Mechanistic insights into catalytic linear cross-dimerization between conjugated dienes and styrenes by a ruthenium(0) complex

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ABSTRACT

The mechanistic studies for linear cross-dimerization between 2,3-dimethylbuta-1,3-diene and styrene by a Ru(0) complex, Ru(η^6-naphthalene)(η^4-1,5-COD) (**1**), are performed both by kinetic and computational studies. This reaction is basically zero-order to both of the diene and styrene concentrations and first-order to the catalyst concentration. The Hammett plot using *p*-substituted styrenes gives a linear relationship with a positive slope ($\rho = +0.482$). The deuterium isotope experiment clearly shows the present reaction being a formal 1,4-addition of a C−H bond in styrene to *cisoid*-1,3-diene. These kinetic studies show the reaction proceeding via oxidative coupling mechanism that is also supported by the DFT calculations.

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1. Introduction

Direct carbon−carbon bond formation by use of simple commodity chemicals has garnered much attention as a straightforward transformation process to give complex and valuable molecules with high atom and step economy [1]. The cross-dimerizations between conjugated dienes and alkenes have been documented by using the Ziegler-type catalyst systems, and combinations of transition-metal salt with alkylaluminum [2]. Similar catalytic 1,4-addition reactions of styrene to conjugated diene are recently documented by in situ reductions of Fe(II) [3] and Co(II) [4] with Mg and Zn metals, respectively. Although the cross-dimerization catalyzed by the Fe(II)/Mg system is proposed to proceed by an oxidative coupling mechanism, this pioneering work does not report the conclusive mechanistic evidence. The other potential mechanisms for a cross-dimerization are hydride-insertion mechanism [5] and C−H bond activation mechanism [6].

We have documented a series of homo- and cross-dimerization reactions between conjugated compounds and/or substituted alkenes by a Ru(0) catalyst. A considerable mechanistic breakthrough was isolation of a ruthenacyclopentane, *trans*-[Ru[C^{1}H(CO$_2$Me) C$_2$H$_4$C^{4}H(CO$_2$Me)-κ^2-C^1C^4](η^4-1,5-COD)(NCMe)$_2$] out of the reaction of [Ru(η^6-naphthalene)(η^4-1,5-COD)] (**1**) with methyl acrylate (Scheme 1), and the isolated ruthenacyclopentane also catalyzed tail-to-tail dimerization of methyl acrylate [7].

These findings were the first solid evidence in support of an oxidative coupling mechanism for tail-to-tail dimerization *between substituted alkenes*. On another front, we have also documented catalytic cross-dimerization *between conjugated dienes and substituted alkenes* [8]. However, we do not have adequate mechanistic evidence for the cross-dimerization. Although we have observed the formation of an η^1:η^3-ruthenacycle by the treatment of [Ru(η^4-buta-1,3-diene)(η^4-1,5-COD)(NCMe)] with vinyl acetate [Eq. (1)], this compound does not show the catalytic activity and therefore we cannot exclude the possibility of this compound being a dead-end species.

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(1)
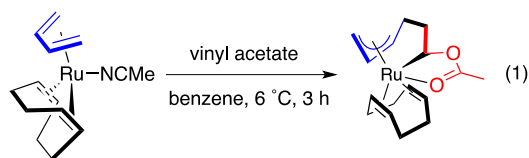
In this paper, we now disclose a solid evidence to support an oxidative coupling mechanism by the kinetic studies and DFT calculations for a catalytic cross-dimerization between conjugated diene and substituted alkenes.

2. Results and discussion

2.1. Cross-dimerization between diene and styrenes

The naphthalene complex **1** (2 mol%) catalyzed the cross-dimerization between 2,3-dimethylbuta-1,3-diene (**2**) and styrene (**3a**) in toluene at 60 °C for 2 h to give the coupling products **4a** (71%) and **5a** (9%) along with 6 minor isomers (12% in total) [Eq. (2)]. No homo-dimers were observed in this reaction. The upmost minor product is **5a**, a regioisomer of the C=C bond of the major product **4a**. Notably, the relative **4a**/**5a** ratio diminished with increase of the catalyst concentration (Table 1).
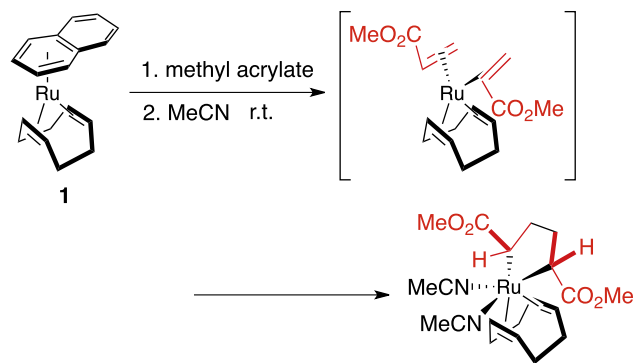

(2)
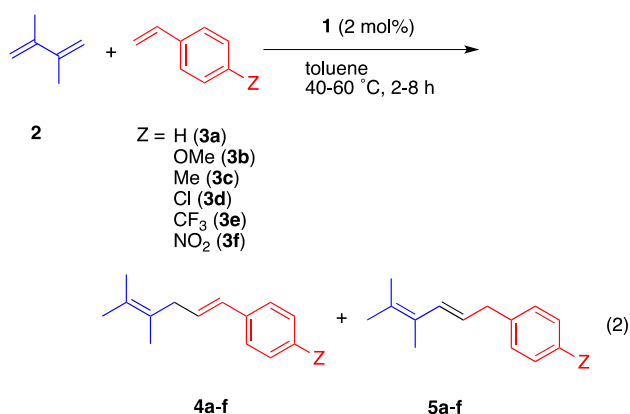
The isolated **4a** did not cause spontaneous conversion into **5a** at 40 °C in benzene-d_6 but the treatment of **4a** with a catalytic amount of **1** (10 mol%) under the same conditions gave a mixture of **4a** and **5a**. The final **4a**/**5a** ratio was 1/2 under these conditions after 148 h. These facts suggest the primary kinetic product **4a** being converted into the thermodynamic product **5a** by a Ru catalyst, and an equilibrium exists between them [Eq. (3)].

(3)
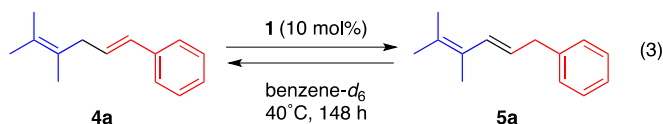
2.2. Kinetic studies

The time-course curves for the reaction of 2,3-dimethylbuta-1,3-diene with styrene by **1** were monitored by GLC, and the total sum yield of the cross-dimers, **4a** and **5a**, showed a linear increase with time, suggesting a zero-order reaction. Fig. 1 shows the double logarithm plots for the relation of the formation rate of the products (v_p) with the diene (Fig. 1A), styrene (Fig. 1B) and catalyst concentrations (Fig. 1C). Although a slight dependence of the rate

on the diene and styrene concentrations was observed in this range, this reaction is roughly regarded as a zero-order reaction to both of the concentrations [9]. The double logarithmic plot for the catalyst concentration and the rate at 40 °C shows a good linear relationship with a positive slope of +0.878, which is consistent with the first-order to the catalyst concentration. Therefore, the present reaction can be summarized as the zero-order to both of diene and styrene concentrations and first-order to the catalyst concentration.

Fig. 2 shows Hammett plot for cross-dimerization between 2,3-dimethylbuta-1,3-diene and a series of *p*-substituted styrenes **3a-f** in toluene, showing the linear dependence with a positive slope ($\rho = +0.482$) (Fig. 2).

Eyring plot for overall formation reaction of **4a** and **5a** by **1** (2 mol%) was measured in toluene: $\Delta H^{\neq} = 70.2$ kJ mol^{-1}, $\Delta G^{\neq}_{298} = 104$ kJ mol^{-1}, and $\Delta S^{\neq} = -115$ J K^{-1} mol^{-1}. The large negative entropy of activation suggests involvement of a distorted transition state.

In order to confirm whereabouts of the cleaved hydrogen, we have employed styrene-β,β'-d_2 (95 atom % D) for this cross-dimerization. In the cross-dimer, the deuterium atoms were distributed among the (*Z*)-1-, 4-, and 5-positions, and the deuterium atoms were not found in the other positions in the product **4a** (Table 2).

Based on the time-course of the reaction monitored by NMR, the deuterium atoms exclusively located among the (*Z*)-1- and 5-positions at the initial stage, and then a H/D exchange reaction occurs between the 4- and 5-positions while the deuterium content at the (*Z*)-1-position remains intact throughout the reaction. The total sum of deuterium atoms in **4a** roughly indicates two D atoms being incorporated in **4a** regardless of the reaction time, suggesting the following H/D exchange reaction between the 4- and 5-positions to be an *intramolecular process* in **4a**-d_2. Note that only the methyl group [(*Z*)-C(1)], *cis* to the styryl fragment, was deuterated and no incorporation of the D atom was observed in the *trans*-methyl [(*E*)-C(1')] position (Scheme 2). These facts suggest the present initial reaction being regarded as a 1,4-addition of

Scheme 1. Isolation of *trans*-2,5-bis(methoxycarbonyl)ruthenacyclopentane.

Table 1
The relation between catalyst concentration and major/minor ratio.

Entry	**1a**/mol%	Total yield/%	**4a/5a**
1	0.5	39	6/1
2	1.0	52	6/1
3	2.0	74	6/1
4	4.0	74	4.5/1
5	10	65	2.6/1
6	20	61	1.3/1

Conditions: [**2**]/[**3a**] = 1.3/1, 40 °C, in toluene, 8 h.