Low Valent Ruthenium Catalyzed Bond-Forming Reactions with Olefins

0 Introduction

Excellent reviews of Ru-Catalyzed reactions.

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

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1 Dimerization of 2.5-norbornadiene

1.1 History
Metal-catalyzed [2+2] cycloaddition


\[
\text{Ru} + [\text{Ir} \text{cod}]_2 \text{Cl}_2 + \text{CO} \rightarrow \text{CA} \rightarrow \text{Nu} \text{lod} \text{dime} \text{ry} \text{ lumate} \]

ca. 35% y.


\[
\text{Ni} + \text{cod} \text{P} \text{Ph}_3 \rightarrow \text{CA} \rightarrow \text{Nu} \text{lod} \text{dime} \text{ry} \text{ lumate} \]

48% y.


\[
\text{Ru} + \text{Ni} \text{lod} \text{dime} \text{ry} \text{ lumate} \rightarrow \text{CA} \rightarrow \text{Nu} \text{lod} \text{dime} \text{ry} \text{ lumate} \]

up to 57% y.

1.2 Discovery

- **Ru(cod)(cot)**
  - N,N-dimethylacrylamide or dimethyl fumarate

\[
\text{PCTD} \quad \text{2a} \quad \text{HCTD} \quad \text{3a} \]

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

<table>
<thead>
<tr>
<th>run</th>
<th>catalyst</th>
<th>olefinic additive</th>
<th>solvent</th>
<th>temp. °C</th>
<th>time, h</th>
<th>2a</th>
<th>3a</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Ru(cod)(cot)</td>
<td>DMAc</td>
<td>NMP</td>
<td>80</td>
<td>10</td>
<td>83</td>
<td>2</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>Ru(cod)(cot)</td>
<td>DMAc</td>
<td>NMP</td>
<td>120</td>
<td>15</td>
<td>82</td>
<td>6</td>
<td>0</td>
</tr>
<tr>
<td>3</td>
<td>Ru(cod)(cot)</td>
<td>DMAc</td>
<td>toluene</td>
<td>120</td>
<td>15</td>
<td>93</td>
<td>5</td>
<td>0</td>
</tr>
<tr>
<td>4</td>
<td>Ru(cod)(cot)</td>
<td>DMAf</td>
<td>THF</td>
<td>80</td>
<td>1</td>
<td>93</td>
<td>5</td>
<td>0</td>
</tr>
<tr>
<td>5</td>
<td>Ru(cod)(cot)</td>
<td>DMAf</td>
<td>toluene</td>
<td>120</td>
<td>24</td>
<td>1</td>
<td>trace</td>
<td>0</td>
</tr>
<tr>
<td>6</td>
<td>Ru(cod)(cot)</td>
<td>DMAf</td>
<td>THF</td>
<td>40</td>
<td>24</td>
<td>1</td>
<td>trace</td>
<td>0</td>
</tr>
<tr>
<td>7</td>
<td>Ru(cod)(cot)</td>
<td>DMAf</td>
<td>toluene</td>
<td>120</td>
<td>24</td>
<td>73</td>
<td>9</td>
<td>0</td>
</tr>
<tr>
<td>8</td>
<td>Ru(cod)(cot)</td>
<td>DMAc</td>
<td>NMP</td>
<td>80</td>
<td>10</td>
<td>2</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>9</td>
<td>Ru(cod)(cot)</td>
<td>DMAm</td>
<td>NMP</td>
<td>40</td>
<td>1</td>
<td>96</td>
<td>2</td>
<td>0</td>
</tr>
<tr>
<td>18</td>
<td>Ru(cod)(cot)</td>
<td>DMAc</td>
<td>DMSO</td>
<td>120</td>
<td>2</td>
<td>23</td>
<td>70</td>
<td>0</td>
</tr>
<tr>
<td>19</td>
<td>Ru(cod)(cot)</td>
<td>DMAc</td>
<td>DMSO</td>
<td>120</td>
<td>2</td>
<td>26</td>
<td>66</td>
<td>0</td>
</tr>
</tbody>
</table>

bicyclo[2.2.1]heptane
skeleton cannot be seen.
What the mechanism ??

- time course study
  - B A + dmmf

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

\[
\text{MeO} = \text{CO}_2 \text{Me} \quad \text{MeO} = \text{CO}_2 \text{Me} \quad \text{MeO} = \text{CO}_2 \text{Me} \]

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\text{MeO} = \text{CO}_2 \text{Me} \quad \text{MeO} = \text{CO}_2 \text{Me} \quad \text{MeO} = \text{CO}_2 \text{Me} \]

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\text{MeO} = \text{CO}_2 \text{Me} \quad \text{MeO} = \text{CO}_2 \text{Me} \quad \text{MeO} = \text{CO}_2 \text{Me} \]

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\[
\text{MeO} = \text{CO}_2 \text{Me} \quad \text{MeO} = \text{CO}_2 \text{Me} \quad \text{MeO} = \text{CO}_2 \text{Me} \]
What`s the mechanism ??

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

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1.3 Formation of Divalent Ruthenacycles


Scheme 1. Possible Pathways for the Formation of 4

Ambiguity of the hapticity contributed to giving unoccupied orbital


Proposed mechanism

X-ray structure of 5

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 cleavage of C-C single bond occurred.

- Ru-carbonyl oxygene interaction is essential?
  $\rightarrow$ Ru was directed to b-H and via 5 membered ring coordination, $sp^2$ C-H activation was promoted

- Electron deficient olefin played key role to accelerate the reaction.
  $\rightarrow$ 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.

$\text{MeO}^-$
2 Ruthenium Aqua Complex


Interestingly, dmfm ligand coordinated with Ru to same enantiopair,
(re, re) & (re, re) or (si, si) & (si, si)


Characters of Ru aqua complex 4

$^1$H NMR

H$_2$O $\delta$ 4.68

-25°C
-0°C
-20°C
-40°C

Shoulder

5
4

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

(1) At -40 °C, peak corresponding to H$_2$O became sharp temporary.
(2) Under -70 °C two different peaks of H$_2$O appeared, (split)

At higher temperature, H$_2$O is equivalent.

That is because...

(1) rotation
(2) exchange with outer H$_2$O

2 73% $\mu_3$-oxotetraathenium cluster
Kondo, T. and Mitsudo, T.-A. et al.
DFT calculations

What is the shoulder peak at -40 °C.

Metal aqua complex as an asymmetric catalyst

(1) chiral center is close to the substrates
   Effectively enantio-induction occurs?!
(2) different kinds of interactions of substrates
   Wider ranges of substrates are applicable.

(1) Examples of (S)-QUINAP complex

(2) multifunctional complex

EBCP calculations

2nd generation LLB
3 Codimerization of Olefins

Reviews

3.1 History

\[
\begin{align*}
\text{H}_2\text{C}=\text{CH}_2 & \xrightarrow{\text{RhCl}_3\cdot\text{H}_2\text{O}} \text{H}_2\text{C}-\text{CH}_3 + \text{H}_2\text{C}=-\text{CH}_3 \\
\text{400 atm} & \quad \text{78\%} \quad \text{20\%} \quad \text{2\%}
\end{align*}
\]

Nickel-hydride catalyzed reaction

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

3.2 Low Valent Ru Catalyzed Reaction

\[
\text{run} \quad \text{catalyst} \quad \text{yield\% (trans:cis)}^b
\]

<table>
<thead>
<tr>
<th>run</th>
<th>catalyst</th>
<th>yield% (trans:cis)$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td><a href="1">RuCl$_2$(tpy)</a> (0.050 mmol)</td>
<td>87 (&gt;40:1)</td>
</tr>
<tr>
<td>2</td>
<td><a href="1">RuCl$_2$(tpy)</a> (0.050 mmol)</td>
<td>0</td>
</tr>
<tr>
<td>7</td>
<td>[RuCl$_2$(p-cymene)$_2$]</td>
<td>19</td>
</tr>
<tr>
<td>9</td>
<td>[RuCl$_2$(cyclohexene)$_2$]</td>
<td>7</td>
</tr>
</tbody>
</table>

Ru$^{III}$ catalyst itself had no activity. Dissociation of arene was difficult.

Proposed mechanisms:
Path A
Path B
Red. elim.
β-elim.
Ruthenacyclopentane

Scheme 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 predominant formation of trans-isomer.
How did active catalys [Ru]-H generated ??

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


![Scheme 1. Possible reaction pathways. [Ru] = ruthenium complex.](image)

Authors suggested path C. However, the observed phenomena is incompatible.
Is path B the most reasonable mechanism??

![Chemical structure](image1)

- Induction period
- D distribution
- Regioselectivities

Further mechanistic study is required.


![Chemical structure](image2)

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

### 3 Outlook & Remark

![Graphical representation](image3)

- Catalytic activity
- Reaction condition
- Ru-catalyzed reactions
  - Reactivities, substrate scopes

condition B

<p>| | |</p>
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condition A