Homogeneous Catalytic Dimerization of Terminal Alkynes by $C_5Me_5Ru(L)H_3$ (L = PPh_3, PCy_3, PMe_3)

Chae S. Yi* and Nianhong Liu

Department of Chemistry, Marquette University, Milwaukee, Wisconsin 53201-1881

Received February 14, 1996[⊗]

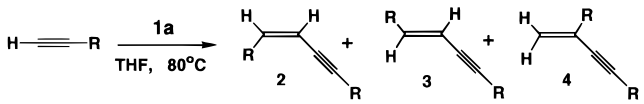
The ruthenium hydride complexes $C_5Me_5Ru(L)H_3$ (L = PPh_3 (**1a**), PCy_3 (**1b**), PMe_3 (**1c**)) were found to catalyze the dimerization reaction of terminal alkynes RC≡CH (R = Ph, *t*-Bu, $SiMe_3$, CH_2Ph, C_4H_9) to produce *cis*- and *trans*-1,4-disubstituted enynes RCH=CHC≡CR and 1,3-disubstituted enynes CH_2=C(R)C≡CR. The selective product formation was effected by modulating both the catalyst environment and the alkyne substrates. A rare form of dimer, cumulene $PhCH_2CH$=C=C=$CHCH_2Ph$ (**5d**), was cleanly obtained from the dimerization of HC≡CCH_2Ph with **1b**. A mechanistic interpretation is presented on the basis of the product distribution.

Introduction

Transition metal-catalyzed dimerization of terminal alkynes is an effective method of forming enynes, but its synthetic application in organic synthesis has been limited due to low selectivity on dimeric products.[1] Recent advances in transition metal-mediated selective dimerization reactions fueled a resurgence of interest in the catalytic dimerization of terminal alkynes.[2−5] While the formations of 1,3-disubstituted enynes from the head-to-tail dimerization of alkynes[2c,3] and of 1,4-disubstituted enynes[4] and cumulenes[5] from the head-to-head dimerization have been reported, the factors influencing different dimeric product formations have not been clearly understood. Herein, we report a selective formation of three different types of linear dimers, 1,3-disubstituted and 1,4-disubstituted enynes and cumulene, from the dimerization of terminal alkynes by using well-defined organoruthenium catalysts C_5Me_5-$Ru(L)H_3$ (L = PPh_3 (**1a**), PCy_3 (**1b**), PMe_3 (**1c**)).[6]

Results and Discussion

While studying the reactivity of organoruthenium complexes toward carbon dioxide and alkynes,[7] we recently discovered that **1a** is an effective catalyst for the dimerization of terminal alkynes. In a sealed NMR tube, excess PhC≡CH (22 μL, 0.20 mmol) and **1a** (10 mg, 0.020 mmol) in 0.5 mL of C_6D_6 solution was heated for 24 h at 80 °C. The reaction mixture was periodically monitored by ^{1}H NMR, which showed a gradual formation of *cis*- and *trans*-1,4-disubstituted enynes **2a** and



R = Ph (a), *t*-Bu (b), $SiMe_3$ (c), CH_2Ph (d), C_4H_9 (e)

3a (**2a**:**3a** = 67:33, 85% yield) and a small amount of styrene (~3%). The relatively smaller coupling constants between two vinyl protons (J = 11.8 Hz) for **2a** compared to **3a** (J = 16.2 Hz) established the stereochemistry for both compounds.[8]

To explore the scope of the catalytic reaction, the dimerization reactions of other terminal alkynes were investigated under similar reaction conditions (Table 1). For example, the dimerization reaction of HC≡$CC(CH_3)_3$ (75 μL, 0.6 mmol) by the catalyst **1a** (10 mg, 0.020 mmol) in THF (10 mL) produced mostly 1,3-disubstituted enyne **4b** over 1,4-enynes (entry 2). The small geminal coupling constants between two vinyl protons (J = 3.4 Hz) and the detection of the dimeric parent ion by GC-MS readily established the terminal enyne structure **4b**. Similar dimerization reaction of HC≡$CSiMe_3$ by **1a** also produced the 1,3-enyne **4c** predominantly (entry 3). The

⊗ Abstract published in *Advance ACS Abstracts,* September 1, 1996.

(1) (a) Parshall, G. W.; Ittel, S. D. *Homogeneous Catalysis,* 2nd ed.; John Wiley & Sons: New York, 1992. (b) Keim, W.; Behr, A.; Röper, M. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: New York, 1982; Vol. 8.

(2) Recent reviews: (a) Winter, M. J. In *The Chemistry of the Metal-Carbon Bond*; Hartley, F. R., Patai, S., Eds.; Wiley & Sons: Chichester, U.K., 1985; Vol. 3. (b) Grotjahn, D. B. In *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon Press: New York, 1995; Vol. 12. (c) Trost, B. M. In *Homogeneous Transition Metal Catalyzed Reactions*; Moser, W. R., Slocum, D. W., Eds.; American Chemical Society: Washington, DC, 1992.

(3) Leading references: (a) Trost, B. M.; Chan, C.; Ruhter, G. *J. Am. Chem. Soc.* **1987**, *109*, 3486. (b) Ohshita, J.; Furumori, K.; Matsuguchi, A.; Ishikawa, M. *J. Org. Chem.* **1990**, *55*, 3277 and references therein. (c) Horton, A. D. *J. Chem. Soc., Chem. Commun.* **1992**, 185. (d) Barluenga, J.; González, J. M.; Llorente, I.; Campos, P. J. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 893. (e) Straub, T.; Haskel, A.; Eisen, M. S. *J. Am. Chem. Soc.* **1995**, *117*, 6364.

(4) (a) Bianchini, C.; Peruzzini, M.; Zanobini, F.; Frediani, P.; Albinati, A. *J. Am. Chem. Soc.* **1991**, *113*, 5453. (b) Bianchini, C.; Frediani, P.; Masi, D.; Peruzzini, M.; Zanobini, F. *Organometallics* **1994**, *13*, 4616. (c) Bianchini, C.; Innocenti, P.; Peruzzini, M; Romerosa, A.; Zanobini, F.; Frediani, P. *Organometallics* **1996**, *15*, 272. (d) Duchateau, R.; van Wee, C. T.; Meetsma, A.; Teuben, J. H. *J. Am. Chem. Soc.* **1993**, *115*, 4931. (e) Barbaro, P.; Bianchini, C.; Peruzzini, M.; Polo, A.; Zanobini, F. *Inorg. Chim. Acta.* **1994**, *220*, 5. (f) Jun, C.-H.; Lu, Z.; Crabtree, R. H. *Tetrahedron Lett.* **1992**, *33*, 7119. (g) Matsuzaka, H.; Takagi, Y.; Ishii, Y.; Nishio, M.; Hidai, M. *Organometallics* **1995**, *14*, 2153.

(5) (a) Wakatsuki, Y.; Yamazaki, H.; Kumegawa, N.; Satoh, T.; Satoh, J. Y. *J. Am. Chem. Soc.* **1991**, *113*, 9604. (b) Wakatsuki, Y.; Koga, N.; Yamazaki, H.; Morokuma, K. *J. Am. Chem. Soc.* **1994**, *116*, 8105. (c) Heeres, H. J.; Nijhoff, J.; Teuben, J. H.; Rogers, R. D. *Organometallics* **1993**, *12*, 2609.

(6) (a) Suzuki, H.; Lee, D. H.; Oshima, N.; Moro-oka, Y. *Organometallics* **1987**, *6*, 1569. (b) Arliguie, T.; Border, C.; Chaudret, B.; Devillers, J.; Poilblanc, R. *Organometallics* **1989**, *8*, 1308. (c) Johnson, T. J.; Huffman, J. C.; Caulton, K. G. *J. Am. Chem. Soc.* **1992**, *114*, 2725. (d) Moreno, B.; Sabo-Etienne, S.; Chaudret, B.; Rodriguez, A.; Jalon, F.; Trofimenko, S. *J. Am. Chem. Soc.* **1995**, *117*, 7441.

(7) Yi, C. S.; Liu, N. *Organometallics* **1995**, *14*, 2616.

(8) Spectroscopic data for some dimeric compounds are reported in refs 3−5.

S0276-7333(96)00111-2 CCC: $12.00

Table 1. Ruthenium Complexes 1a−c Catalyzed Dimerization of Terminal Alkynes

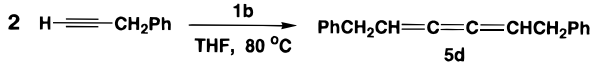
entry	substrate	catalyst	product ratio **2**:**3**:**4**	% yield[a]
1	HC≡CPh	**1a**	67:33:0	85
2	HC≡CC(CH$_3$)$_3$	**1a**	5[b]:95	91
3	HC≡CSiMe$_3$	**1a**	2[b]:98	100
4	HC≡CCH$_2$Ph	**1a**	0:27:73	80
5	HC≡CC$_4$H$_9$	**1a**	0:37:63	88 (3)
6	HC≡CPh	**1b**	90:10:0	86
7	HC≡CC(CH$_3$)$_3$	**1b**	17:35:48	17
8	HC≡CSiMe$_3$	**1b**	5[b]:95	58
9	HC≡CCH$_2$Ph	**1b**	>95% of **5d**	93[c]
10	HC≡CC$_4$H$_9$	**1b**	<5[b]:>95	14 (23)
11	HC≡CPh	**1c**	10:90:0	82
12	HC≡CC(CH$_3$)$_3$	**1c**	33:39:12[d]	87
13	HC≡CSiMe$_3$	**1c**	10:28:62	83
14	HC≡CCH$_2$Ph	**1c**	14:62:24	78
15	HC≡CC$_4$H$_9$	**1c**	24:26:50	79 (12)

[a] Reaction conditions: THF (5 mL); 0.1 mmol of alkyne and 3−5 mol % of the catalyst, **1**; 80 °C; 24 h. The product yields were determined from the GC-MS using hexamethylbenzene as an internal standard. Numbers in parentheses represent the % yield of trimeric products. [b] The combined ratio of both **2** and **3**. [c] Trace amount of other dimeric products was observed. The reaction was run at 80 °C for 60 h. [d] 16% of cumulene **5b** was also formed. The spectroscopic data for **5b** was described in: Wakatsuki, Y.; Satoh, M.; Yamazaki, H. *Chem. Lett.* **1989**, 1585.

dimerization of HC≡CCH$_2$Ph and HC≡CC$_4$H$_9$ by **1a** produced mixtures of *trans*-1,4-enynes and 1,3-enynes, **3d** and **4d** and, **3e** and **4e**, respectively (entries 4 and 5). All of the dimeric products were completely characterized by spectroscopic methods.[8]

Changing the ligand environment of the metal catalyst was found to dramatically influence the product distribution. For example, the dimerization reaction of HC≡CPh using bulky PCy$_3$-substituted **1b** resulted in selective formation for *cis*-enyne **2a** over **3a** (**2a**:**3a** = 90:10) (entry 6). In contrast, the dimerization of HC≡CPh by PMe$_3$-containing catalyst **1c** produced predominantly *trans*-enyne **3a** over the cis isomer **2a** (entry 11). For all three catalysts **1a**−**c**, selective formation of 1,4-disubstituted enynes from the head-to-head dimerization was observed for HC≡CPh, while the formation of 1,3-enynes from the head-to-tail dimerization was prevalent for alkyl- and silyl-substituted alkynes. The dimerization reactions of alkyl-substituted alkynes by **1b** were noticeably sluggish resulting in low conversion (entries 7 and 10), probably due to the unfavorable steric interactions between PCy$_3$ ligand and the alkyl groups. Poor selectivity was generally observed for dimerization reactions catalyzed by **1c** (entries 12−15). No significant amount of higher oligomers was formed, except for HC≡CC$_4$H$_9$, in which case a mixture of dimeric and other linear and cyclic trimeric products was produced (entries 5, 10, and 15). The reactions of smaller alkynes HC≡CCH$_3$ and HC≡CCO$_2$CH$_3$ produced mostly cyclotrimeric and other higher oligomeric products. The formation of cyclotrimeric compounds has been commonly observed in the metal-catalyzed oligomerization of alkynes.[2b]

Unexpected product formation was observed during the dimerization of HC≡CCH$_2$Ph. The dimerization of HC≡CCH$_2$Ph in the presence of **1b** resulted in the clean formation of cumulene **5d** (entry 9). The downfield-shifted vinyl proton (δ 6.03) and the quaternary carbon (δ 210.1) signals by NMR and the detection of dimeric parent ion peak by GC-MS established the cumulene structure **5d**, but its stereochemistry could not be determined unambiguously by spectroscopic methods.[5a,b] Similar dimerization reactions by **1a** and **1c** did not produce a significant amount of the cumulene, although a small amount of cumulene **5b** along with other dimeric products was formed during the **1c**-catalyzed dimerization reaction of HC≡CC(CH$_3$)$_3$ (entry 12). The formation of cumulenes from the dimerization of terminal alkynes has been rarely observed, in part due to their relative thermodynamic instability compared to enynes.[9]



Although detailed mechanism of the reaction and the nature of intermediate species have not been clearly elucidated, the outcome of the catalytic dimerization suggested some mechanistic insights, as illustrated in Scheme 1. It was found that the treatment of complex **1b** with D$_2$ (1 atm) and CO in THF at 70 °C produced C$_5$Me$_5$(PCy$_3$)RuD$_3$ and C$_5$Me$_5$(PCy$_3$)Ru(CO)H, respectively. Also, complex **1b** and other similar ruthenium hydride complexes are known to exist as equilibrium mixtures of the classical metal hydride and η^2-hydrogen complexes.[6b,10] These results suggest that the dihydrogen ligand of **1** was initially displaced by an incoming alkyne. The insertion of an alkyne to Ru−H bond, followed by σ-bond metathesis with another alkyne and the elimination of an alkene, would generate the acetylide intermediate **6**.[11]

Attempts have been made to detect the acetylide intermediate **6** independently. The reaction of Tilley's complex C$_5$Me$_5$Ru(PCy$_3$)Cl[12] with LiC≡CPh in C$_6$D$_6$ did not generate the anticipated acetylide complex as monitored by ^{1}H NMR. Instead, small amounts of the dimers **2a** and **3a** were formed as the starting materials slowly decomposed. The reaction of C$_5$Me$_5$Ru(PCy$_3$)Cl (20 mg, 0.036 mmol) with LiC≡CPh (4 mg, 0.036 mmol) in the presence of 10 equiv of HC≡CPh in C$_6$D$_6$ at room temperature produced the same mixture of enynes **2a** and **3a** with a similar ratio. No new Cp*-containing products was seen by ^{1}H NMR during the reaction. Qualitatively, initial rate of product formation for this system was comparable to **1b**-catalyzed reactions, but the catalytic activity gradually diminished after 1 h (65% conversion after 12 h).

The formation of 1,4-enynes has been previously explained by invoking an acetylene-to-vinylidene rearrangement.[4,5] For a pseudo-three-legged piano stool geometry, the vinylidene ligand is well-known to adopt a configuration where the plane of the vinylidene ligand is orthogonal to the plane bisecting the ancillary

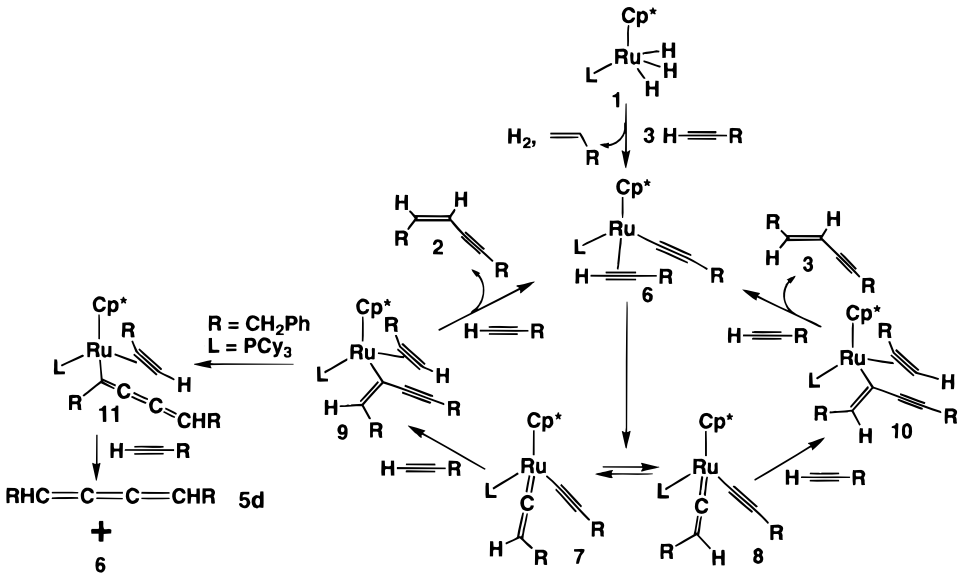
(9) (a) Huzinaga, S. *J. Chem. Phys.* **1965**, *42*, 1293. (b) Dunning, T. H., Jr. *J. Chem. Phys.* **1971**, *55*, 3958. (c) Stockis, A.; Hoffman, R. *J. Am. Chem. Soc.* **1980**, *102*, 2952.

(10) (a) Kubas, G. J. *Acc. Chem. Res.* **1988**, *21*, 120. (b) Crabtree, R. H. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 789. (c) Jessop, P. G.; Morris, R. H. *Coord. Chem. Rev.* **1992**, *121*, 155. (d) Heinekey, D. M.; Oldham, W. J., Jr. *Chem. Rev.* **1993**, *93*, 913.

(11) In a preliminary investigation, we observed that the phosphine ligand of **1b** was not labile on the NMR time scale in the temperature range 25−70 °C.

(12) (a) Campion, B. K.; Heyn, R. H.; Tilley, T. D. *J. Chem. Soc., Chem. Commun.* **1988**, 278. (b) Loren, S. D.; Campion, B. K.; Heyn, R. H.; Tilley, T. D.; Bursten, B. E.; Luth, K. W. *J. Am. Chem. Soc.* **1989**, *111*, 4712.

Scheme 1. Mechanistic Rationale on the Ruthenium-Catalyzed Alkyne Dimerization Reaction for the Formation of *cis*- and *trans*-1,4-Disubstituted Enynes, 2 and 3 and Cumulene 5d



ligands.[13] The salient feature of the present catalytic system is that the intramolecular acetylene-to-vinylidene rearrangement of **6** for aryl-substituted alkynes (R = Ph and CH_2Ph) should generate a mixture of two rotamers, **7** and **8**. Thus, when bulky PCy_3-substituted catalyst **1b** is employed, the formation of the rotamer **7** would be favored over **8**, on the basis of the greater steric repulsion between the vinylidene R group and PCy_3. The preferential formation of *cis*-1,4-enyne **2a** over **3a** is readily explained by the intramolecular acetylide migration to the α-vinylidene carbon from **7**.[14] The predominant formation of the trans isomer **3a** by PMe_3-substituted **1c** (entry 11) is similarly rationalized by invoking the preferential formation of **8** due to the smaller steric interactions between R group and PMe_3. The ratio of products for the dimerization of PhC≡CH can be correlated with the phosphine's cone angle of the catalysts **1a**−**c**.[15]

Since the acetylene-to-vinylidene step is known to be sluggish for nonaromatic alkynes,[13a] the direct insertion of these alkynes (R = *t*-Bu, $SiMe_3$, C_4H_9) from **6** would produce predominantly 1,3-enynes **4**.[3] For smaller alkynes (R = CH_3, CO_2Me), the insertion of another alkyne before elimination would produce trimeric and higher oligomeric products. In all cases, regeneration of the acetylide intermediate **6** would be achieved by the elimination of dimeric products from the intermediates **9**−**11** and the subsequent coordination of another alkyne. Recently, several metal−enynyl complexes have been isolated as an η^3-coordinated form.[4a−c,13a−c]

Formation of the cumulene **5d** should require a 1,3-metal migration from the vinyl intermediate **9** or **10**.[16] From the molecular modeling study of $(PPh_3)_2(Cl)_2Ru$-[C(=CHBu^t)C≡CHBu^t], Wakatsuki and co-workers rationalized that the steric interaction between PPh_3 and the butenynyl group is the dominant factor for promoting the 1,3-metal migration to form (*Z*)-cumulenes.[5a] In our case, steric interactions between PCy_3 and the benzyl group may also be an important factor in facilitating the 1,3-metal migration to form the cumulenyl intermediate **11**. Simple molecular mechanics calculations (PCMODEL, version 5.0) supported this hypothesis in that the phenyl group of the minimized cumulenyl structure **11** pointed directly to the PCy_3 group, whereas the benzyl analog of the cumulenyl structure **11** was significantly bent away from the PCy_3 group. Clearly, further studies are warranted to identify the factors governing this transformation.

In summary, we have shown that the ruthenium hydride complexes **1a**−**c** are versatile catalysts for the dimerization of terminal alkynes. The selective formation of different dimeric products, 1,3- and 1,4-enynes and cumulenes, has been achieved by modulating both the catalyst and the alkyne substrates. Studies on elucidating the mechanism of the reaction and on improving selectivity of the product formation are currently underway.

Experimental Section

General Methods. All materials were manipulated in an inert-atmosphere glovebox or by standard high-vacuum and

(13) (a) Bruce, M. I. *Chem. Rev.* **1991**, *91*, 197 and references therein. (b) Lomprey, J. R.; Selegue, J. P. *J. Am. Chem. Soc.* **1992**, *114*, 5518. (c) Kelley, C.; Lugan, N.; Terry, M. R.; Geoffroy, G. L.; Haggerty, B. S.; Rheingold, A. L. *J. Am. Chem. Soc.* **1992**, *114*, 6735. (d) Feng, S. G.; White, P. S.; Templeton, J. L. *J. Am. Chem. Soc.* **1994**, *116*, 8613. (e) Gamasa, M. P.; Gimeno, J.; Martin-Vaca, B. M.; Borge, J.; García-Granda, S.; Perez-Carreño, E. *Organometallics* **1994**, *13*, 4045. (f) Le Lagadec, R.; Roman, E.; Toupet, L.; Müller, U.; Dixneuf, P. H. *Organometallics* **1994**, *13*, 5030.

(14) For recent examples on the intramolecular alkyl migration to the vinylidene ligand for Ru and Os complexes, see: (a) Hill, A. F. In *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon Press: New York, 1995; Vol. 7. For other recent examples: (b) Jia, G.; Meek, D. W. *Organometallics* **1991**, *10*, 1444. (c) McMullen, A. K.; Selegue, J. P.; Wang, J.-G. *Organometallics* **1991**, *10*, 3421. (d) Selnau, H. E.; Merola, J. S. *J. Am. Chem. Soc.* **1991**, *113*, 4008. (e) Wiedemann, R.; Steinert, P.; Schäfer, M.; Werner, H. *J. Am. Chem. Soc.* **1993**, *115*, 9864. (f) Hughes, D. L.; Jimenez-Tenorio, M.; Leigh, G. J.; Rowley, A. T. *J. Chem. Soc., Dalton Trans.* **1993**, 3151. We thank a reviewer for bringing some of these references to our attention.

(15) (a) Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313. (b) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987.

(16) For recent examples on the 1,3-metal migrations, see: (a) Fisher, H.; Troll, C. *J. Organomet. Chem.* **1992**, *427*, 77. (b) Terry, M. R.; Mercando, L. A.; Kelley, C.; Geoffroy, G. L.; Nombel, P.; Lugan, N.; Mathieu, R.; Ostrander, R. L.; Owens-Waltermire, B. E.; Rheingold, A. L. *Organometallics* **1994**, *13*, 843.

Schlenk line techniques unless otherwise mentioned. Tetrahydrofuran and benzene were distilled from purple solutions of sodium and benzophenone immediately prior to use. C_6D_6 was dried from activated molecular sieves (4 Å). Ruthenium complexes $C_5Me_5Ru(L)H_3$ (L = PPh_3 (**1a**), PCy_3 (**1b**), PMe_3 (**1c**))[6] and $C_5Me_5Ru(PCy_3)Cl$[12] were prepared according to literature procedures. Organic alkynes were received from the commercial sources and used without further purification. The ^1H and ^{13}C NMR spectra were recorded on GE GN-Omega 300 MHz FT-NMR spectrometer. Mass spectra were recorded on Hewlett-Packard HP 5970 GC/MS spectrometer.

General Procedure for Catalytic Dimerization Reaction. In a 25 mL Schlenk tube equipped with a Teflon stopcock, ruthenium catalyst **1** (0.02 mmol, 3−5 mol %) was dissolved in 5−10 mL of THF. Excess alkyne (0.60 mmol) was added to the solution, and the reaction mixture was heated for 24 h at 80 °C under a closed system. After the reaction mixture was cooled to room temperature, a small sample was drawn out from the solution and was analyzed by GC-MS. The remaining solution was evaporated under high vacuum. The residue was extracted with Et_2O and chromatographed on silica gel (hexane/Et_2O) in air to obtain a mixture of dimeric products. For volatile dimeric products (R = CH_3, $SiMe_3$), the product containing THF solution was directly analyzed by GC-MS without isolation.

NMR Reaction of the Catalytic Dimerization of HC≡CPh by 1a. In an NMR tube, HC≡CPh (22 μL, 0.20 mmol) was added via syringe to a C_6D_6 solution containing the ruthenium catalyst **1a** (10 mg, 0.020 mmol) and hexamethylbenzene (5 mg, internal standard). The tube was flame-sealed and was heated in an oil bath at 80 °C for 24 h. The reaction was periodically monitored by ^1H NMR.

NMR Reaction of $C_5Me_5Ru(PCy_3)Cl$ with LiC≡CPh and HC≡CPh. In an NMR tube, the complex $C_5Me_5Ru(PCy_3)Cl$ was generated by mixing $[C_5Me_5RuCl]_4$ (10 mg, 0.009 mmol) and PCy_3 (10 mg, 0.036 mmol) in C_6D_6 by following the literature procedure.[12] To this deep blue solution, LiC≡CPh (4 mg, 0.036 mmol) and HC≡CPh (40 μL, 0.36 mmol) were added at room temperature. The color of solution turned red-brown upon shaking the tube. The reaction was monitored by ^1H NMR at ambient temperature.

Spectroscopic Data for Dimeric Products. ***cis*-PhCH=CHC≡CPh (2a).** ^1H NMR (C_6D_6, 300 MHz): δ 8.10−6.80 (m, Ph), 6.40 (d, J = 11.8 Hz, =CHPh), 5.79 (d, J = 11.8 Hz, =CHC≡C). $^{13}C\{^1H\}$ NMR (C_6D_6, 75 MHz): δ 139.1 (=CHPh), 137.1, 131.7, 129.2, 128.7, 128.5, 128.4, 124.0 (Ph carbons), 107.7 (=*C*HC≡C), 96.7 (=CH*C*≡CPh), 88.9 (=CHC≡*C*Ph). GC-MS: m/z = 204 (M^+).

***cis*-Me$_3$CCH=CHC≡CCMe$_3$ (2b).** ^1H NMR (C_6D_6, 300 MHz): δ 5.56 (d, J = 12.0 Hz, =CHCMe$_3$), 5.47 (d, J = 12.0 Hz, =C*H*C≡C), 1.24 and 1.18 (s, CMe$_3$). $^{13}C\{^1H\}$ NMR (C_6D_6, 75 MHz): δ 152.9 (=*C*HCMe$_3$), 118.5 (=*C*HC≡C), 106.4 (=CH*C*≡C), 67.3 (=CHC≡*C*), 29.8 and 27.3 (CMe$_3$). GC-MS: m/z = 164 (M^+).

***cis*-Me$_3$SiCH=CHC≡CSiMe$_3$ (2c).** ^1H NMR (C_6D_6, 300 MHz): δ 6.23 (d, J = 14.7 Hz, =CHSiMe$_3$), 6.00 (d, J = 14.7 Hz, =CHC≡CSiMe$_3$), 0.17 and 0.12 (SiMe$_3$). $^{13}C\{^1H\}$ NMR (C_6D_6, 75 MHz): δ 146.4 (=*C*HSiMe$_3$), 124.4 (=*C*HC≡CSiMe$_3$), 105.7 (=CHC≡*C*SiMe$_3$), 98.6 (=CH*C*≡CSiMe$_3$), −1.00 and −0.28 (SiMe$_3$). GC-MS: m/z = 196 (M^+).

***cis*-C$_4$H$_9$CH=CHC≡CC$_4$H$_9$ (2e).** ^1H NMR (C_6D_6, 300 MHz): δ 5.65 (dt, J = 11.2, 6.7 Hz, =C*H*C$_4$H$_9$), 5.52 (d, J = 11.2 Hz, =C*H*C≡CC$_4$H$_9$), 2.5−0.5 (m, C$_4$H$_9$). $^{13}C\{^1H\}$ NMR (C_6D_6, 75 MHz): δ 142.1 (=*C*HC$_4$H$_9$), 110.3 (=*C*HC≡CC$_4$H$_9$), 88.7 (*C*≡CC$_4$H$_9$), 80.0 (C≡*C*C$_4$H$_9$), 30.1, 22.6, 19.5, and 14.1 (C$_4$H$_9$ carbons). GC-MS: m/z = 164 (M^+).

***trans*-PhCH=CHC≡CPh (3a).** ^1H NMR (C_6D_6, 300 MHz): δ 8.10−6.80 (m, Ph), 7.04 (d, J = 16.2 Hz, =CHPh), 6.30 (d, J = 16.2 Hz, =CHC≡C). $^{13}C\{^1H\}$ NMR (C_6D_6, 75 MHz): δ 142.3 (=CHPh), 137.3, 132.2, 129.7, 129.4, 129.2, 127.3, and 124.4 (Ph carbons), 109.0 (=*C*HC≡C), 92.3 (=CH*C*≡CPh), 89.8 (=CHC≡*C*Ph). GC-MS: m/z = 204 (M^+).

***trans*-Me$_3$CCH=CHC≡CCMe$_3$ (3b).** ^1H NMR (C_6D_6, 300 MHz): δ 6.14 (d, J = 16.2 Hz, =CHCMe$_3$), 5.49 (d, J = 16.2 Hz, =CHC≡CCMe$_3$), 1.26 and 1.19 (s, CMe$_3$). $^{13}C\{^1H\}$ NMR (C_6D_6, 75 MHz): δ 150.9 (=*C*HCMe$_3$), 107.8 (=*C*HC≡C), 92.6 (=CH*C*≡C), 79.6 (=CHC≡*C*), 31.0, and 29.1 (CMe$_3$). GC-MS: m/z = 164 (M^+).

***trans*-Me$_3$SiCH=CHC≡CSiMe$_3$ (3c).** ^1H NMR (C_6D_6, 300 MHz): δ 6.25 (d, J = 15.5 Hz, =CHSiMe$_3$), 6.01 (d, J = 15.5 Hz, =CHC≡C), 0.24 and 0.16 (SiMe$_3$). $^{13}C\{^1H\}$ NMR (C_6D_6, 75 MHz): δ 145.8 (=*C*HSiMe$_3$), 125.4 (=*C*HC≡C), 106.1 (C≡*C*SiMe$_3$), 94.9 (*C*≡CSiMe$_3$), −0.01 and −1.84 (SiMe$_3$). GC-MS: m/z = 196 (M^+).

***trans*-PhCH$_2$CH=CHC≡CCH$_2$Ph (3d).** ^1H NMR (C_6D_6, 300 MHz): δ 7.8−6.9 (m, Ph), 6.20 (dt, J = 16.2, 6.6 Hz, =C*H*CH$_2$Ph), 5.51 (d, J = 16.2 Hz, =C*H*C≡CCH$_2$Ph), 3.46 (s, C≡CCH$_2$Ph), 3.04 (d, J = 6.6 Hz, =CHC*H*$_2$Ph). $^{13}C\{^1H\}$ NMR (C_6D_6, 75 MHz): δ 139.0 (=*C*HCH$_2$Ph), 128.9, 128.7, 128.6, 128.1, and 126.5 (Ph carbons), 111.6 (=*C*HC≡C), 88.5 (*C*≡CCH$_2$Ph), 83.6 (C≡*C*CH$_2$Ph), 39.3 (=CH*C*H$_2$Ph), 25.6 (C≡C*C*H$_2$Ph). GC-MS: m/z = 232 (M^+).

***trans*-C$_4$H$_9$CH=CHC≡CC$_4$H$_9$ (3e).** ^1H NMR (C_6D_6, 300 MHz): δ 6.04 (dt, J = 16.2, 6.6 Hz, =C*H*C$_4$H$_9$), 5.51 (d, J = 16.2 Hz, =C*H*C≡CC$_4$H$_9$), 2.2−0.7 (m, C$_4$H$_9$). $^{13}C\{^1H\}$ NMR (C_6D_6, 75 MHz): δ 132.9 (=*C*HC$_4$H$_9$), 110.9 (=*C*HC≡CC$_4$H$_9$), 90.1 (*C*≡CC$_4$H$_9$), 81.7 (C≡*C*C$_4$H$_9$), 31.3, 22.3, 19.2, and 14.0 (C$_4$H$_9$ carbons). GC-MS: m/z = 164 (M^+).

CH$_2$=C(CMe$_3$)C≡CCMe$_3$ (4b). ^1H NMR (C_6D_6, 300 MHz): δ 5.36 (d, J = 1.5 Hz, CH*H*=), 5.12 (d, J = 1.5 Hz, C*H*H=), 1.20 and 1.17 (CMe$_3$). $^{13}C\{^1H\}$ NMR (C_6D_6, 75 MHz): δ 142.3 (CH$_2$=), 116.0 (=*C*C≡C), 99.2 (=C*C*≡C), 67.2 (=CC≡*C*), 31.1 and 29.2 (CMe$_3$). GC-MS: m/z = 164 (M^+).

CH$_2$=C(SiMe$_3$)C≡CSiMe$_3$ (4c). ^1H NMR (C_6D_6, 300 MHz): δ 6.11 (d, J = 3.4 Hz, CH*H*=), 5.54 (d, J = 3.4 Hz, C*H*H=), 0.18 and 0.13 (SiMe$_3$). $^{13}C\{^1H\}$ NMR (C_6D_6, 75 MHz): δ 135.3 (CH$_2$=*C*), 134.9 (*C*H$_2$=C), 107.2 (*C*≡CSiMe$_3$), 98.6 (C≡*C*SiMe$_3$), 0.14 and −2.20 (SiMe$_3$). GC-MS: m/z = 196 (M^+).

CH$_2$=C(CH$_2$Ph)C≡CCH$_2$Ph (4d). ^1H NMR (C_6D_6, 300 MHz): δ 7.8−6.9 (m, Ph), 5.41 (d, J = 1.5 Hz, CH*H*=), 5.05 (d, J = 1.5 Hz, C*H*H=), 3.36 and 3.33 (s, CH$_2$). $^{13}C\{^1H\}$ NMR (C_6D_6, 75 MHz): δ 142.2 (=*C*C≡C), 129.4, 128.7, 128.6, 128.2, and 126.6 (Ph carbons), 121.3 (=CH$_2$), 91.6 (*C*≡CCH$_2$Ph), 87.2 (C≡*C*CH$_2$Ph), 44.1 (=C*C*H$_2$Ph), 25.8 (C≡C*C*H$_2$Ph). GC-MS: m/z = 232 (M^+).

CH$_2$=C(C$_4$H$_9$)C≡CC$_4$H$_9$ (4e). ^1H NMR (C_6D_6, 300 MHz): δ 5.31 (d, J = 1.5 Hz, CH*H*=), 5.06 (d, J = 1.5 Hz, C*H*H=), 2.2−0.7 (m, C$_4$H$_9$). $^{13}C\{^1H\}$ NMR (C_6D_6, 75 MHz): δ 142.9 (=CH$_2$), 119.5 (=*C*C≡C), 84.3 (*C*≡CC$_4$H$_9$), 68.6 (C≡*C*C$_4$H$_9$), 30.8, 22.0, 18.3, and 13.6 (C$_4$H$_9$ carbons). GC-MS: m/z = 164 (M^+).

(CH$_3$)$_3$CCH=C=C=CHC(CH$_3$)$_3$ (5b). ^1H NMR (C_6D_6, 300 MHz): δ 5.49 (s, =CH), 1.11 (s, CH$_3$). $^{13}C\{^1H\}$ NMR (C_6D_6, 75 MHz): δ 160.8 (=*C*=CHCMe$_3$), 118.2 (=*C*HCMe$_3$), 35.1 and 29.9 (CMe$_3$). GC-MS: m/z = 164 (M^+).

PhCH$_2$CH=C=C=CHCH$_2$Ph (5d). ^1H NMR (C_6D_6, 300 MHz): δ 7.5−6.9 (m, Ph), 6.03 (t, J = 6.6 Hz, =CH), 4.84 (d, J = 6.6 Hz, C*H*$_2$Ph). ^{13}C NMR (C_6D_6, 75 MHz): δ 210.1 (s, =*C*=CH), 134.3, 129.0, 128.9, 127.7, 127.3, and 127.0 (Ph carbons), 94.1 (d, J = 164.8 Hz, =*C*HCH$_2$Ph), 78.9 (t, J = 168.5 Hz, *C*H$_2$Ph). GC-MS: m/z = 232 (M^+).

Acknowledgment. Financial support from Marquette University is gratefully acknowledged.

OM9601110