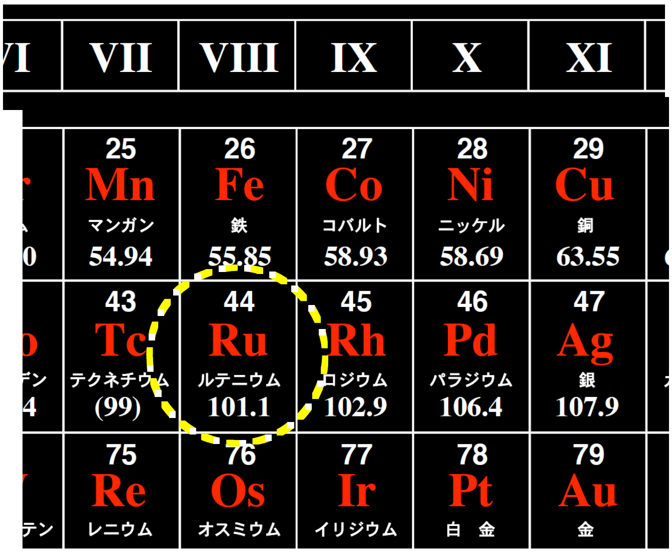
Literature Seminar

2007.11.28 Shinya Handa (D1)

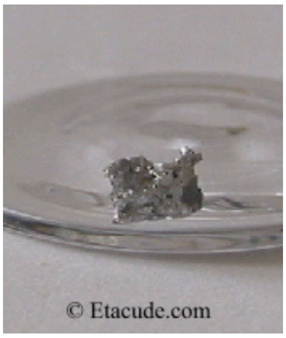
Low Valent Ruthenium Catalyzed Bond-Forming Reactions with Olefins

0 Introduction



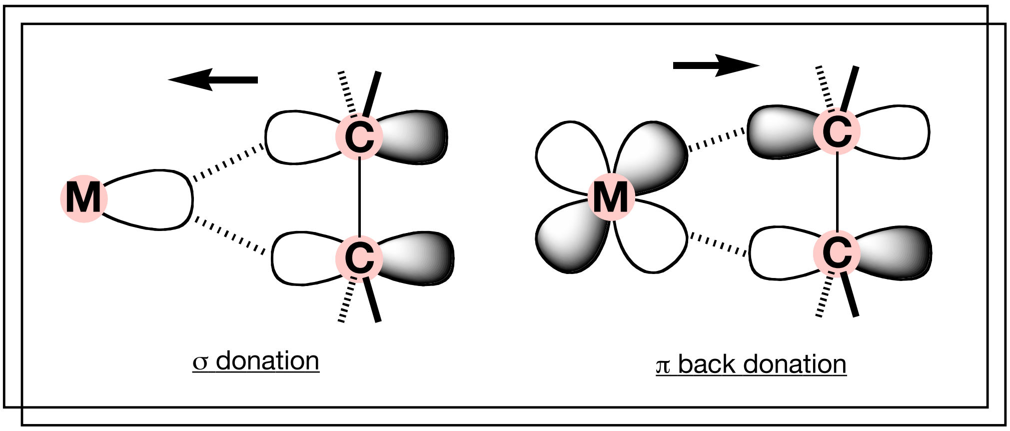
VII	VIII	IX	X	XI
25 Mn マンガン 54.94	26 Fe 鉄 55.85	27 Co コバルト 58.93	28 Ni ニッケル 58.69	29 Cu 銅 63.55
43 Tc テクネチウム (99)	44 Ru ルテニウム 101.1	45 Rh ロジウム 102.9	46 Pd パラジウム 106.4	47 Ag 銀 107.9
75 Re レニウム	76 Os オスミウム	77 Ir イリジウム	78 Pt 白 金	79 Au 金

Ru



The name derives from Ruthenia, the Latin word for Rus', a historical area which includes present-day Ukraine, Belarus, and parts of Russia, Slovakia, and Poland. Karl Klaus named the element in honour of his birthland, as he was born in Tartu, Estonia, which was at the time a part of the Russian Empire.

(from wikipedia in English)



Excellent reviews of Ru-Catalyzed reactions.

Trost, B. M. et al. *Angew. Chem., Int. Ed.* **2005,** *44*, 6630.
Mitsudo, T.-A. et al. *Synlett* **2001**, 309.
Murahashi, S.-I. et al. *Chem. Rev.* **1998**, *98*, 2599.

Other examples (See below)

- Dr. Suto's lit. seminar (2004.10.27); Direct substitution propargyl alcohol
- Morimoto-kun's seminar (2007.11.21); Synergy of transition metal complex with acid/base catalyst

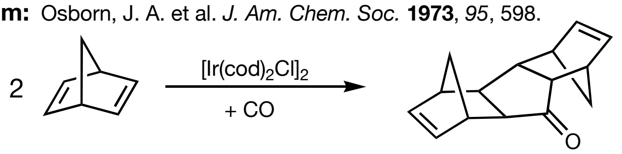
Contents

1 Dimerization of 2.5-norbornadiene

1.1 History

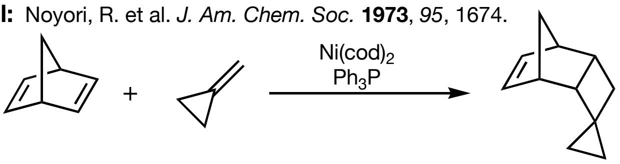
Metal-catalyzed [2+2] cycloaddition

Iridium: Osborn, J. A. et al. *J. Am. Chem. Soc.* **1973**, *95*, 598.



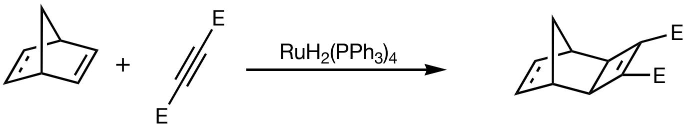
ca. 35% y.

Nickel: Noyori, R. et al. *J. Am. Chem. Soc.* **1973**, *95*, 1674.



48% y.

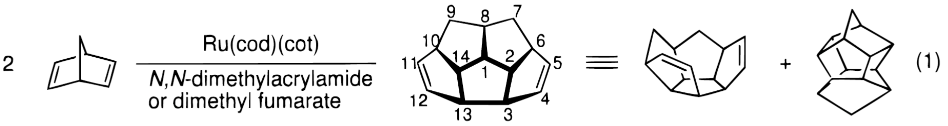
Ruthenium: Mitsudo, T.-A. et al. *J. C. S. Chem. Commun.* **1976**, 722.



up to 57% y.

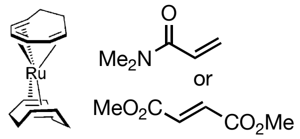
1.2 Discovery

Mitsudo, T.-A. and Watababe, Y. et al. *J. C. S. Chem. Commun.* **1994**, 435.
Mitsudo, T.-A. et al. *J. Am. Chem. Soc.* **1999**, *121*, 1839.



(1)

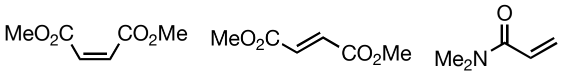
PCTD **2a** **3a** HCTD



PCTD: pentacyclo[6.6.0.0^{2,6}.0^{3,13}.0^{10,14}]tetradeca-4-11-diene
HCTD: heptacyclo[6.6.0.0^{2,6}.0^{3,13}.0^{4,14}.0^{5,9}.0^{10,14}]tetradecane

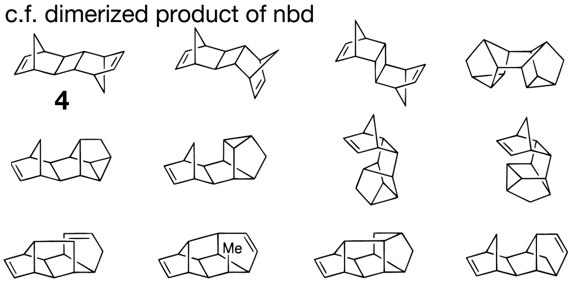
Table 1. Ruthenium Complex-Catalyzed Dimerization of **1a** in the Presence of *N,N*-Dimethylacrylamide or Dimethyl Fumarate[a]

run	catalyst	olefinic additive[b]	solvent[c]	temp., °C	time, h	yield, %[d]		
						2a	**3a**	**4**
1	Ru(cod)(cot)	DMAc	NMP	80	10	83	2	0
2	Ru(cod)(cot)	DMAc	NMP	120	15	82	6	0
3	Ru(cod)(cot)	DMAc	toluene	120	15	93	5	0
4	Ru(cod)(cot)	DMFm	THF	40	1	96	2	0
5	Ru(1-5-η-cyclooctadienyl)$_2$	DMFm	toluene	120	2	92	2	0
6	Ru(1-5-η-cyclooctadienyl)$_2$	DMFm	THF	40	24	1	trace	0
7	Ru$_3$(CO)$_{12}$	DMFm	toluene	120	2	73	9	3
8	Ru$_3$(CO)$_{12}$[e]	DMAc	NMP[f]	80	10	2	0	63
9	Ru(cod)(cot)	DMMl	THF	40	1	96	2	
18	Ru(cod)(cot)	DMAc	DMSO	120	2	23	70	
19	Ru(cod)(cot)	DMFm	DMSO	120	2	26	66	



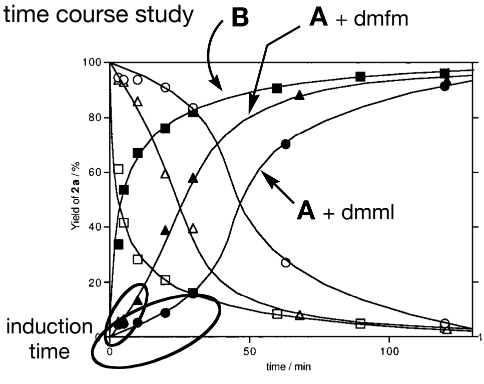
DMMl DMFm DMAc

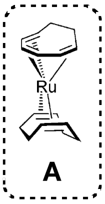
c.f. dimerized product of nbd

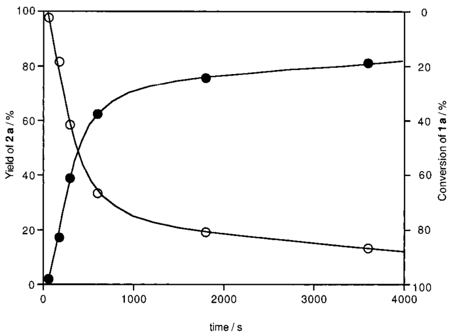


bicyclo[2,2,1]heptane
skeletone cannot be seen.
What the mechanism ??

- time course study

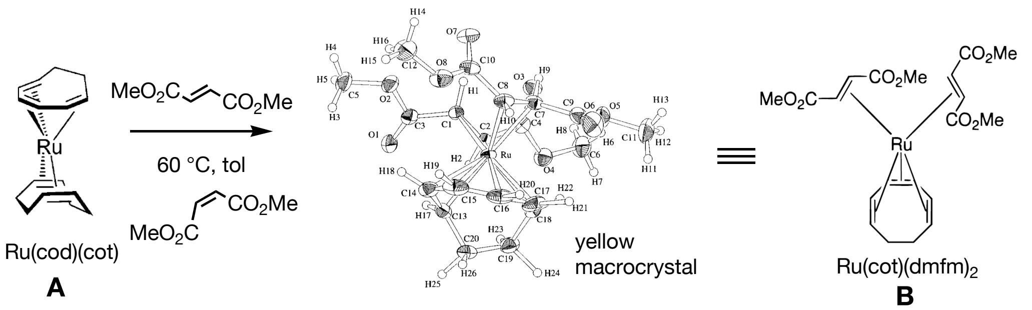






A + dmfm
A + dmml } induction period ⟶ generation of **B**

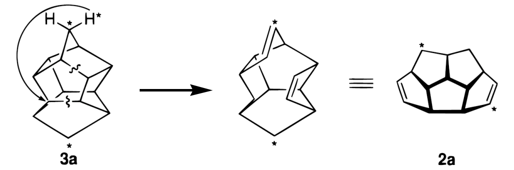
3rd order dependency on nbd
1st order dependency on catalyst



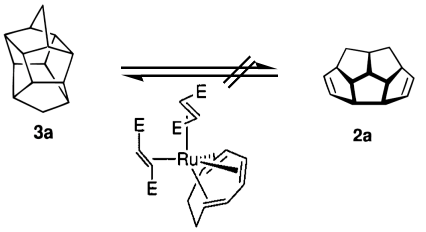
bond length
ax: longer
eq: shorter

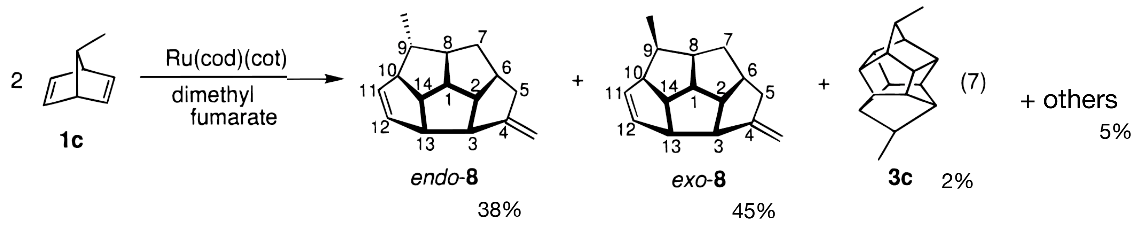
· Complexation with dimethyl maleate gave same crystal

What 's the mechanism ??



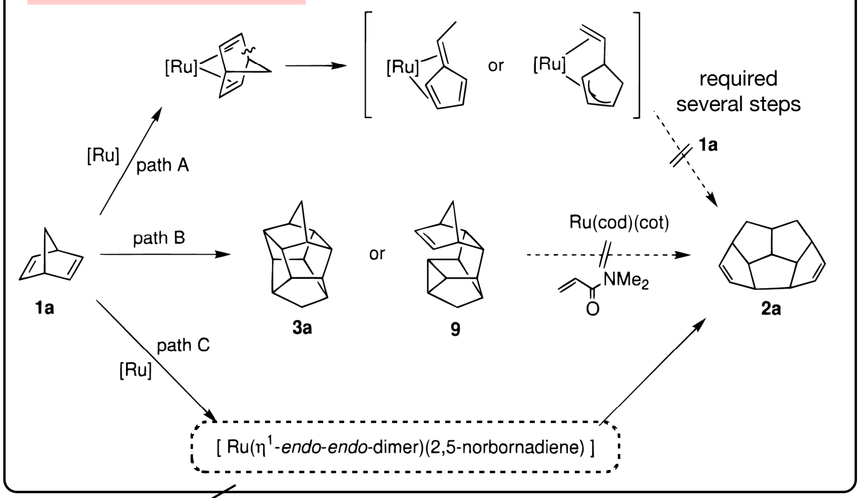
but



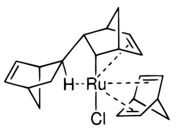


There is no evidence **3a** is the precursor.
At least 2 C-C bond must be cleaved.

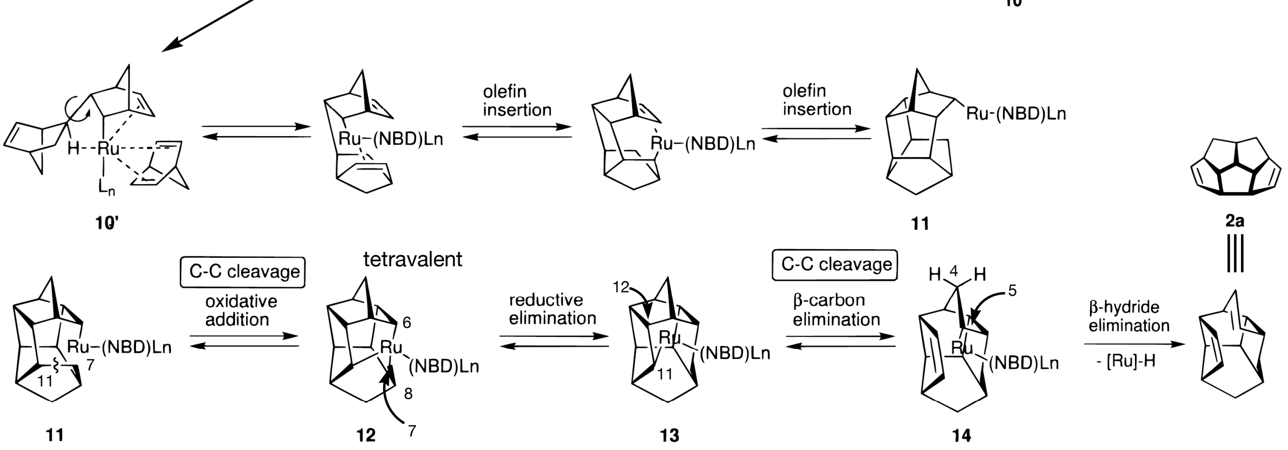
Proposed mechanism



c.f.) Ibers, J. A.et al
J. Am. Chem. Soc. **1981**, *103*, 3014.

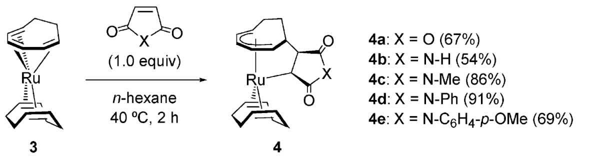


10

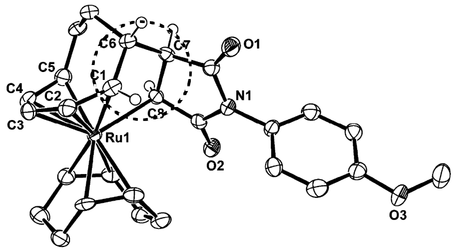


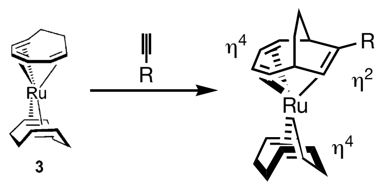
1.3 Formation of Divalent Ruthenacycles

Ura, Y. Mitsudo, T,-A. et al. *Organometallics* **2006**, *25*, 2934.



4a: X = O (67%)
4b: X = N-H (54%)
4c: X = N-Me (86%)
4d: X = N-Ph (91%)
4e: X = N-C_6H_4-*p*-OMe (69%)

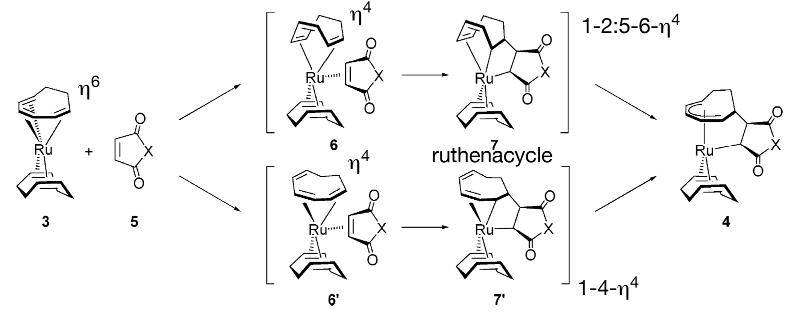




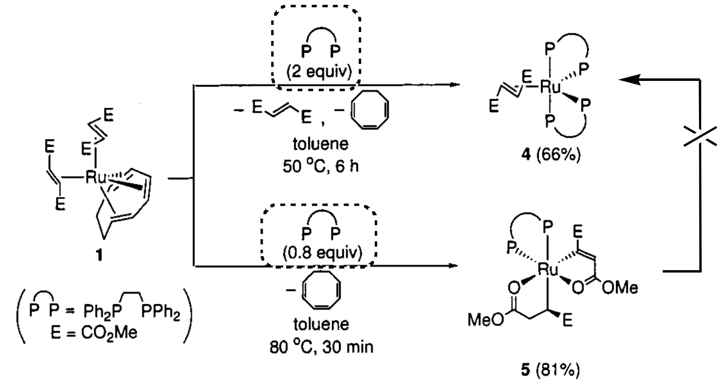
bicyclodecane ligand complex

Ambiguity of the hapticity contributed to giving unoccupied orbital

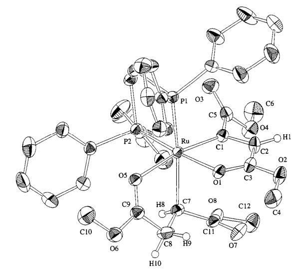
Scheme 1. Possible Pathways for the Formation of 4



Mitsudo, T,-A. et al. *Organometallics* **2000**, *19*, 5733.

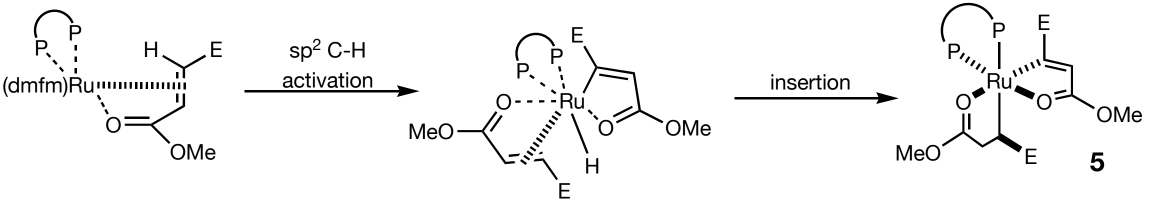


further treatment with bidentate p ligand did not gave isolable complex



X-lay structure of **5**

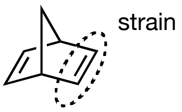
Proposed mechanism



Personal Speculation

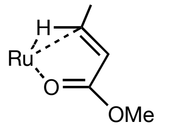
Why does interesting dimerization occur??

· sp^2 C-H bond is activated due to the strain of the C-C double and also creavage of C-C single bond occurred.



· Ru-carbonyl oxygene interaction is essential?

⟶ Ru was directed to b-H and via 5 membered ring coordination, sp^2 C-H activation was promoted



carbonyl direction

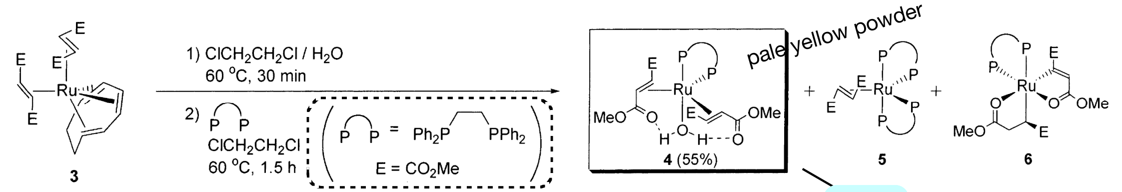
· Electron deficient olefin played key role to acceralate the reaction.

⟶ easy formation of Ru-H species

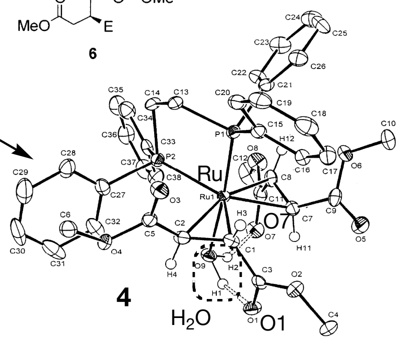
· Coordinative solvent THF made interaction with Ru center. In place of P ligand, sp^2 C-H activation was prompted.

2 Ruthenium Aqua Complex

Mitsudo, T,-A. et al. *Organometallics* **2002**, *21*, 4960.
Mitsudo, T,-A. et al. *Organometallics* **2005**, *24*, 5724.

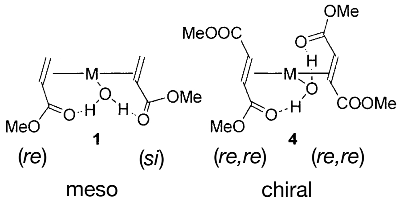


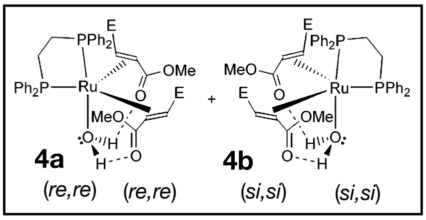
H_2O coordinated with Ru center.
Hydrogen bond with dmfm ligand.



Interestingly, dmfm ligand coordinated with Ru to same enantioface .
(*re,re*)&(*re,re*) or (*si,si*)&(*si,si*)

c.f.) Sustman. J. et al. *J. Organomet. Chem.* **1994**, *470*, 191.





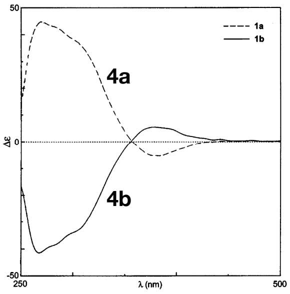
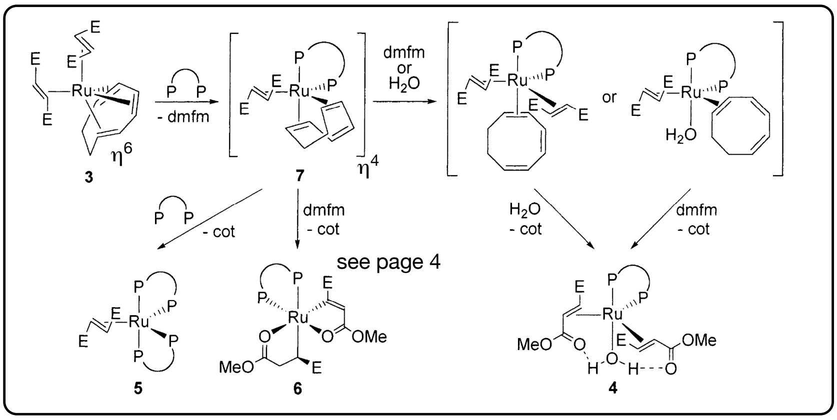


Figure 2. CD spectra of **1a** ($c = 2.5 \times 10^{-5}$ M) and **1b** ($c = 3.7 \times 10^{-5}$ M) in $CHCl_3$. For **1a**: λ_{max} 270 nm ($\Delta\epsilon$ +45), 381 (−5). For **1b**: λ 268 nm ($\Delta\epsilon$ −41), 378 (+5).

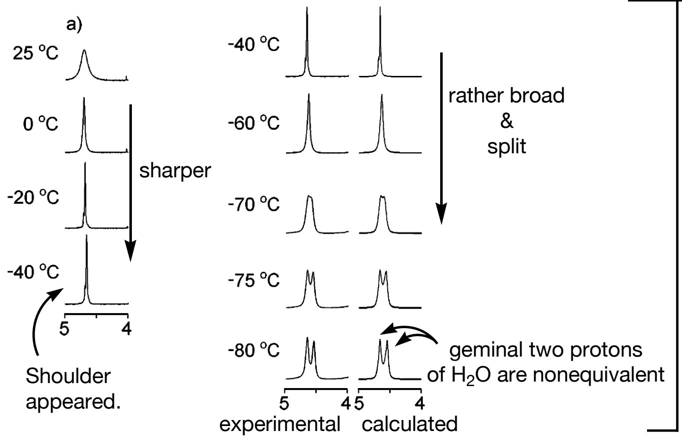


7 was isolated in the case of dppm.
7-dppm was intact with H_2O and extra P ligand.

Characters of Ru aqua complex **4**

^{1}HNMR

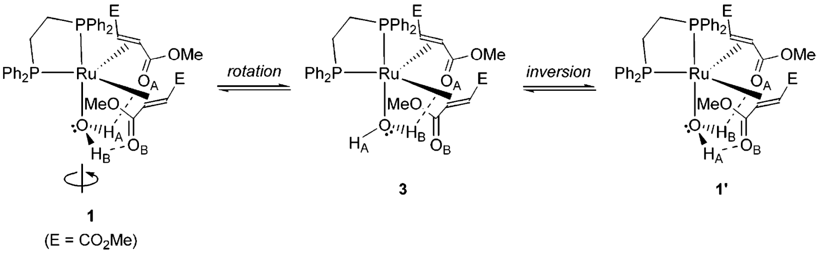
H_2O δ 4.68

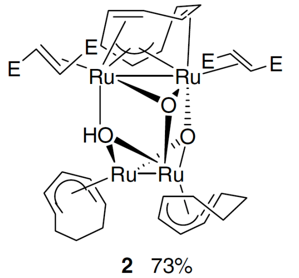


(1) At –40 °C, peak corresponding to H_2O became sharp temporary.
(2) Under -70 °C two different peaks of H_2O appeared. (split)

At higher temperature, H_2O is equivalent.
That is because...
(1) rotation
or
(2) exchange with outer H_2O

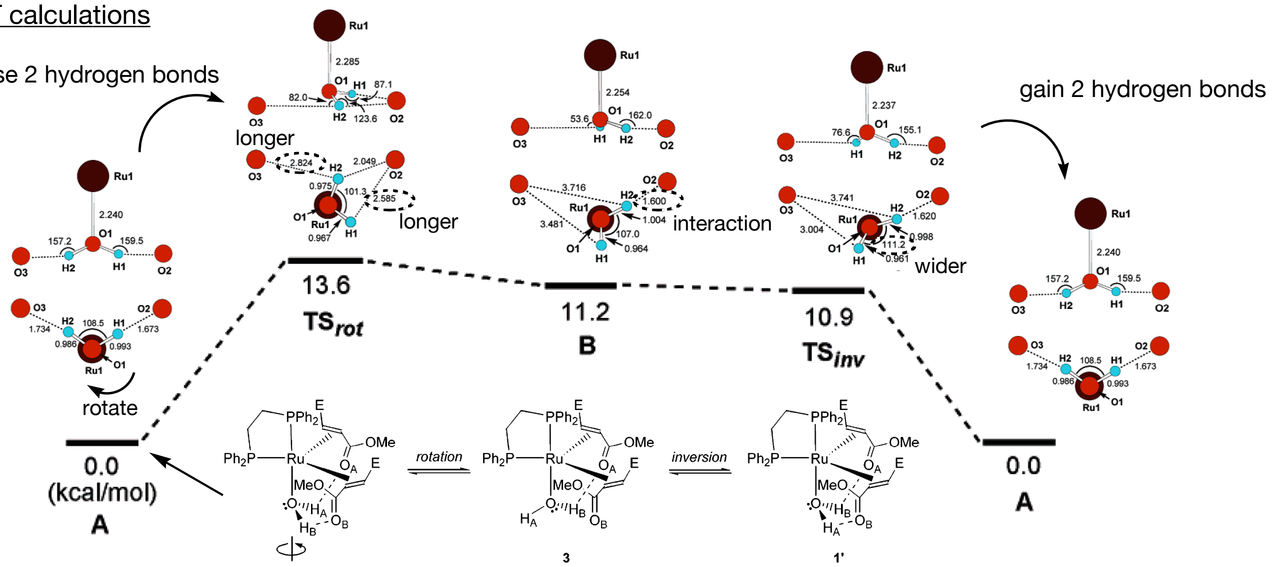
Scheme 1. Possible positional exchange process of the water protons via rotation and inversion





2 73%
μ_3-oxotetraruthenium cluster
Kondo, T. and Mitsudo, T.-A. et al
J Organomet. Chem. **2007**, *692*, 530.

DFT calculations



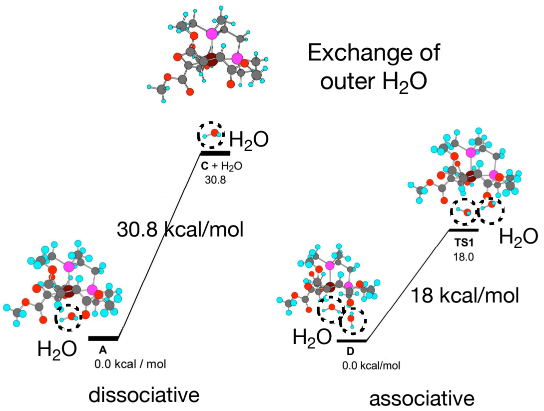
1

(E = CO_2Me)

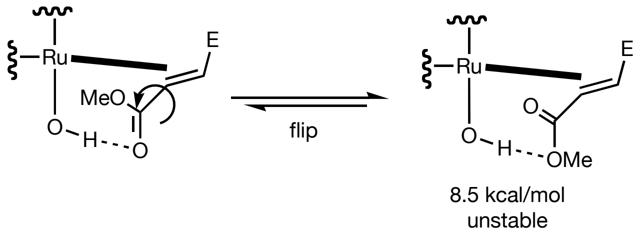
3

1'

Rotation of H_2O is energetically favorable.

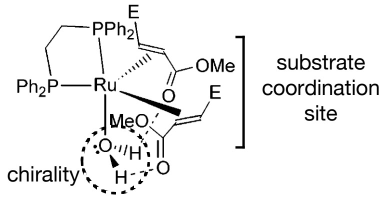


What is the shoulder peak at –40 °C.

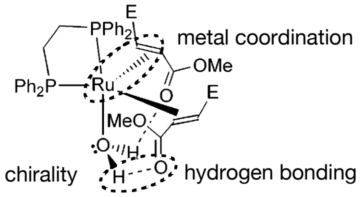


Metal aqua complex as an asymmetric catalyst
（物思いにふけってみました）

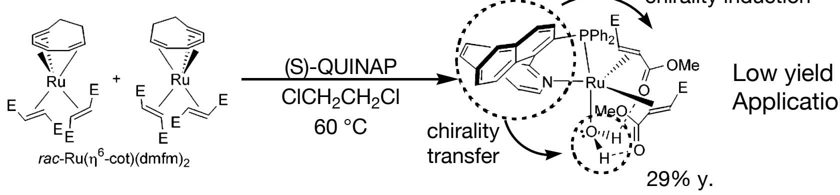
(1) chiral center is close to the substrates
⟶ Effectively enantio-induction occurs?!



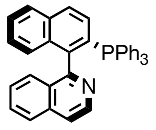
(2) different kinds of interactions of substrates
⟶ Wider ranges of substarates are applicable.



(1) Examples of (*S*)-QUINAP complex

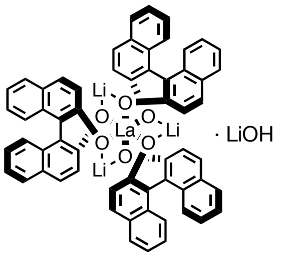


Low yield should be solved.
Application to other metals



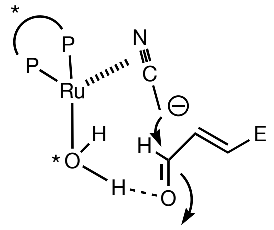
(S)-QUINAP

(2) multifuctional complex



2nd generation LLB

combinations of
Lewis Acid × Lewis Base
Brønsted Acid × Brønsted Base

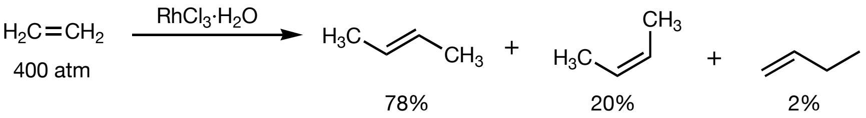


3 Codimerization of Olefins

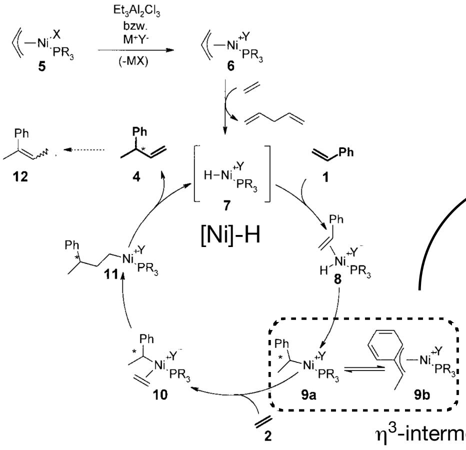
Reviews Gooßen, L. J. *Angew. Chem., Int. Ed.* **2002**, *41*, 3775.
RajanBabu, T. V. *Chem. Rev.* **2003,** *103,* 2845.
Gooßen, L. J. et al. *Angew. Chem., Int. Ed.* **2007**, *46*, 7544.

3.1 History

Alderson, T.; Jenner, E. L.; Lindsey, R. V. Jr. *J. Am. Chem. Soc.* **1965**, *87*, 5638.

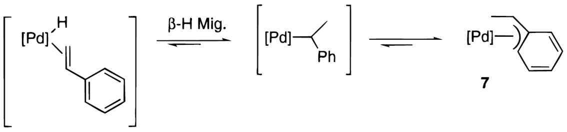


Nickel-hydride catalyzed reaction



η³-intermediate

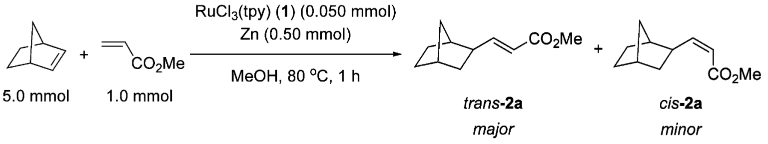
c.f.) Brookhart, M. at al. *J. Am. Chem. Soc.* **1997**, *119*, 906
and references therein.



And also regioselectivity from the view of kinetic and thermodynamic controles, see Handa's lit. Seminar 060715 Pd catalyzed oxidative reactions

3.2 Low Valent Ru Catalyzed Reaction

Mitsudo, T.-A. et al. *J. Org. Chem.* **2005**, *70*, 6623.



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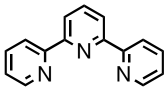
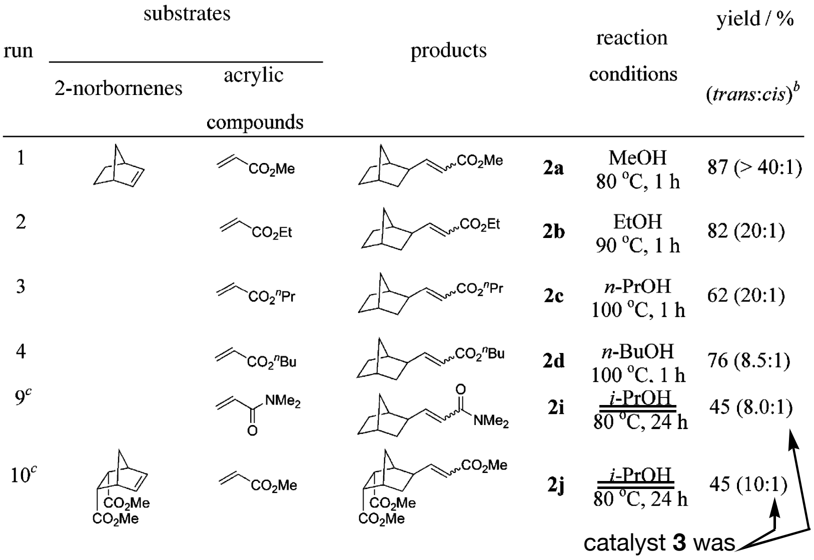


run	catalyst	yield/% (*trans*:*cis*)[b]
1	**1**	87 (>40:1)
2	**1** (without Zn)	0
7	$[RuCl_2(C_6H_6)]_2$ (**3**)	87 (>40:1)
8	$[RuCl_2(p\text{-cymene})]_2$	19
9	$[RuCl_2(C_6Me_6)]_2$	7

Ru^{III} catalyst itself had no activity.

dissociation of arene was difficult

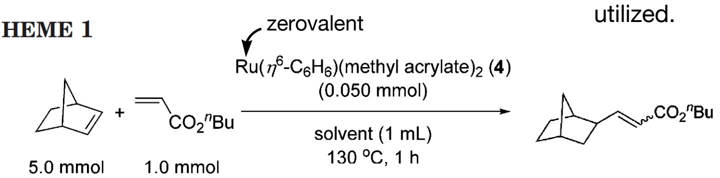


run	substrates: 2-norbornenes	substrates: acrylic compounds	products		reaction conditions	yield / % (*trans*:*cis*)[b]
1		CO_2Me	CO_2Me	**2a**	MeOH 80 °C, 1 h	87 (> 40:1)
2		CO_2Et	CO_2Et	**2b**	EtOH 90 °C, 1 h	82 (20:1)
3		$CO_2{}^nPr$	$CO_2{}^nPr$	**2c**	*n*-PrOH 100 °C, 1 h	62 (20:1)
4		$CO_2{}^nBu$	$CO_2{}^nBu$	**2d**	*n*-BuOH 100 °C, 1 h	76 (8.5:1)
9[c]		NMe_2, O	O, NMe_2	**2i**	*i*-PrOH 80 °C, 24 h	45 (8.0:1)
10[c]	CO_2Me CO_2Me	CO_2Me	CO_2Me CO_2Me CO_2Me	**2j**	*i*-PrOH 80 °C, 24 h	45 (10:1)

catalyst **3** was utilized.

SCHEME 1

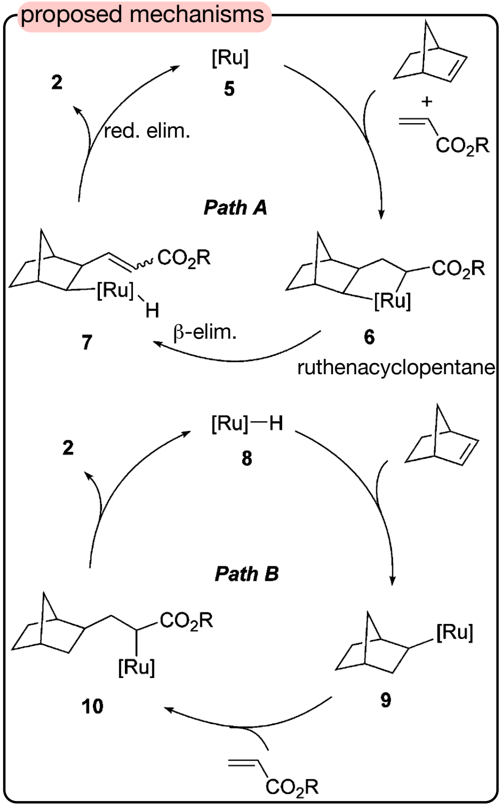
zerovalent



solvent	yield (*trans*:*cis*)
^{n}BuOH	79% (3.6:1)
DMA	81% (3.8:1)
diglyme	67% (2.7:1)

Ru^0 is the active species.

Alcohol is not necessary for dimerization.



Also other mechanism can be thought. (Path C: one candidate)

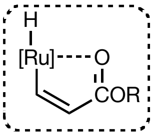
Path B

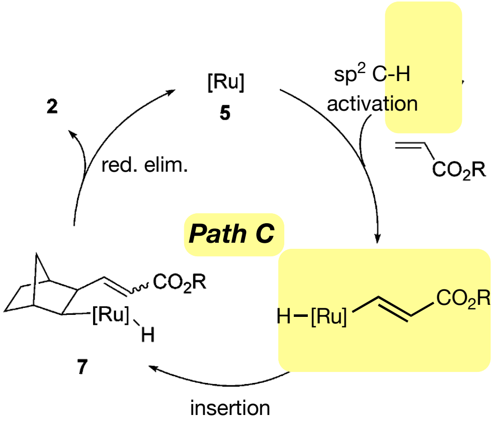
β-H elimination from **7** cannot be explained predominat formation of trans-isomer.

How did active catalys [Ru]-H generated ??

Path C

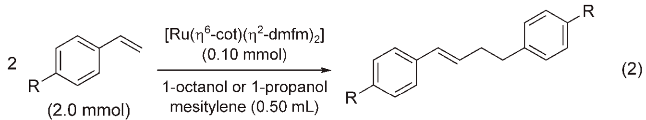
After the C-H activation cis-isomer might be more stable?





Kondo, T. et al. *Angew. Chem., Int. Ed.* **2007**, *46*, 5958.

- no reaction occurred with divalent Ru complex.
- linear adduct formed with (*E*) C=C double bond.
- Primary alcohol is essential (3 equiv.).



1a: R = H
1b: R = CH_3
1c: R = OCH_3
1d: R = F

2a:	80 (53)%	(95% *E* form)
2b:	71%	(95% *E* form)
2c:	(66)%	(97% *E* form)
2d:	67 (56)%	(97% *E* form)

(parehthasis is isolated yield)

Time course study

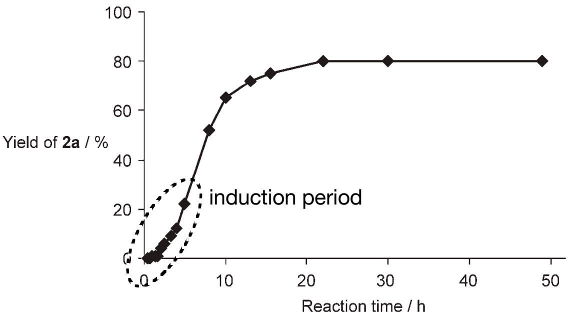


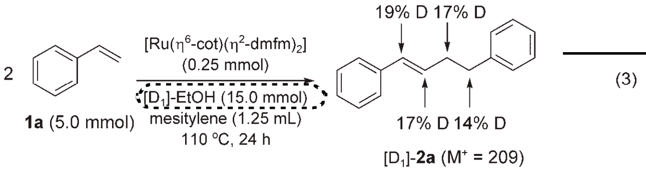
Figure 1. The time-course of the dimerization of **1a** to **2a**.

What is the role of alcohol ?

- Primary alcohol is essential
  (1-propanol, 1-octanol and ehanol)

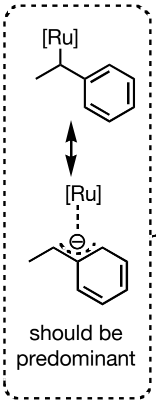
Secondary, tertiary alcohol is not suitable.

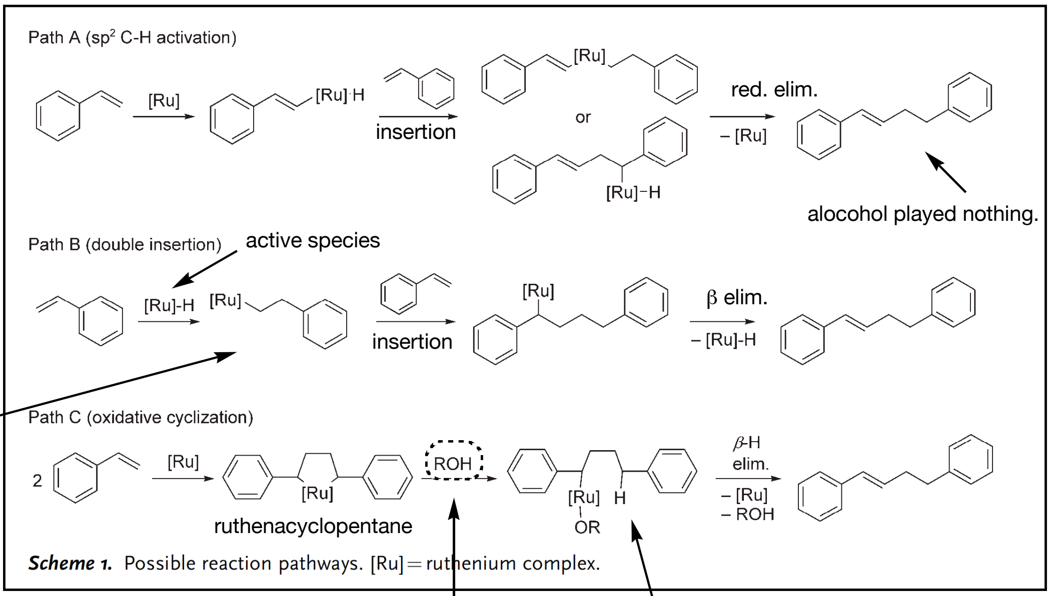
⟶ Alcohol interacted with Ru complex.



⟶ almost no [D_2]-**2a** or [D_3]-**2a**

Generation of [Ru]-H which rapidly reacted with styrene and the product was intact to the active species.





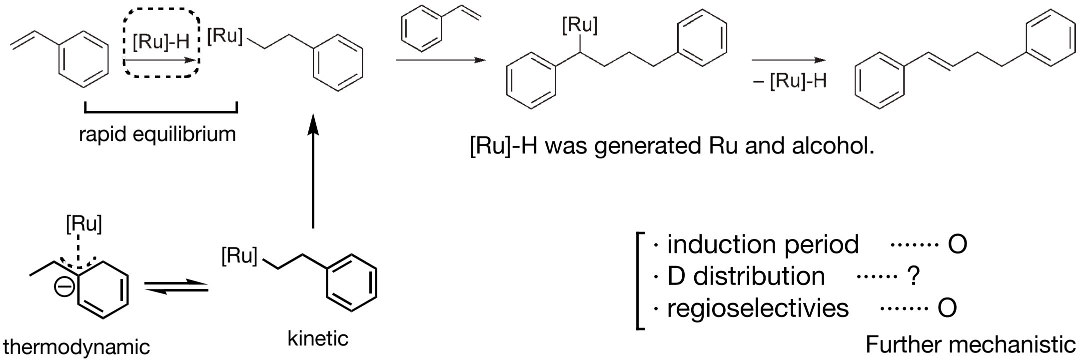
Scheme 1. Possible reaction pathways. [Ru] = ruthenium complex.

acceleration of reaction
or
direct other pathway

D distribution cannot be explained

Authers suggested path C. However, the observed phenomina is imcompatible.

Is path B the most reasonable mechanism??



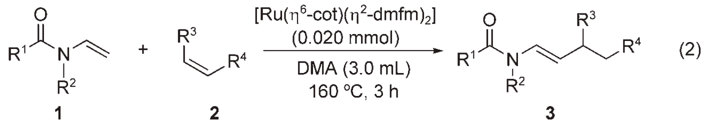
[Ru]-H was generated Ru and alcohol.

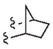
- · induction period ······· O
- · D distribution ······ ?
- · regioselectivies ······· O

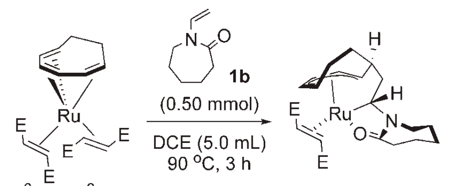
Further mechanistic study is required.

c.f.) Stahl, S. S. et al. *J. Am Chem Soc.* **2005**, *127*, 17888.

Ura, Y., Kondo, T. et al. *Angew. Chem., Int. Ed.* **2007**, *46*, 5160.



1 1.1 mmol	**2** 1.0 mmol	**3**
1a: $R^1 = R^2 = Me$	**2b:** $R^3 = H$, $R^4 = CO_2\mathit{t}Bu$	**3b:** 77 (61)% (88% *E* form)
1a: $R^1 = R^2 = Me$	**2c:** $R^3 = H$, $R^4 = COEt$	**3c:** 70 (48)% (94% *E* form)
1a: $R^1 = R^2 = Me$	**2d:** $R^3 = R^4 = CO_2Me$	**3d:** 76 (52)% (98% *E* form)
1a: $R^1 = R^2 = Me$	**2e:** $R^3 = R^4 =$ 	**3e:** 33% (99% *E* form, and *exo* only)[a]
1a: $R^1 = R^2 = Me$	**2f** : $R^3 = R^4 = H$	**3f** : 16% (97% *E* form)[b]
1b: $R^1, R^2 = -(CH_2)_5-$	**2a:** $R^3 = H$, $R^4 = CO_2Et$	**3g:** 60 (50)% (88% *E* form)

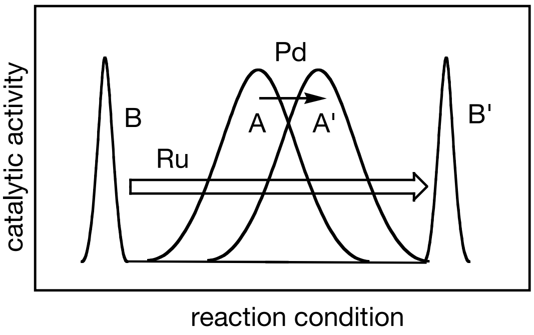


[Ru(η6-cot)(η2-dmfm)2]
(0.50 mmol)
(E = CO_2Me)

8a
(27% yield)

[6+2] cycloaddition
consumed the substrate some extent.

3 Outlook & Remark



Ru-catalyzed reactions
Reactivities, substrate scopes