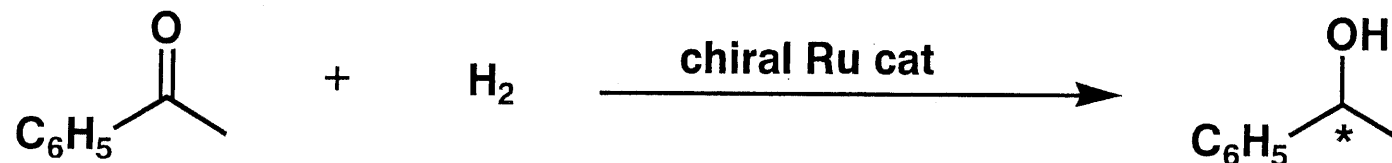


ASYMMETRIC HYDROGENATION OF KETONES



chiral Ru cat:

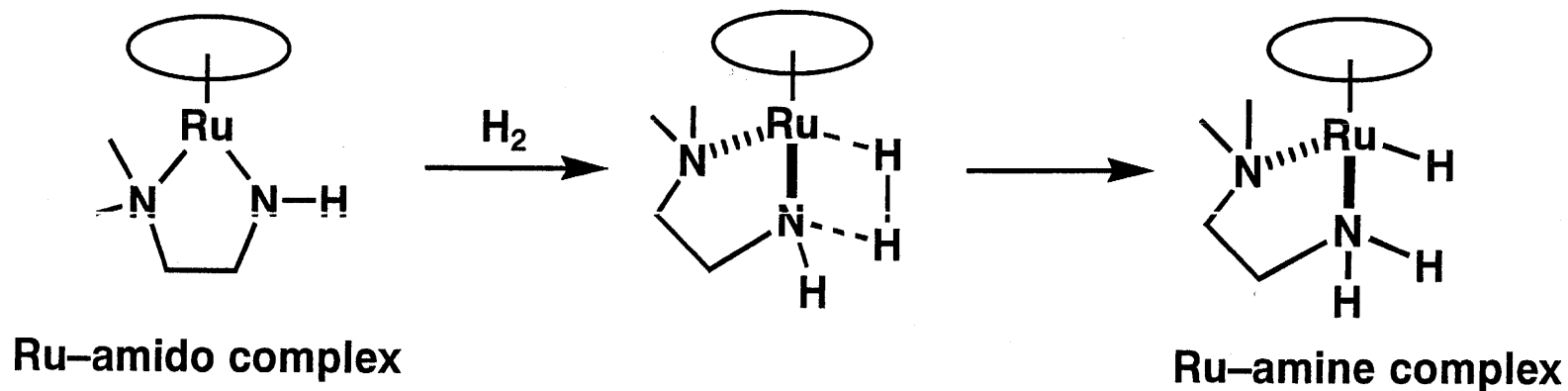
■ $\text{RuCl}_2(\text{binap}) \cdot (\text{chiral diamine}) + \text{base}$

Ohkuma, Noyori, 1995, 1998

■ $\text{Cp}^*\text{RuCl}(\text{cod}) + \text{chiral diamine} + \text{base}$

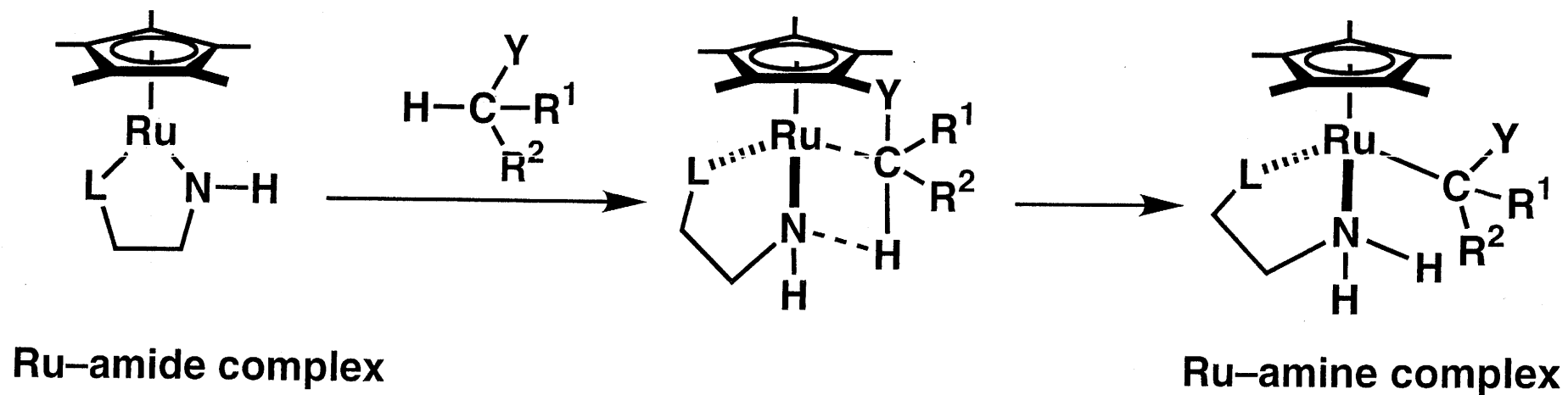
Ito, Hirakawa, Ikariya, 1998

A key step of H_2 activation



C-H BOND ACTIVATION BY Cp*Ru—amine COMPLEX

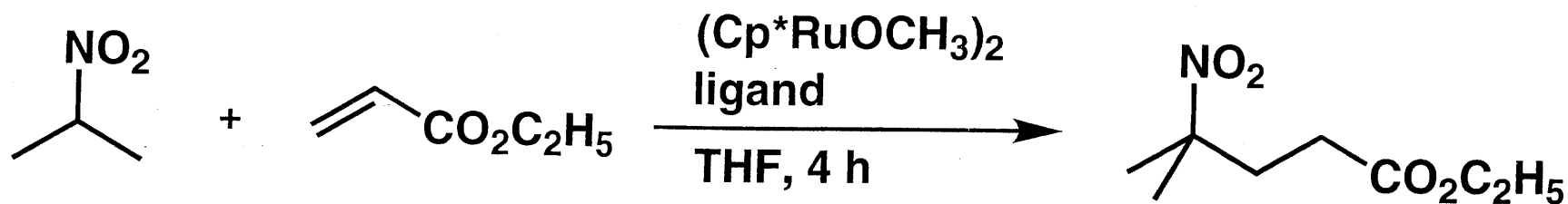
A possible mechanism



L: P, N

Y: electron withdrawing group

MICHAEL ADDITION REACTION WITH Ru–Amine CATALYSTS

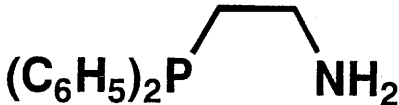
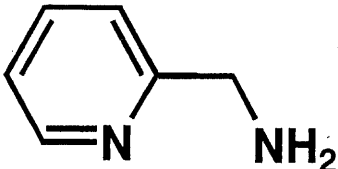
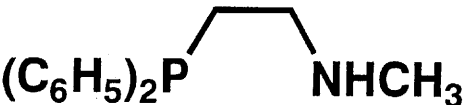
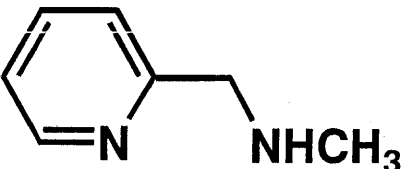
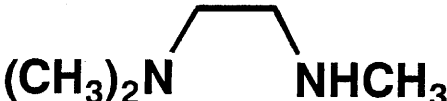
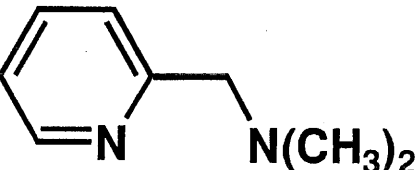


ligand	yield, % ^a
none	1
$(\text{C}_6\text{H}_5)_2\text{P}-\text{CH}_2\text{CH}_2-\text{NH}_2$	49
	97
$(\text{CH}_3)_2\text{N}-\text{CH}_2\text{CH}_2-\text{NH}_2$	18

Conditions: Ru cat 0.02–0.04 mmol,
 RNO_2 :olefin:Ru:amine=100:100:1:1, rt.

^aDetermined by GC.

EFFECT OF STRUCTURES OF LIGANDS

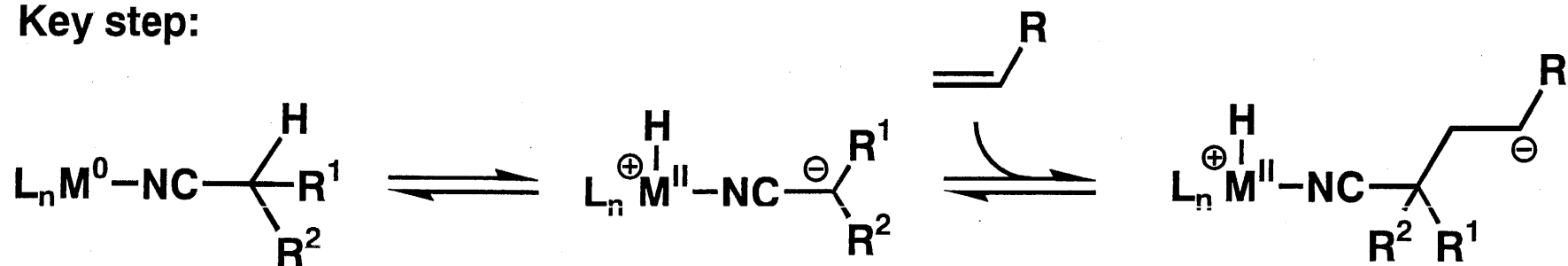
ligand	yield, % ^a	ligand	yield, % ^a	ligand	yield, % ^a
	49		97		18
	27		88		1
	1		1		1

Conditions: Ru cat 0.02–0.04 mmol, RNO_2 :olefin:Ru:amine=100:100:1:1, rt, THF, 4 h. ^aDetermined by GC.

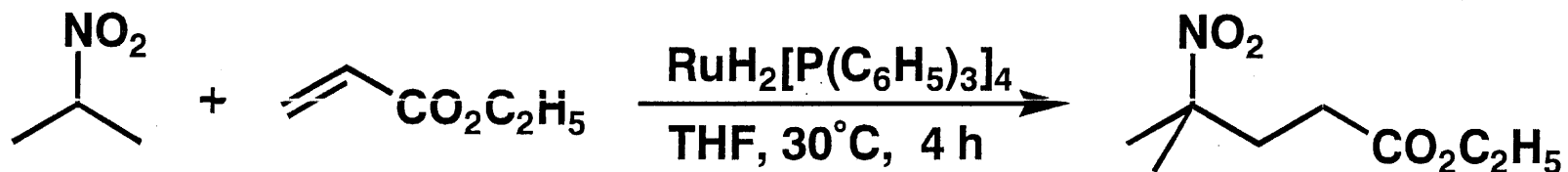
LOW-VALENT Ru⁽⁰⁾ CATALYZED MICHAEL REACTION

RuH₂[P(C₆H₅)₃]₄: Murahashi, S.-I.; Komiya, S. 1995

Key step:



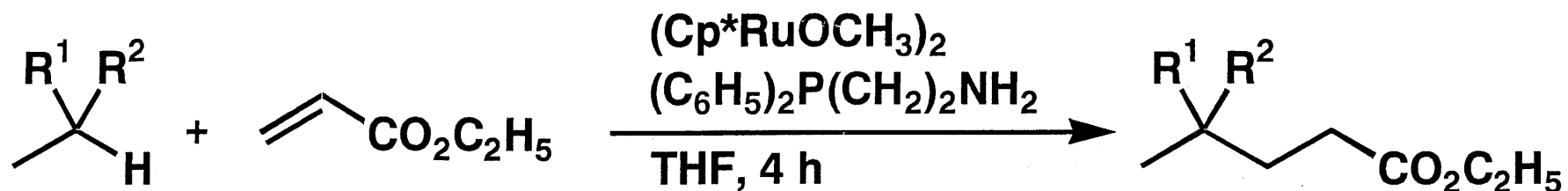
oxidative addition



NO₂R:olefin:Ru = 100:100:1

yield: 1 %

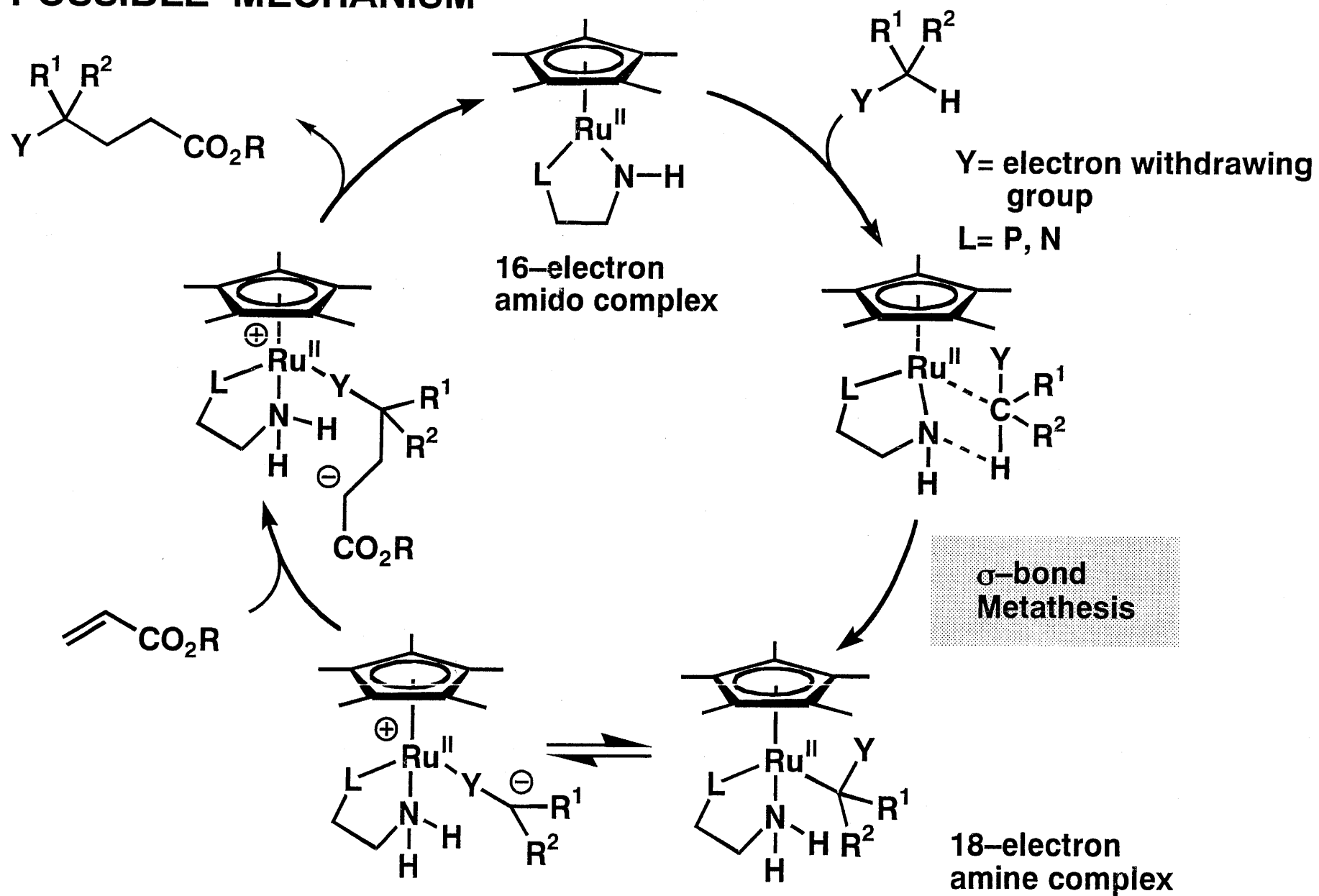
MICHAEL ADDITION OF VARIOUS SUBSTRATES



R^1	R^2	pK_a	conv, % ^a
CN	$\text{CO}_2\text{C}_2\text{H}_5$	9	100
COCH_3	COCH_3	9	60
NO_2	CH_3	10	86
COCH_3	$\text{CO}_2\text{C}_2\text{H}_5$	11	66
$\text{CO}_2\text{C}_2\text{H}_5$	$\text{CO}_2\text{C}_2\text{H}_5$	13	17

Conditions: Ru cat 0.02–0.04 mmol, substrate:olefin:Ru: amine = 100:100:1:1, rt. ^a Determined by GC.

A POSSIBLE MECHANISM



SYNTHESIS OF Cp*Ru-amine COMPLEX

