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Chain-Selective and Regioselective Ethylene and Styrene Dimerization Reactions Catalyzed by a Well-Defined Cationic Ruthenium Hydride Complex: New Insights on the Styrene Dimerization Mechanism

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The cationic ruthenium hydride complex $[(\eta^6\text{-}C_6H_6)(PCy_3)(CO)RuH]^+BF_4^-$ was found to be a highly regioselective catalyst for the ethylene dimerization reaction to give 2-butene products (TOF = 1910 h^{-1}, >95% selectivity for 2-butenes). The dimerization of styrene exclusively produced the head-to-tail dimer (*E*)-PhCH(CH_3)CH=CHPh at an initial turnover rate of 2300 h^{-1}. A rapid and extensive H/D exchange between the vinyl hydrogens of styrene-d_8 and 4-methoxystyrene was observed within 10 min without forming the dimer products at room temperature. The inverse deuterium isotope effect of $k_H/k_D = 0.77 \pm 0.10$ was measured from the first-order plots on the dimerization reaction of styrene and styrene-d_8 in chlorobenzene at 70 °C. The pronounced carbon isotope effect on both vinyl carbons of styrene as measured by using Singleton's method (^{13}C(recovered)/^{13}C(virgin) at $C_1 = 1.096$ and $C_2 = 1.042$) indicates that the C−C bond formation is the rate-limiting step for the dimerization reaction. The Eyring plot of the dimerization of styrene in the temperature range of 50−90 °C led to $\Delta H^\ddagger = 3.3(6)$ kcal/mol and $\Delta S^\ddagger = -35.5(7)$ eu. An electrophilic addition mechanism has been proposed for the dimerization of styrene.

Introduction

Transition-metal-catalyzed olefin dimerization and oligomerization reactions constitute one of the most important industrial processes for forming α-olefins.[1−3] Ziegler-type Ti and Ni catalysts have been successfully utilized for the commercial processes of ethylene dimerization (IFP Alphabutol process) and α-olefins (Dimersol process), respectively.[2] Extensive research efforts have led to two distinctively different dimerization reaction mechanisms: the Cosse-Arlman mechanism of sequential alkene insertion for Ziegler catalysts[1d,2b] and the oxidative coupling mechanism via the formation of metallacycles for Ti and Ta catalysts.[3] More recently, Periana and co-workers proposed a novel ethylene dimerization mechanism via vinyl C−H activation, which is mediated by an electrophilic Ir−vinyl catalyst, on the basis of both experimental and computational analyses.[4] Since the ethylene oligomerization reaction typically produces a range of olefin products (C_4−C_{26}) which require tedious and energy-consuming separation steps, one of the enduring challenges is to design effective catalytic processes that would result in chain-selective and regioselective olefin products. The chain-selective ethylene trimerization reaction by soluble Cr and Ti catalysts has been a notable advance in this context.[5]

In recent years, considerable research has been focused on utilizing electrophilic late-transition-metal catalysts to achieve selective dimerization and oligomerization of olefins.[1d,6] Brookhart and co-workers investigated detailed kinetic and mechanistic aspects of the ethylene dimerization by using well-defined cationic Pd and Pt catalysts, where the energy of activation for the turnover-limiting olefin insertion

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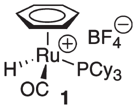
step has been estimated to be 19.5 kcal/mol for cationic (P−N)Pd−alkyl complexes and 29.8 kcal/mol for (diimine)Pt^{II} complexes.[7] Jordan also found significant steric and electronic effects of the bis(pyrazolyl) and diimine ligands in modulating the activity of cationic (N−N)Pd^{II}−alkyl catalysts for the ethylene dimerization and oligomerization reactions.[8] While a number of selective formations of 1-butene have been recently reported by using well-defined Ziegler-type catalysts,[9] most late-transition-metal catalysts have been found to produce a mixture of 1- and 2-butenes.[2] In a notable case, Roddick reported the regioselective formation of 2-butenes from the ethylene dimerization reaction by using Pt and Pd catalysts with perfluorinated diphosphine ligands in strongly acidic media (340 turnovers/h with 100 psi of C_2H_4 at 25 °C).[10] Regioselective formation of 2-butenes from the dimerization of ethylene is of considerable synthetic importance in homogeneous catalysis, since 2-butenes are a common precursor for both industrially significant SHOP metathesis[11] and Wacker-type olefin oxidation processes.[12]



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We have recently disclosed that the in situ formed cationic ruthenium hydride complexes are highly effective catalysts for the dehydrative coupling reaction of aryl ketones and 1-alkenes, in which the coupling reactions apparently involved olefin isomerization and vinyl C−H activation steps.[13] In an effort to elucidate the coupling reaction mechanism, we have undertaken a series of investigations on the alkene dimerization/oligomerization reactions by using well-defined electrophilic ruthenium hydride catalysts. This report delineates a highly regioselective and chain-selective ethylene and styrene dimerization reaction by using a well-defined cationic ruthenium hydride catalyst, $[(\eta^6\text{-}C_6H_6)(PCy_3)(CO)RuH]^+BF_4^-$ (**1**).[14]

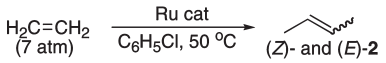
Results and Discussion

The catalytic activity of selected ruthenium complexes was initially surveyed for the ethylene dimerization reaction. Thus, the mixture of ethylene (26 mmol, 7 atm) and a Ru catalyst (0.02−0.03 mol %) in C_6H_5Cl in a Fisher−Porter pressure tube was stirred at 50 °C for 30 min (eq 1). The initial turnover rate of the dimeric and oligomeric products was determined by the pressure−volume method from a high-vacuum line with a Hg manometer.[15] Among the selected ruthenium catalysts, complex **1** exhibited uniquely high activity and selectivity for the formation of 2-butenes (**2**) over 1-butene and other oligomers, as analyzed by both NMR and GC (> 95% selectivity, (*E*)-**2**/(*Z*)-**2** = 4:1) (Table 1). Among the initially screened solvents, C_6H_5Cl was found to be most suitable for the catalyst **1**; CH_2Cl_2 was also found to be an acceptable solvent (initial TOF ~1000 h^{-1}), but with a considerably lower selectivity for 2-butenes.

Table 1. Catalyst Survey for the Ethylene Dimerization Reaction[a]

entry	catalyst	additive	**2** (*E*:*Z*)[b]	TOF[c]
1	**1**		82:18	1910
2[d]	$[RuH(CO)(PCy_3)]_4(O)(OH)_2$			0
3[d]	$[RuH(CO)(PCy_3)]_4(O)(OH)_2$	$HBF_4 \cdot OEt_2$	70:30	790
4	$RuHCl(CO)(PCy_3)_2$	$HBF_4 \cdot OEt_2$		0
5	$RuH_2(CO)(PPh_3)_3$	$HBF_4 \cdot OEt_2$		20
6	$RuCl_2(PPh_3)_3$	$HBF_4 \cdot OEt_2$		0
7	[(*p*-cymene)$RuCl_2]_2$	$HBF_4 \cdot OEt_2$		0
8	$Ru_3(CO)_{12}$	NH_4PF_6		0
9	$[RuH(CO)(PCy_3)_2(CH_3CN)_2]^+BF_4^-$			0
10	$RuCl_3 \cdot 3H_2O$			0
11	$HBF_4 \cdot OEt_2$			0

[a] Reaction conditions: ethylene (0.74 g, 26 mmol), catalyst (5−7 mg, 0.033 mol %), $HBF_4 \cdot OEt_2$ (1−2 μL, 1.0 equiv), C_6H_5Cl (1 mL), 50 °C, 0.5 h. [b] Determined by ^1H NMR. [c] TOF = (mol of ethylene consumed)(mol of catalyst)$^{-1}$ h^{-1}. [d] See ref 14a for the synthesis and structure of the complex.



(1)

Ethylene Dimerization Reaction. The catalytic activity of **1** for the ethylene dimerization reaction was examined. The rate of formation of the products was measured by GC in 10 min intervals from the treatment of ethylene (0.74 g, 26.4 mmol) with **1** (5 mg, 8.7 μmol) in C_6H_5Cl (2 mL) in a 100 mL Fisher−Porter pressure tube at 50 °C. The initial turnover rate, which was measured to be ca. 2440 h^{-1} after 10 min, was steadily decreased to 1340 h^{-1} after 1 h, at which time ~45% of ethylene was converted to 2-butenes. Due to the product inhibition, the reaction rate slowed further, giving only about 10 000 TON (50% conversion) after 24 h. The rate of the dimerization reaction was found to be linearly dependent on the pressure of ethylene gas (Figure S1, Supporting Information), and the first-order plot of ln[ethylene] vs time resulted in $k_{obs} = 0.76\ h^{-1}$ (Figure 1).

In an effort to detect possible intermediate species, the treatment of ethylene (4 mg, 4 equiv) with **1** (20 mg, 35 μmol) in CD_2Cl_2 (0.5 mL) was monitored by NMR. The formation of ethane (δ 0.23 ppm) along with a small amount of 1-butene was detected by ^1H NMR after 10 min, but no detectable amount of 2-butenes was formed at room temperature. When the temperature was raised to 50 °C, 2-butenes were formed rapidly within 5 min, without changing the amount of 1-butene significantly over time (((*E*)- and (*Z*)-**2**):1-butene = 95:5). Though the formation of free benzene molecules

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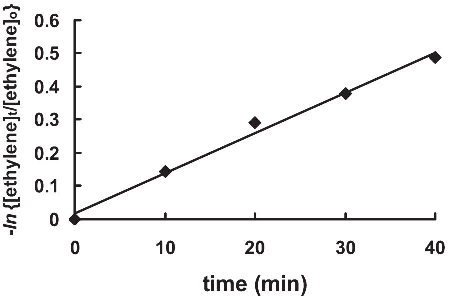
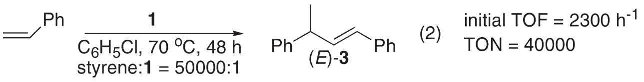


Figure 1. Plot of ln [ethylene] vs time at 50 °C.

was observed (the ratio of free benzene to coordinated benzene was 35:65 after 10 min), we were not able to detect/identify any new ruthenium species under these conditions.

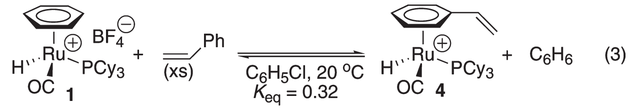
To gauge the rate of ethylene dimerization vs olefin isomerization, 1-pentene (1.83 g, 26 mmol) was treated with **1** (0.02 mol %) in C_6H_5Cl at 50 °C. The initial turnover rate for the isomerization of 1-pentene to 2-pentenes was found to exceed 20 000 h^{-1}, which is an order of magnitude higher than the dimerization rate under comparable conditions. Also, the catalyst **1** was found to mediate a rapid isomerization of 2-butenes to produce the same mixture as that formed from the ethylene dimerization reaction (((*E*)- and (*Z*)-**2**): 1-butene = 94:6). These results showed that the rate of olefin isomerization is much higher than that of the dimerization reaction and further suggest that the initially formed 1-alkenes would have been rapidly isomerized under the catalytic reaction conditions.

Styrene Dimerization Reaction. Among the initially screened α-olefins, the catalyst **1** was found to be particularly effective for regioselective and chain-selective dimerization of styrene and vinylarenes. Thus, the treatment of styrene (45 g, 9.4 mmol) with **1** (5 mg, styrene:**1** = 50 000:1) in C_6H_5Cl (1 mL) at 70 °C led to the head-to-tail dimer product (*E*)-**3** exclusively at an initial TOF of 2300 h^{-1} (eq 2). No other oligomeric or polymeric products were detected by GC. Furthermore, the catalyst **1** was found to be active for a prolonged reaction time, giving a TON of ~40 000 in 48 h. Again, the turnover rate was found to steadily decrease as the concentration of the dimer product **3** increased. Though regioselective dimerization of styrene and related vinylarenes has been achieved by using electrophilic palladium[16] and ruthenium[17] catalysts, the mechanism of the dimerization reaction has not been clearly established. To the best of our knowledge, the activity and selectivity of **1** are uniquely high among non-Ziegler types of late-transition-metal catalysts for the styrene dimerization reaction.



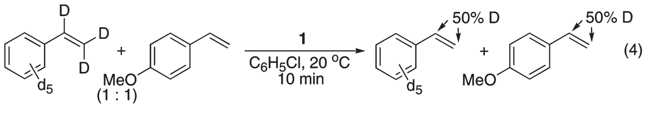
(2)

Kinetics and Mechanistic Study for the Styrene Dimerization Reaction. We performed the following experiments to gain mechanistic insights into the styrene dimerization reaction. First, the formation of the styrene-coordinated complex $[(\eta^6\text{-}C_6H_5CH{=}CH_2)RuH(CO)(PCy_3)]^+BF_4^-$ (**4**) was detected along with ethylbenzene and free benzene molecules when the treatment of styrene (0.87 mmol) with **1** (17 μmol) in CD_2Cl_2 (0.5 mL) was monitored by NMR at 40 °C (eq 3).[15] Assuming [styrene] remains constant during the exchange reaction, the equilibrium constant (K_{eq}) for the reaction was estimated to be 0.32 at 20 °C from the ^{31}P NMR analysis. Several attempts to isolate the complex **4** in pure form were not successful.



(3)

To examine the H/D exchange rate on the alkene substrate, a 1:1 mixture of styrene-d_8 and 4-methoxystyrene (1.4 mmol) in the presence of **1** (3 mg) in CH_2Cl_2 (0.5 mL) was monitored by NMR at room temperature. A rapid and extensive H/D exchange between the vinyl hydrogens of styrene-d_8 and 4-methoxystyrene was observed within 10 min without formation of the dimer products (eq 4). In a separate experiment, the partially deuterated complex **1**-*d* (40 mg, 69 μmol; 64% Ru-D) was treated with 5 equiv of styrene in CH_2Cl_2 (0.5 mL) at room temperature (eq 5). A complete H/D exchange at the vinyl positions of styrene occurred rapidly within 30 min at room temperature along with the formation of deuterated ethylbenzene (33% D) as monitored by ^2H NMR. In this case, the formation of the dimer **3** was observed after ~1 h. The formation of ethylbenzene suggested that the ruthenium hydride complex **1** is acting as a hydrogenation agent, but we have not been able to detect/identify any other ruthenium species under the reaction conditions.



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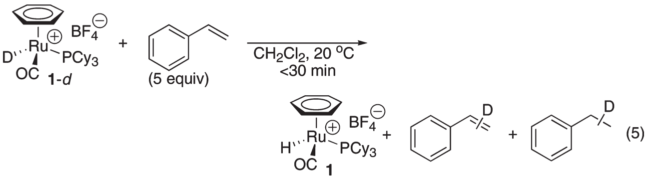

(5)

The deuterium isotope effect of the dimerization reaction was measured under relatively dilute conditions. Thus, the rate of disappearance of styrene was analyzed by GC periodically from the treatment of styrene (0.54 g, 5.2 mmol) with **1** (3 mg, 0.1 mol %) in C_6H_5Cl (2 mL) at 70 °C. The first-order plots of the dimerization reaction rate vs time for both styrene and styrene-d_8 led to $k_{obs} = 0.37$ and 0.48 h^{-1}, respectively, which translated to an inverse isotope effect of $k_H/k_D = 0.77 \pm 0.10$ (Figure 2). No significant temperature effect on the isotope effect was observed in the range of 50−90 °C, giving the nearly equal $k_H/k_D = 0.67 \pm 0.10$ at 50 °C and $k_H/k_D = 0.68 \pm 0.10$ at 90 °C. In transition-metal-mediated C−H activation reactions, inverse deuterium isotope effects have been commonly observed for the stepwise reactions involving rapid pre-equilibrium followed by a

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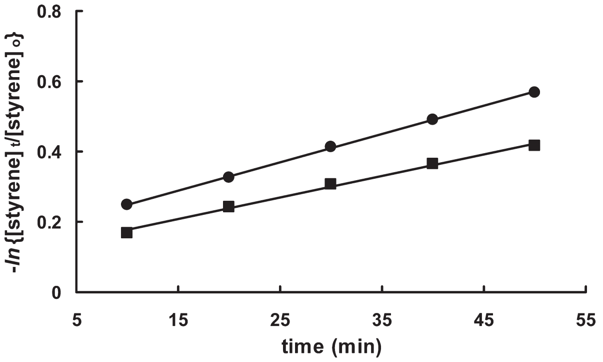


Figure 2. First-order plots of the dimerization of styrene (■) and styrene-d_8 (●) at 70 °C.

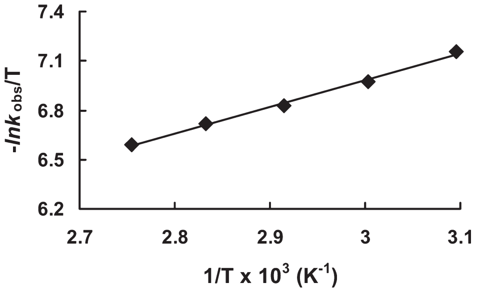
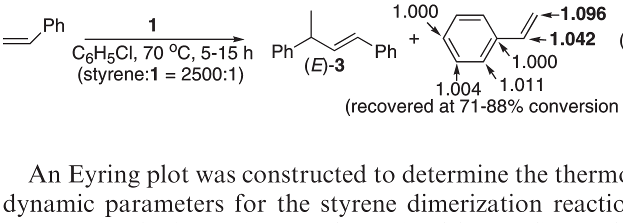


Figure 3. Eyring plot for the styrene dimerization.

rate-limiting step.[18] In our case, the observation of an inverse isotope effect on the dimerization reaction is consistent with rapid and reversible styrene coordination and hydride insertion steps followed by a rate-limiting C−C bond formation step.[19]

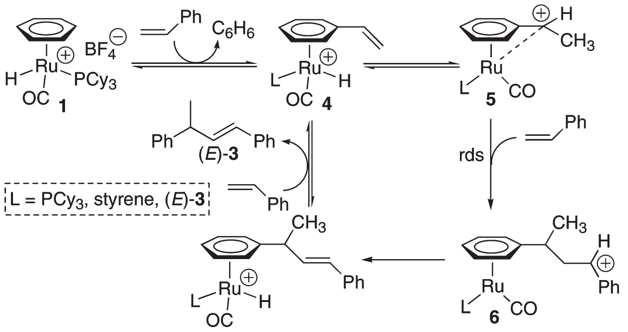
To further discern the rate-limiting step of the dimerization reaction, we next examined the carbon isotope effect for the styrene dimerization by employing Singleton's isotope measurement technique at natural abundance.[20] The treatment of styrene (4.5 g, 44 mmol) with **1** (10 mg, 17 μmol) in C_6H_5Cl (1 mL) at 70 °C was stopped after 5−15 h at 71−88% conversion (eq 6). A pronounced carbon isotope effect was observed on both vinyl carbons when the ^{13}C ratio of recovered styrene was compared to that of the virgin sample (^{13}C(recovered)/^{13}C(virgin) at $C_1 = 1.096$ and $C_2 = 1.042$, average of three runs) (Table S1, Supporting Information). The observation of a significant carbon isotope effect on both vinyl carbons clearly indicates that the C−C bond formation is the rate-limiting step for the dimerization reaction.



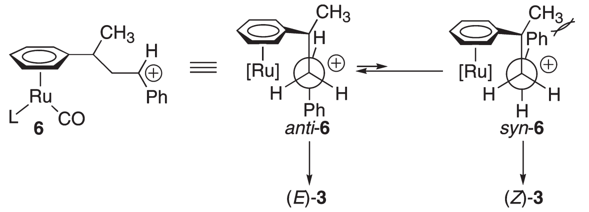
(6)

An Eyring plot was constructed to determine the thermodynamic parameters for the styrene dimerization reaction (Figure 3). The k_{obs} value was determined from a first-order plot of $-\ln\{[\text{styrene}]_t/[\text{styrene}]_0\}$ vs time in the treatment of styrene (0.54 g, 5.2 mmol) with **1** (3 mg, 5.2 μmol) in C_6H_5Cl (2 mL) for the temperature range of 50−90 °C. The Eyring plot of $-\ln(k_{obs}/T)$ vs $1/T$ led to $\Delta H^{\ddagger} = 3.3(6)$ kcal/mol and $\Delta S^{\ddagger} = -35.5(7)$ eu. A relatively large negative $\Delta S^{\ddagger}$ value is consistent with an organized transition state formed from combining two styrene molecules.

Scheme 1. Proposed Mechanism of the Styrene Dimerization Reaction



Scheme 2



Proposed Mechanism of the Styrene Dimerization Reaction. These results provide support for an electrophilic addition mechanism for the styrene dimerization reaction (Scheme 1). We propose that the benzylic carbocation ruthenium arene species **5** is generated from the initial arene exchange reaction and the hydride migration to the coordinated styrene. Both rapid H/D arene exchange results and the observation of styrene complex **4** suggest that the initial hydride migration and elimination steps are facile and reversible. The electrophilic addition of the second styrene molecule would form the chain-extended carbocation species **6**. The inverse deuterium isotope effect and the carbon isotope effect studies imply that the C−C bond formation is the rate-limiting step for the dimerization reaction. The subsequent deprotonation and arene exchange steps should result in the dimer product **3** and the regeneration of the Ru−H species **4**.

The proposed mechanism can readily explain the exclusive formation of (*E*)-**3** product resulting from the deprotonation step of the benzylic carbocation species **6** (Scheme 2). From a purely steric point of view, the formation of the "anti" benzyl carbocation species *anti*-**6** would be favored over the "syn" isomer *syn*-**6**, and the deprotonation of a methylene hydrogen from *anti*-**6** should lead to the trans product (*E*)-**3** preferentially. Similar electrophilic addition mechanisms have been commonly proposed for the dimerization/oligomerization reactions mediated by electrophilic metal catalysts, but the reactions typically have been found to give a *E*/*Z* mixture of the dimeric products.[16]

The Cosse−Arlman type of insertion mechanism is not likely for the styrene dimerization reaction, because the mechanism would require a regioselective insertion of the

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(18) (a) Jones, W. D. *Acc. Chem. Res.* **2003**, *36*, 140–146. (b) Parkin, G. *Acc. Chem. Res.* **2009**, *42*, 315–325.

(19) We previously observed a similar inverse deuterium isotope effect in ruthenium-catalyzed hydrogenation of olefins: Yi, C. S.; Lee, D. W. *Organometallics* **1999**, *18*, 5152–5156.

(20) (a) Singleton, D. A.; Thomas, A. A. *J. Am. Chem. Soc.* **1995**, *117*, 9357–9358. (b) Frantz, D. E.; Singleton, D. A.; Snyder, J. P. *J. Am. Chem. Soc.* **1997**, *119*, 3383–3384.

second styrene molecule to form a sterically hindered secondary alkyl species and the subsequent β-H elimination would result in an E/Z mixture of the dimeric products.[1,2] Previously, Periana and Goddard proposed a novel dimerization mechanism invoking a vinyl C$-$H activation on the basis of synthetic and computational studies of the ethylene dimerization reaction mediated by electrophilic Ir catalysts.[4] However, in their case, the reaction was performed at a relatively high temperature (150 °C), and the formation of Ru$-$vinyl species under our reaction conditions (50$-$70 °C) is less likely, though it cannot be rigorously excluded at this time. We also observed that the rate of olefin isomerization is much higher than the rate of ethylene dimerization, and this result provides support for the Cosse$-$Arlman type of insertion and isomerization mechanism for the ethylene dimerization reaction.[2] It is certainly possible that the cationic ruthenium hydride catalyst **1** could assist both vinyl C$-$H activation and Cosse$-$Arlman insertion/olefin isomerization mechanistic pathways under certain conditions, and we are currently looking into this mechanistic possibility for the ethylene dimerization reaction.

Conclusions

A highly efficient and regioselective dimerization of ethylene and styrene has been achieved by using the well-defined cationic ruthenium hydride catalyst **1**. Kinetic and mechanistic studies for the styrene dimerization reaction provide support for an electrophilic addition mechanism involving the formation of benzylic carbocation species and the rate-limiting C$-$C bond formation step. Efforts to establish a detailed mechanism for the ethylene dimerization reaction as well as to extend the synthetic utility of the dimerization reaction are currently being pursued.

Experimental Section

Representative Procedure of the Ethylene Dimerization Reaction. In a glovebox, complex **1** (5 mg, 8.7 μmol) was dissolved in chlorobenzene (2 mL) in a 100 mL Fisher$-$Porter pressure tube equipped with a magnetic stirring bar. The tube was brought out of the box and was degassed three times by freeze$-$pump$-$thaw cycles. Ethylene gas (0.74 g, 26.4 mmol) was condensed into the tube via a vacuum line. The tube was slowly warmed to room temperature, and the contents were stirred for 30 min in an oil bath which was preset at 50 °C. After the tube was cooled in a dry ice/ethylene glycol bath ($-$25 °C) for 10 min, the reaction tube stopcock was slowly opened to a vacuum line connected to a Hg manometer. The turnover number was determined by measuring the difference of the vapor pressure exerted by the ethylene gas at $-$25 °C. After evaporation of unreacted ethylene at $-$25 °C under high vacuum, a ~4:1 mixture of 2-butene products was obtained (> 95% pure as analyzed by NMR and GC).

Deuterium Isotope Effect Study. In a glovebox, complex **1** (3 mg, 5.2 μmol) and styrene (0.54 g, 5.2 mmol) or styrene-d_8 (0.58 g, 5.2 mmol) were dissolved in chlorobenzene (2 mL). The solution was divided into equal amounts (~0.45 g), and each solution was placed into six different 25 mL Schlenk tubes equipped with a Teflon stopcock and a magnetic stirring bar. The tubes were brought out of the box, and the contents were stirred in an oil bath (preset at 50, 70, and 90 °C). Each reaction tube was taken out of the oil bath in 10 min intervals and was immediately cooled in a dry ice/acetone bath. After it was filtered through a small silica gel column (2:1 hexanes/EtOAc), the solution was analyzed by GC to measure the disappearance of the styrene. The k_{obs} value was determined from a first-order plot of $-\ln\{[\mathrm{styrene}]_t/[\mathrm{styrene}]_0\}$ vs time (Figures S2 and S3, Supporting Information).

Carbon Isotope Effect Study. In a glovebox, complex **1** (10 mg, 17.4 μmol) and styrene (4.52 g, 43.5 mmol) were dissolved in chlorobenzene (1 mL) in three separate 25 mL Schlenk tubes equipped with a Teflon screw cap stopcock and a magnetic stirring bar. The tubes were brought out of the box, and the contents were stirred for 5, 10, and 15 h, respectively, in an oil bath which was preset at 70 °C. After it was filtered through a small silica gel column (2:1 hexanes/EtOAc), the solution was analyzed by GC (71, 80, and 88% conversion). Unreacted styrene was collected separately via vacuum transfer for the ^{13}C{^{1}H} NMR analysis.

The ^{13}C{^{1}H} NMR analysis of the recovered and virgin samples of styrene was performed by following Singleton's ^{13}C NMR method.[20] The NMR sample of virgin and recovered styrene was prepared identically by dissolving styrene (100 mg) in $CDCl_3$ (0.5 mL) in a 5 mm high-precision NMR tube. The ^{13}C{^{1}H} NMR spectra were recorded with H-decoupling and 45° pulses. A 60 s delay between pulses was imposed to minimize T_1 variations (d1 = 60 s at 5.0 s, np = 245 098, nt = 704). The data are summarized in Table S1 in the Supporting Information.

Formation of $[(\eta^6\text{-}C_6H_5CH{=}CH_2)RuH(CO)(PCy_3)]^+BF_4^-$ (4). In a glovebox, complex **1** (20 mg, 34.8 μmol) and styrene (18 mg, 5 equiv) in a J. Young NMR tube equipped with a screw cap were dissolved in CD_2Cl_2 (0.5 mL). The NMR tube was brought out of the box and was analyzed by both ^{1}H and ^{31}P NMR in the temperature range of 0$-$50 °C. Two sets of isomers (3:1) for **4** as well as a ~1:1 ratio of free benzene and ethylbenzene were detected by ^{1}H and ^{31}P NMR.

Selected spectroscopic data are as follows. Major isomer of **4**: ^{1}H NMR (400 MHz, CD_2Cl_2) δ 6.75 (m, CH=), 6.6$-$6.4 (m, Ar), 6.04 (d, J = 17.5 Hz, =CH_2), 5.65 (d, J = 10.9 Hz, =CH_2), $-$10.75 (d, J_{PH} = 26.5 Hz, Ru$-$H); ^{31}P{^{1}H} NMR (162 MHz, CD_2Cl_2) δ 73.7 (s, PCy_3). Minor isomer of **4**: ^{1}H NMR (400 MHz, CD_2Cl_2) δ $-$10.66 (d, J_{PH} = 26.4 Hz, Ru$-$H); ^{31}P{^{1}H} NMR (162 MHz, CD_2Cl_2) δ 73.1 (s, PCy_3).

General Procedure for Rate Measurement and Eyring Plot. In a glovebox, complex **1** (3 mg, 5.2 μmol) and styrene (0.54 g, 5.2 mmol) were dissolved in chlorobenzene (2 mL). The solution was divided into equal amounts (~0.45 g) and placed in six different 25 mL Schlenk tubes, each equipped with a Teflon stopcock and a magnetic stirring bar. The tubes were brought out of the box and were stirred in an oil bath preset at 50$-$90 °C. Each reaction tube was taken out of the oil bath in 10 min intervals and was immediately cooled in a dry ice/acetone bath. After the mixture was passed through a small silica gel column (2:1 hexanes/EtOAc), the disappearance of the styrene was analyzed by GC. The k_{obs} value was determined from a first-order plot of $-\ln\{[\mathrm{styrene}]_t/[\mathrm{styrene}]_0\}$ vs time (Figure S4, Supporting Information).

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Supporting Information Available: Text, figures, and tables giving experimental procedures and spectroscopic data of organic products. This material is available free of charge via the Internet at http://pubs.acs.org.