Rhodium-Catalyzed Unstrained C-C Bond Cleavage of Ketones

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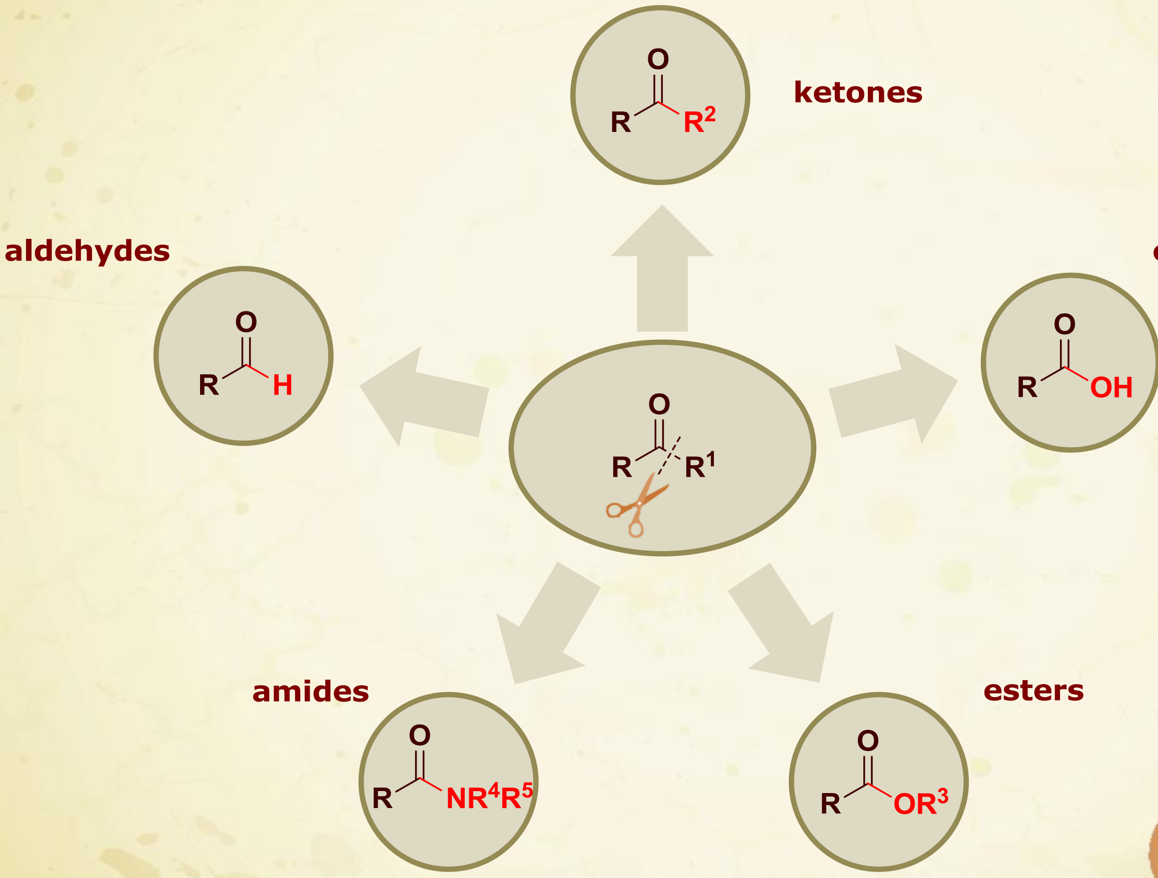
Introduction: Background of C-C Bond Cleavage

Strategies for Unstrained C-C Bond Cleavage of Ketones

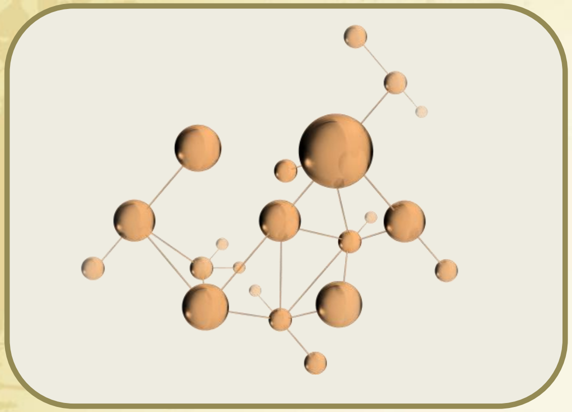
Summary and Outlook

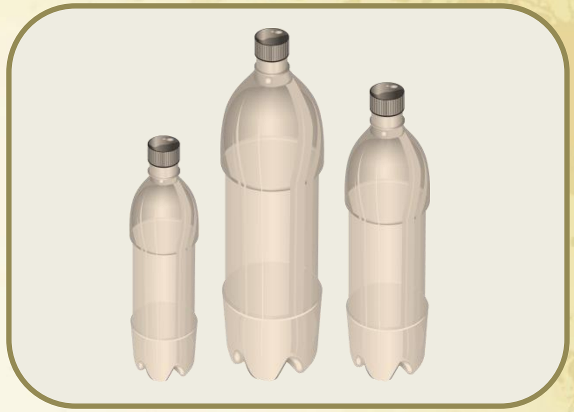
Introduction: Background of C-C Bond Cleavage

C-C Bond Cleavage of Ketones



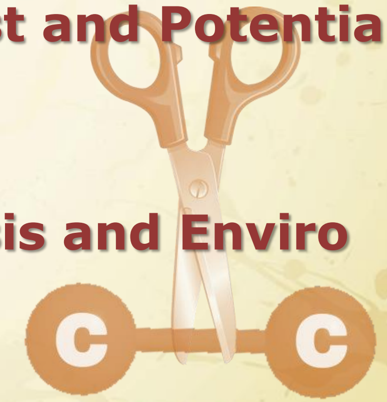
Introduction: Background of C-C Bond Cleavage





C-C Bond Cleavage:

- To Find Its Fundamental Scientific Interest and Potential Ability in Organic Synthesis
- To Reduce the Pressure of the Energy Crisis and Enviro-mental Pollution



Reference: 1

Introduction: Background of C-C Bond Cleavage

C-C Bond: Thermodynamic Stability

- **To Increase the Energy State of the Starting Materials**
  - To Relieve Ring Energy
  - To Induce Aromatic Stabilization

- **To Lower the Energy State of the C-C Bond Cleaved Complexes**
  - To Form Stable Metallacyclic Complexes

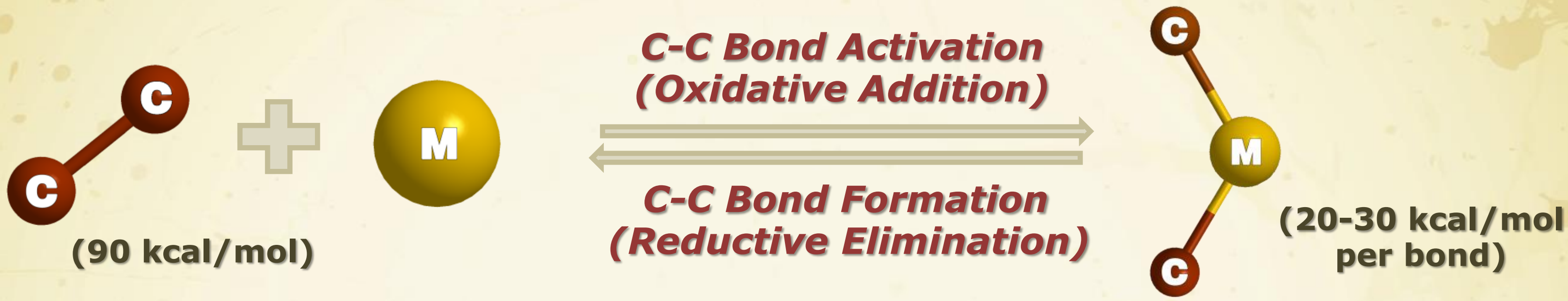
↓

Transition-Metal-Mediated

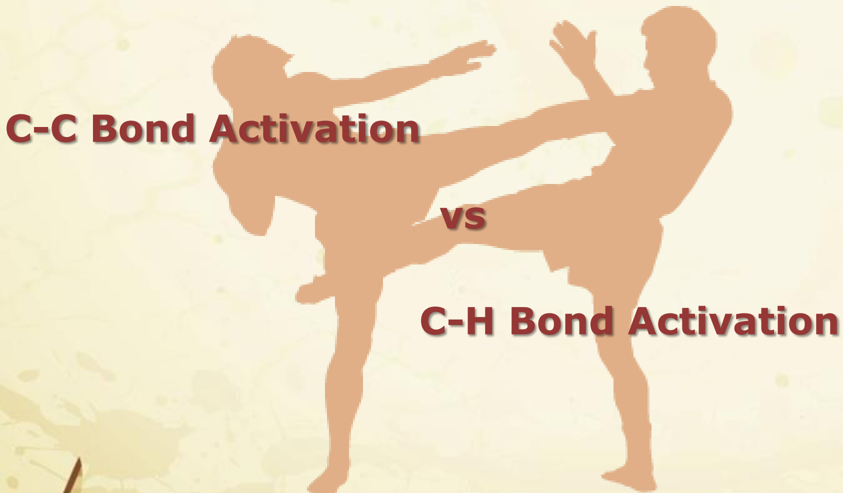
Reference: 2

Introduction: Background of C-C Bond Cleavage

- **C-C Bond Activation is Thermodynamically Much Less Favored than the C-C Bond Formation**

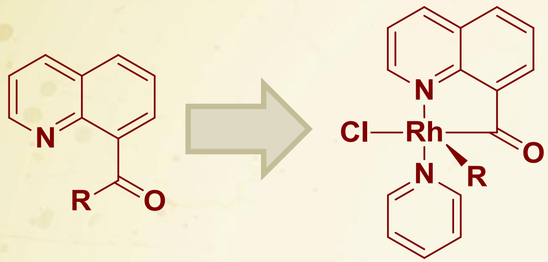


- **Several Factors Favor C-H over C-C Bond Activation**

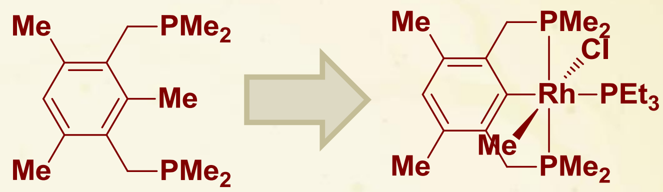


Reference: 3

C-C Bond Cleavage: Chelation Assistance



Suggs, J. W. 1984



Milstein, D. 1995

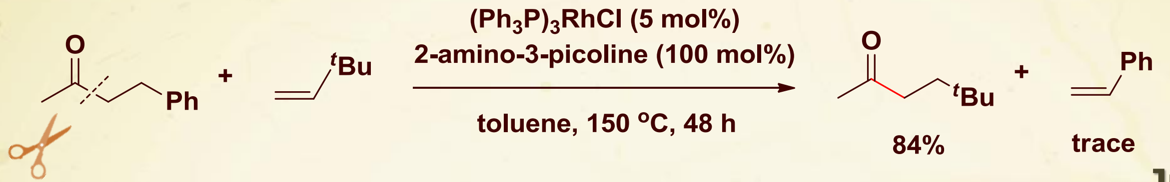
Stoichiometric Reactions

Catalytic Reactions

References: 4-6

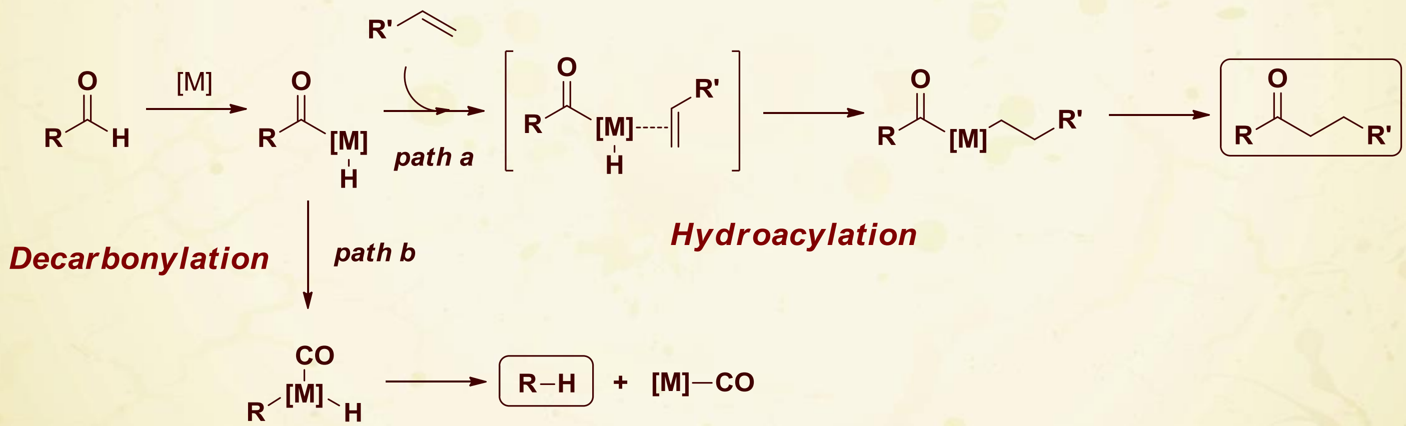
Chelation Assistance

Metal-Organic Cooperative Catalysis (MOCC)



Jun, C. H. 1999

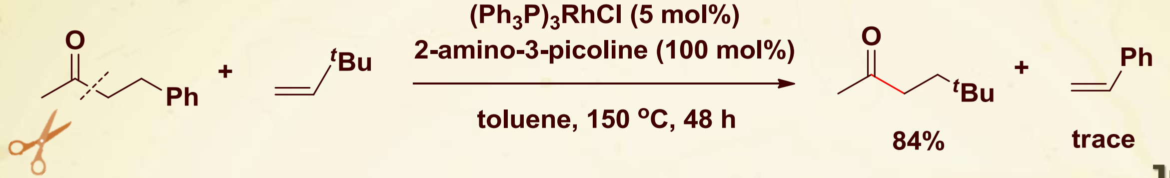
Hydroacylation of Olefin with Aldehydes



Reference: 7

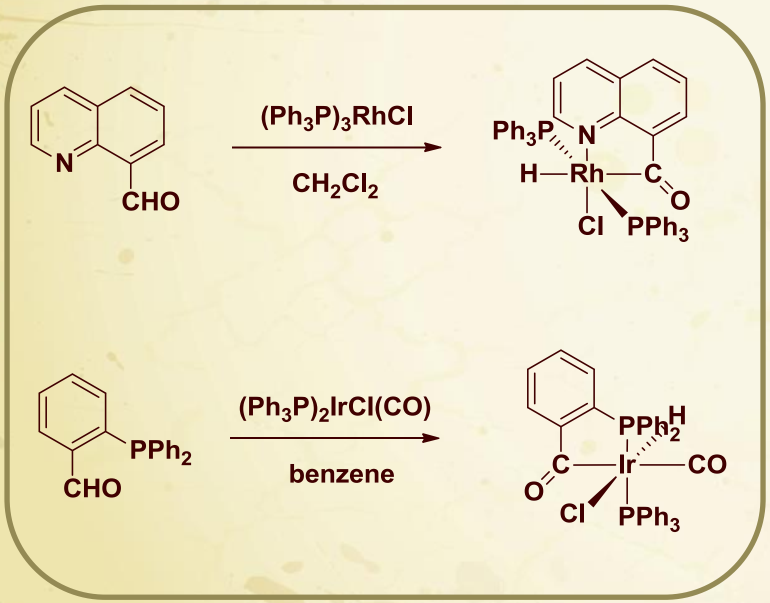
Strategies for Unstrained C-C Bond Cleavage of Ketones

Metal-Organic Cooperative Catalysis (MOCC)

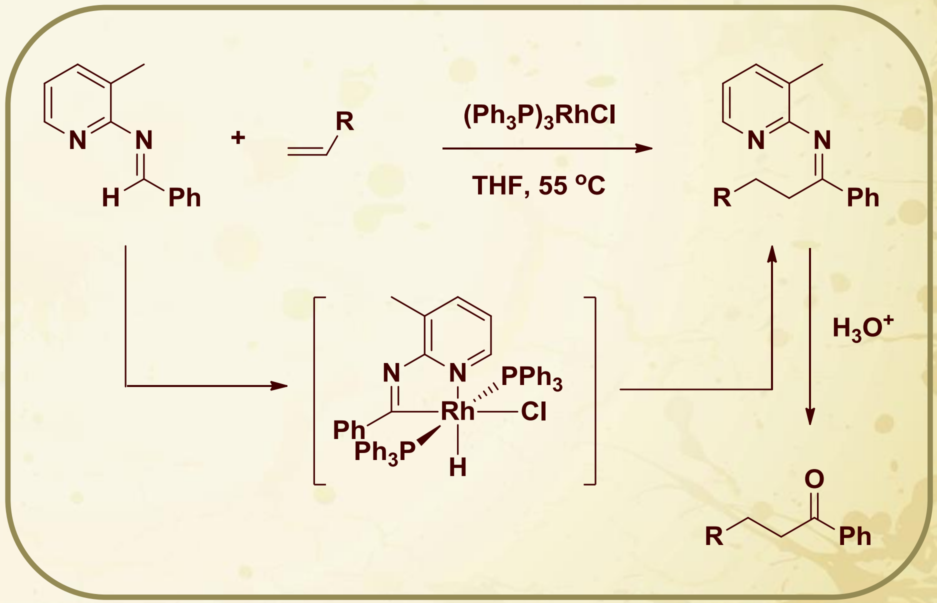


Jun, C. H. 1999

Cyclometalation Models



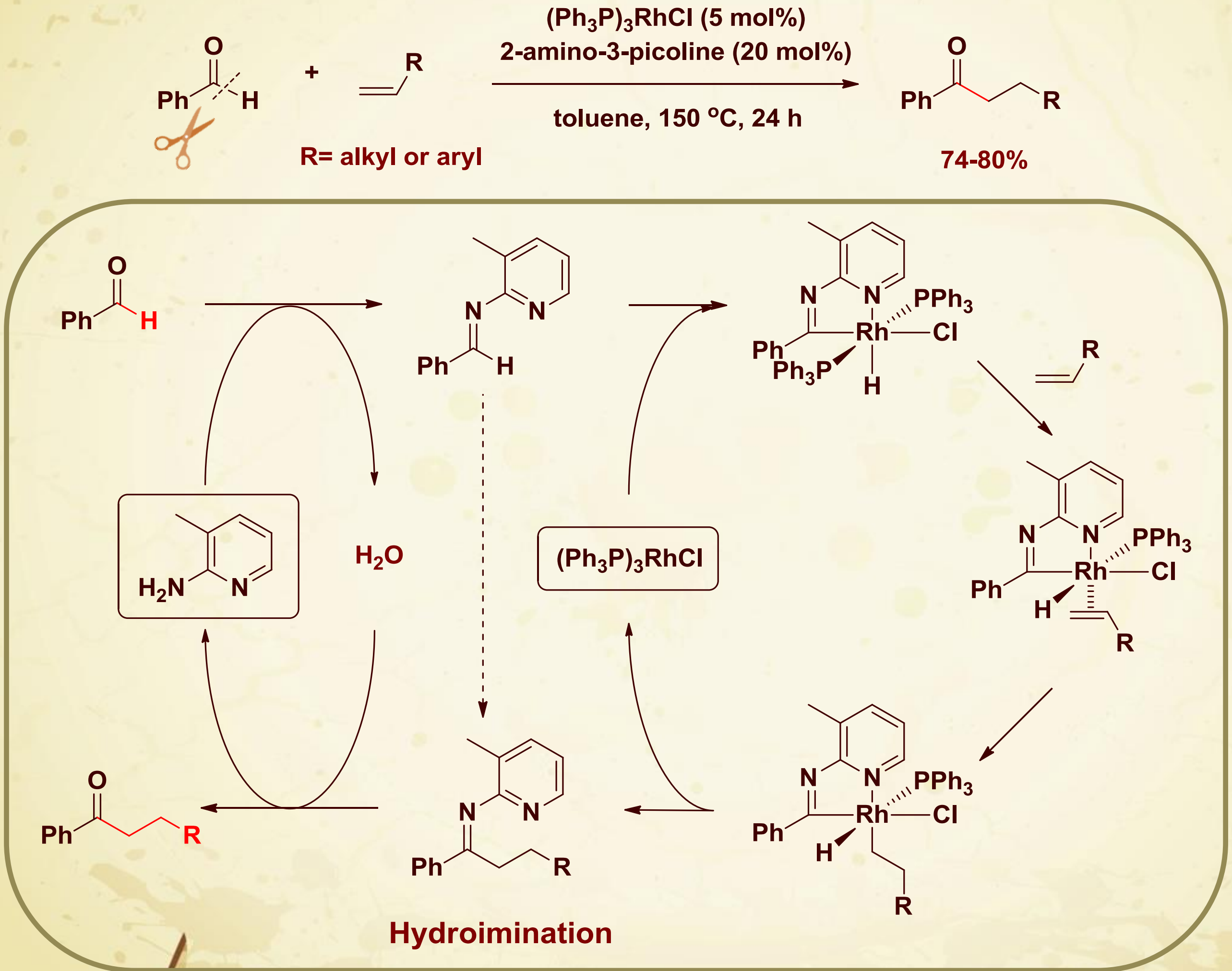
Hydroiminoacylation of Olefin with Aldimines



References: 8-10

Strategies for Unstrained C-C Bond Cleavage of Ketones

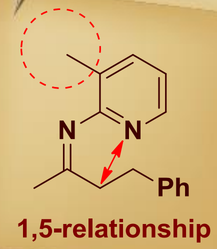
Hydroacylation of Olefin with Aldehydes

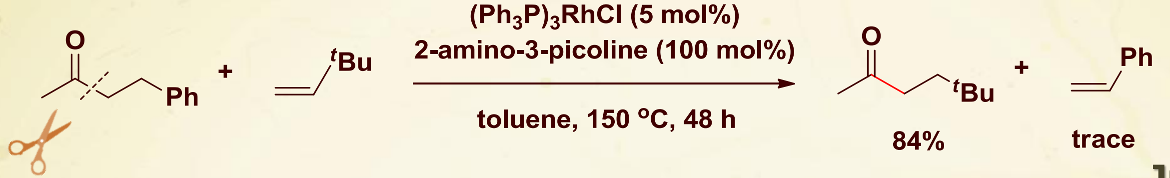


References: 11-12

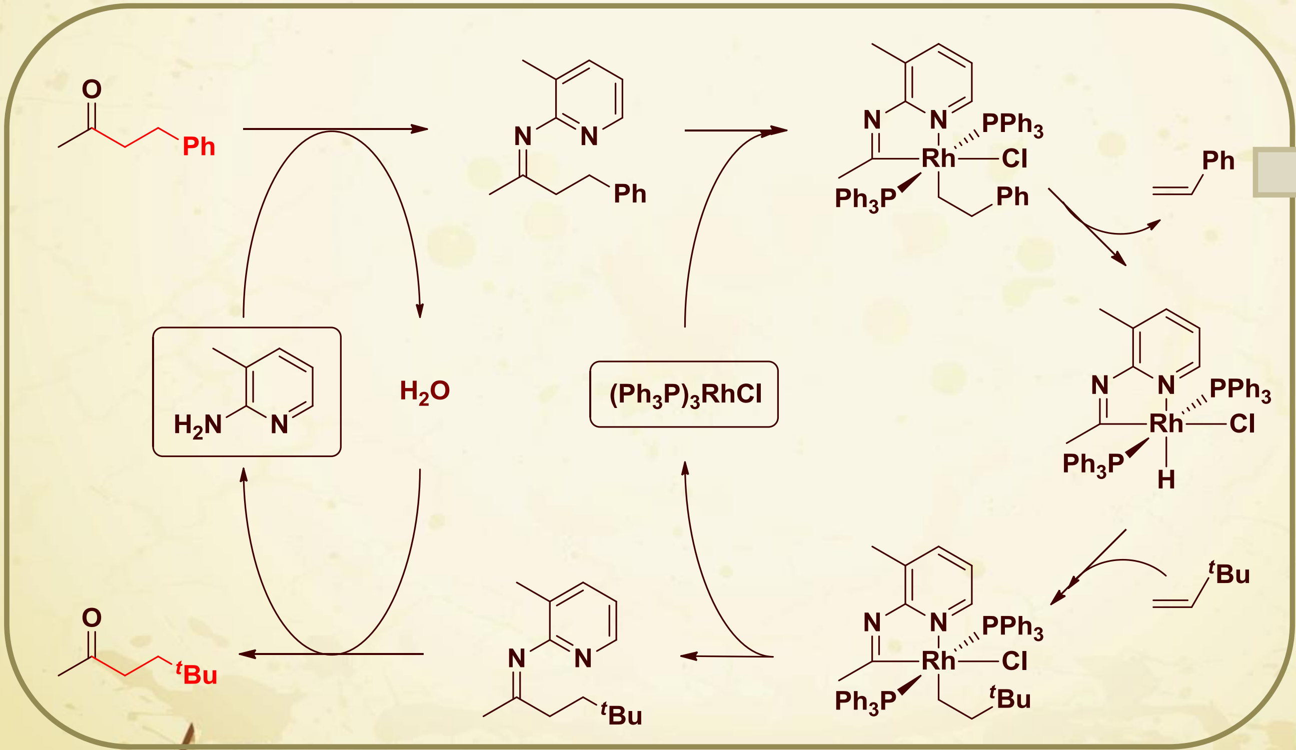
Strategies for Unstrained C-C Bond Cleavage of Ketones

Metal-Organic Cooperative Catalysis (MOCC)





Jun, C. H. 1999

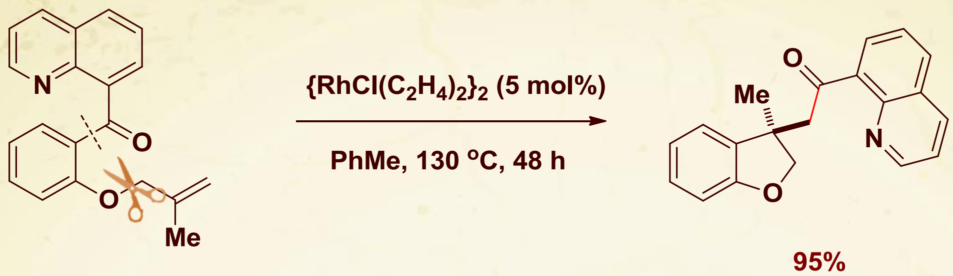


Driving Force: Polymerization

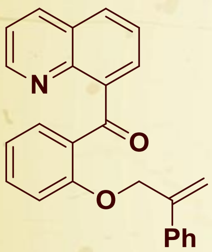
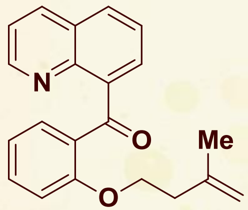
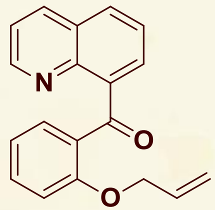
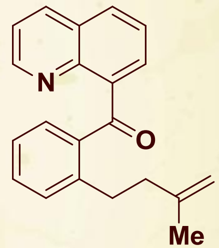
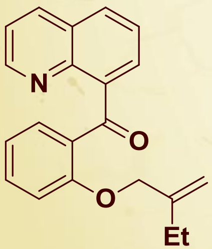
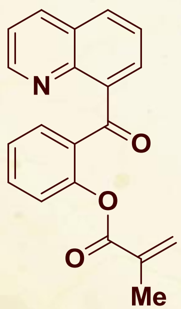
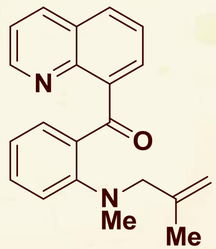
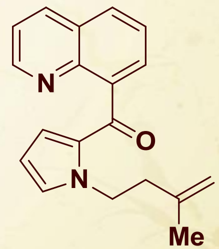
References: 12-13

Strategies for Unstrained C-C Bond Cleavage of Ketones

Chelation Assistance



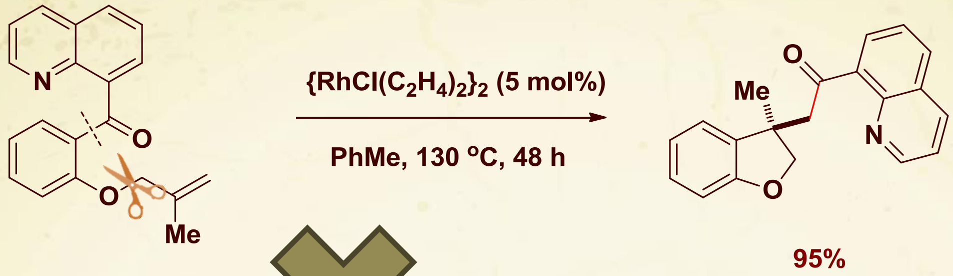
Douglas, C. J. 2009

substrate	condition yield [a]	substrate	condition yield [a]	substrate	condition yield [a]	substrate	condition yield [a]
	A 94%		A 81%		B 25%		A 93%
	A 82%		A 80% [b]		C 75%		A 63%

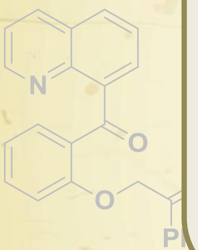
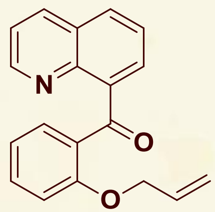
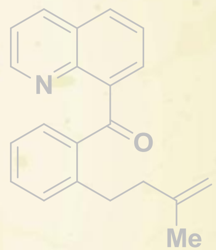
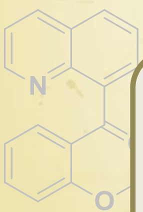
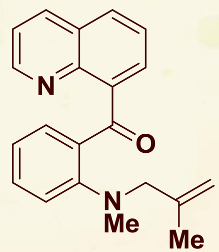
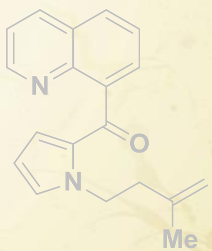
[a] Isolated yield after chromatography with SiO_2. [b] Reaction stopped after 24 h. [c] Condition A: 5 mol% $\{RhCl(C_2H_4)_2\}_2$, PhMe, 130 °C, 48 h. Condition B: 5 mol% $Rh(OTf)(COD)_2$, PhMe, 130 °C, 24 h. Condition C: 10 mol% $RhCl(PPh_3)_3$, PhMe, 130 °C, 24 h.

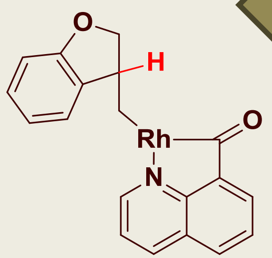
Reference: 14

Strategies for Unstrained C-C Bond Cleavage of Ketones



Douglas, C. J. 2009

substrate	condition yield [a]	substrate	condition yield [a]	substrate	condition yield [a]
			B 25%		A 93%
			A 10%, C 75%		A 63%



β-H elimination

C-C activation step is slower: electron donation from the 2-amino group

[a] Isolated yield after chromatography with SiO_2. [b] Reaction stopped after 24 h. [c] Condition A: 5 mol% $\{RhCl(C_2H_4)_2\}_2$, PhMe, 130 °C, 48 h. Condition B: 5 mol% $Rh(OTf)(COD)_2$, PhMe, 130 °C, 24 h. Condition C: 10 mol% $RhCl(PPh_3)_3$, PhMe, 130 °C, 24 h.

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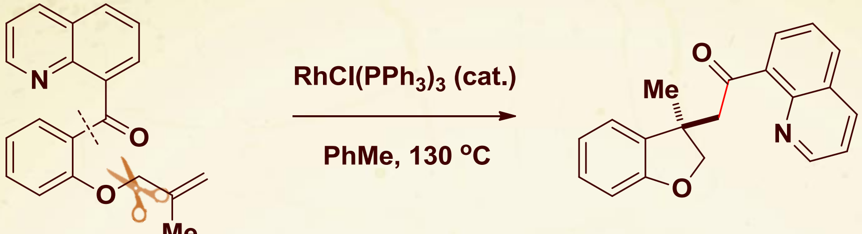
Strategies for Unstrained C-C Bond Cleavage of Ketones

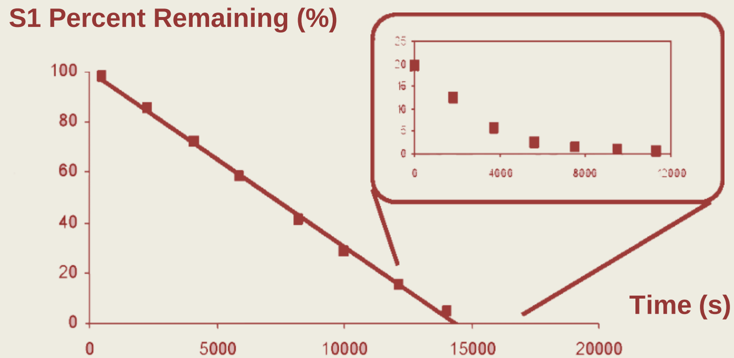
Chelation Assistance



S1 P1

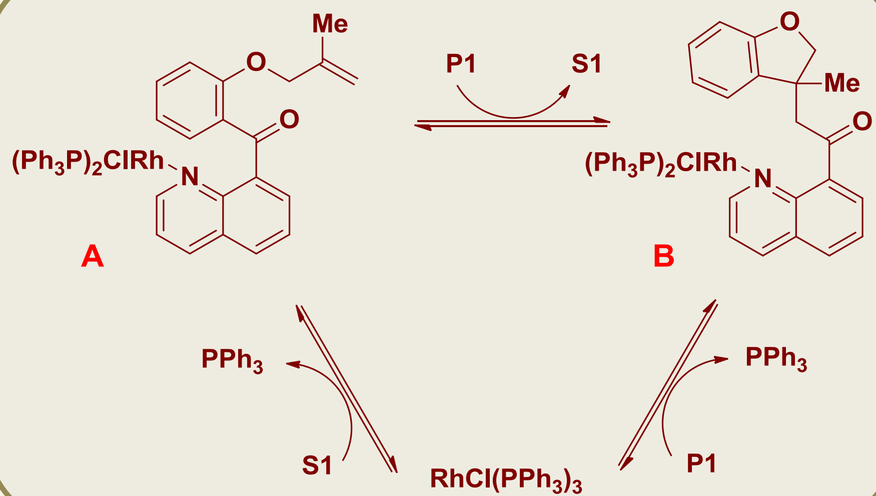
Johnson, J. B. 2011

Rate Law



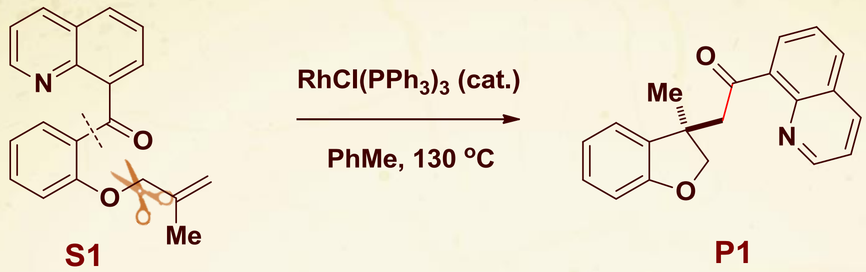
$$-\frac{d[S1]}{dt} = k[Rh]^1[S1]^0 \qquad k = 4.98*10^{-4}\ s^{-1}$$

Equilibrium between Complex A and B



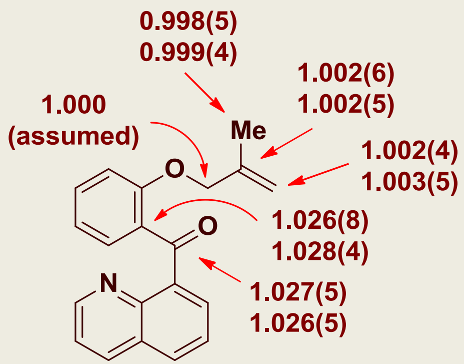
Reference: 15

Strategies for Unstrained C-C Bond Cleavage of Ketones

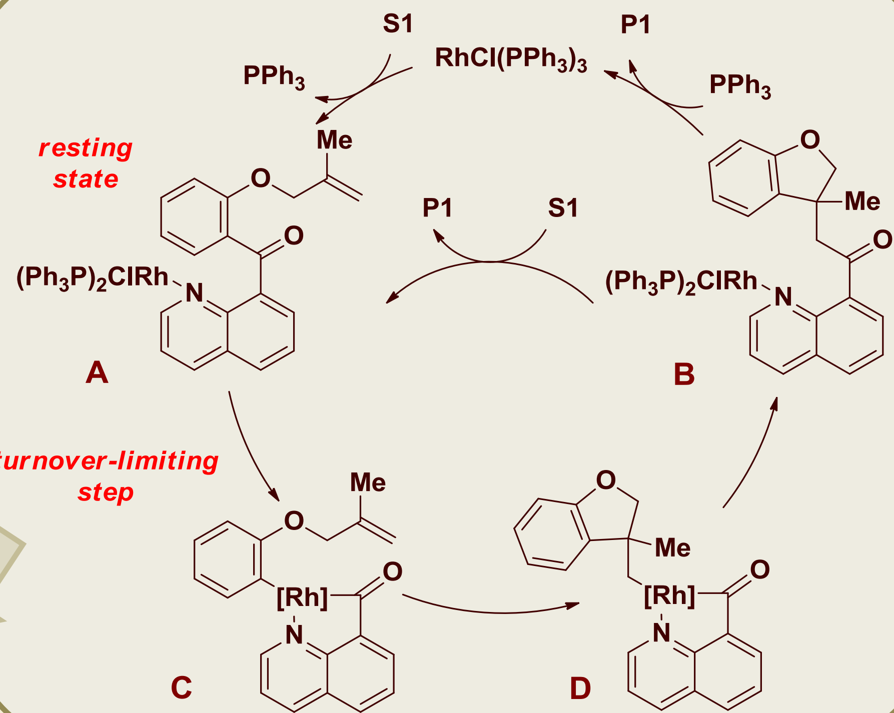


Johnson, J. B. 2011

$^{12}C/^{13}C$ Kinetic Isotope Effects

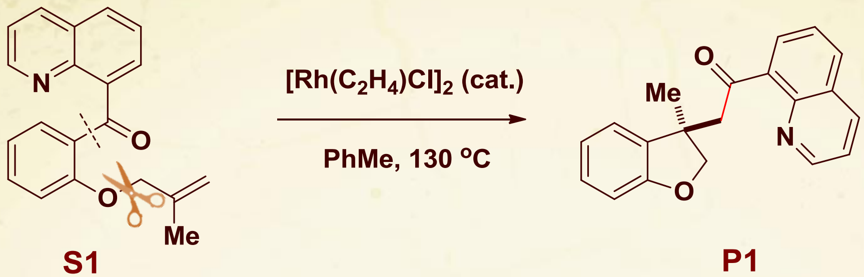


$\Delta H^{‡}$ = 27.8 ± 1.0 kcal/mol
$\Delta S^{‡}$ = -4.3 ± 2.4 eu.



Reference: 15

Strategies for Unstrained C-C Bond Cleavage of Ketones

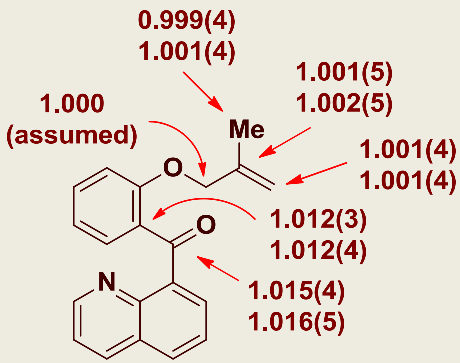


Johnson, J. B. 2012

Rate Law

$$-\frac{d[S1]}{dt} = k[Rh]^1[S1]^1 \qquad k = 7.59*10^{-2}\ M^{-1}s^{-1}$$

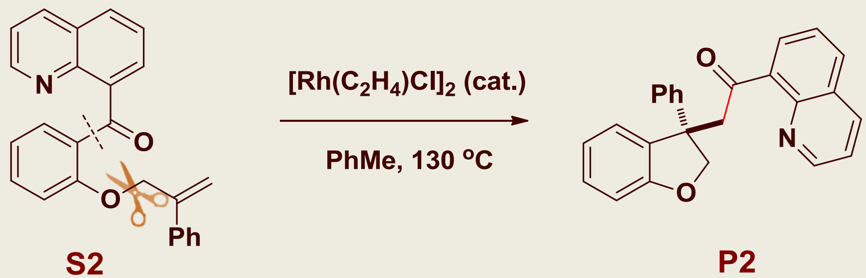
$^{12}C/^{13}C$ Kinetic Isotope Effects



Activation Parameters

$\Delta H^{\ddagger}$ = 28.4 ± 1.3 kcal/mol
$\Delta S^{\ddagger}$ = -26.4 ± 2.6 eu.

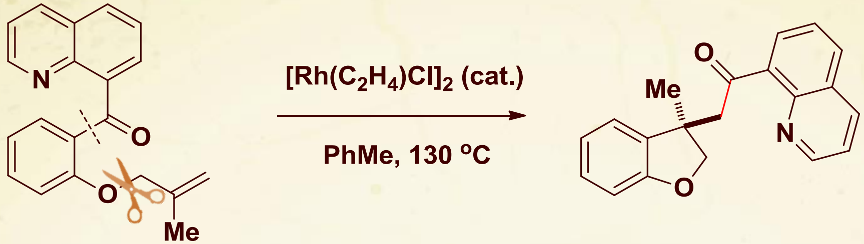
Alkene Substitution Effect



$k = 2.62*10^{-2}\ M^{-1}s^{-1}$

Reference: 16

Strategies for Unstrained C-C Bond Cleavage of Ketones



S1 P1

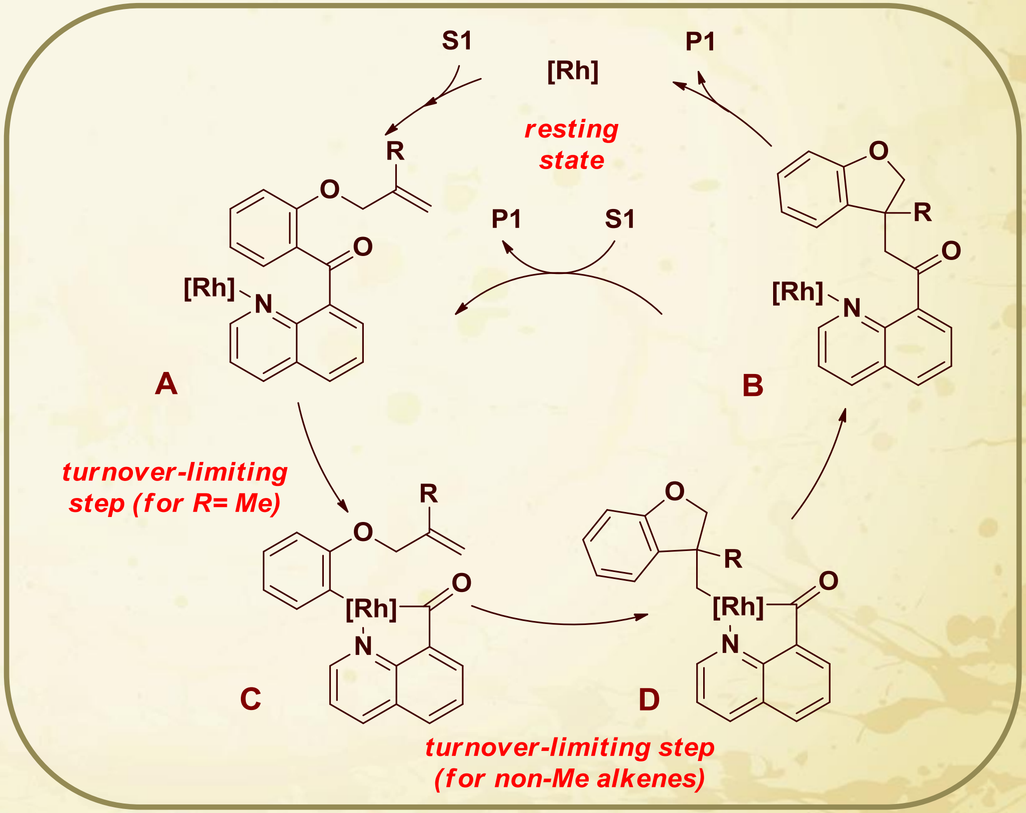
Johnson, J. B. 2012

The Energy Barriers to C-C Bond Activation and Alkene Insertion are Quite Similar

Turnover-limiting Step:

C-C Bond Activation
(for R= Me)

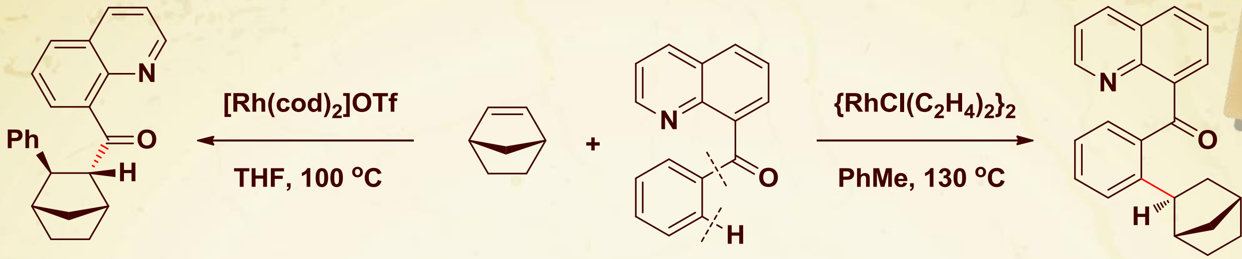
Alkene Insertion
(for non-Me alkenes)



Reference: 16

Strategies for Unstrained C-C Bond Cleavage of Ketones

Chelation Assistance



C-C activation
50%

C-H activation
79%

Douglas, C. J. 2009

C-H Activation is More Favorable than C-C Activation

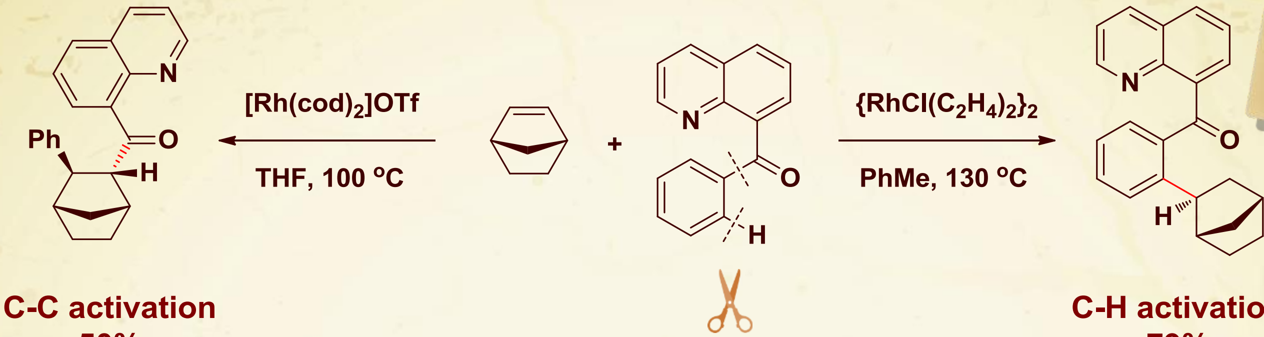
Kinetic Consideration:

- The Generally Easier Approach of the Metal Center to C-H Bonds
- The Higher Activation Energy for the Insertion of Transition-Metal Atoms into C-C Bonds

References: 17-18

Strategies for Unstrained C-C Bond Cleavage of Ketones

Chelation Assistance



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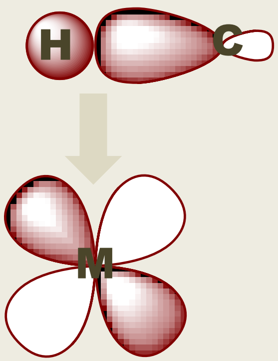
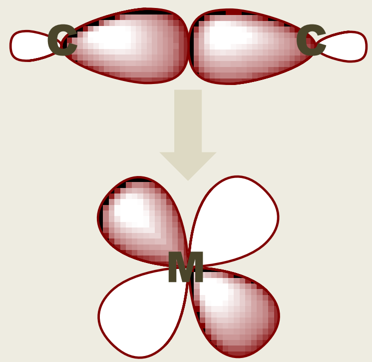


C-H Orbital Directionality

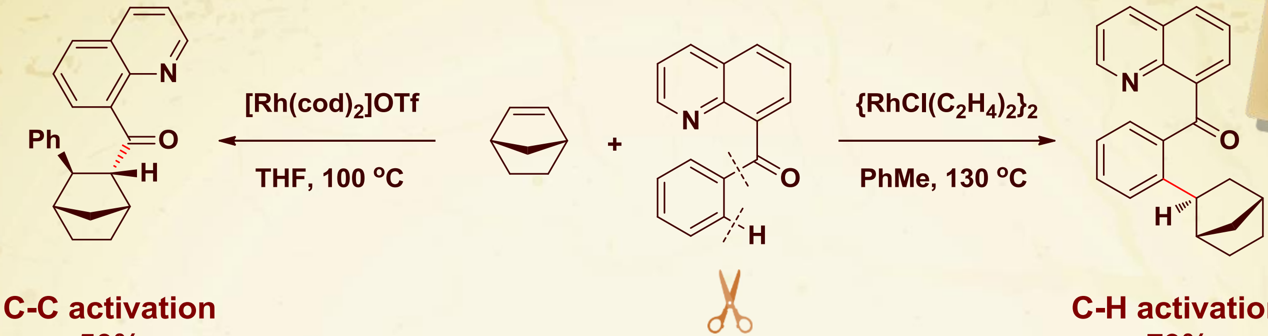


C-C Orbital Directionality

References: 17-18

Strategies for Unstrained C-C Bond Cleavage of Ketones

Chelation Assistance



C-C activation
50%

C-H activation
79%

Douglas, C. J. 2009

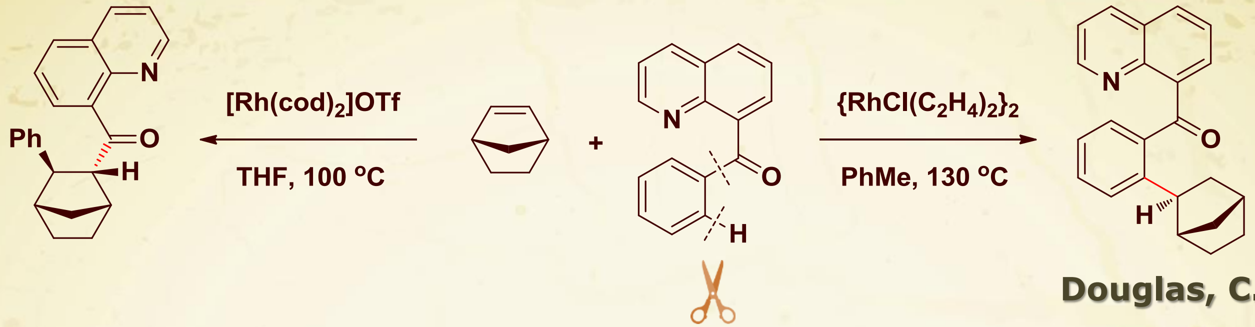
C-H Activation is More Favorable than C-C Activation

Thermodynamic Consideration:

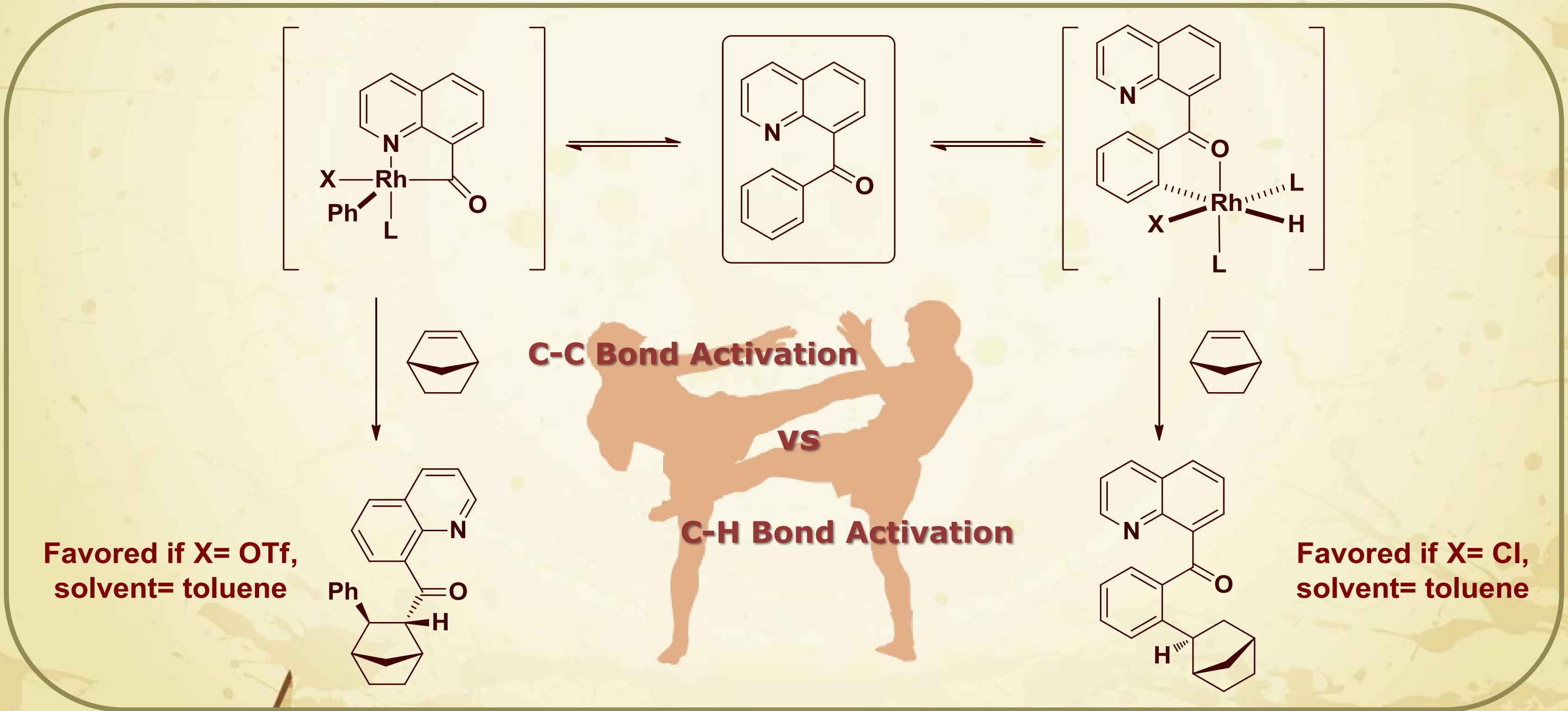
- The Higher Bond Dissociation Energy of C-C Bonds
- The Generally Considerably Higher Strengths of M-H Bonds

References: 17-18

Strategies for Unstrained C-C Bond Cleavage of Ketones



Douglas, C. J. 2009



References: 17-18

Strategies for Unstrained C-C Bond Cleavage of Ketones

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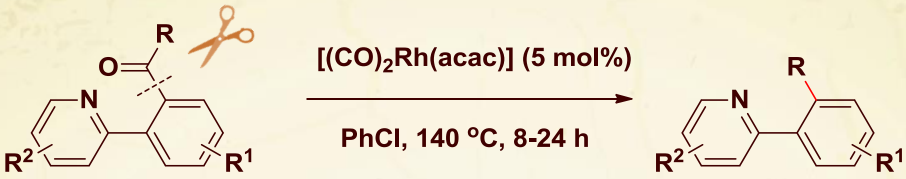
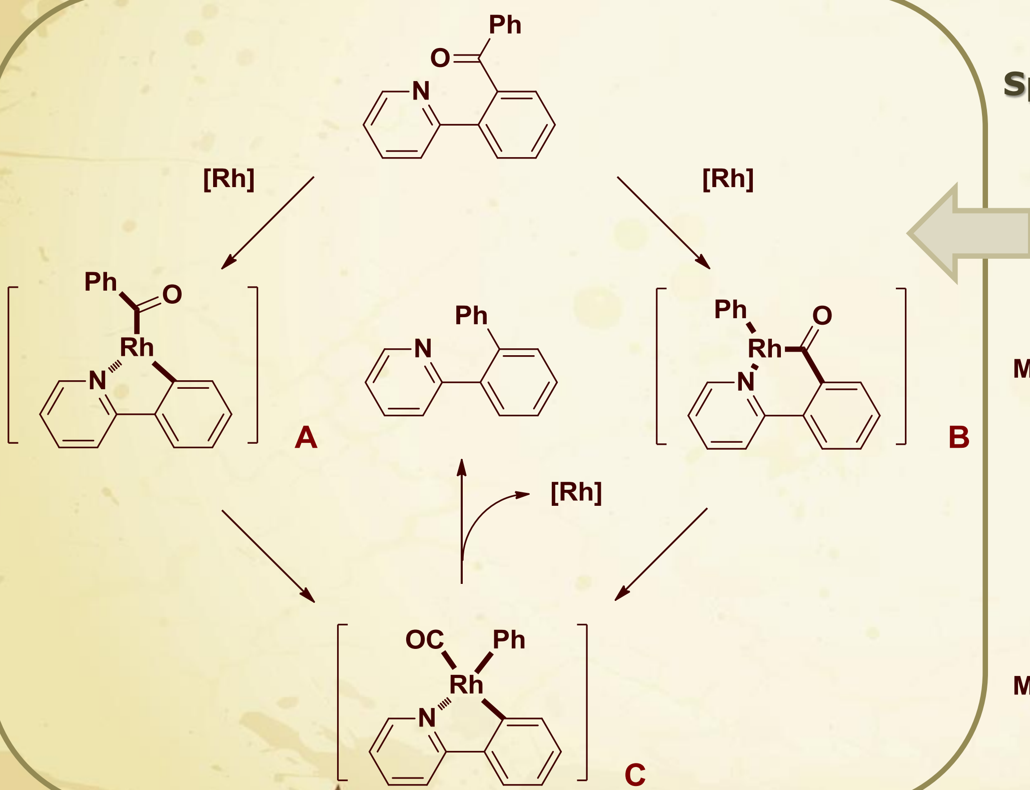
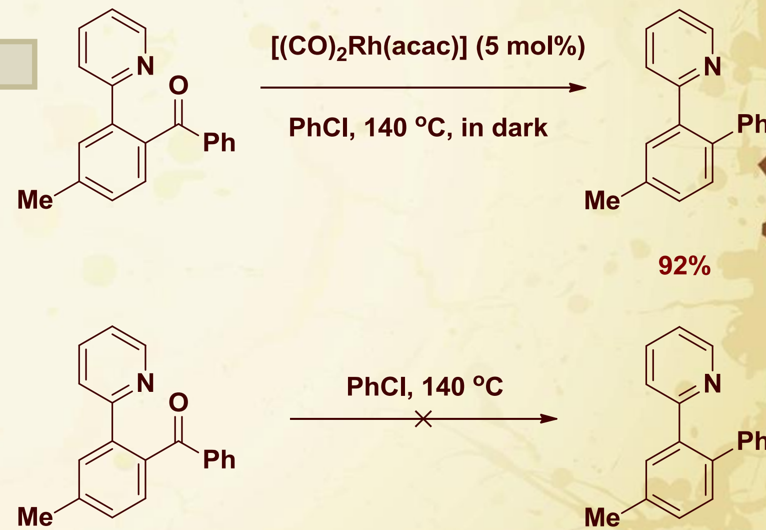


Shi, Z. J. 2012



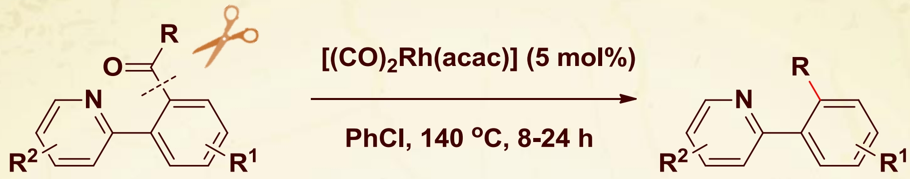
Rhodium Complex is the Catalytic Species Performing the Decarbonylation.



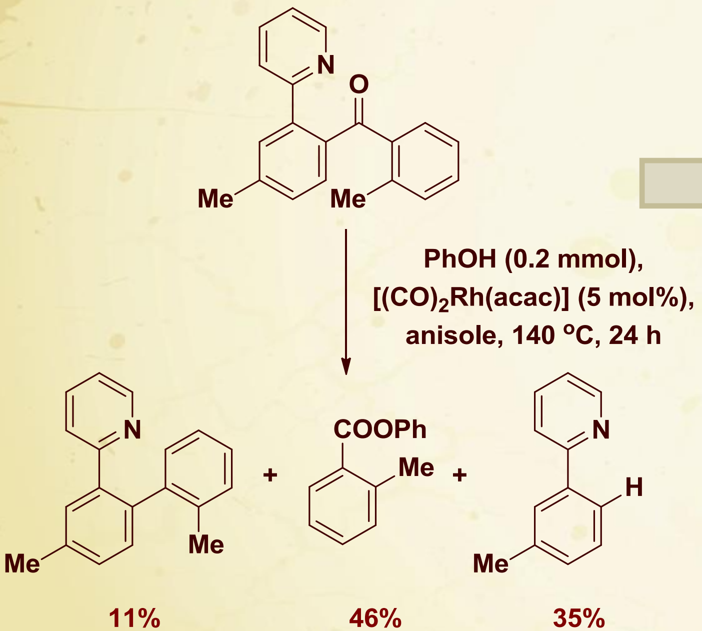
Reference: 19

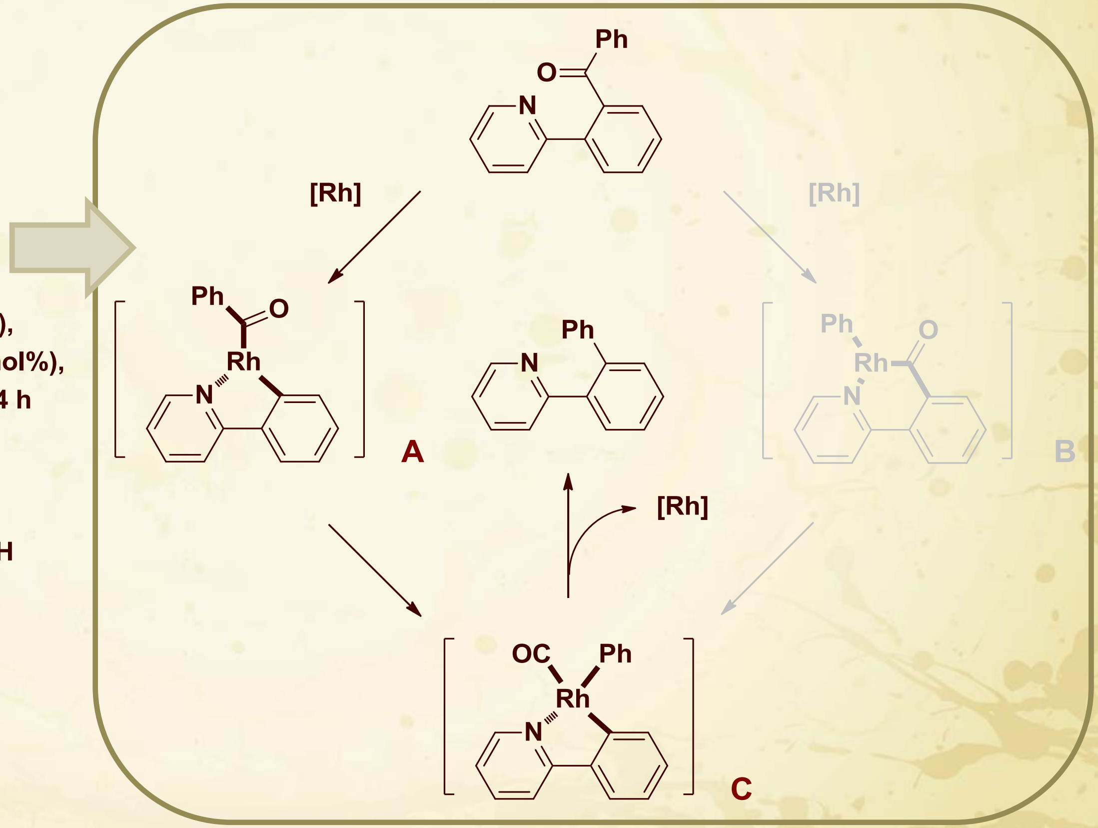
Strategies for Unstrained C-C Bond Cleavage of Ketones

Chelation Assistance



Shi, Z. J. 2012





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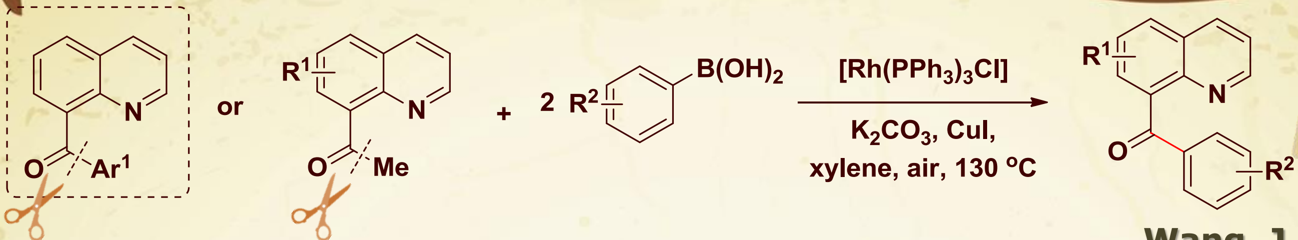
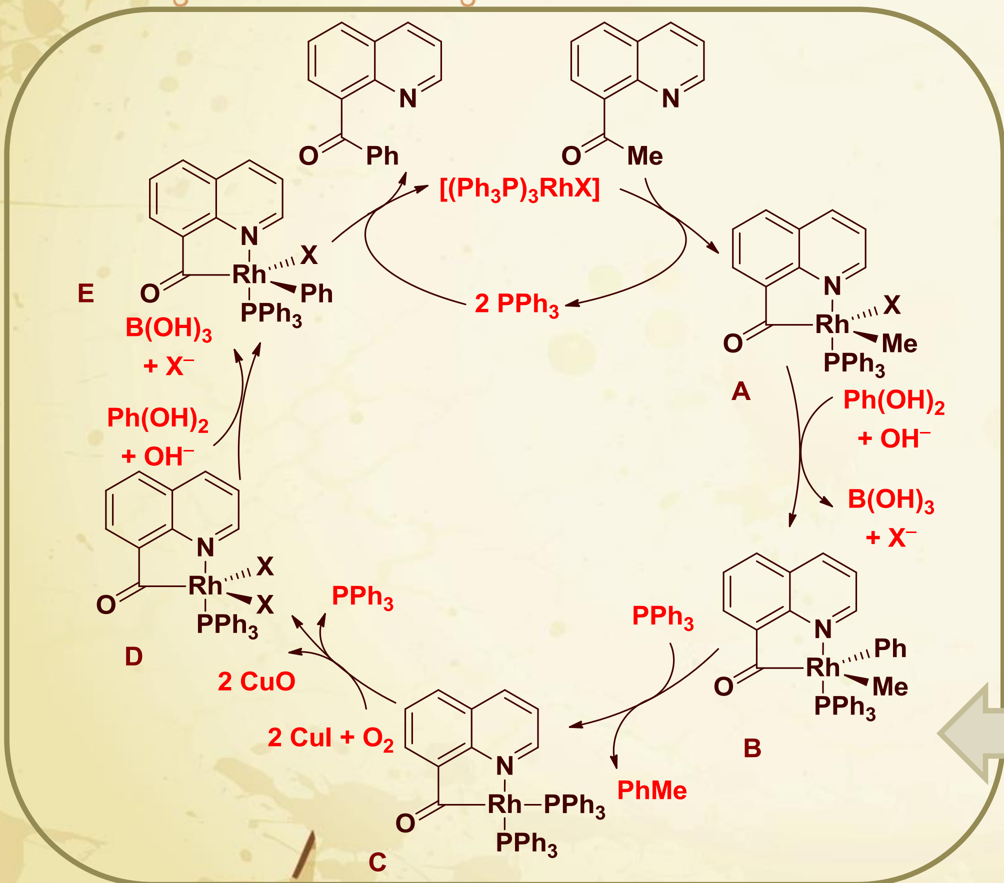
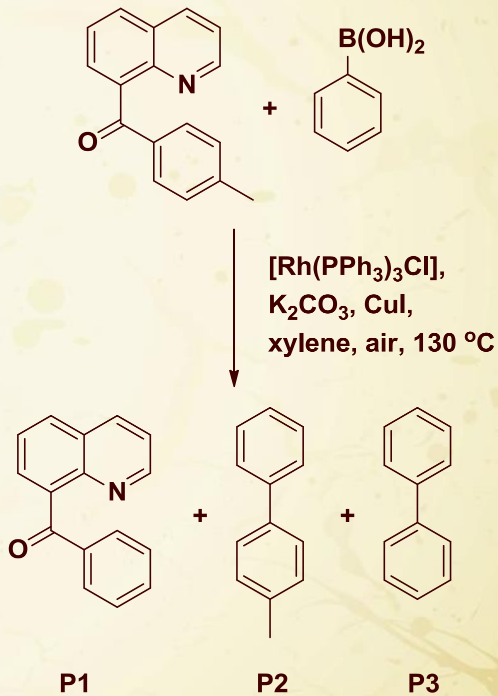


Wang, J. H. 2012



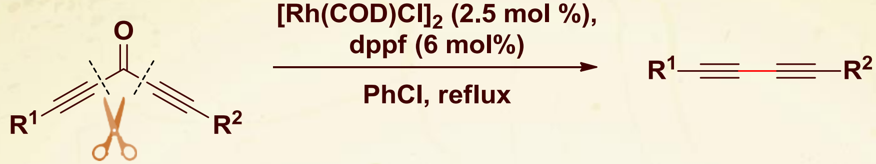


molar ratio of P1: P2= 1: 0.9

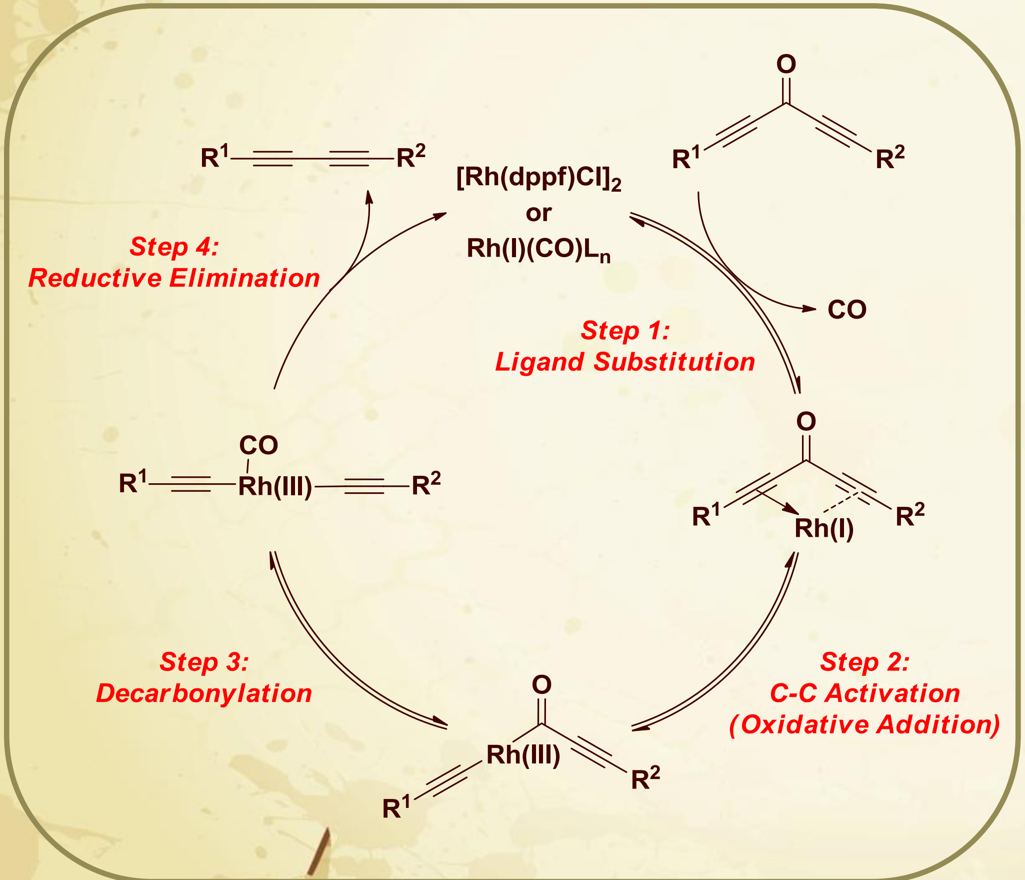
Reference: 20

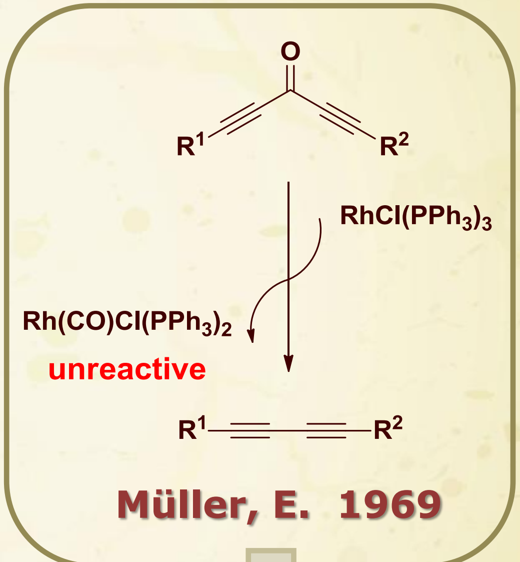
Strategies for Unstrained C-C Bond Cleavage of Ketones

Chelation Assistance



Dong, G. B. 2013





Bidentate Phosphine Ligand:

To Accelerate CO Dissociation and Reductive Elimination

Reference: 21

Summary and Outlook

Chelation Assistance

The Appropriately Located Coordinating Group Attracts The Metal Complex in Proximity to the C-C Bond to be Cleaved and the Stable Metallacycle is Formed.

Further Development of New C-C Bond Cleavage Reactions in this Field will be Expected to Explore New Catalytic Systems with Inexpensive Transition-metal Catalysts, under Mild Conditions, with Green and Sustainable Oxidants, and with a Wide Substrate Scope.

Thanks for your attention!

Jiang Fanzhou

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