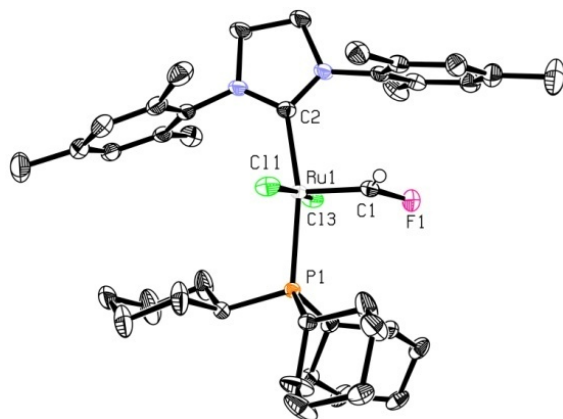
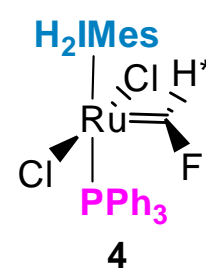
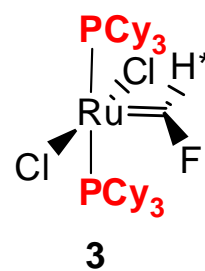
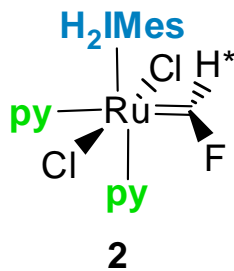
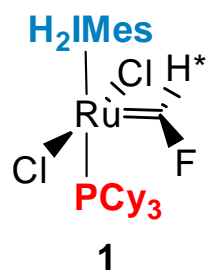


# Monofluoromethylidene Complexes



XRD of 1



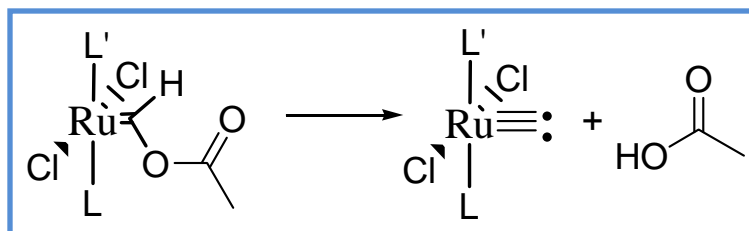
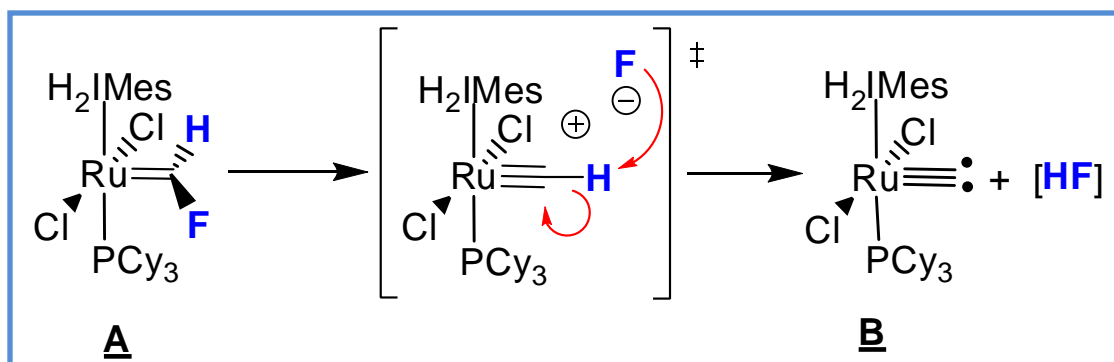
*The first isolable monofluoromethylidene complexes of any transition metal*

NMR (C <sub>6</sub> D <sub>6</sub> )	<sup>1</sup> H* (ppm)	<sup>19</sup> F (ppm)	<sup>31</sup> P (ppm)	<sup>2</sup> J <sub>HF</sub> (Hz)	<sup>3</sup> J <sub>PF</sub> (Hz)	<sup>13</sup> C (ppm)	<sup>1</sup> J <sub>CF</sub> (Hz)
1	13.1 (d)	113.7 (d)	32.6 (s)	106	N/A	283	416
2	13.4 (d)	130.4 (d)	N/A	90	N/A	-	-
3	14.2 (d)	127.0 (dt)	34.1 (d)	110	14	-	-
4	12.8 (d)	137.3 (dd)	35.0 (d)	108	54	-	-

**All four compounds decompose in solution to form the corresponding carbides**

# Why Current Catalysts Fail for Cross Metathesis with Vinyl Fluorides

- 1) **Decomposition** of monohalomethylidene species through C-X bond scission
- X=Cl, Br is more problematic than X=F
  - All four monofluoromethylidene compounds **eventually decompose in solution (over days)** to form the corresponding carbides



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

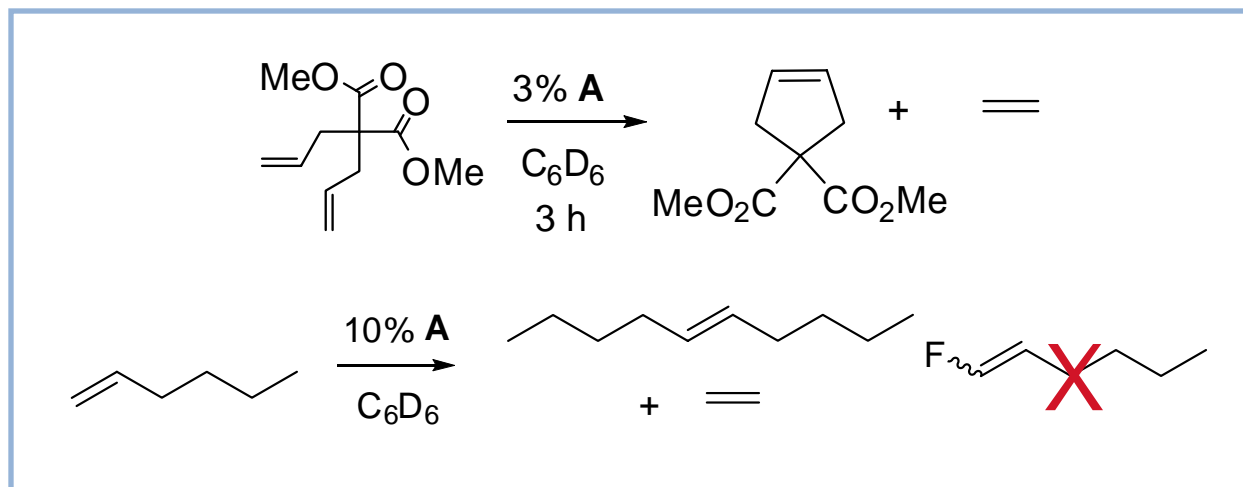
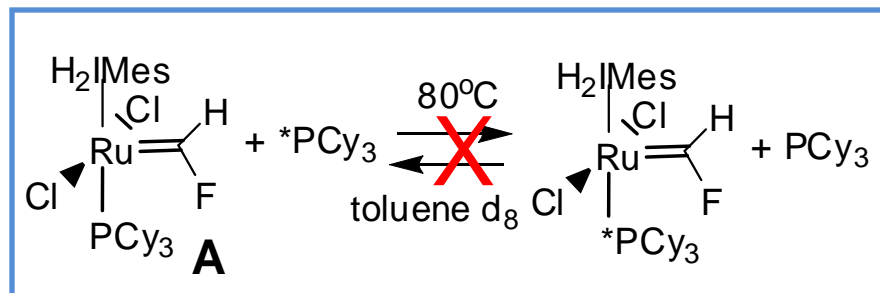
Caskey, S.R., Stewart, M.H., Kivela, J.E., Sootsman, J.R., Johnson, M.J.A., Kampf, J.W. *J. Am. Chem. Soc.* **2005**, 127, 16750

# Why Current Catalysts Fail for Cross Metathesis with Vinyl Fluoride

1) Decomposition (takes days)

2) **Phosphine loss is hindered** by the presence of  $\alpha$ -X group

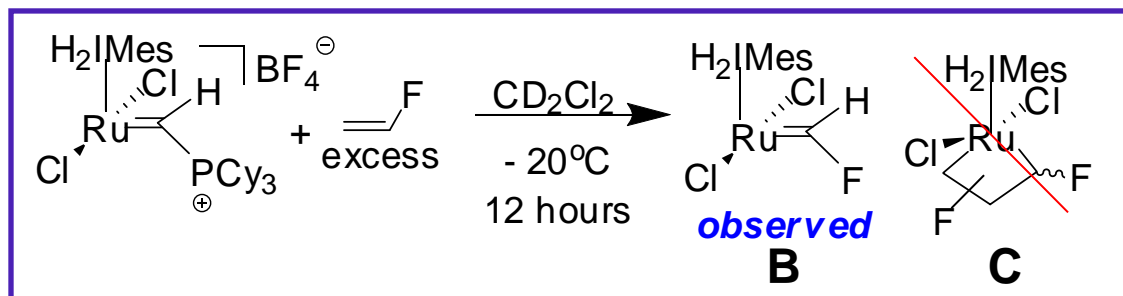
▪ **No phosphine exchange is observed** (on an NMR time scale) via  $^{31}\text{P}$ -Magnetization Transfer NMR for **A**



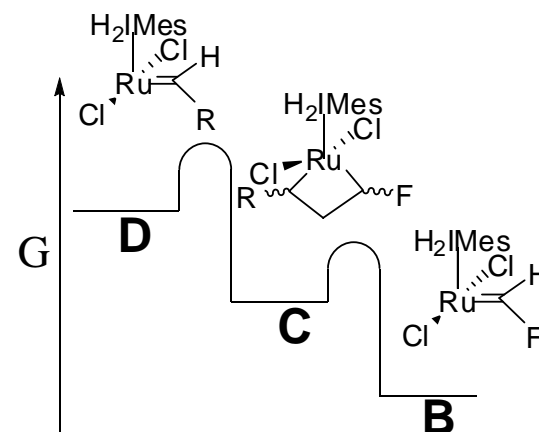
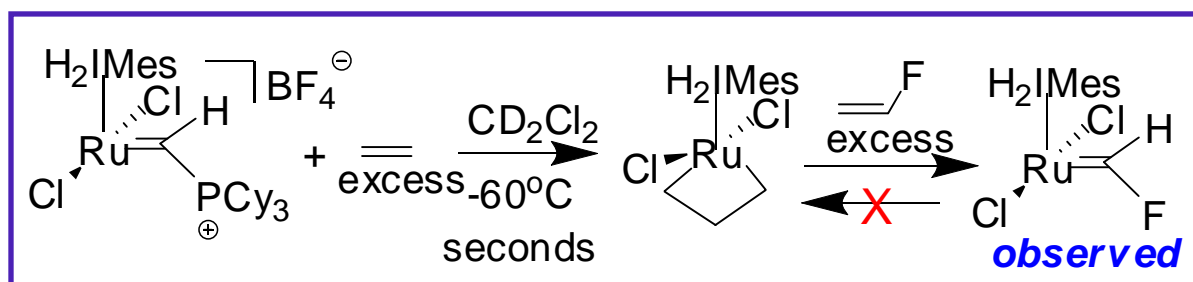
▪ **A** is a sluggish *OM* catalyst

# Why Current Catalysts Fail for Cross Metathesis with Vinyl Fluoride

- 1) Decomposition (takes days)
- 2) Phosphine loss is hindered (but still occurs)
- 3) **Thermodynamic Stability:** The most pressing problem with vinyl fluorides



▪ Only B was observed (may be dimeric)



▪ **DFT calculations** indicate that **B** is more stable than its corresponding metalacycles (**C**) and 14-electron alkylidene complexes (**D**)

▪ Romero, P.E., Piers W.E. *J. Am. Chem. Soc.* **2005**, 127, 5032-5033

# Conclusions

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- Four monofluoromethylidene complexes have been isolated and characterized
  - All decompose slowly in solution to their corresponding carbide
- Vinyl fluoride is a viable substrate in enyne metathesis with current catalysts
- *More thermally stable* catalysts to initiate olefin metathesis with vinyl fluorides are needed
- Tunable tridentate (XLX) ligands may afford viable catalyst for olefin metathesis with vinyl fluoride along with other directly substituted olefins