Synthesis of 1,1-Disubstituted Alkenes via a Ru-Catalyzed Addition

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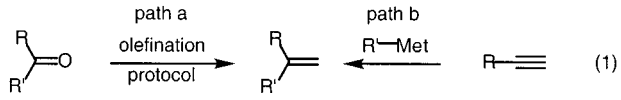
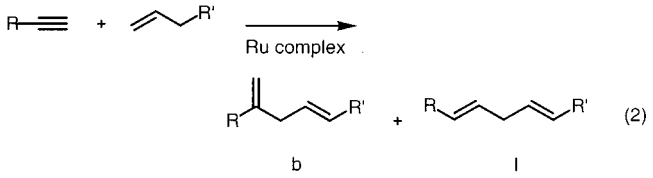
Abstract: The synthesis of 1,1-disubstituted alkenes typically involves reactions that lack atom economy such as olefination protocols. The use of various ruthenium complexes to effect the addition of terminal alkynes to alkenes is explored as an atom economical strategy. Two new ruthenium complexes have been discovered that effect this reaction at ambient temperature, cyclopentadienylruthenium (triphenylphosphine) camphorsulfonate and cyclopentadienylruthenium tris(acetonitrile) hexafluorophosphate. Using these complexes as catalysts, reactions proceed at ambient temperature in acetone or DMF, respectively. Regioselectivity favoring the formation of a 1,1-disubstituted over a 1,2-disubstituted alkene typically ranges from 9:1 to >25:1. The reaction demonstrates extraordinary chemoselectivity—even di- and trisubstituted alkenes such as present in the products do not compete with the starting monosubstituted alkene. Free hydroxyl groups as well as silyl and PMB ethers are tolerated as are ketones, esters, and amides. The mechanism of the reaction is believed to invoke formation of a metallacyclopentene. To account for the chemo- and regioselectivity, the initial formation of the metallacycle is believed to be reversible. While formation of the 2,5-disubstituted ruthenacyclopentene, which produces the linear product, is believed to be kinetically preferred, the rate of β-hydrogen elimination from the 2,4-disubstituted ruthenacyclopentene, which produces the branched product, is believed to be faster. Thus, the competition between the rate of β-hydrogen elimination and cycloreversion rationalizes the results.

Introduction

The development of new synthetic methods that are atom economical is an important goal.[1] Ideally, reactions involve additions that proceed chemo- and regioselectively to generate complex products from simple building blocks. The synthesis of 1,1-disubstituted alkenes illustrates the issue (eq 1). The strategy that almost immediately jumps



to mind is an olefination protocol.[2] While chemoselectivity issues do arise in such a strategy, a major deficiency is the poor atom economy of such a process (path a). A better strategy employs the more atom economical addition of an organometallic to a terminal alkyne.[3] While this route clearly still retains issues of atom economy, a large issue is chemoselectivity. We have been developing an atom economical alternative to 1,1-disubstituted alkenes based upon a ruthenium-catalyzed addition as shown in eq 2.[4,5] This strategy is highly atom economical, but it suffers with



respect to the issue of regioselectivity. Branched-to-linear ratios (b/l) typically ranged from 3 to 6:1. In this paper, we report two new ruthenium complexes competent to effect this reaction and the remarkable influences of ligand and, in some cases, alkene substrate on the regioselectivity of this process.[6] With regioselectivities typically 9 to >25:1 b/l, an excellent approach to 1,1-disubstituted alkenes has resulted.

Catalysts. Scheme 1 outlines the working hypothesis for the mechanism of the Ru-catalyzed alkene/alkyne coupling. The initial coordination (step 1) and the tautomerization of **1a**/**1b** to metallacycles **2a**/**2b** (steps 2) are believed to be reversible, at least to some extent. The product ratio then depends on the conversion of **2** to **3**. If step 3 is faster than the reversal of step 2, then the product ratio derives from the initial ratio of **2a**/**2b**. If step 3 is slower than the reversal of step 2, then a Curtin−Hammett situation ensues. The product ratio will depend on

(1) Trost, B. M. *Science* **1991**, *254*, 1471. Trost, B. M. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 259.

(2) Kelly, S. E. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Schreiber, S. L., Eds.; Pergamon: Oxford, U.K., 1991; Vol. 1, pp 729−818.

(3) Knochel, P. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Schreiber, S. L., Eds.; Pergamon: Oxford, U.K., 1991; Vol. 4, pp 865−911.

(4) Trost, B. M.; Indolese, A. F.; Müller, T. J. J.; Treptow, B. *J. Am. Chem. Soc.* **1995**, *117*, 615. Trost, B. M.; Indolese, A. F. *J. Am. Chem. Soc.* **1993**, *115*, 4361.

(5) For a review, see: Trost, B. M.; Krische, M. J. *Synlett* **1998**, 1.

(6) For a preliminary report of a portion of this work, see: Trost, B. M.; Toste, F. D. *Tetrahedron Lett.* **1999**, *40*, 7739.

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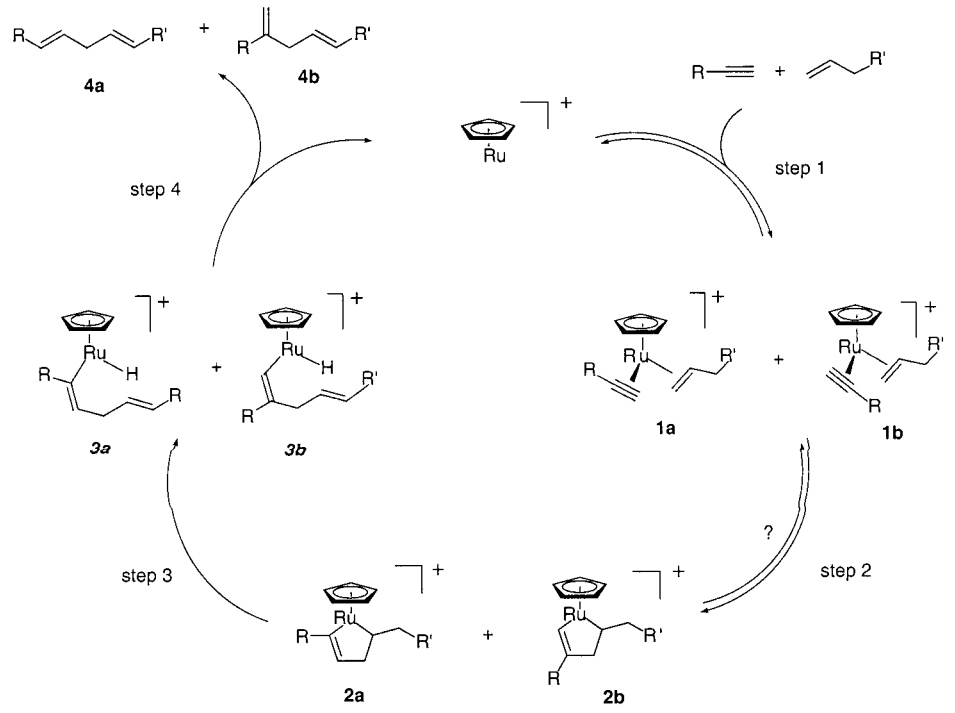
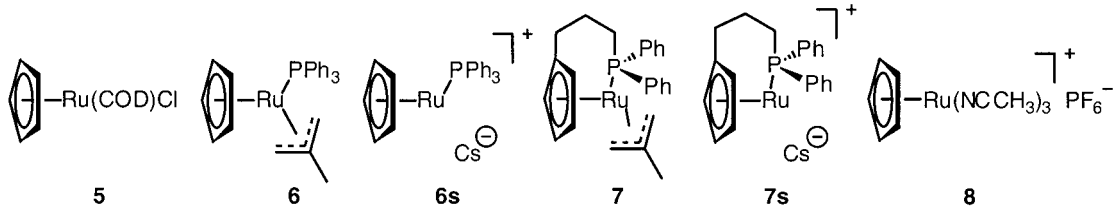
Scheme 1. Mechanistic Hypothesis for the Ru-Catalyzed Alkene−Alkyne Addition[a]



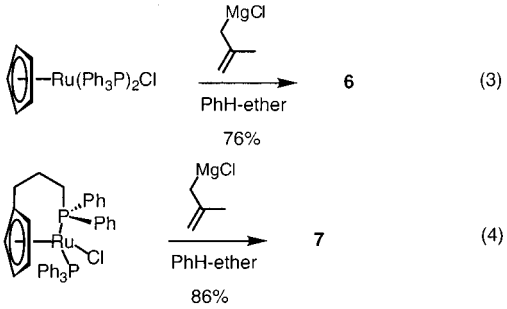
[a] Any open coordination site(s) in these complexes would be anticipated to be occupied by some ligand present including solvent.

Chart 1



the relative rate of the β-hydrogen elimination of **2a** versus **2b**. In this catalytic cycle, it should be noted that at least one open coordination site on Ru exists and, in some cases, two. Thus, the regioselectivity may be affected by the occupants of the open coordination site.

Our first-generation catalyst **5**[7] possesses a chloride, which may serve as a ligand at any stage of the catalytic cycle. Such an anionic ligand is believed to be detrimental to the rate of the reaction. Cationic complexes were envisioned to be kinetically more competent and would allow for a greater diversity in the choice of a ligand. Placing a bulky substituent on Ru might favor **2b** over **2a** and therefore enhance the regioselectivity favoring the branched isomer. Our second-generation cationic catalysts **6s** and **7s** (Cs = camphorsulfonate; Chart 1) would derive by protonation of the methallyl group of **6** and **7** with camphorsulfonic acid. Although the phosphine might slow the reaction, this negative rate effect would be countermanded by the cationic nature of the complex. Complexes **6**[8] and **7**[9] are readily accessed according to eqs 3 and 4, the former according



to a literature procedure.[8] The quality of the Grignard reagent was crucial, and preactivation of the magnesium by the method of Brown et al.[10] was preferred. Removal of the liberated triphenylphosphine by sublimation was preferred over distillation. An X-ray structure of **7** (Figure 1) reveals a transoid relationship of the central carbon of the allyl group and phosphorus. This structure remains constant in solution as revealed by its NMR spectra, which are similar to those reported for **6**. Anticipating a rate retardation by the presence of a phosphine ligand, a cationic ruthenium complex lacking this substituent was sought. The tris-acetonitrile complex **8**[11] nicely meets this requirement. Although it possesses a sterically small

(7) Albers, M. O.; Robinson, D. J.; Shaver, A.; Singleton, E. *Organometallics* **1986**, *5*, 2199. For a review, see: Davies, S. G.; McNally, J. P.; Smallridge, A. J. *Adv. Organomet. Chem.* **1990**, *30*, 1.

(8) Lehmkuhl, H.; Mauermann, H.; Benn, R. *Liebigs Ann. Chem.* **1980**, 754.

(9) For the precursor, see: Trost, B. M.; Vidal, B.; Thommen, M. *Chem. Eur. J.* **1999**, *5*, 1055.

(10) Baker, K. V.; Brown, J. M.; Hughes, N.; Skarnulis, A. J.; Sexton, A. *J. Org. Chem.* **1991**, *56*, 698.

(11) Gill, T. P.; Mann, K. R. *Organometallics* **1982**, *1*, 485.

(12) Cf. Trost, B. M.; Krause, L.; Portnoy, M. *J. Am. Chem. Soc.* **1997**, *119*, 11319. Trost, B. M.; Portnoy, M.; Kurihara, H. *J. Am. Chem. Soc.* **1997**, *119*, 836.

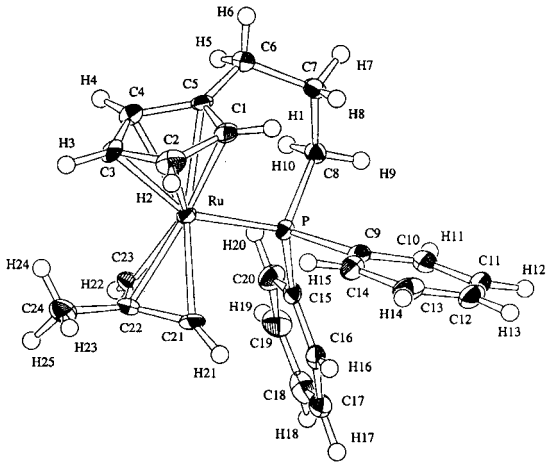
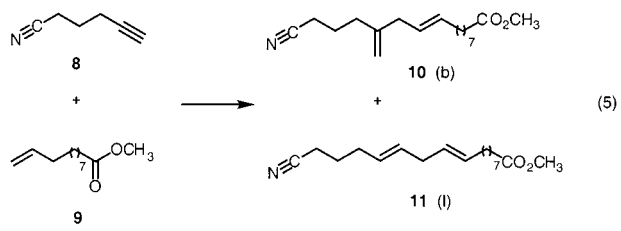


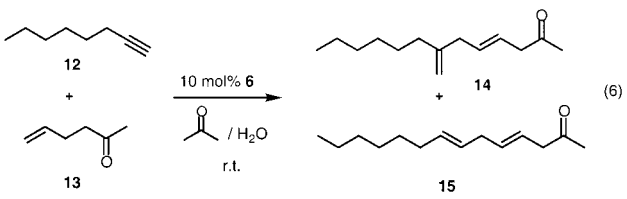
Figure 1. ORTEP plot of **7**.

ligand, acetonitrile, it offers the prospect of exchanging it for other ligands as desired.

Second-Generation Catalyst Reactions. Equation 5 illustrates the initial reaction examined using complexes **6** and **7** as precatalysts. Using the typical conditions[4] for complex **5** (3:1 DMF/water, 100 °C), a 41% yield of a 5:1 b/l ratio of adducts **10** and **11** was isolated. Treating complex **6** (10 mol %) with camphorsulfonic acid (CSA, 15 mol %) gave the camphorsulfonate (Cs^-) salt **6s**. Peforming the reaction at 100 °C in DMF gave only a 30% yield of a 3.7:1 ratio of b/l adducts. In acetone at reflux, a 48% yield of a 3.4:1 ratio of b/l isomers was isolated. Interestingly, the reaction even proceeded at ambient temperature wherein the b/l ratio improved to 5.0:1.0. The presence of water in acetone had a dramatic effect on the reaction. Using 5:1 to 2:1 acetone/water ratios at ambient temperature gave 76−66% yields of 5.9:1.0−5.2:1.0 b/l ratios, respectively. In the case of 5:1 acetone/water, raising the temperature to reflux gave the same 76% yield but the ratio dropped to 3.8:1.0 from 5.9:1.0. Varying the amount of CSA had little effect on the reaction. However, addition of indium triflate as a cocatalyst had a significant effect.[12] Adding anywhere from 10 to 40 mol % gave little change in yield (70−74%) but significantly reduced the regioselectivity to 1.8:1.0 b/l. Switching to complex **7** as the precatalyst gave similar results.

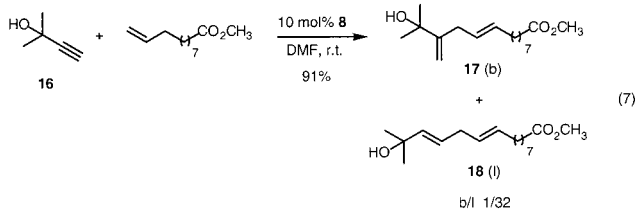


A more striking example is illustrated in eq 6. Using our first-generation catalyst **5** in methanol at reflux gave a 50% yield of a 3.8:1.0 ratio of **14**/**15**.[4] With our second-generation catalyst **6s** in 5:1 acetone/water at room temperature, the yield and regioselectivity increased to 67% and a 26:1.0 b/l ratio. Thus, an excellent selectivity for the 1,1-disubstituted alkene was now in hand.



Third-Generation Catalyst Reactions. Initial studies with our third generation catalyst **8** under conditions similar to those above (30% CSA, acetone, 60 °C) gave a 78% yield of **10** and **11** but a disappointing 1:1.1 ratio. Using alternative additives such as indium triflate, HMPA, and TMU did not have a beneficial effect. In the absence of any additives at room temperature in acetone, a 73% yield of a 1.2:1 b/l ratio was obtained. In contrast to our second-generation catalyst, using DMF as solvent had a dramatic effect on the b/l ratio favoring b. The reaction still proceeded at room temperature within 2 h to give an 82% yield of a 9:1 b/l ratio. With this excellent result, a range of substrates was examined and is summarized in the Table.

The examples in the table clearly show good to excellent regioselectivity. The lower regioselectivities of entries 1 and 2 are somewhat baffling given the examples in the rest of the table. At the same time, it is difficult to see trends as to what factors contribute to higher b/l ratios. Entry 3 comes closest to a totally unbiased system, yet a 7.2:1 b/l ratio was still observed. Curiously, the unfunctionalized 1-decene gave regioselectivities as high as 15.3:1 (entry 15). More remarkable, methyl 10-undecenoate, an alkene substrate whose ester functional group is so far removed from the alkene that it should function more like a simple hydrocarbon, reacted with some alkynes to give the branched isomer as the only detectable one (entries 21 and 22). There does appear to be some role for substituents on the alkyne influencing regioselectivity. Steric bulk or coordinating groups proximal to the alkyne may be helpful. However, the steric hindrance, if at the propargylic position, can reverse the regioselectivity. Indeed, as shown in eq 7, the linear isomer **18**



was virtually the exclusive product of the reaction with alkyne **16**. On the other hand, moving the quaternary center one atom away from the alkyne and the regioselectivity completely reverses giving only the branched product (Table, entry 21).

A functional group two or three atoms away from the alkyne appears helpful. A comparison of entries 8−11 indicates that an aromatic ring may be sufficient. Hydroxyl groups two atoms away also play this role. Conversion of the hydroxyl group to its PMB ether significantly reduces the regioselectivity (entry 2 vs 13). Running the reaction of entry 13 in acetone as solvent gave the adduct in 46% yield as a 2:1 b/l ratio, again showing the superiority of DMF as solvent. On the other hand, a hydroxyl group three atoms away leads to a 2:1 adduct in addition to the desired product, both with low b/l ratios (eq 8). In this case, it appears

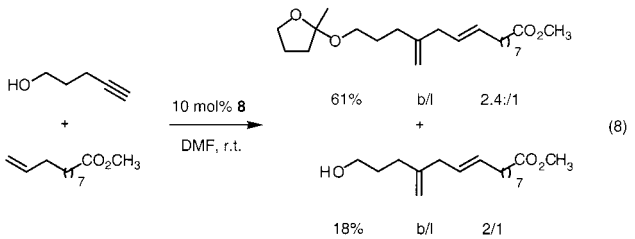
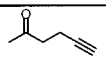
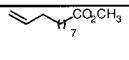
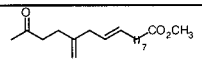
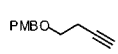
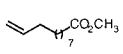
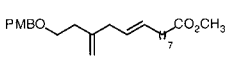
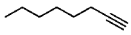
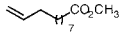
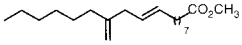
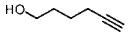
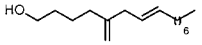
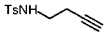
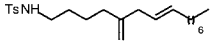
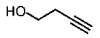
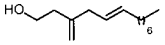
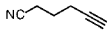
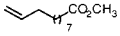
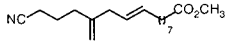
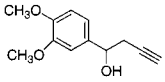
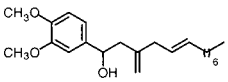
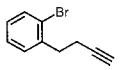
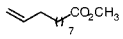
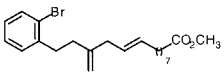
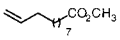
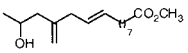
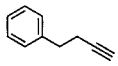
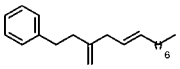
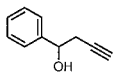
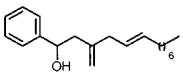
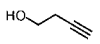
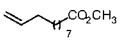
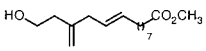


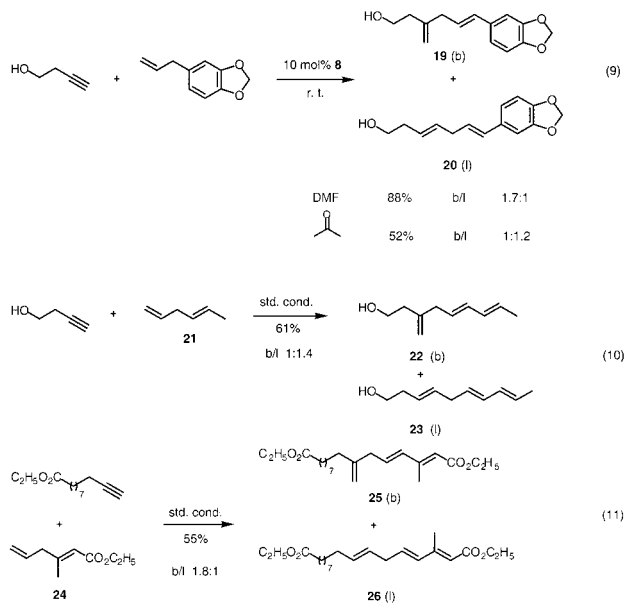
Table 1. A Synthesis of 1,1-Disubstituted Alkenes via a Ru Catalyzed Addition[a]

Entry	Alkyne	Alkene	Product	Isolated Yield	b/l
1				86%	4.8 : 1
2				74%	5.3 : 1
3				72%	7.2 : 1
4				62%	7.4 : 1
5				73%	7.4 : 1
6				66%	8.9 : 1
7				82%	8.9 : 1
8				69%	9.1 : 1
9				75%	9.7 : 1
10				74%	9.8 : 1
11				73%	10.5 : 1
12				68%	10.5 : 1
13				75%	11.3 : 1
14				69%	14.2 : 1
15				84%	15.3 : 1
16				72%	16.7 : 1
17				58%	17.4 : 1
18				59%	>25 : 1
19				67%	>25 : 1
20				25%	>25 : 1
21				72%	>25 : 1
22				84%	>25 : 1

[a] All reactions were performed with 10 mol % **8**, 1.2 equiv of alkene, and 1.0 equiv of alkyne at 0.5 M in DMF at room temperature.

that cycloisomerization of the alkynol to 2-methylenetetrahydrofuran also occurs, the latter then derivatizing the primary alcohol to form an acetal of either the starting alkynol or the adduct, either of which may account for the final product acetal.

There were several alkene substrates that gave low regioselectivities (eqs 9−11). In the reaction of safrole (eq 9), the



reaction proceeded readily at room temperature in both DMF and acetone. While the regioselectivity was rather poor in both, the major regioisomer in acetone was the linear one and in DMF the branched one. For comparison, the same reaction catalyzed by the first-generation catalyst **5** required methanol at reflux and only gave a 46% yield of a 1:1 mixture of **19** and **20**. Similarly, the allylic substrates **21** and **24** also participate but also give low regioselectivity. The formation of 1,3-dienes is quite interesting. The latter reaction (eq 11) required methanol at reflux with catalyst **5**, but the results were better—a 54% yield of a 4:1 ratio of **25** and **26**. While these three examples demonstrate the scope and limitation for good regioselectivity, they help provide insight into the mechanism of this process.

Discussion

The mechanistic hypothesis outlined in Scheme 1 generally accounts for the observations to date. The ability to form a ruthenacyclopentene (from an alkyne and alkene) compared to a ruthenacyclopentadiene (from two alkynes) or a ruthenacyclopentane (from two alkenes) can be understood by envisioning metallacycle formation being reversible. The much higher coordinating affinity of an alkyne compared to an alkene should lead to the rate of metallacycle formation decreasing in the order metallacyclopentadiene > metallacyclopentene ≫ metallacyclopentane.[14] The current results can be understood in the context of this scheme if metallacyclopentene formation is reversible and the relative rates of β-hydrogen elimination and metallacycle formation are competitive. Significant data suggest that steric interactions between the two carbons involved in C−C bond formation of the metallacycle normally dominate and lead to preference of transition state I_l over I_b to favor metallacycle II_l (see Scheme 2).[15] Thus, to the extent that the rate of β-hydrogen elimination is faster than reversal of metallacycle formation, then linear products should dominate. Indeed, to the extent that β-hydrogen elimination is made faster, the amount of the linear product increases. Thus, when the β-hydrogen in II_b or II_l is benzylic or allylic which, by decreasing the C−H bond strength should increase the rate of β-H elimination, the amount of the linear product increases and may even become dominant, albeit slightly.

However, that circumstance appears to be more the exception than the rule. In most cases, the β-hydrogen elimination is slower than reversal of metallacycle formation—a situation that brings the reaction toward Curtin−Hammett control. The solvent effects are in accord with this analysis. The better coordinating solvent, DMF, favors branched over linear product with complex **8**. Since β-hydrogen elimination requires open coordination sites on the metal,[16] to the extent such sites are occupied by solvent, this reaction is slowed. Thus, DMF more effectively retards β-hydrogen elimination in both cases, thus making reversal of metallacycle formation faster than β-hydrogen elimination. In the case of complex **6** as catalyst, no solvent effect on the regioselectivity was noted since triphenylphosphine occupies one of the open coordination sites in the metallacycle, which makes it difficult for any other ligand to enter the coordination sphere of the Ru(+4).

In the domain wherein metallacycle equilibration is faster than β-hydrogen elimination—i.e., k_b, k_{-b}, k_l, and k_{-l} are larger than k_{2b} and k_{2l}—then the product ratio depends on k_{2b}/k_{2l}. Steric hindrance associated with the transition state leading to III_l makes $k_{2b} > k_{2l}$ and thus favors the branched product. To the extent that potential coordinating groups are present in R, any such coordination would disfavor β-hydrogen elimination in the case of II_l due to saturation of the metal, therefore further increasing the ratio of k_{2b}/k_{2l} and the amount of branched product.

Among the catalysts explored to date, the tris-acetonitrile complex **8** represents the most practical and general. Reactions proceed readily at room temperature normally within a few hours. The mild conditions undoubtedly also contribute to the excellent selectivity. The reaction has excellent chemoselectivity. It is not sensitive to water or oxygen although we do perform the reactions under an inert atmosphere. A broad range of functionality is compatible. It is important to note that the products, which are alkenes, do not react further under the reaction conditions—a fact that indicates a monosubstituted alkene is a much better substrate than a disubstituted one. In comparison to other methods to form 1,1-disubstituted alkenes, this simple addition has the benefit of being highly atom economical and very simple to perform. The formation of 1,4-dienes constitutes a bonus since it provides a second alkene for elaboration as well. For example, the formation of allyl alcohols as in the table, entries **18** and **19**, sets the stage for further reactions such as allylic alkylations, Claisen rearrangements, etc. This reaction should prove to be a valuable addition to the arsenal of atom economic C−C bond forming reactions.

Experimental Section

Ru-Catalyzed Reaction with Complex 6: 7-Methylene-4-tridecen-2-one (14). To a mixture of 9.6 mg (0.02 mmol) of **6** and 18.6 mg (0.08 mmol) of CSA under nitrogen was added 1.5 mL of dried acetone

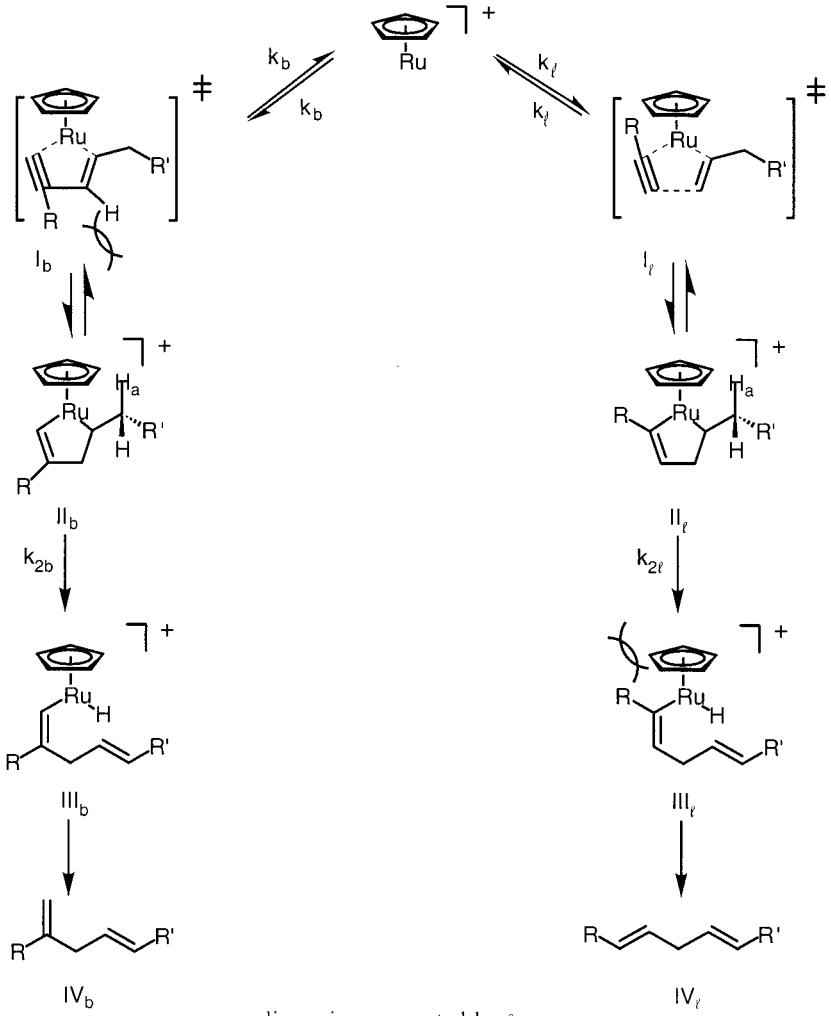
(13) For a few other reactions involving a ruthenacyclopentene intermediate, see: Mitsudo, T.; Kokuryo, K.; Shinsugi, T.; Nakagawa, Y.; Watanabe, Y.; Takegami, Y. *J. Org. Chem.* **1979**, *44*, 4492. Trost, B. M.; Imi, K.; Indolese, A. F. *J. Am. Chem. Soc.* **1993**, *115*, 8831. Warrener, R. N.; Abhenants, A.; Kennard, C. H. L. *J. Am. Chem. Soc.* **1994**, *116*, 3645. Mitsudo, T.; Naruse, H.; Kondo, T.; Ozaki, Y.; Watanabe, Y. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 580. Marimoto, T.; Chatani, N.; Fukumoto, Y.; Murai, S. *J. Org. Chem.* **1997**, *62*, 3762. Kondo, T.; Ozaki, Y.; Watanabe, Y. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 580. Marimoto, T.; Chatani, N.; Fukumoto, Y.; Murai, S. *J. Org. Chem.* **1997**, *62*, 3762. Kondo, T.; Suzuki, N.; Okada, T.; Mitsudo, T. *J. Am. Chem. Soc.* **1997**, *119*, 6187. Matsushima, Y.; Kikuchi, H.; Uno, M.; Takahashi, S. *Bull. Chem. Soc. Jpn.* **1999**, *72*, 2475. Dérien, S.; Ropartz, L.; Le Paih, J.; Dixneuf, P. H. *J. Org. Chem.* **1999**, *64*, 3524.

(14) Trost, B. M.; Toste, F. D.; Pinkerton, A. B. *Chem. Rev.* **2001**, *101*, 2067−2096.

(15) Vollhardt, K. P. C. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 539.

(16) Cross, R. J. In *The Chemistry of the Metal−Carbon Bond*; Hartley, R. F., Patai, S., Eds.; Wiley: New York, 1985; Vol. 2, Chapter 8. Also see: Schmidt, G. F.; Brookhart, M. *J. Am. Chem. Soc.* **1985**, *107*, 1443.

Scheme 2. Competitive Ruthenacycle Formation and β-Hydrogen Elimination



to form an orange solution. 1-Octyne (24.2 mg, 0.22 mmol) and 5-hexen-2-one (19.6 mg, 0.20 mmol) were added sequentially. The reaction was complete after 3 h. It was evaporated and the residue directly chromatographed (1:8 ethyl acetate/hexane) to give 27.8 mg (67% yield) of **14**. GC analysis revealed a 26:1 ratio of **14** (retention time 10.35 min) to **15** (retention time 10.59 min): IR (neat) 1720, 1645, 1430m 1358, 1156, 1018 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 5.56−5.59 (m, 2H), 4.72 (s, 1H), 3.15 (d, J = 4.6 Hz, 2H), 2.75 (d, J = 4.2 Hz, 2H), 2.16 (s, 3H), 2.00 (t, J = 7.6 Hz, 2H), 1.21−1.31 (m, 8H), 0.89 (t, J = 6.8 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 208.01, 149.19, 133.42, 124.07, 110.25, 47.87, 39.69, 36.25, 31.98, 29.57, 29.25, 27.78, 22.82, 14.25; HRMS calcd for $C_{14}H_{24}O$ 208.1827, found 208.1844 (4.3).

General Procedure with Ruthenium Complex 8. The alkyne (1 equiv) and alkene (1.2 equiv) were dissolved in the solvent (to give 0.5 M solution) and then added to $CpRu(CH_3CN)_3PF_6$ (10 mol %) in a test tube. The reaction was stirred under nitrogen for 2 h. The solvent was then removed in vacuo and the crude mixture was analyzed by proton NMR. The residue was then subjected to silica gel chromatography.

A typical example is given as follows: 5-Hexyn-1-ol (24.5 mg, 0.25 mmol) and 1-decene (42.1 mg, 0.3 mmol) were dissolved in DMF (0.5 mL) and then added to $CpRu(CH_3CN)_3PF_6$ (10.9 mg, 0.025 mmol) in a test tube. The reaction was stirred under nitrogen for 2 h. The reaction was then subjected to silica gel chromatography (2:1 petroleum ether/ether) to give 37 mg of **9** (62%) as a 7.4:1 ratio of the branched to the linear isomers, as determined by relative integration of the following signals in the proton NMR: δ 5.48−5.38 (representing all four protons from the linear isomer, and two protons from the branched isomer) and two singlets at δ 4.76 and 4.75 (representing the branched isomer).

5-Methylene-pentadec-7-en-1-ol (9). Colorless oil. R_f = 0.29 (2:1 petroleum ether/ether); IR (neat) 3331, 3078, 2926, 2860, 2358, 1642, 1450, 1375, 1156, 1062, 970, 891 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 5.48−5.38 (m, 2H), 4.76 (s, 1H), 4.75 (s, 1H), 3.68 (t, J = 6.4 Hz, 2H), 2.71 (d, J = 6.4 Hz, 2H), 20.8−1.99 (m, 4H), 1.62−1.51 (m, 4H), 1.40−1.29 (m, 11H), 0.90 (t, J = 6.9, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.9, 132.4, 127.5, 109.5, 62.9, 39.5, 35.5, 32.5, 32.4, 31.9, 29.5, 29.2, 29.1, 23.7, 22.7, 14.1. Additional peaks for linear isomer: δ 131.2, 130.4, 192.2, 128.4, 35.6. Anal. Calcd for $C_{16}H_{30}O$: C, 80.61; H, 12.68. Found: C, 80.48; H, 12.43.

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Supporting Information Available: Experimental details for all reactions as well as characterization data and X-ray data (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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