson

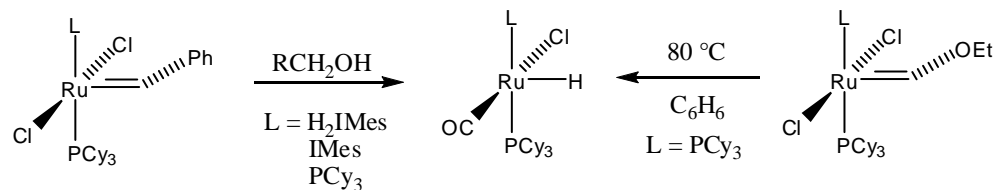
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Funding:

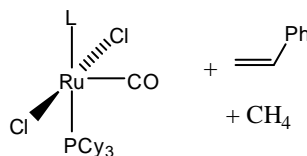
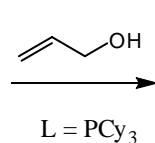
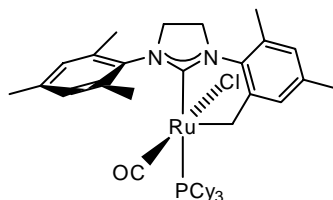
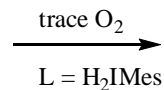
NSF
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Known Decomposition Products

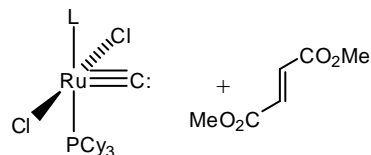
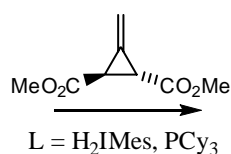


Grubbs & co-workers, *J. Am. Chem. Soc.* **2003**, 125, 2546

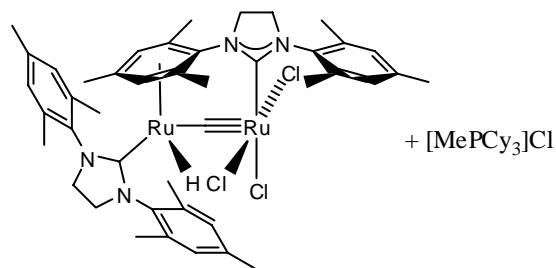
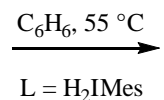
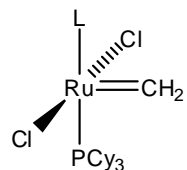
Louie & Grubbs, *Organometallics* **2002**, 21, 2153



Werner & co-workers, *Organometallics* **2003**, 22, 1558

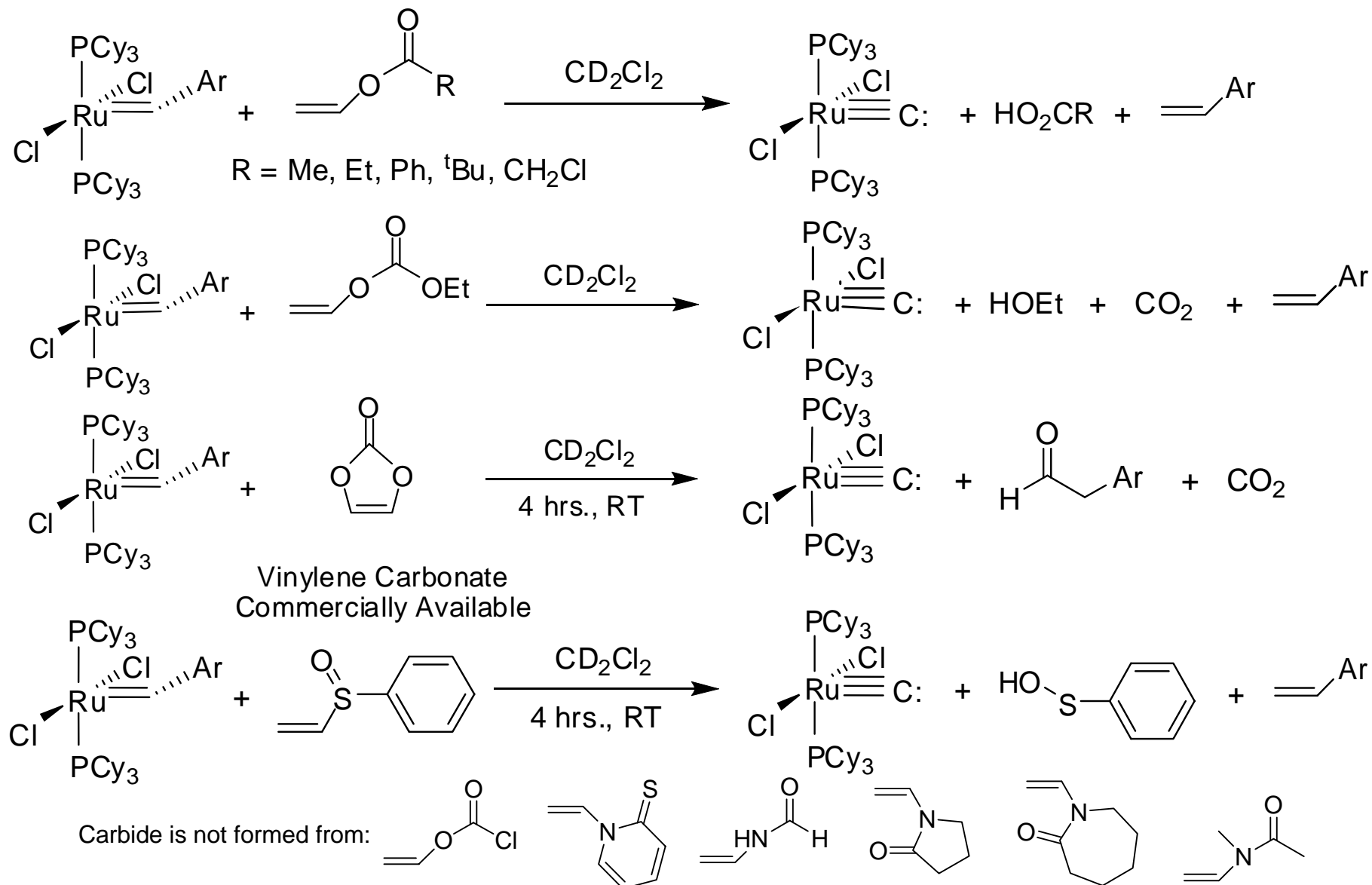


Heppert & co-workers, *J. Am. Chem. Soc.* **2002**, 124, 1580

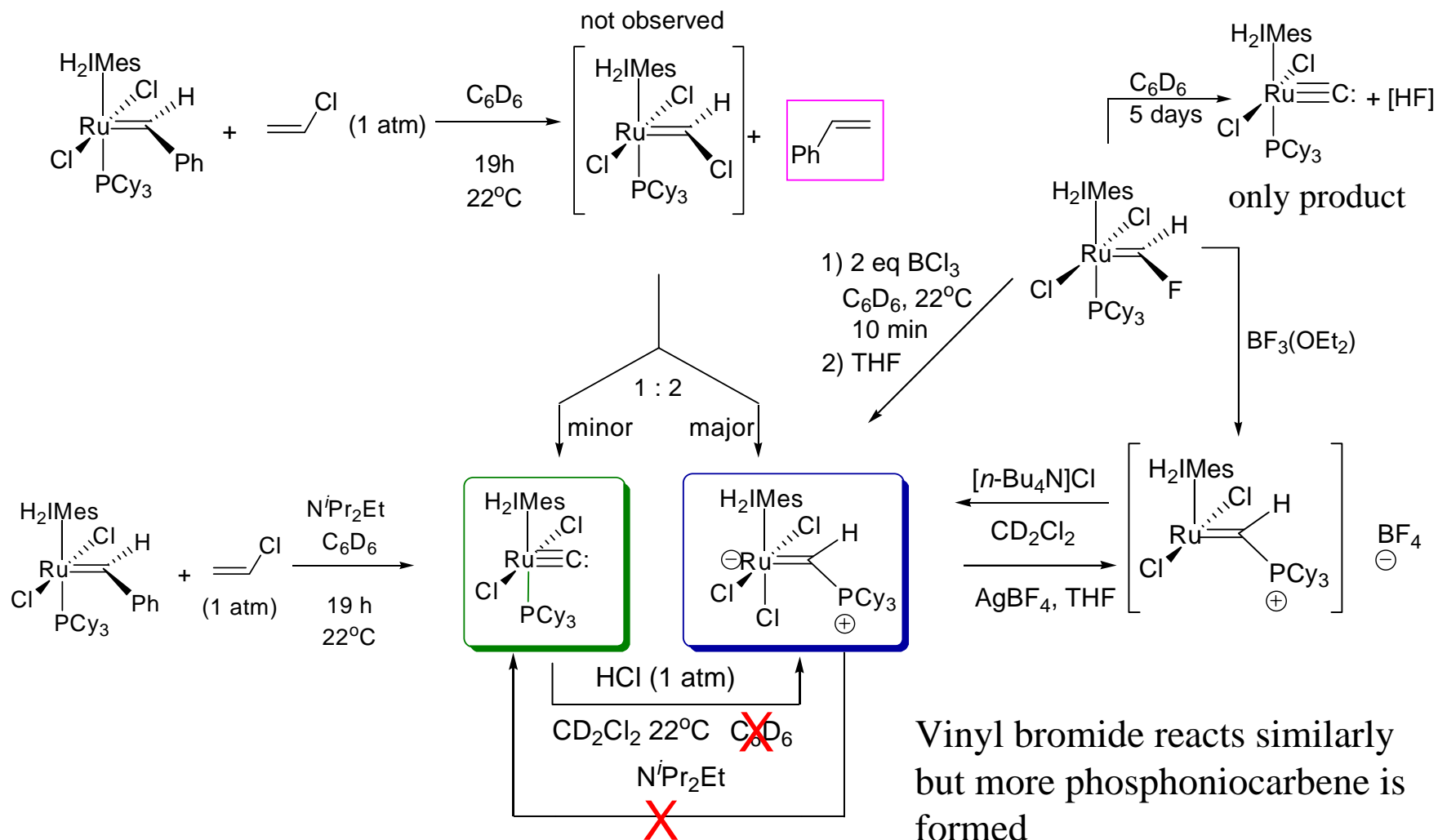


Hong & Grubbs, *J. Am. Chem. Soc.* **2004**, 126, 7414; *J. Am. Chem. Soc.* **2007**, 129, 7961

New Carbide-Forming Reaction: Acid Expulsion



Reactions Involving Monohalomethylidene

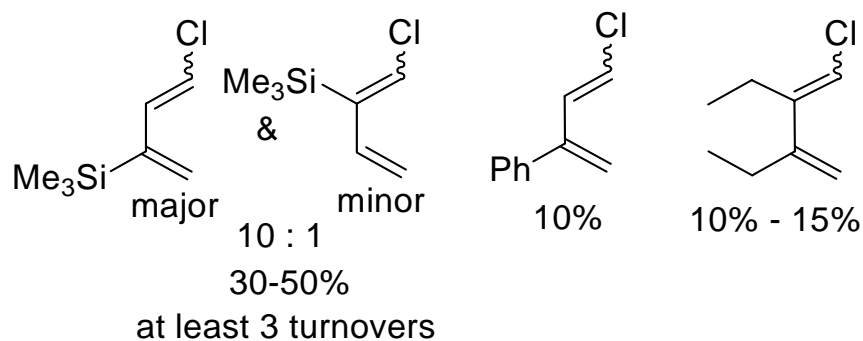
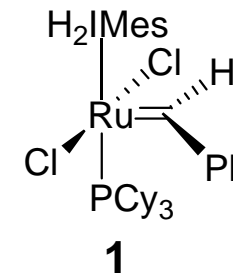
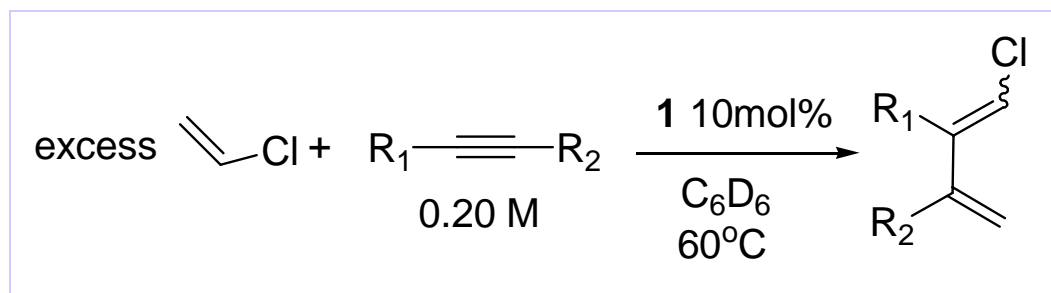


Macnaughtan M.L, Kampf, J.W., Johnson, M.J.A, *J. Am. Chem. Soc.* **2007**, 129, 7708

Macnaughtan M.L, Kampf, J.W., Johnson, M.J.A *Organometallics*, **2007**, 26, 780

Interception of the Ru=CHCl Unit

• Enyne metathesis



- Confirmation: ¹H NMR and GC-MS
- Sole initiation product is styrene
- Multiple turnovers – Ru=CHCl can be trapped

Summary

- Terminal carbido complex formation is a common decomposition pathway for many Fischer carbene complexes (explains many CM failures)
- Carbido ligands in these complexes are very weak bases
- Phosponiocarbene complexes form upon protonation of carbide ligand
- Rate of decomposition to carbide/phosponiocarbene complexes depends on C-X bond strength
- Carbide/phosponiocarbene ratio reflects acidity of HX
- $[\text{Ru}]=\text{CHO}_2\text{CR}$ undergoes exchange of O_2CR group with $\text{HO}_2\text{CR}'$
- Two thermodynamic strategies for avoiding carbide formation:
 - 5th ligand weak or absent
 - ligand trans to incipient carbide