Stoichiometric and Catalytic Cross Dimerization between Butadiene and Methyl Acrylate Promoted by a Ruthenium(0) Complex

Masafumi Hirano,* Yasutomo Arai, Nobuyuki Komine, and Sanshiro Komiya

Department of Applied Chemistry, Graduate School of Engineering, Tokyo University of Agriculture and Technology, 2-24-26 Nakacho, Koganei, Tokyo 184-8588, Japan

*Summary: Treatment of Ru(η^4-butadiene)(η^4-1,5-COD)(NCMe) (**1a**) with methyl acrylate in benzene for 3 h at 6 °C produces Ru{cisoid-η^4-(2E,4E)-(methyl hepta-2,4-dienoate)}(η^4-1,5-COD)- (NCMe) (**2a**) in 97% yield. Complex **1a** (2 mol %) catalyzes the chemoselective cross dimerization between butadiene and methyl acrylate in benzene to give a mixture of the regio- isomers of methyl heptadienoate in 43% yield by the oxidative coupling reaction.*

Selective dimerizations of substituted olefins catalyzed by cationic Ru(II) complexes with Cp or Cp* ligands are regarded as one of the promising zero-emission processes for preparing monomers for condensation polymerization as well as other starting materials.[1] Although a highly Lewis basic Ru(0) species is expected to enhance the susceptibility toward the oxidative coupling reaction, the mechanism is not well understood and explored. We recently obtained explicit examples in support of oxidative coupling of acrylates on a zerovalent ruthenium compound, Ru(η^6-naphthalene)- (η^4-1,5-COD)[2] (COD = cyclooctadiene (C$_8$H$_{12}$)), by the addition of ancillary ligands such as PMe$_3$ or MeCN to the catalytic system, giving {κ^4-(methyl methacrylate)}- {η^2-(methyl methacrylate)}ruthenium(0) (**I**) in the case of methyl methacrylate[3] and *trans*-2,5-bis(methoxycarbonyl)- ruthenacyclopentane (**II**) in the case of methyl acrylate[4] (Chart 1). Notably, **II** is an effective catalyst for the tail-to- tail type coupling reaction of methyl acrylate.

One promising and valuable outlet of olefin dimerization reactions is chemoselective cross dimerization of substituted olefins, since it would provide an easy and versatile synthetic methodology for a variety of organic molecules having functional groups. Herein we disclose the stoichiometric and catalytic chemo- selective cross dimerization of butadiene and methyl acrylate.

Treatment of Ru(η^4-butadiene)(η^4-1,5-COD)L[5] (**1a**: L = MeCN) with methyl acrylate in benzene at 6 °C followed by workup procedures produced a brown oil of Ru{cisoid-η^4- (2E,4E)-(methyl hepta-2,4-dienoate)}(η^4-1,5-COD)L (**2a**: L = MeCN) in 97% yield (Scheme 1).

Chart 1

Scheme 1

1a: L = MeCN   **2a**: L = MeCN, 97%

2b: L = PPh$_3$, 36%
2c: L = CO, 53%

Complex **2a** was characterized by ^{1}H NMR and ^{1}H−^{1}H COSY.[6] The most interesting feature of **2a** is the ethyl group attached to the conjugated diene moiety. It is worthy to note that a conjugated diene fragment is produced by the coupling reaction of the coordinated butadiene with methyl acrylate. The methylene protons in the ethyl group are observed as diastereotopic, suggesting the conjugated diene moiety is coordinated to the ruthenium center. These observations are consistent with the formation of the η^4-(2E,4E)-methyl hepta-2,4-dienoate fragment on ruthenium. The formation of the conjugated diene moiety was also confirmed by the iodolysis of **2a** to give (2E,4E)-methyl hepta-2,4-dienoate[7] in 80% yield.

*To whom correspondence should be addressed. Tel and fax: +81 423 88 7044. E-mail: hrc@cc.tuat.ac.jp.

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(6) ^{1}H NMR (300 MHz, C$_6$D$_6$, rt): δ 0.82 (s, 3H, NC*Me*), 0.99 (t, J_{H-H} = 7.2 Hz, 3H, 7-*Me*), 1.22 (q, J_{H-H} = 7.0 Hz, 1H, 5-C*H*), 1.30 (dqui, J_{H-H} = 13.8, 7.0 Hz, 1H, 6-C*H$_2$*), 1.39 (d, J_{H-H} = 7.1 Hz, 1H, 2-C*H*), 1.48 (dqui, J_{H-H} = 13.8, 7.0 Hz, 1H, 6-C*H$_2$*), 1.95−2.1 (m, 4H, COD), 2.15−2.3 (m, 2H, COD), 2.4−2.55 (m, 2H, COD), 3.0−3.1 (m, 1H, COD), 3.3−3.45 (m, 2H, COD), 3.49 (s, 3H, O*Me*), 4.52−4.57 (m, 1H, COD), 4.86 (dd, J_{H-H} = 7.0, 5.1 Hz, 1H, 4-C*H*), 6.10 (dd, J_{H-H} = 7.1, 5.1 Hz, 1H, 3-C*H*).
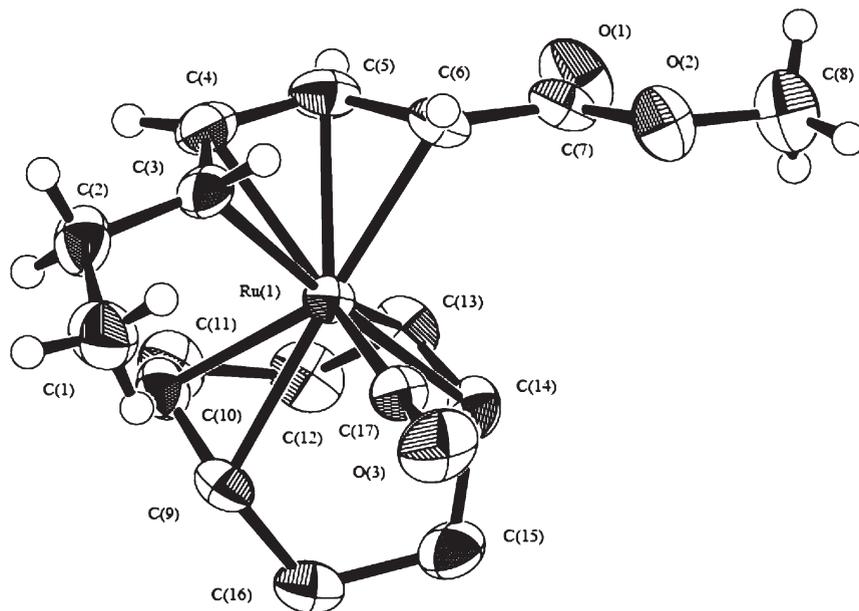
Figure 1. Molecular structure of **2c** with numbering schemes. Ellipsoids indicate 50% probability. Hydrogen atoms in the 1,5-COD ligand are omitted for clarity.

This compound was more unambiguously characterized by the X-ray structure analyses of its PPh$_3$ and CO analogues. For example, exposure of **2a** to an atmosphere of CO (0.1 MPa) for 3 h at room temperature followed by workup procedures involving recrystallization from cold Et$_2$O gave pale yellow needles of **2c** (L = CO) in 53% yield. The overall molecular structure consists of the *cisoid-η^4-(2E,4E)*-methyl hepta-2,4-dienoate complex of Ru(0) with 1,5-COD and CO ligands (Figure 1).[8]

The bond distances C(1)−C(2) [1.509(5) Å] and C(2)−C(3) [1.509(3) Å] clearly show their single-bond character, and C(3)−C(4) [1.416(3) Å], C(4)−C(5) [1.407(3) Å], and C(5)−C(6) [1.431(4) Å] suggest a slight contribution of the ene-diyl type coordination. The IR spectrum of **2c** in KBr shows an intense band at 1976 cm^{-1}, which is assignable to the stretching vibration of the CO ligand. Since a monocarbonyl complex of Ru(0), Ru($η^4$-1,5-COD)($η^4$-1,3,5-COT)(CO), has been reported to show a $ν$CO band at 1985 cm^{-1},[9] the $ν$CO band in **2c** suggests the formal zerovalent state of **2c**.

Treatment of **2b** with excess butadiene at room temperature released (2E,4E)-methyl hepta-2,4-dienoate in 49% yield by re-formation of a *cisoid-η^4*-butadiene complex, Ru($η^4$-butadiene)($η^4$-1,5-COD)(PPh$_3$) (**1b**), in 80% yield (eq 1).
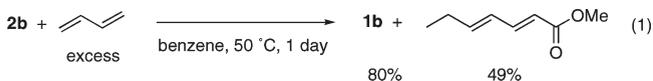
Encouraged by this stoichiometric reaction, the catalytic cross dimerization was performed. The chemoselective cross dimerization reaction between butadiene and methyl acrylate was achieved by **1a** (2 mol %) at 80 °C for 4 h to give (2E,5Z)-methyl hepta-2,5-dienoate[10] (32%) and (2E,4E)-methyl hepta-2,4-dienoate (11%) with a trace of the isomers (eq 2).[11]

$$\text{butadiene} + \text{methyl acrylate (OMe)} \xrightarrow[\substack{80\ °C,\ 4\ h \\ benzene}]{\textbf{1a}\ (2\ mol\%)} \text{(2E,5Z) OMe } 32\% + \text{(2E,4E) OMe } 11\% \quad (2)$$
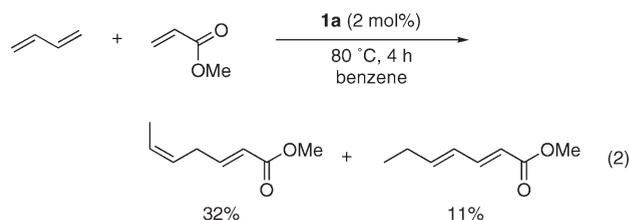
When **2b** was employed in this reaction, (2E,5Z)-methyl hepta-2,5-dienoate (27%) and (2E,4E)-methyl hepta-2,4-dienoate (5%) were produced, suggesting the isolated **2b** to also be an active catalyst. It is notable that the dominant product in catalysis is (2E,5Z)-methyl hepta-2,5-dienoate, while the stoichiometric reaction exclusively gives (2E,4E)-methyl hepta-2,4-dienoate (*vide infra*). Such cross dimerization has also been catalyzed by (allyl)cobalt(I)[12] and *in situ*-formed (hydrido)ruthenium(II) species,[13] but they give (3E,5Z)-methyl hepta-3,5-dienoate as the dominant product, which is not observed in the present catalysis. Both

$$\textbf{2b} + \text{butadiene} \xrightarrow[\substack{excess}]{benzene,\ 50\ °C,\ 1\ day} \textbf{1b}\ 80\% + \text{OMe } 49\% \quad (1)$$

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(8) Selected crystallographic and physical data for **2c**: triclinic, $P\bar{1}$, $a = 7.715(4)$ Å, $b = 8.091(4)$ Å, $c = 14.138(7)$ Å, $α = 101.756(4)°$, $β = 95.319(4)°$, $γ = 108.580(6)°$, $V = 807.1(7)$ Å^3, $Z = 2$, temp = 200.0 K, reflns number total = 3590, parameters = 287, GOF = 1.072, R_1 = 0.0281, wR_2 = 0.0744.

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(10) Feldman, K. S.; Grega, K. C. *J. Organomet. Chem.* **1990**, *381*, 251.

(11) The moderate total yield (43%) is probably due to deactivation of the active species. A stoichiometric reaction of **2a** with excess butadiene produced a homocoupling complex of butadiene, *supine,prone*-[Ru($η^3$:$η^3$-2,7-octadiene-1,8-diyl)($η^4$-1,5-COD)] (54%), with liberation of (2E,4E)-methyl hepta-2,4-dienoate (49%). The $η^3$:$η^3$-2,7-octadiene-1,8-diyl complex is a very stable compound under these conditions. Therefore, we believe the oxidative coupling reaction between butadiene molecules on Ru(0) to be the major deactivation process. The comprehensive oxidative coupling reactions of conjugated dienes on Ru(0) will be reported elsewhere.

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Scheme 2. Proposed Catalytic Cycle
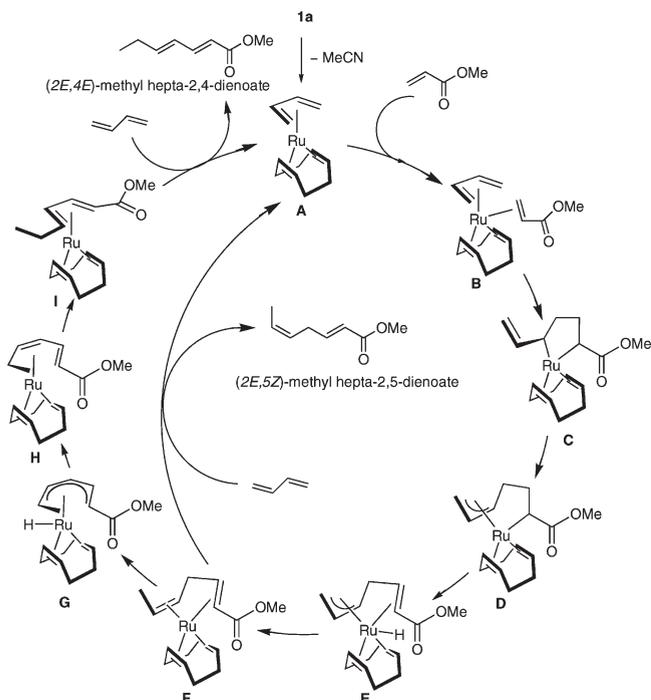
reports have brought forward the hydrido-insertion mechanism without detailed experimental support.

The present chemoselective cross dimerization is consistent with the catalytic cycle as shown in Scheme 2. In the first step, facile liberation of MeCN from **1a** initiates the catalysis to give **A**. The highly basic zerovalent ruthenium(0) species **A** favors coordination of an electron-withdrawing methyl acrylate to give **B**. Formation of such a (κ^4-conjugated compound)-(η^2-conjugated compound)ruthenium(0) complex has been demonstrated in the mechanistic study of catalytic tail-to-tail dimerization of methyl methacrylate promoted by ruthenium-(0) by us (Chart 1).[3] Then a ruthenacyclopentane **C** is formed

by the oxidative coupling. An analogous ruthenacyclopentane is also formed in the selective dimerization of methyl acrylate (Chart 1).[4] The $\sigma-\pi$ rearrangement of the allyl produces the intermediate **D**. The η^3-allylic moiety should have an *anti* configuration to reflect the *cisoid* conformation of the η^4-butadiene ligand in **B**. Then, the β-hydride elimination and successive reductive elimination produces the intermediate **F**. This unconjugated diene ligand may be labile, and the presence of butadiene induces facile liberation of the unconjugated diene. This scenario well accounts for the predominant formation of (2E,5Z)-methyl hepta-2,5-dienoate in the catalysis. On the other hand, the intermediate **F** can also cause further isomerization to give the more thermodynamically stable conjugated species **I** by the C–H bond cleavage reaction process. This process accounts for the exclusive formation of **2a** by the stoichiometric reaction in the absence of butadiene.

In summary, the present work provides a ruthenium-promoted stoichiometric and catalytic chemoselective cross dimerization reaction between butadiene and methyl acrylate via an oxidative coupling mechanism. The chemoselectivity is probably induced by the facile η^4-coordination of butadiene on ruthenium(0) followed by the η^2-coordination of electron-withdrawing methyl acrylate on the Lewis basic site. Further detailed mechanistic studies and tolerance of substrates are now in progress.

Supporting Information Available: Text, tables, and figures giving full experimental details involving the characterizations of **2a**, **2b**, **2c**, and **1b**, ^{1}H NMR spectrum of **2a**, reactions of **2a**, **2b**, and **2c** with iodine and butadiene, GLC chart for catalysis between butadiene and methyl acrylate, and crystallographic analyses of **2b** and **2c** and CIF files giving X-ray crystal data. This material is available free of charge via the Internet at http://pubs.acs.org.