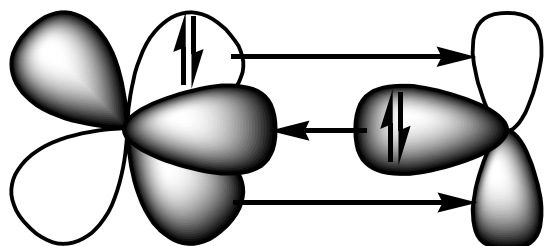
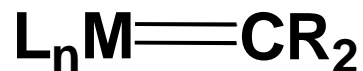
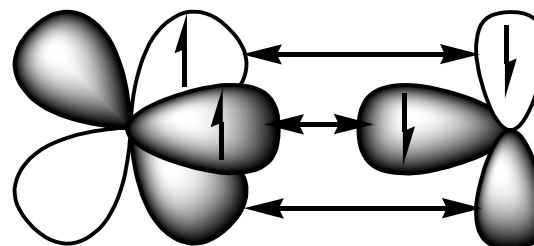


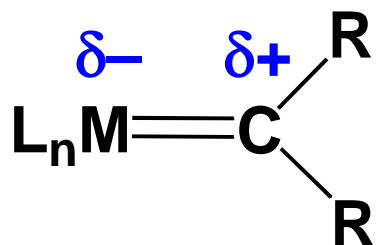
Metal Carbene Complexes



Carbene

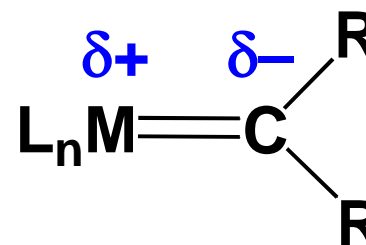


Alkylidene



Electrophilic

- usually possess heteroatom (electronegative) substituents



Nucleophilic

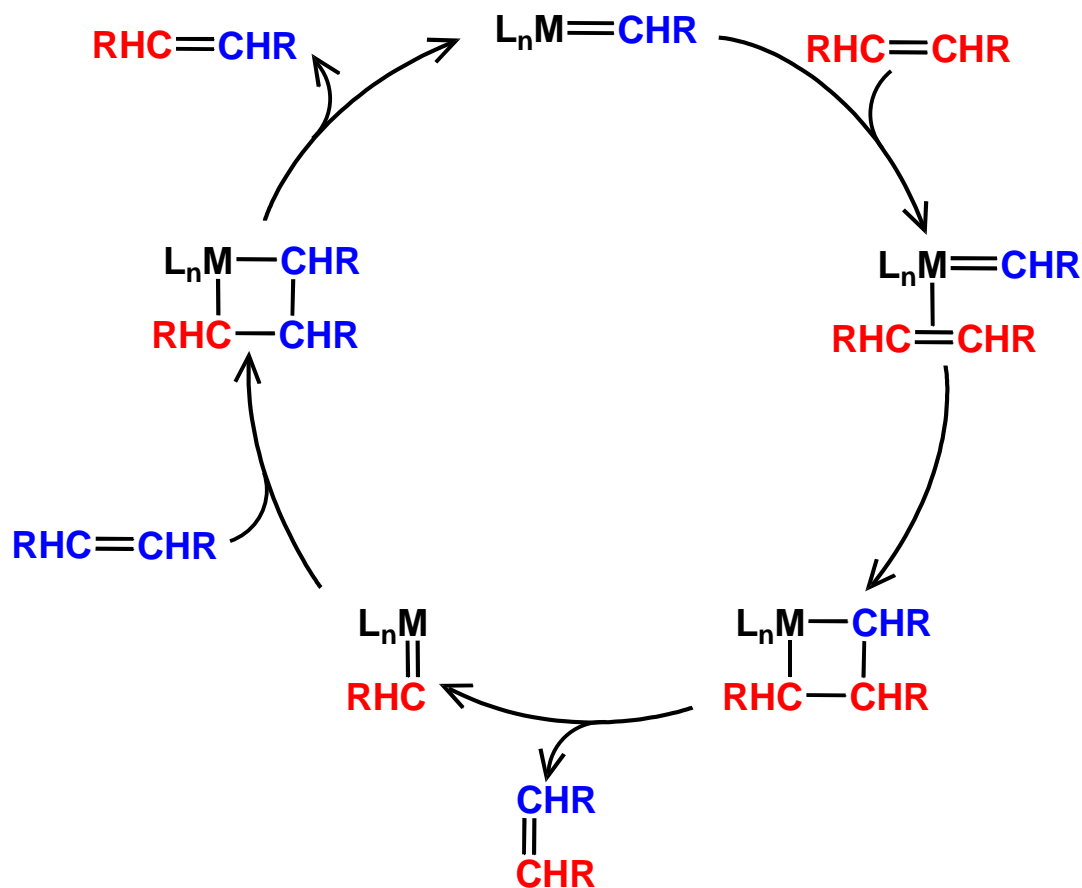
- usually possess alkyl or hydrogen substituents

$L_nM=CR_2$ Chemistry

2005 Nobel Prize: Chauvin, Grubbs, Schrock



Catalytic Olefin Metathesis:

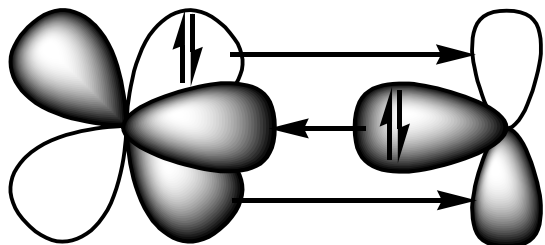
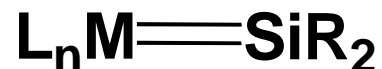


$L_nM=CR_2$ vs. $L_nM=SiR_2$

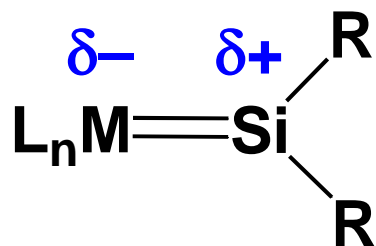
	$L_nM=CR_2$	$L_nM=SiR_2$
First Prepared	1964 (Fischer) 1974 (Schrock)	1990 (Tilley)
Known Compounds	thousands	hundreds
Reactivity	Nucleophilic and electrophilic	Electrophilic Only
Synthetic Utility	-Olefin metathesis -Organic synthesis -Metal carbyne precursors	-Proposed in numerous catalytic processes -Largely unexplored

- Main Group – Pronounced differences in chemistry within the same group

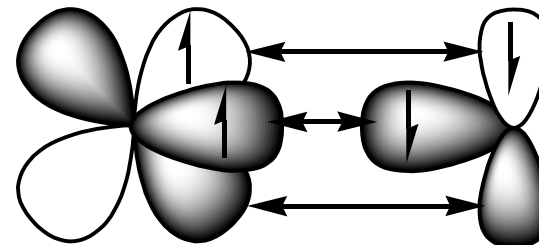
Metal Silylene Complexes



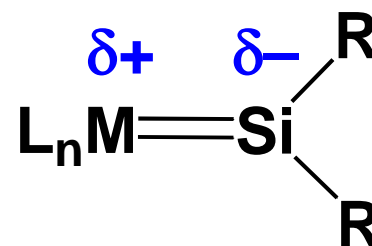
Silylene



Electrophilic



Silylidene

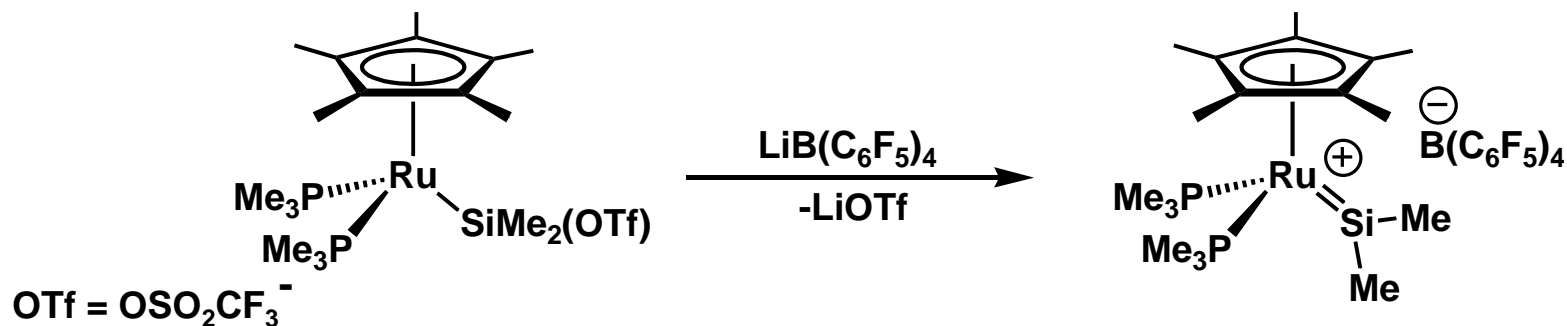


Nucleophilic

- No known complexes with silylidene character
- $\chi(C) = 2.55$, $\chi(Si) = 1.90$ – free silylenes have singlet character

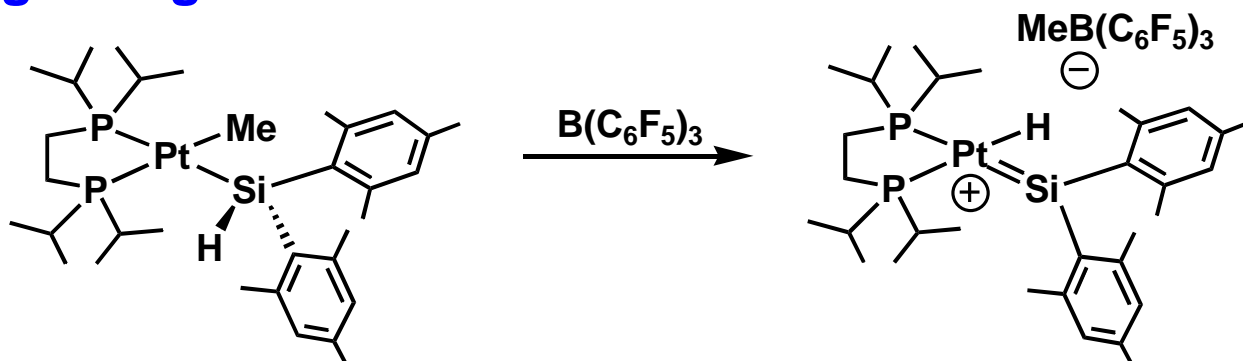
Synthetic Strategies for M=Si Compounds

Anionic Substituent Abstraction



Grubbine, S. K.; Tilley, T. D. *J. Am. Chem. Soc.* **1994**, *116*, 5495.

α-Hydrogen Migration

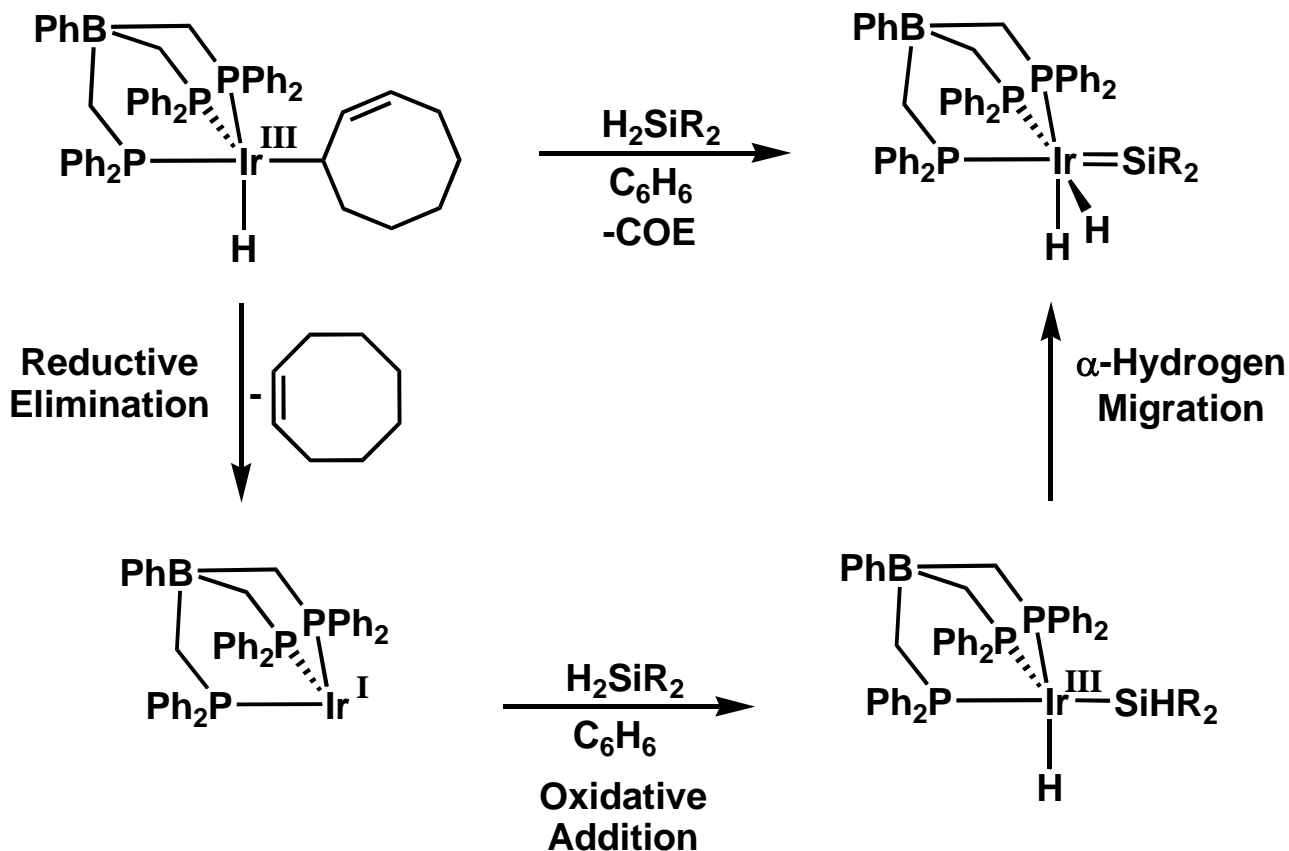


Mitchell, G. P.; Tilley, T. D. *Angew. Chem. Int. Ed.* **1998**, *37*, 2524.

Waterman, R.; Hayes, P. G.; Tilley, T. D. *Acc. Chem. Res.* **2007**, *40*, 712.

Synthetic Strategies for $L_nM=SiR_2$ Compounds

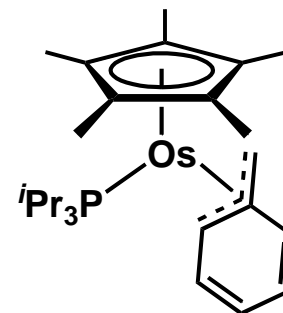
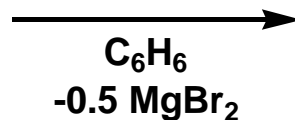
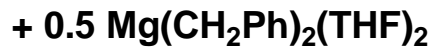
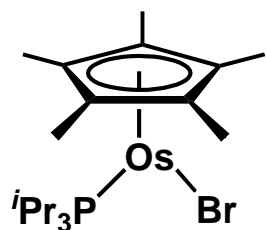
Double Si-H Activation (Silylene Extrusion)



Peters, J. C.; Feldman, J. D.; Tilley, T. D. *J. Am. Chem. Soc.* **1999**, *121*, 9871.

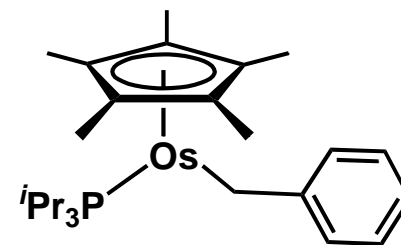
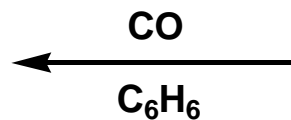
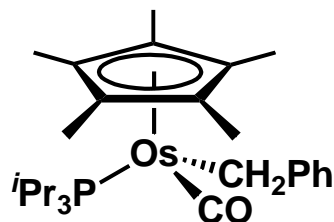
Waterman, R.; Hayes, P. G.; Tilley, T. D. *Acc. Chem. Res.* **2007**, *40*, 712.

$Cp^*(iPr_3P)OsCH_2Ph$



- 16 e⁻
- 4 steps from OsO_4

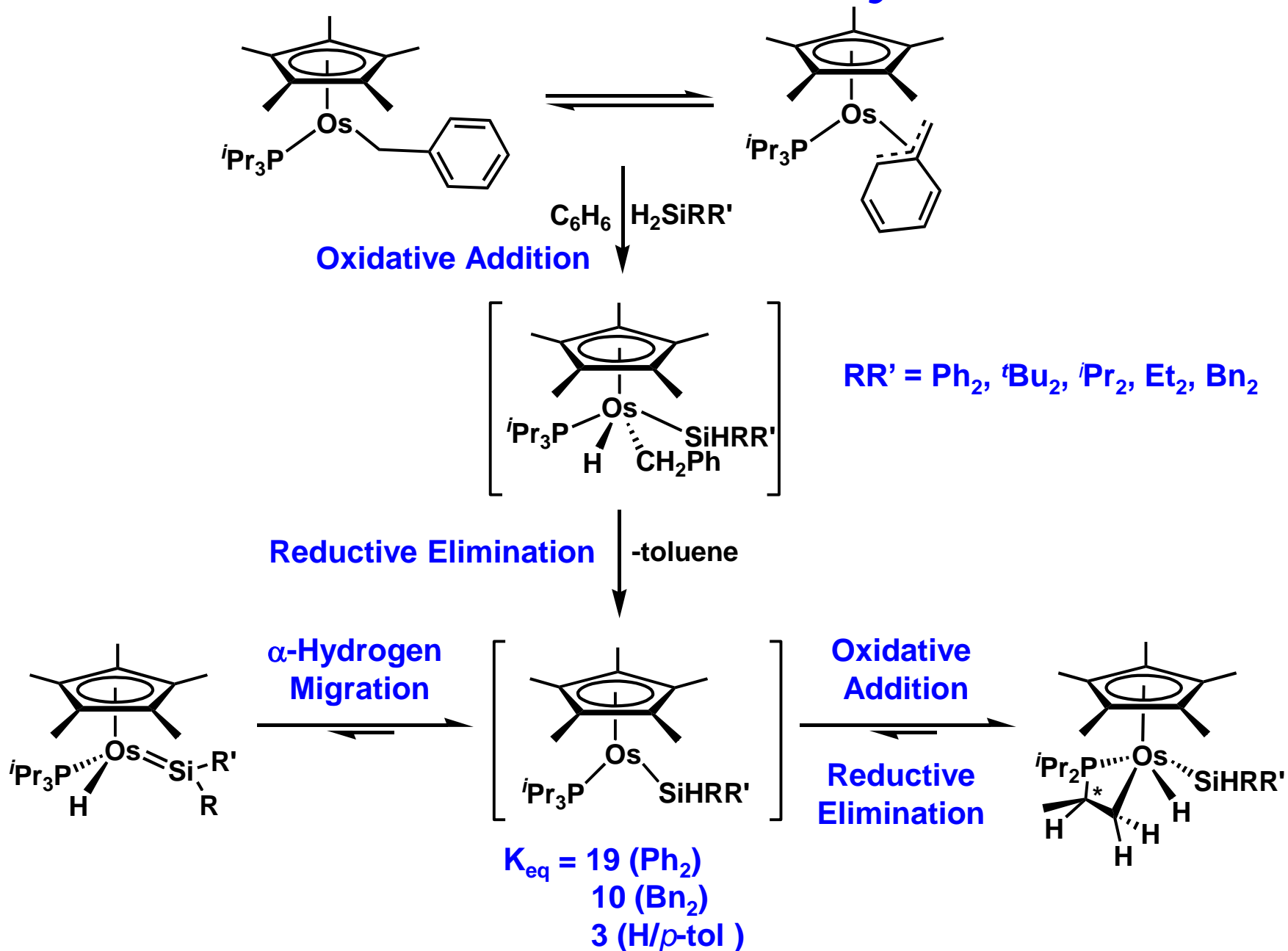
Glaser, P. B.; Tilley, T. D. *Eur. J. Inorg. Chem.* **2001**, 2747.



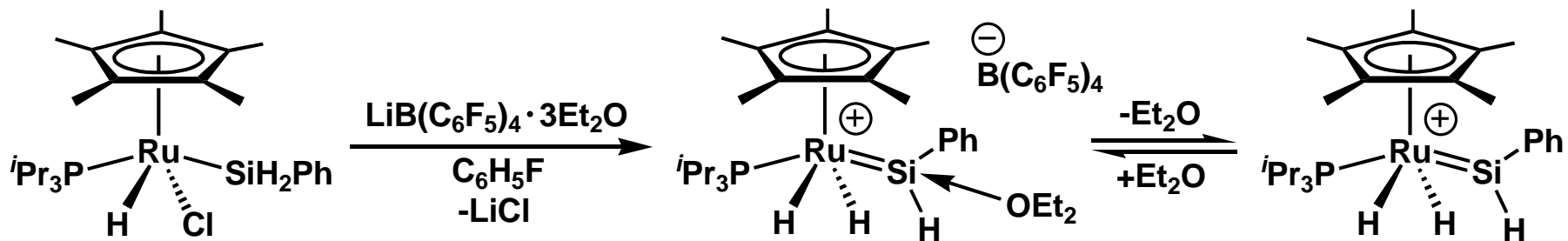
- Pale yellow crystals (62%)
- ^{13}C NMR (CO): δ 193
- ν_{CO} : 1883 cm^{-1}

- Fluxional
- ^{31}P NMR: δ 22
- $t_{1/2} \sim 1$ hour at RT

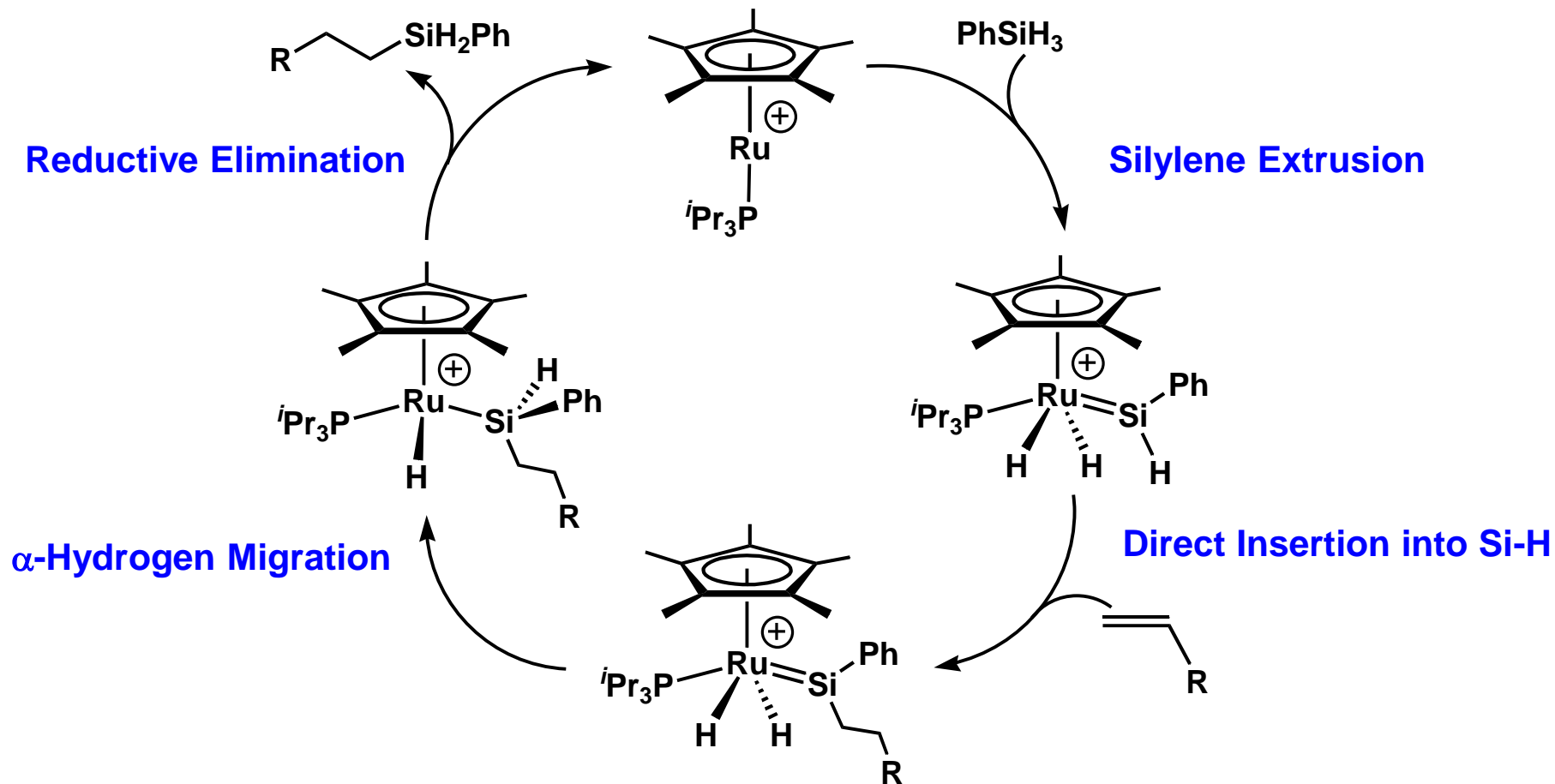
Reactions with Secondary Silanes



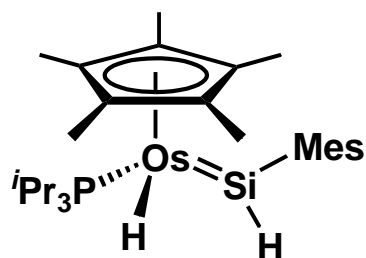
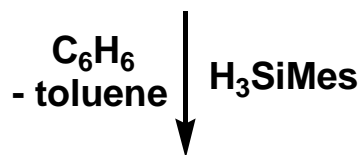
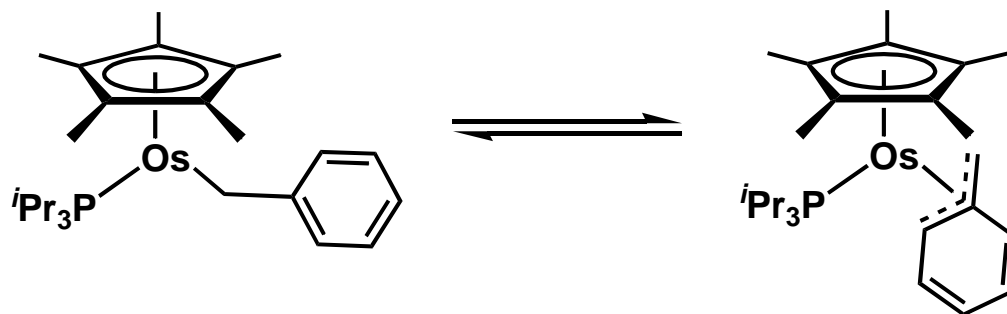
H-Substituted Silylene Compounds



Glaser, P. B.; Tilley, T. D. *J. Am. Chem. Soc.* **2003**, *125*, 13640.

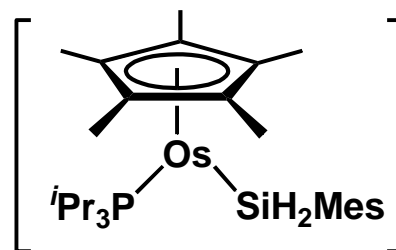


Reaction with MesSiH_3

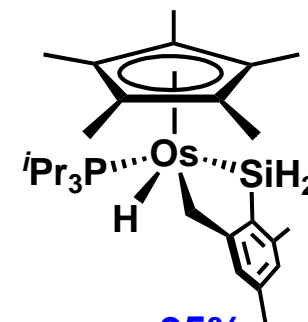


5%

- ^{31}P NMR: δ 41.0
- ^1H NMR: δ -15.9 (Os-H)
 δ 12.1 (Si-H)



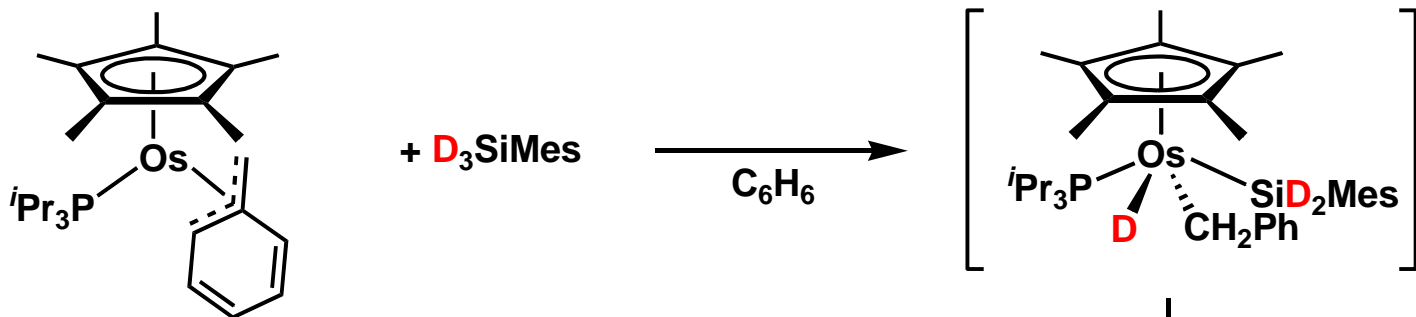
Beige solid (74%)



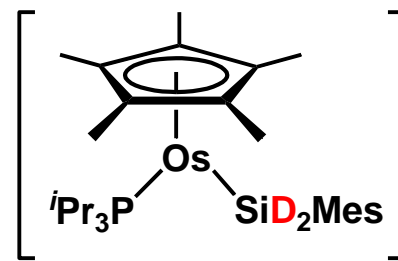
95%

- ^{31}P NMR: δ 41.2
- ^1H NMR: δ -15.7 (Os-H)
 δ 4.91, 6.45 (Si-H)
- ^{29}Si NMR: δ -21

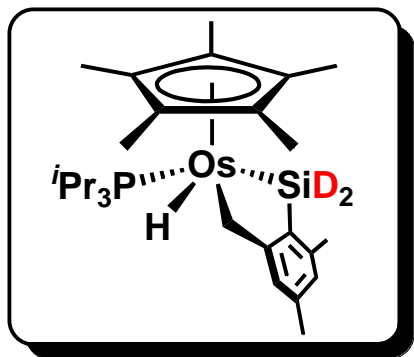
Mechanism of C-H Activation



$-d_1$ -toluene

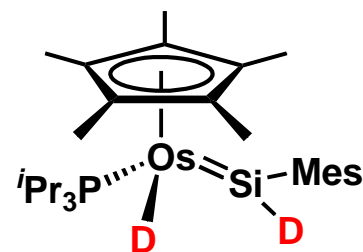


Path A:
Direct Addition

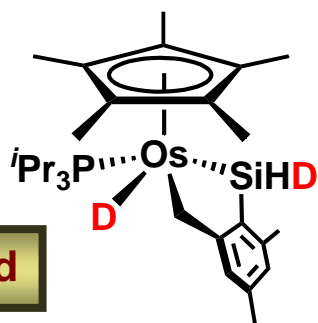


Exclusive
Product

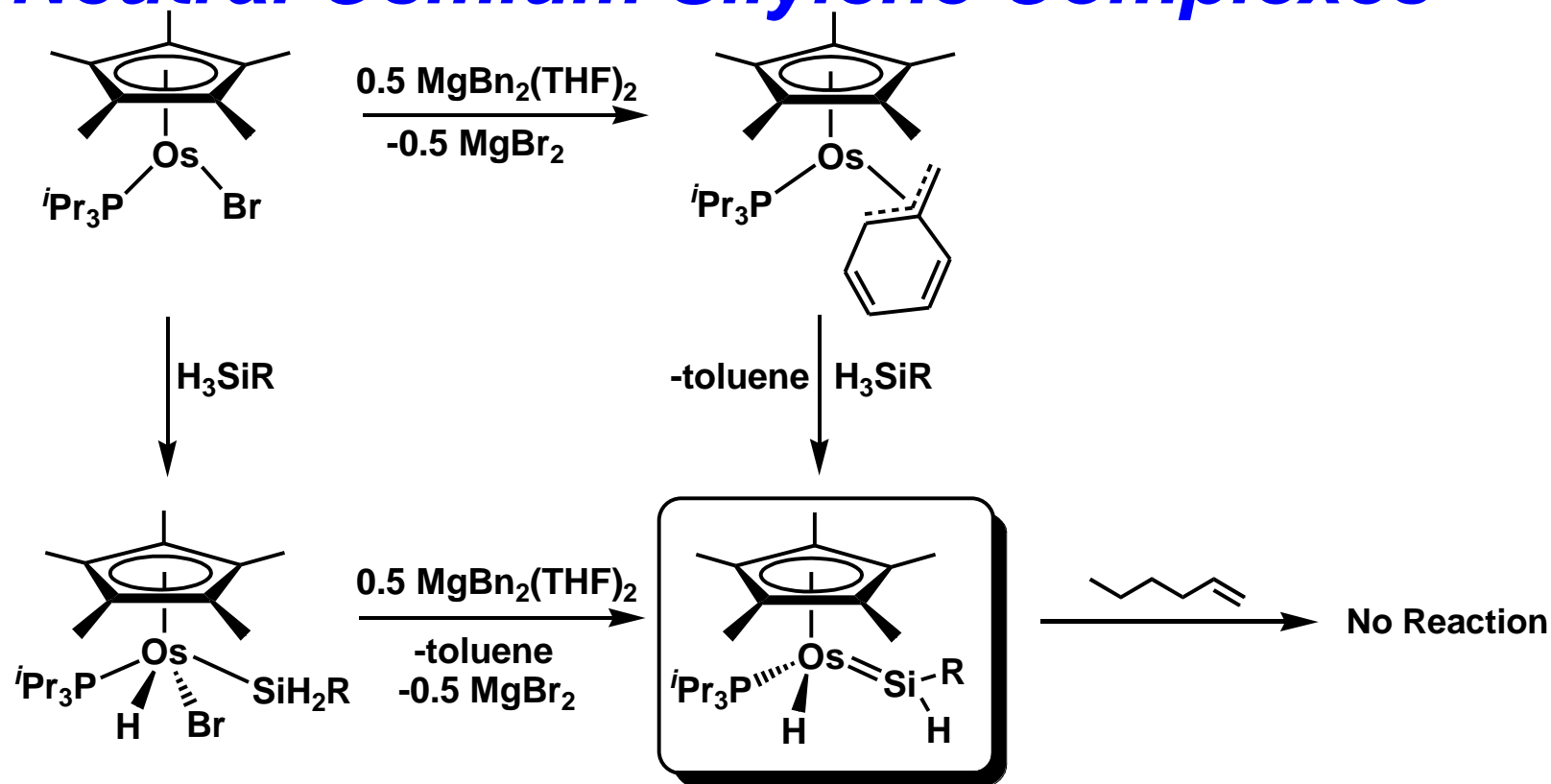
Path B:
C-H Addition
Across $Os=Si$



Not Observed

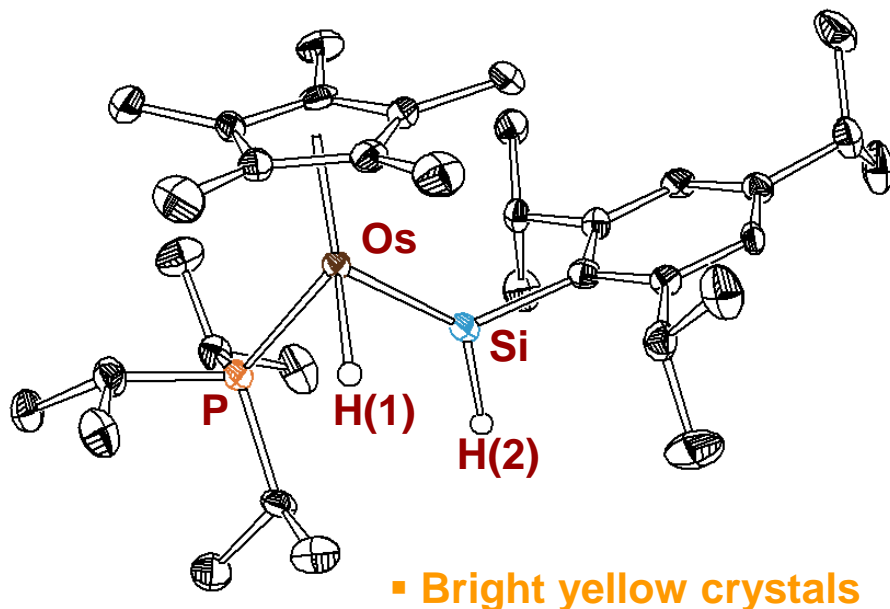


Neutral Osmium Silylene Complexes



NMR	R = 2,4,6- <i>i</i> Pr ₃ C ₆ H ₂ (trip)	R = 2,6-Mes ₂ C ₆ H ₃ (dmp)	R = 2,4,6-(CF ₃) ₃ -C ₆ H ₂ (Mes ^F)
¹ H (δ)	12.1 (SiH) -16.0 (OsH)	11.6 (SiH) -16.9 (OsH)	11.2 (SiH) -16.5 (OsH)
²⁹ Si (δ)	229	217	N/A
¹ J _{Si-H} (Hz)	144	149	N/A
² J _{Si-H} (Hz)	6.6	7.7	N/A

Solid State Structure of $Cp^*(iPr_3P)(H)Os=SiH(trip)$

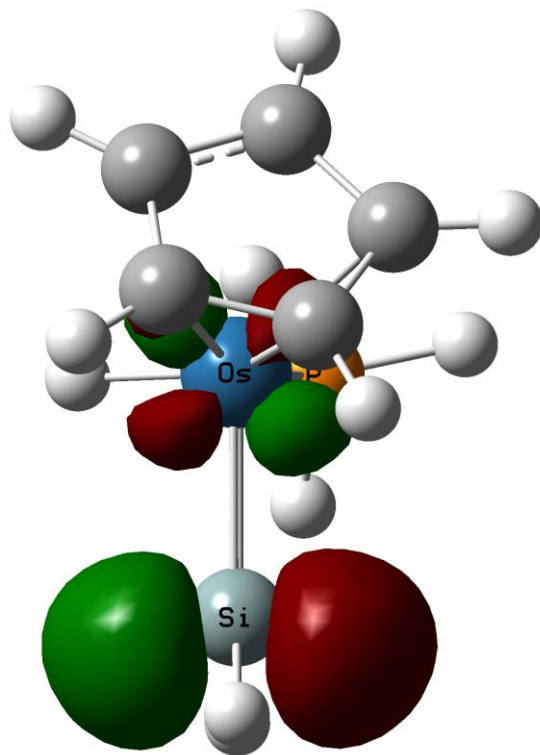


- Crystals grown from cold pentane
- Sum of angles at Si = 359.8°

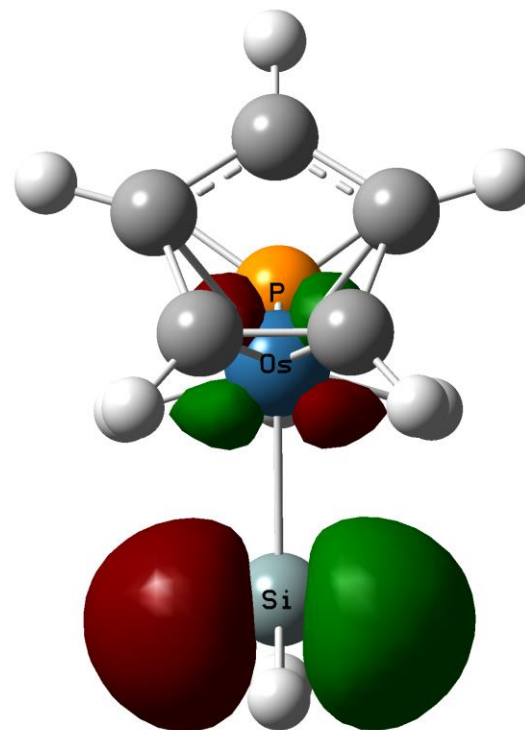
Bond Lengths (Å)	
Os-Si	2.219(1)
Os-P	2.293(1)
Os-Cp*	2.218(5) – 2.351(5)
Os-H(1)	1.87(1)
Si-H(2)	1.48(1)

Bond/Dihedral Angles (°)	
Os-Si-C	129.7(2)
P-Os-Si	90.9(1)
Os-Si-H(2)	131.5(2)
C-Si-H(2)	98.6(2)
H(1)-Os-Si-H(2)	53.2(2)
P-Os-Si-C	19.7(2)

Calculated LUMOs for Silylene Complexes



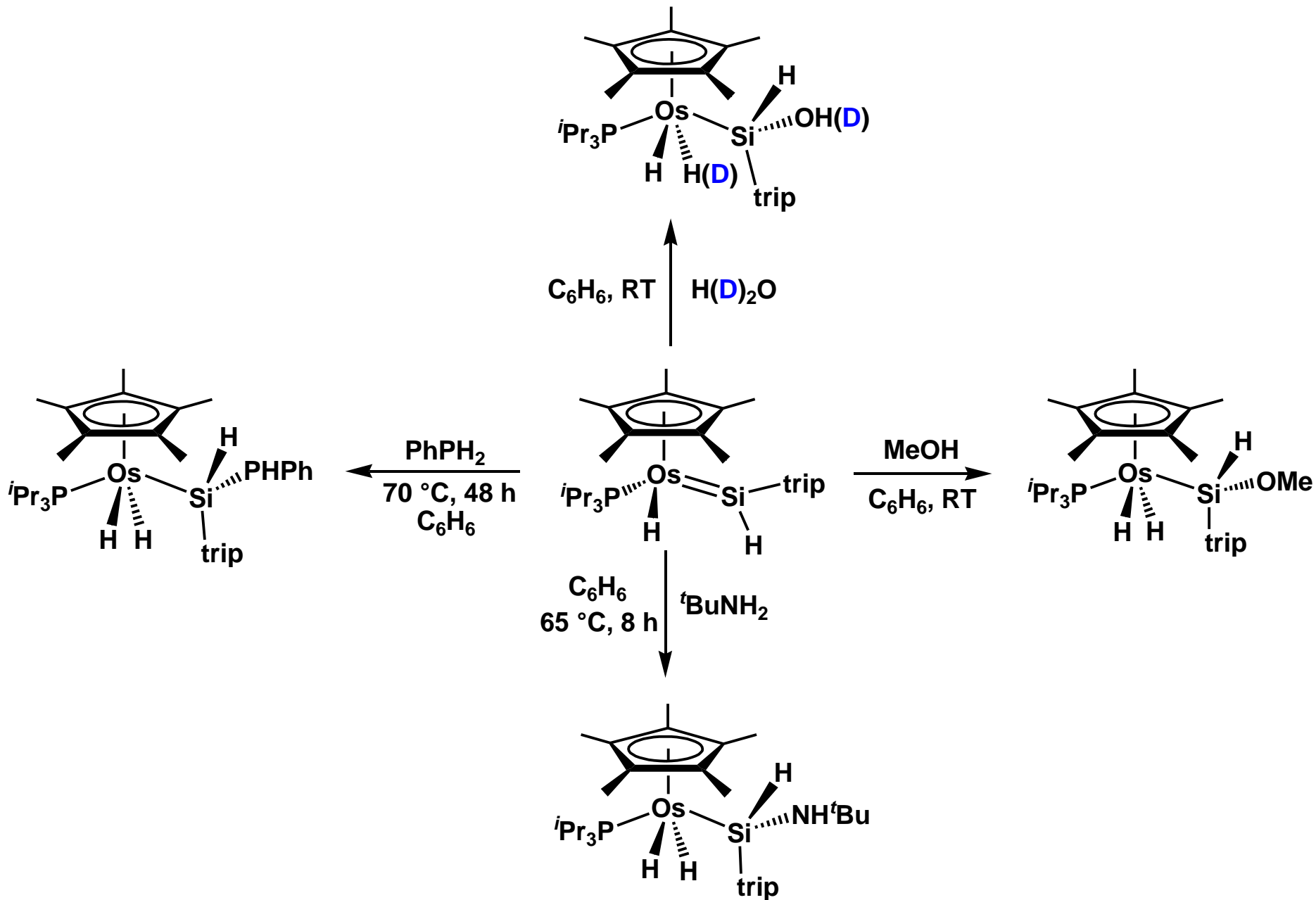
LUMO of $\text{Cp}(\text{H}_3\text{P})(\text{H})\text{Os}=\text{SiH}_2$
(-0.051 eV)



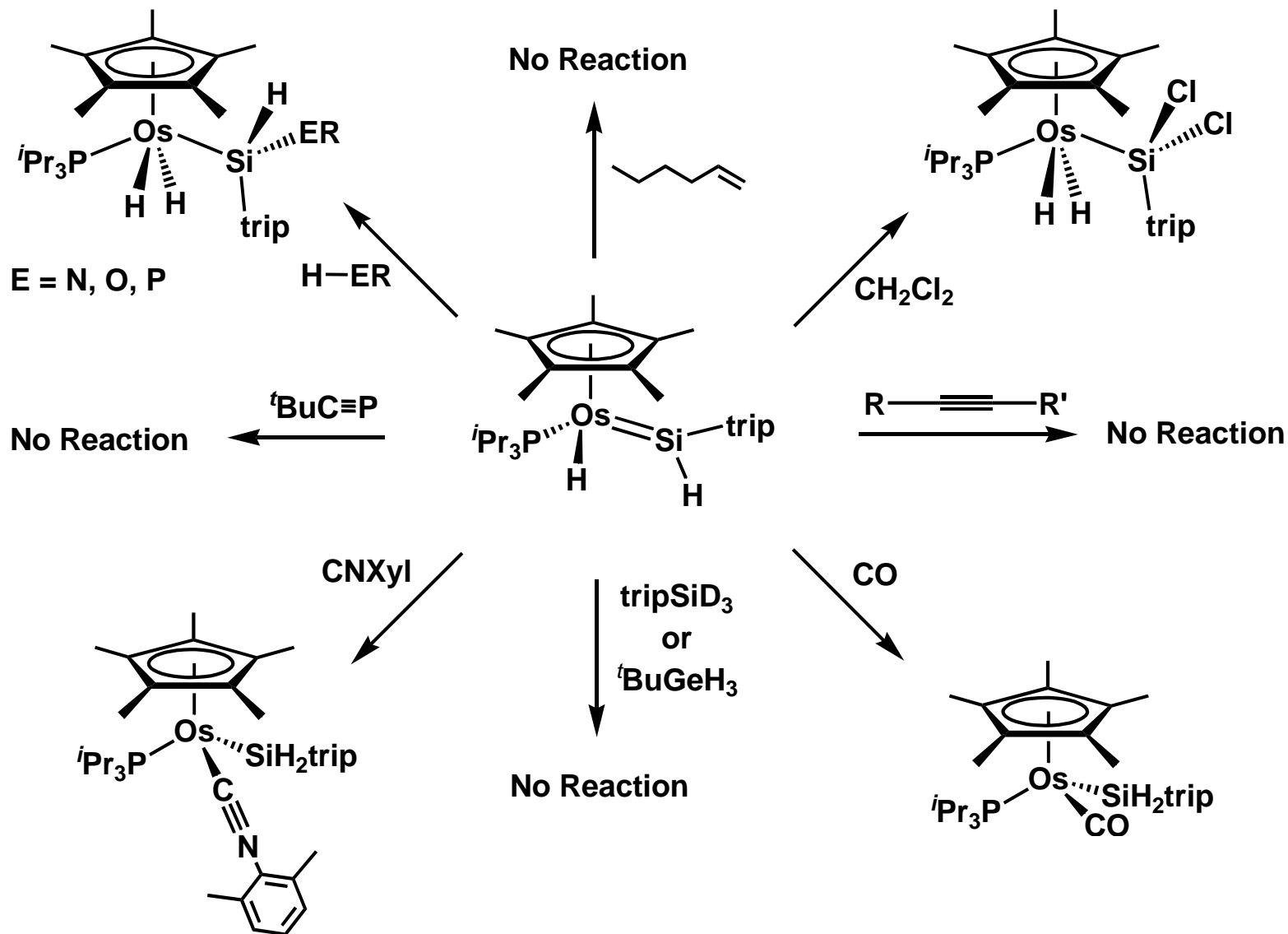
LUMO of $\text{Cp}(\text{H}_3\text{P})(\text{H})_2\text{Os}=\text{SiH}_2^+$
(-0.232 eV)

- LUMO is primarily a Si p -orbital
- Coordination of olefin to Si involves interaction of $\text{Os}=\text{Si}$ LUMO with the olefin HOMO
- LUMO of charged species is much closer in energy to HOMO of olefin (-0.267eV)

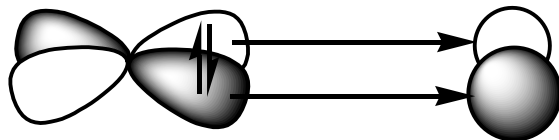
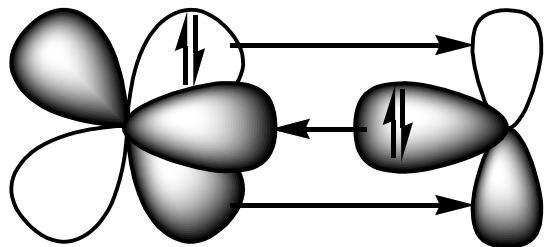
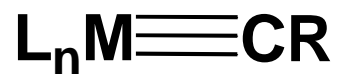
Activation of E-H Bonds



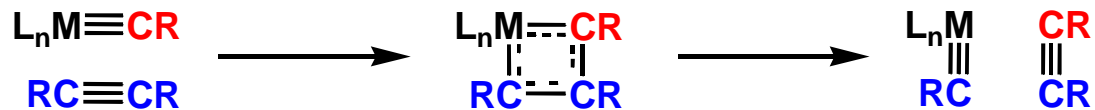
Summary of Small Molecule Reactivity



Metal Carbyne Complexes

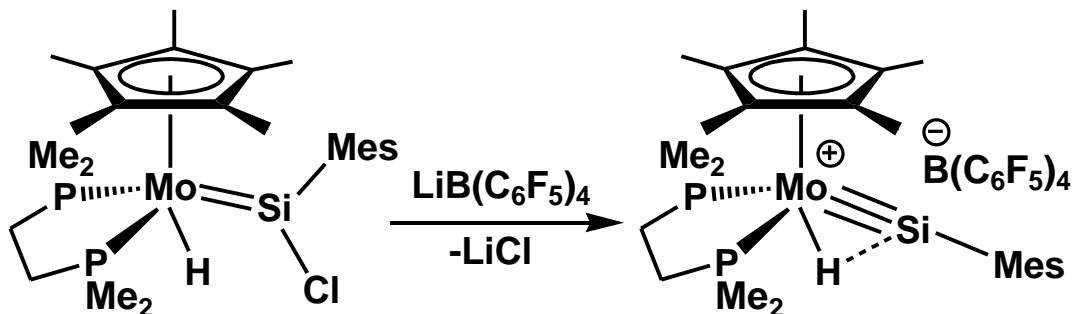


Alkyne Metathesis:

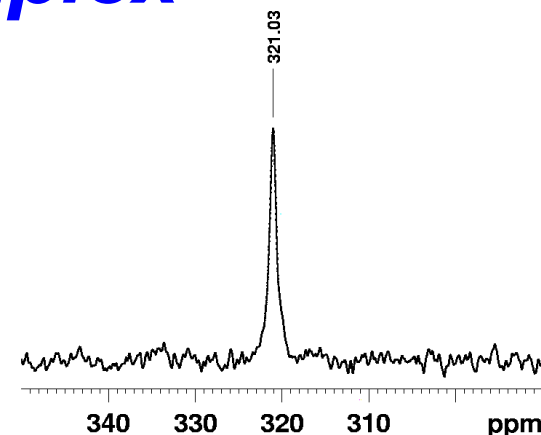
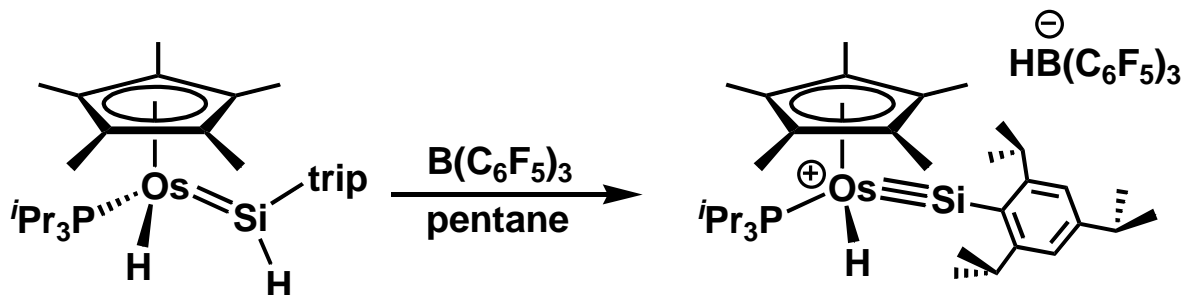


$L_nM\equiv CR$ vs. $L_nM\equiv SiR$

	$L_nM\equiv CR$	$L_nM\equiv SiR$
First Prepared	1973 (Fischer)	2003 (Tilley)
Known Compounds	>1000	<100
Reactivity	Nucleophilic and electrophilic	?
Synthetic Utility	-Alkyne metathesis -Alkyne polymerization -Carbide precursors	?



Osmium Silylyne Complex



▪ ^{29}Si NMR: δ 229

▪ Deep red powder (58%)

▪ ^1H NMR: δ -14.5 (Os-H)
 δ 4.39 (B-H)

▪ $t_{1/2} \sim 30$ mins at RT ($\text{C}_6\text{D}_5\text{Br}$)

▪ ^{29}Si NMR: δ 321

▪ whh = 86 Hz

▪ $^2J_{\text{SiH}} = ?$

Cation-Anion Interaction?

Spectroscopic parameters for free $\text{RB}(\text{C}_6\text{F}_5)_3^-$:

▪ ^{11}B NMR: δ -20 to -25

▪ ^{19}F NMR: $\Delta_{\text{m,p}}\delta < 3$

▪ Coordinated Anion $\Delta_{\text{m,p}}\delta$ 3-6

$[\text{Cp}^*(i\text{Pr}_3\text{P})(\text{H})\text{Os}\equiv\text{Si}(\text{trip})][\text{HB}(\text{C}_6\text{F}_5)_3^-]$:

▪ ^{11}B NMR: δ -25

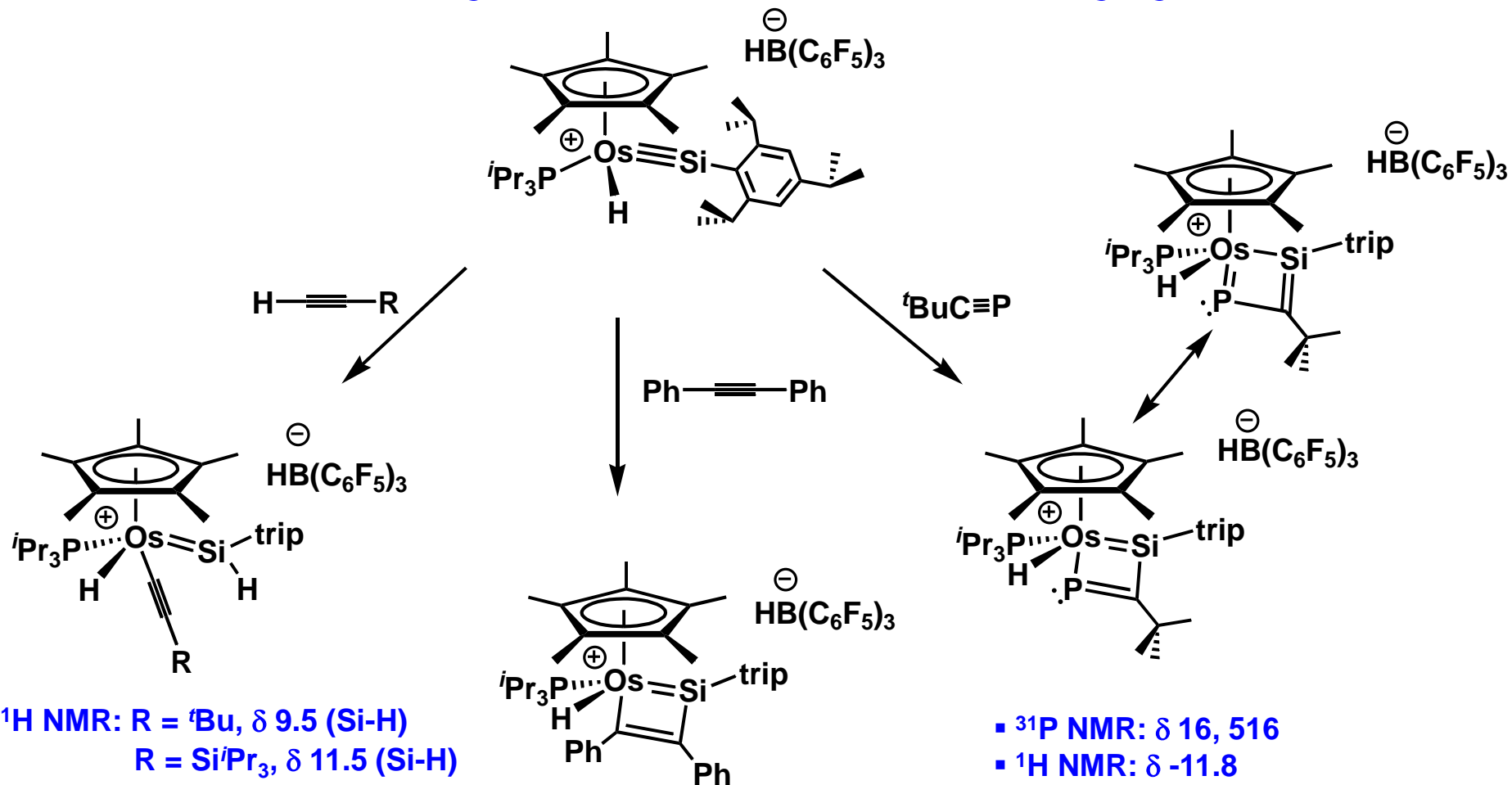
▪ ^{19}F NMR: δ -131.2, -162.9, -165.5
 $\Delta_{\text{m,p}}\delta$ 2.6

Horton, A. D. *Organometallics* **1996**, *15*, 2675.

⇒ Noncoordinated $\text{HB}(\text{C}_6\text{F}_5)_3^-$

Hayes, P. G.; Beddie, C.; Hall, M. B.; Waterman, R.; Tilley, T. D. *J. Am. Chem. Soc.* **2013**, *135*, 11780.

Reactivity of an Osmium Silylyne



- ^1H NMR: R = $t\text{Bu}$, δ 9.5 (Si-H)
R = Si^iPr_3 , δ 11.5 (Si-H)

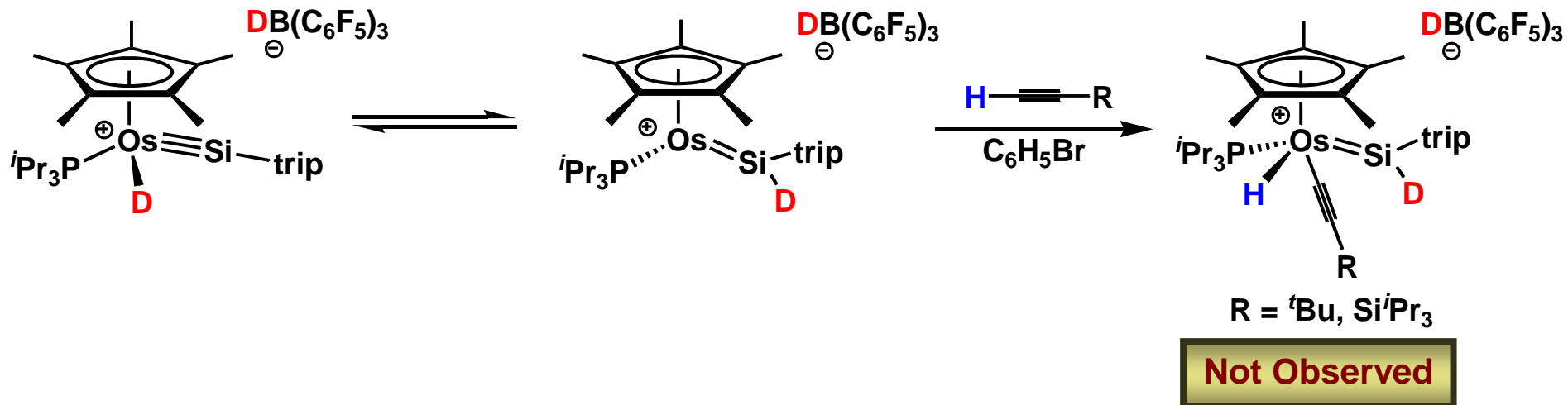
▪ yellow solid (68%)

- ^{13}C NMR: δ 164 (C_α ; $^2J_{\text{CP}} = 13$ Hz)
 δ 197 (C_β ; $^3J_{\text{CP}} = 3$ Hz)

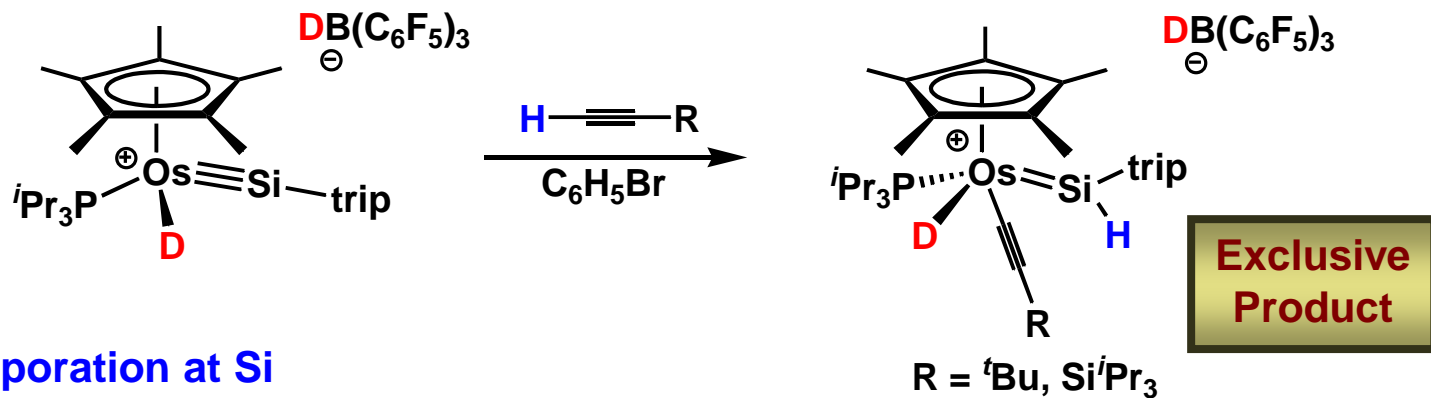
- ^{31}P NMR: δ 16, 516
- ^1H NMR: δ -11.8
- ^{29}Si NMR: δ 82
- ^{13}C NMR: δ 278

Mechanism of C-H Activation

Path A: Oxidative Addition at Os

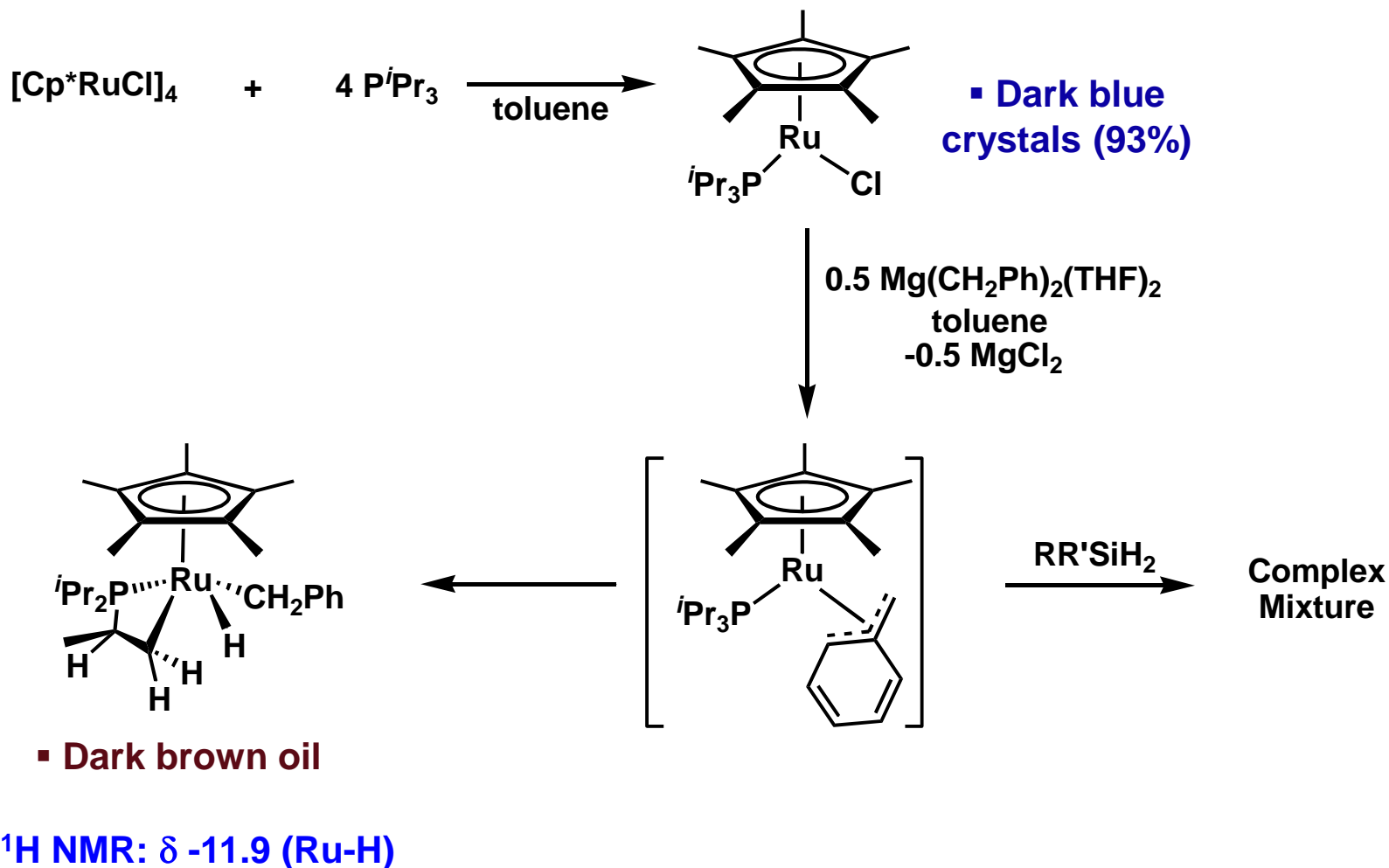


Path B: C-H Addition Across Os=Si

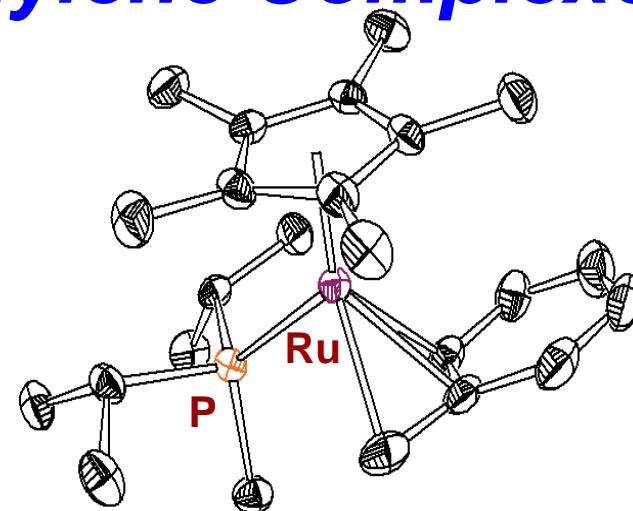
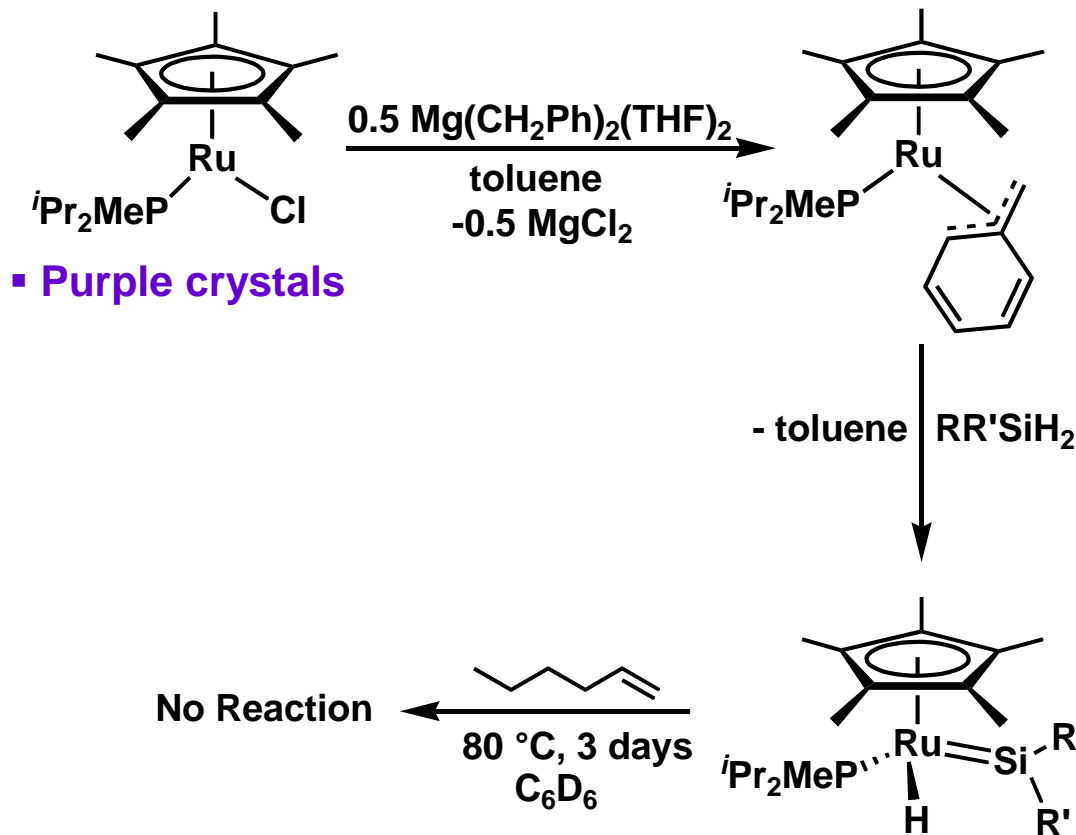


- No D incorporation at Si
- No H incorporation at Os or B
- No Os-D/Si-H or Si-H/B-D exchange observed after 6 hours at RT

Exploring Routes to Neutral Ruthenium Silylene Complexes



Stable Neutral Ruthenium Silylene Complexes



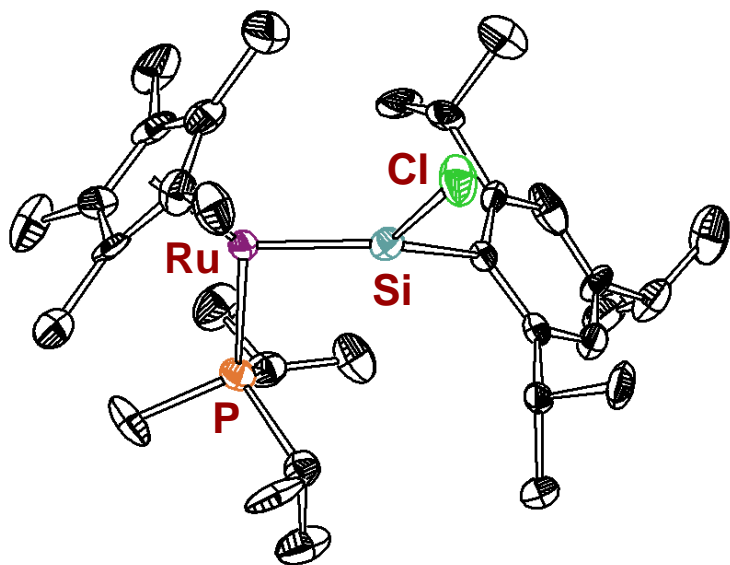
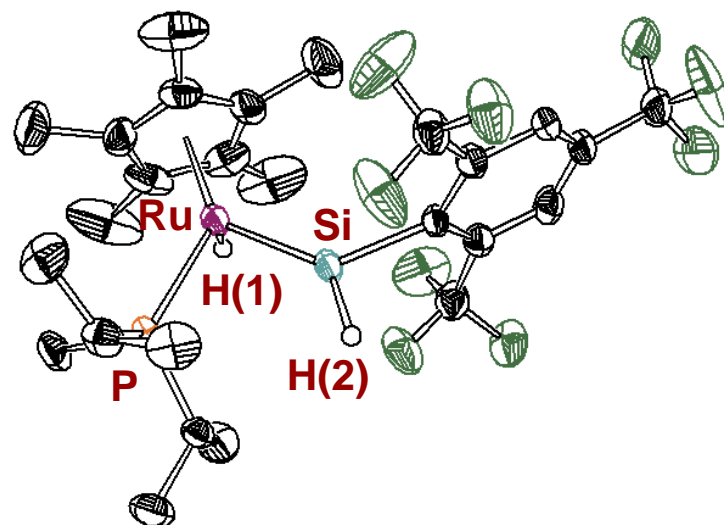
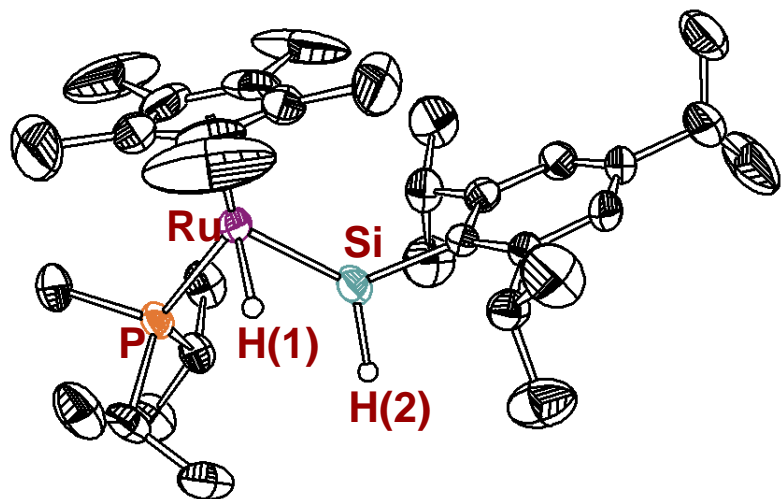
▪ ^{31}P NMR: δ 47.4

▪ $t_{1/2} \sim 24 \text{ h}$
(25°C , C_6D_6)

▪ Red crystals (47%)

NMR	R,R' = H, trip	R,R' = H, Mes ^F	R,R' = Cl, trip	R,R' = H, dmp	R,R' = Ph, trip
^1H (δ) Si-H	9.4	N/A (br)	N/A	8.0	N/A
Ru-H	-13.5	-13.3 (br)	-16.0	-14.4	-12.6
^{29}Si (δ)	N/A	N/A	222	204, $^2J_{\text{Si-H}} = 8.6$	229
^{31}P (δ)	55.5	53.6	56.9	48.5	55.7

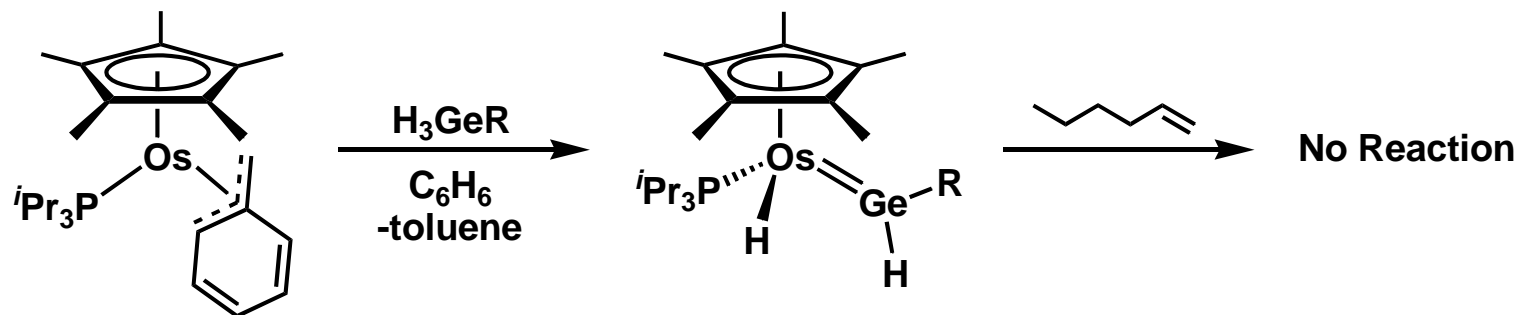
Ruthenium Silylene X-ray Crystal Structures



Bond Lengths and Angles (Å and °)

	R,R' = H, trip	R,R' = H, Mes ^F	R,R' = Cl, trip
Ru–Si	2.205(2)	2.181(1)	2.183(4)
Ru–P	2.272(1)	2.285(1)	2.286(4)
Ru–Cp*	2.226(4) – 2.264(6)	2.223(4) – 2.257(4)	2.223(2) – 2.282(2)
Σ angles at Si	359.4	359.9	357.7

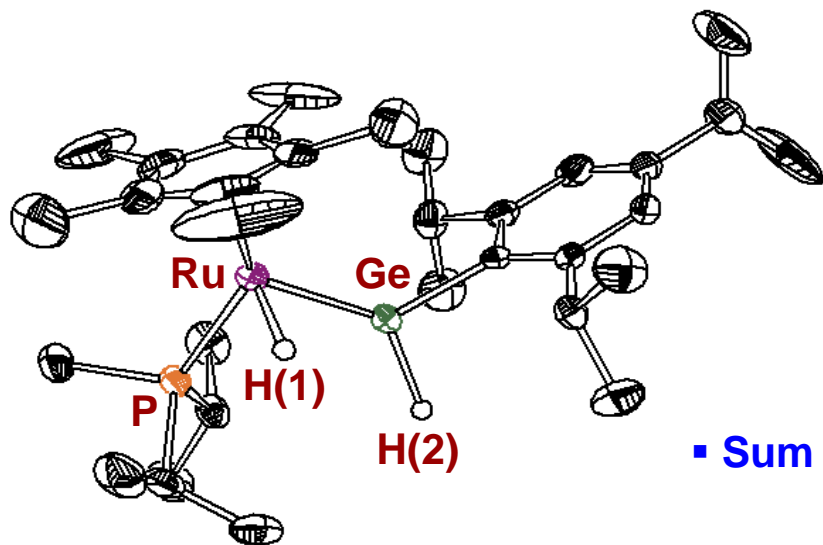
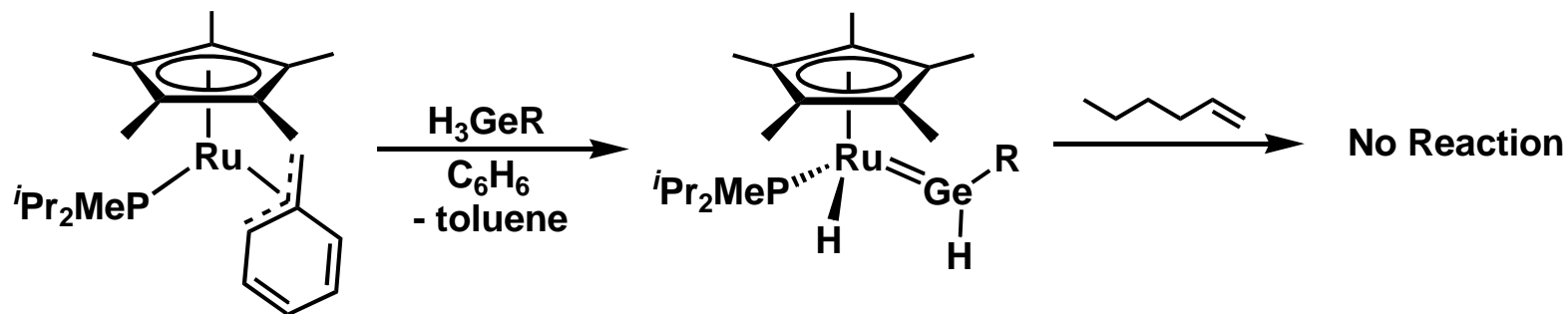
Osmium Germylene Complexes



NMR	R = <i>t</i> Bu	R = Ph	R = trip
^1H (δ)	14.0 (GeH) -15.7 (OsH)	14.3 (GeH) -15.6 (OsH)	15.0 (GeH) -15.7 (OsH)
^{31}P (δ)	45.9	43.0	37.5

- First hydrogen-substituted germylene complexes

Ruthenium Germylene Complexes



▪ Sum of angles about germanium = 359.1°

NMR	R = ^t Bu	R = trip
¹ H (δ)	11.7 (GeH)	12.4 (GeH)
	-12.8 (RuH)	-12.8 (RuH)
³¹ P (δ)	61.1	57.6

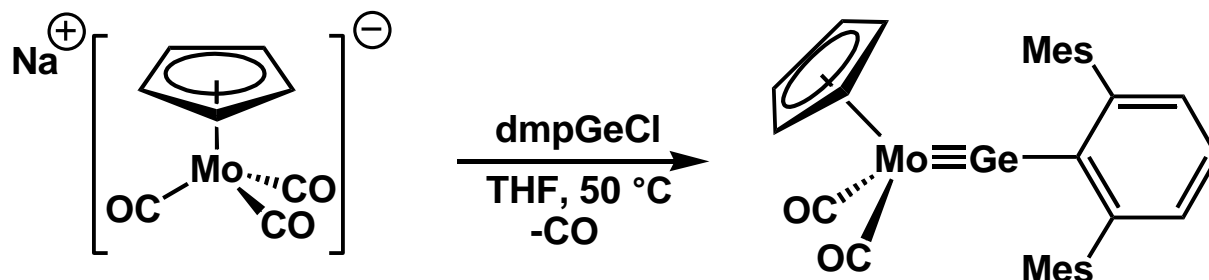
Bond Lengths (Å)

Ru–Ge	2.282(2)
Ru–Cp*	2.209(7) – 2.255(6)
Ru–P	2.272(2)

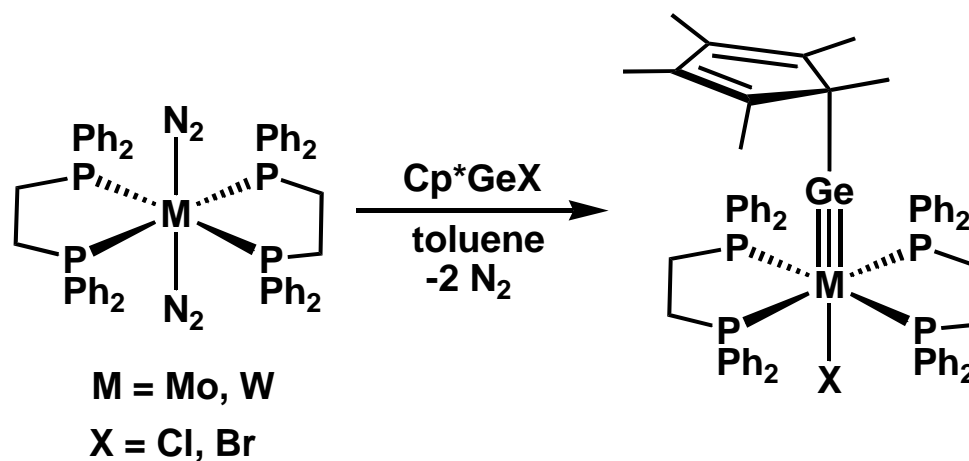
Bond/Torsion Angles (°)

Ru–Ge–C	129.33(2)
H–Ru–Ge–H	50.4(2)
P–Ru–Ge–C	161.3(3)

Metal Germylyne Complexes



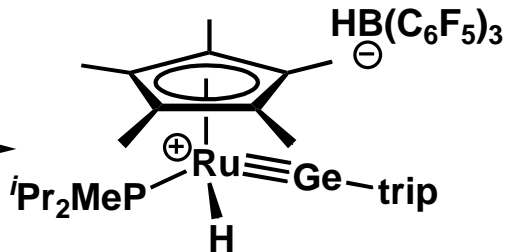
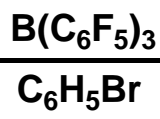
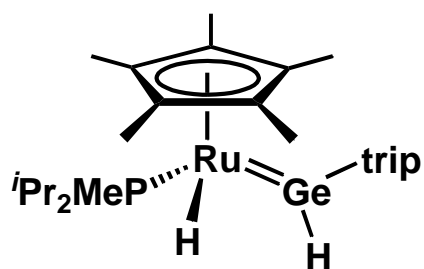
Filippou, Philippopoulos, Portius and Neumann *Angew. Chem. Int. Ed.* **2000**, *39*, 2778; *Organometallics* **2002**, *21*, 653.



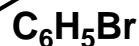
Simmons, Pu, Twamley, Haubrich, Olmstead, Mork and Power *J. Am. Chem. Soc.* **1996**, *118*, 11966; **2000**, *122*, 650.

- All known routes utilize E(II) precursors

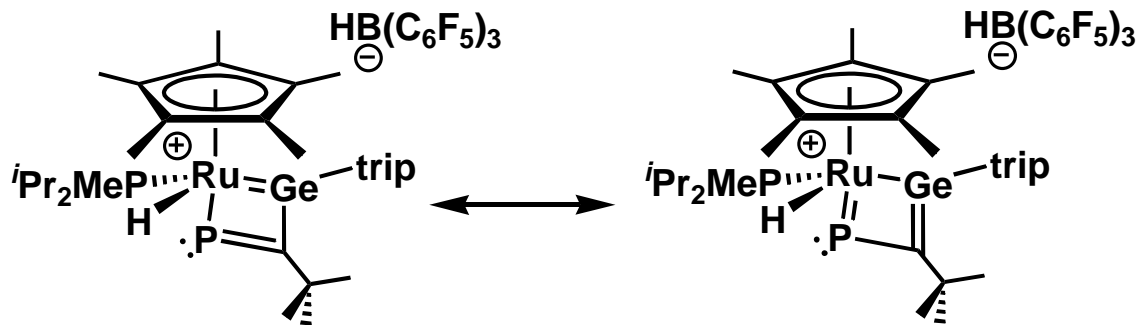
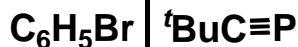
Ruthenium Germylyne Complex



- ^{31}P NMR: δ 60.1
- 1H NMR: δ -11.2 (Ru-H)
 δ 4.4 (B-H)
- ^{19}F NMR: δ -131.1, -162.9, 165.6
 $\Delta_{m,p}\delta = 2.7$
- ^{11}B NMR: δ -24

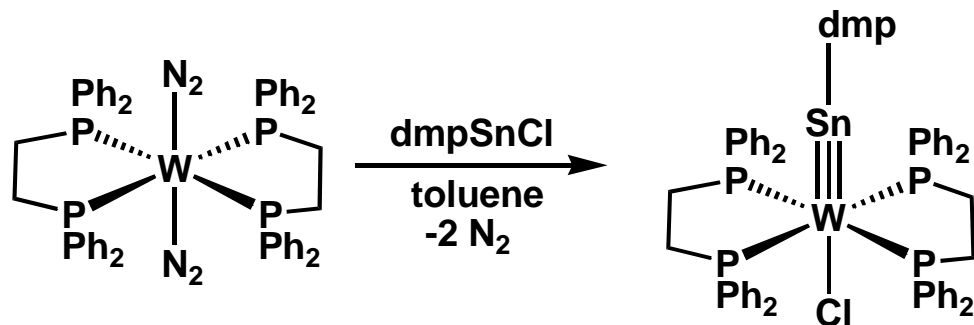


No Reaction

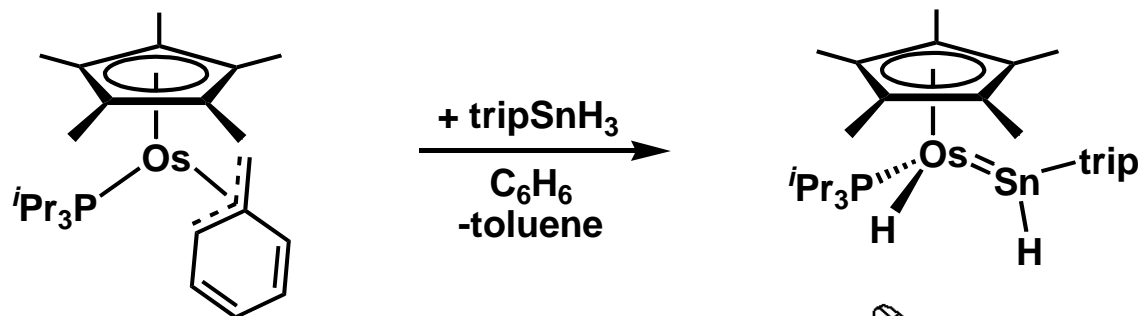


- ^{31}P NMR: δ 39.5, 60.2
- 1H NMR: δ -9.2 (Ru-H)
 δ 4.5 (B-H)
- ^{19}F NMR: δ -131.2, -163.0, 165.7
 $\Delta_{m,p}\delta = 2.7$
- ^{11}B NMR: δ -25

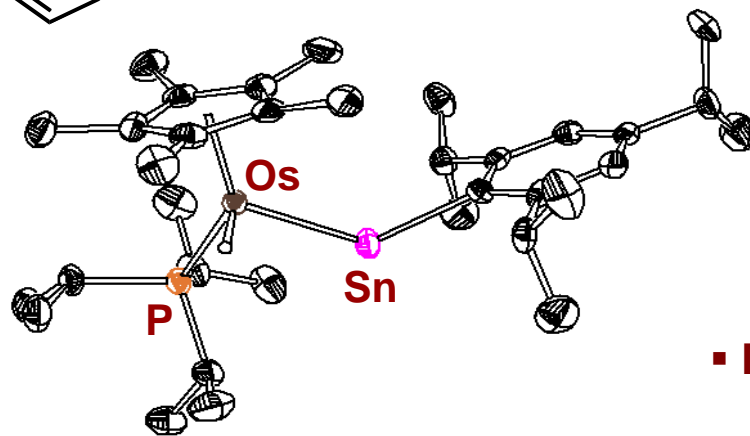
Osmium Stannylene/Stannylyne Complexes



Filippou, A. C.; Philippopoulos, A. I.; Schnakenburg, G.; Rohde, H.; Portius, P. *Organometallics* **2003**, *22*, 3339; *Angew. Chem. Int. Ed.* **2003**, *42*, 445.



- ^{31}P NMR: δ 40.9 ppm
- ^{119}Sn NMR: δ 786
- ^1H NMR: δ 19.4 ppm (Sn-H)
- $^1J_{\text{Sn-H}} = 775$ Hz



- Photochemically sensitive
- Dark red crystals (42%)

Hayes, P. G.; Gribble, C. W.; Waterman, R.; Tilley, T. D. *J. Am. Chem. Soc.* **2009**, *131*, 4606.

Osmium Stannylene Reactivity

