DOI: 10.1002/adsc.201300743

# A Rhodium-Catalyzed Tandem Alkyne Dimerization/ 1,4-Addition Reaction

Ronald V. Lerum,[a] Christopher M. Russo,[a] Jocellie E. Marquez,[a] and John D. Chisholm[a,*]

[a] Department of Chemistry, Syracuse University, 1-014 Center for Science and Technology, Syracuse, NY 13244, USA
Fax: (+1)-315-443-4070; phone: (+1)-315-443-6894; e-mail: jdchisho@syr.edu

Received: August 16, 2013; Revised: October 2, 2013; Published online: November 13, 2013

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/adsc.201300743.

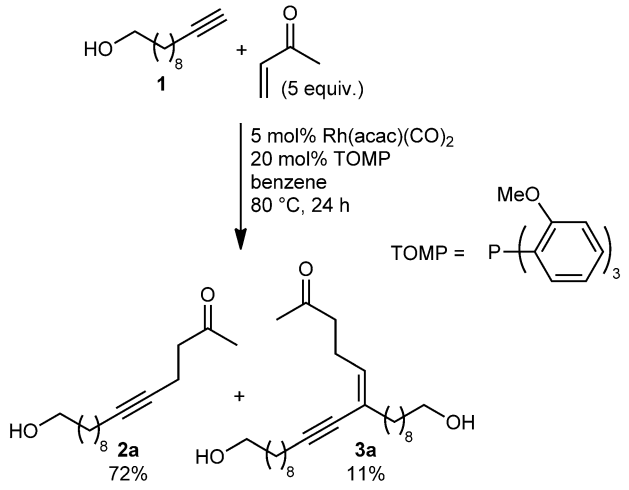
**Abstract:** A convenient three-component coupling reaction for the construction of conjugated enynes using rhodium catalysis is reported. Dimerization of a monosubstituted alkyne followed by trapping of the vinyl metal intermediate with an electron-deficient alkene, such as methyl vinyl ketone, provided moderate to good yields of these enynes. The use of the hindered electron-rich tris(*ortho*-tolyl)phosphine as a ligand for the rhodium catalyst provided the best conversions to these complex products.

**Keywords:** 1,4-addition; alkynes; enynes; multicomponent reactions; rhodium

One of the most challenging goals of synthetic chemistry is the development of methods to elaborate simple and readily available starting materials into significantly more complex products in a single step. Pursuant to this goal much effort has been devoted to the development of multicomponent reactions.[1] Interest in this area has been spurred in recent years by the use of such transformations in the synthesis of diverse chemical libraries, which are often used in screening efforts to develop new pharmaceuticals and small molecule probes of biological systems.[2]

Transition metals have also been shown to catalyze multicomponent reactions.[3] During the course of our studies on the rhodium-catalyzed 1,4-addition of alkynes to α,β-unsaturated ketones,[4] we serendipitously isolated a distinct π-conjugated enyne adduct that was comprised of two alkyne units and one equivalent of methyl vinyl ketone (MVK) (compound **3a**, Scheme 1). The dimerization of alkynes is a well precedented reaction,[5] often used in organic synthesis.[6] The use of the alkyne dimerization reaction as a starting point for a multicomponent coupling, however, is far more rare.[7] Recently Tanaka highlighted a similar process[8] where triisopropylsilylacetylene was added to an alkynyl ester using rhodium catalysis, with the resultant vinylrhodium species being trapped by an electron-deficient alkene to form complex enyne products similar to **3a**. Also relevant are reports by Sato and Ikeda on the use of a nickel-catalyzed tandem coupling reaction of alkynylstannanes, alkynes and enones to form similar enynes.[9] A distinguishing feature of the nickel-catalyzed process is the requirement for activation of an alkyne as an alkynylstannane, which is not necessary for the rhodium-catalyzed reactions. As enynes similar to **3a** have found uses in transition metal-catalyzed cycloadditions[10] and in materials science,[11] the reaction was further examined to optimize for the dimerization/addition product and determine the substrate scope.

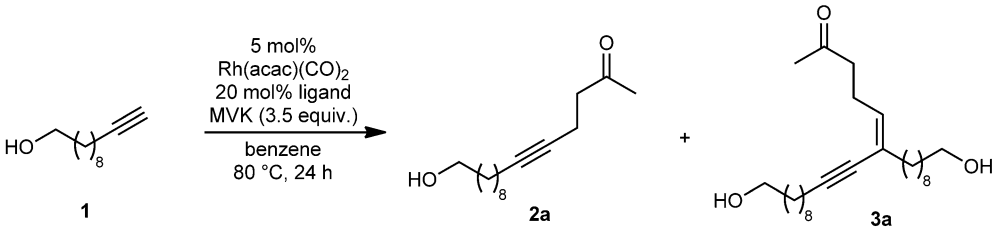
Initial attempts to influence the product distribution of the reaction focused on varying the phosphine ligand (Table 1). The use of tris(*ortho*-tolyl)phosphine (TOTP) significantly increased the yield of the dime-




**Scheme 1.** Isolation of an enyne side product in the Rh-catalyzed 1,4-addition reaction.

 © 2013 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim 

**Table 1.** Phosphine ligand screen.




| Entry | Ligand | **2a**[a] | **3a**[a] |
|---|---|---|---|
| 1 | tris(*ortho*-methoxyphenyl)phosphine (TOMP) | 72 | 11 |
| ***2*** | ***tris(ortho-tolyl)phosphine (TOTP)*** | ***24*** | ***76*** |
| 3 | tris(*para*-methoxyphenyl)phosphine[b] | 14 | 23 |
| 4 | tris(2,4,6-trimethoxyphenyl)phosphine[b] | 19 | 0 |
| 5 | triphenylphosphine | 26 | 16 |
| 6 | tris(2,4,6-trimethylphenyl)phosphine | 8 | 7 |
| 7 | tris(pentafluorophenyl)phosphine | 16 | 10 |
| 8 | tris(*para*-trifluoromethylphenyl)phosphine | 28 | 17 |
| 9 | tris(*para*-fluorophenyl)phosphine | 15 | 44 |
| 10 | 1,2-bis(diphenylphosphino)benzene[c] | 0 | 0 |
| 11 | none | 17 | 5 |
| 12 | tris(*ortho*-tolyl)phosphine (TOTP)[d] | 23 | 36 |
| 13 | tris(*ortho*-tolyl)phosphine (TOTP)[e] | 34 | 8 |
| 14 | tris(*ortho*-tolyl)phosphine (TOTP)[f] | 8 | trace |

[a] Isolated yields [%].
[b] Baylis–Hillman product **4** was also isolated.
[c] Ether **5** was isolated.
[d] $Rh(acac)(ethylene)_2$ was used as catalyst.
[e] $[Rh(COD)Cl]_2$ (2.5 mol%) was used as catalyst.
[f] $[Rh(Cl)(CO)_2]_2$ (2.5 mol%) was used as catalyst.

rization/addition product while suppressing the formation of the 1,4-addition product (entry 2). The alkyne starting material could be completely accounted for in the two products when using the ligand TOTP. No apparent trends as a result of the phosphine's nature (electron-rich, electron-deficient, size of cone angle, mono- or bidentate) could be identified. Additional experiments suggest that the active catalyst was generated *in situ* from both the rhodium complex $Rh(acac)(CO)_2$ and the phosphine. A control experiment with only the rhodium pre-catalyst present gave both 1,4-addition and dimerization/addition products in 17% and 5% yields, respectively (entry 11). When no rhodium precatalyst was applied and just the phosphine was used, the alkyne starting material **1** was isolated quantitatively. Other rhodium sources {such as $Rh(acac)(ethylene)_2$, $[Rh(COD)Cl]_2$ and $[Rh(Cl)(CO)_2]_2$} were less effective. Based on this study, both the rhodium pre-catalyst and TOTP are required for the reaction to perform efficiently.

In some cases products other than alkyne **2** and enyne **3** were detected during the phosphine screening. The use of the electron-rich phosphines tris(*para*-methoxyphenyl)phosphine (Table 1, entry 2) and tris(2,4,6-trimethoxyphenyl)phosphine (entry 3) led to a competing reaction, dimerizing the MVK to form the Baylis–Hillman product **4** (Figure 1). Both rhodium complexes[12] and phosphines[13] have been reported to dimerize enones, forming 1,5-diketones like **4**, so either the phosphine or the rhodium complex formed with these phosphines may be responsible for this mode of reactivity. The use of 1,2-bis(diphenylphosphino)benzene as a ligand (entry 10) failed to give either alkyne **2** or enyne **3** but instead gave the *O*-Michael addition product **5** (Figure 1). This reaction is precedented from the work of Louie,[14] but the ligand dependence is notable as in her report rhodium salts [including $Rh(acac)(CO)_2$] were used as catalysts in the presence of added $Na_2CO_3$ without added phosphine ligands.

Having optimized the phosphine ligand to favor the dimerization/addition product, the substrate scope of the reaction was investigated. Outlined in Table 2 are the comparative yields of the 1,4-addition adduct **2**

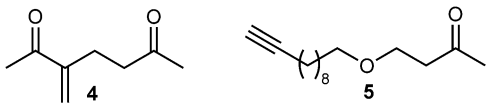
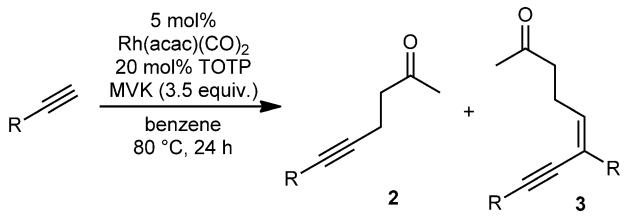



**Figure 1.** Side products observed during the phosphine screening.

 © 2013 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim 

**Table 2.** Variation of alkynes in the dimerization/addition reaction.




| Entry | R Group | **2**[a] | **3**[a] |
|---|---|---|---|
| 1 | $(CH_2)_9OH$ | 24 (**2a**) | 76 (**3a**) |
| 2 | $(CH_2)_3OH$ | 30 (**2b**) | 51 (**3b**) |
| 3 | $(CH_2)_2OH$ | 30 (**2c**) | 63 (**3c**) |
| 4 | $CH_2OH$ | 0 (**2d**) | 21 (**3d**) |
| 5 | $CH_2OTBDPS$ | 3 (**2e**) | 29 (**3e**) |
| 6 | $(CH_2)_3OBz$ | 20 (**2f**) | 67 (**3f**) |
| 7 | $(CH_2)_9NPhth$ | 29 (**2g**) | 38 (**3g**) |
| 8 | $(CH_2)_5CH_3$ | 24 (**2h**) | 47 (**3h**) |
| 9 | Ph | 0 (**2i**) | 0 (**3i**) |
| 10 | TIPS | 75 (**2j**) | 0 (**3j**) |

[a] Isolated yields [%].

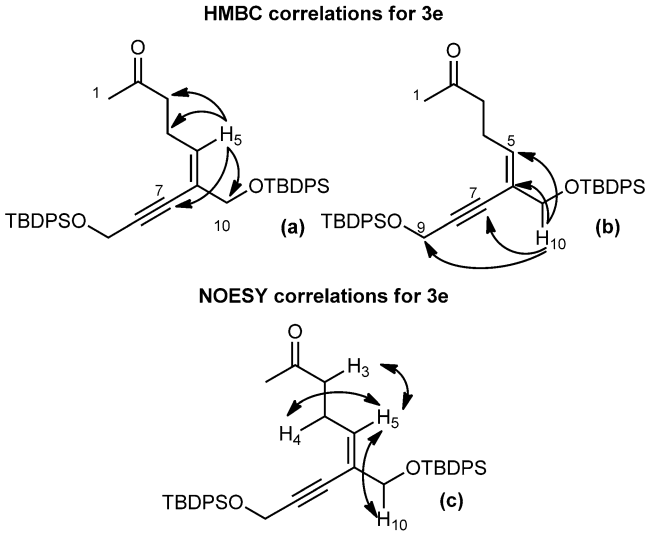



**Figure 2.** HMBC correlations (a) and (b) and NOESY correlations (c) on enyne **3e**.

*versus* the enyne product **3** using various alkynes. Alkynes containing primary alcohols, esters, and phthalamide-protected amines were found to participate in the dimerization/addition reaction (Table 2). These substrates afforded modest to satisfactory yields of dimerization/addition product **3**. Propargyl alcohol itself was a poor substrate (entry 4), perhaps ionizing to an inert rhodium allenylidene complex by dehydration. Similar organometallic structures have been isolated by Werner.[15] Phenylacetylene (entry 9) yielded only an inseparable mixture of products that did not appear to contain either alkyne **2** or enyne **3**. The use of triisopropylsilylacetylene led only to the 1,4-addition adduct (entry 10). This selectivity is dictated by the presence of the bulky TIPS group, which inhibits the dimerization reaction. Hayashi observed a similar reactivity pattern in the 1,4-addition reactions of alkynes.[16]

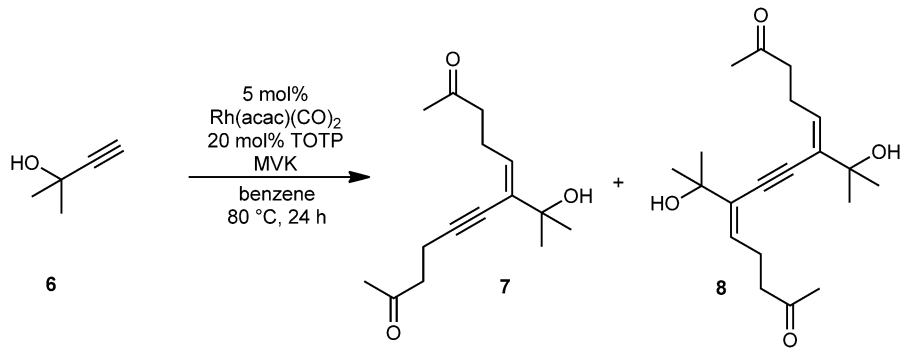
While the gross structure of the dimerization/addition product was clear, the stereochemistry of the trisubstituted alkene was as yet undetermined. NMR studies were therefore undertaken with enyne **3e** to determine the alkene stereochemistry. After the assignment of all protons and carbons of **3e** using COSY and HSQC experiments, an HMBC was performed which confirmed the connectivity of the structure. Specifically, the HMBC spectrum confirmed the dimerization of the alkyne component to form an $sp$–$sp^2$ bond, as indicated by correlations of H-10 to C-5, C-6, C-7 and C-9 and of H-5 to C-3, C-4, C-7 and C-10 (Figure 2). The *Z* stereochemistry of the alkene was also established by NMR, using a NOESY experiment, which showed a significant correlation between H-5 and H-10. The stereochemistry of the other enyne products was assigned in analogy to these findings.

In contrast to other alkynes, the reaction of 2-methyl-3-butyn-2-ol **6** with methyl vinyl ketone afforded two different alkyne products, **7** and **8** (Table 3). Alkyne **7** appeared to be the result of an alkyne dimerization/addition reaction that was followed by loss of acetone and 1,4-addition of the resulting alkyne to a second equivalent of MVK. Alkyne **8** was identified as a symmetrical alkyne adduct of 2-methyl-3-butyn-2-ol **6** and MVK. Attempts were made to determine if the yields of the alkyne products **7** and **8** were dependent on the ratio of alkyne to MVK (Table 3). Since both the alkyne and the MVK must compete for a coordination site on the transition metal catalyst, increasing the amount of MVK was expected to provide an improved ratio favoring product **7**. When equal ratios of both starting materials were used, a small amount of (17%) product **7** was isolated along with product **8** in 54% yield (entry 1). Use of 2.5 equiv. of MVK gave 50% of **7** and 41% of **8** (entry 2, a 55:45 ratio of **7**:**8**). Use of a large excess of MVK resulted in a further improvement in the ratio of **7**:**8** (71:29), although the yield of product **7** was only 53% compared to 22% of product **8** (entry 3). The requirement for a large excess of enone is likely due to the MVK being an inferior ligand for the rhodium relative to the alkyne.

Studies were also performed to determine the compatibility of other electron-deficient alkenes with the reaction conditions (Table 4). Reactions with ethyl vinyl ketone, phenyl vinyl ketone and acryloyloxazolidinone[17] proceeded to give the respective dimer addition products in more modest yields when compared to MVK. The greater amount of the 1,4-addition

 © 2013 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim 

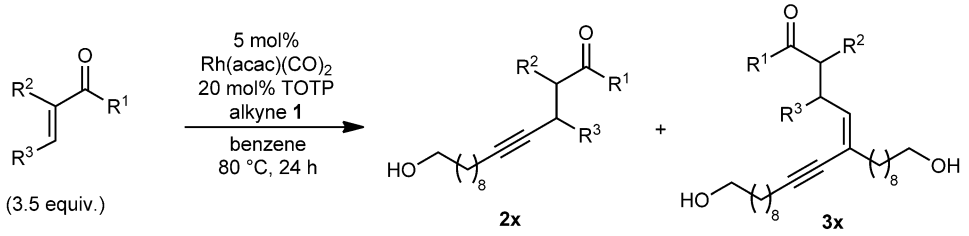
**Table 3.** Reaction of 2-methyl-3-butyn-2-ol **6**.

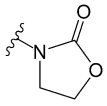
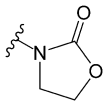
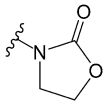



| Entry | Equiv MVK | **7**[a] | **8**[a] | Ratio **7**:**8** |
|---|---|---|---|---|
| 1 | 1 | 17 | 54 | 24:76 |
| 2 | 3.5 | 50 | 41 | 55:45 |
| 3 | 10 | 53 | 22 | 71:29 |

[a] Isolated yields [%].

**Table 4.** Variation of electron-deficient alkenes in the dimerization/addition reaction.




| Entry | $R^1$ | $R^2$ | $R^3$ | **2**[a] | **3**[a] |
|---|---|---|---|---|---|
| 1 | Me | H | H | 24 (**2a**) | 76 (**3a**) |
| 2 | Et | H | H | 34 (**2k**) | 46 (**3k**) |
| 3 | Ph | H | H | 36 (**2l**) | 45 (**3l**) |
| 4 |  | H | H | 44 (**2m**) | 45 (**3m**) |
| 5[b] |  | H | H | 18 (**2m**) | 23 (**3m**) |
| 6[c] |  | H | H | 8 (**2m**) | 16 (**3m**) |
| 5 | OEt | H | H | 0 (**2n**) | 0 (**3n**) |
| 6 | $NMe_2$ | H | H | 0 (**2o**) | 0 (**3o**) |
| 7 | Ph | Me | H | 0 (**2p**) | 0 (**3p**) |
| 8 | Me | H | Bu | 0 (**2q**) | 0 (**3q**) |

[a] Isolated yields [%].
[b] 2.2 equiv. of alkene were used.
[c] 1.1 equiv. of alkene were used.

products **2k**, **2l** and **2m** formed may be due to the lower volatility of the alkenes in these cases. With MVK some loss by evaporation may occur, leading to more dimerization/addition, but with less volatile substrates a greater concentration of alkene may compete more effectively for the rhodium with the alkyne, leading to a more significant amount of the alkyne product **2**. Attempts were made to probe this

 © 2013 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim 

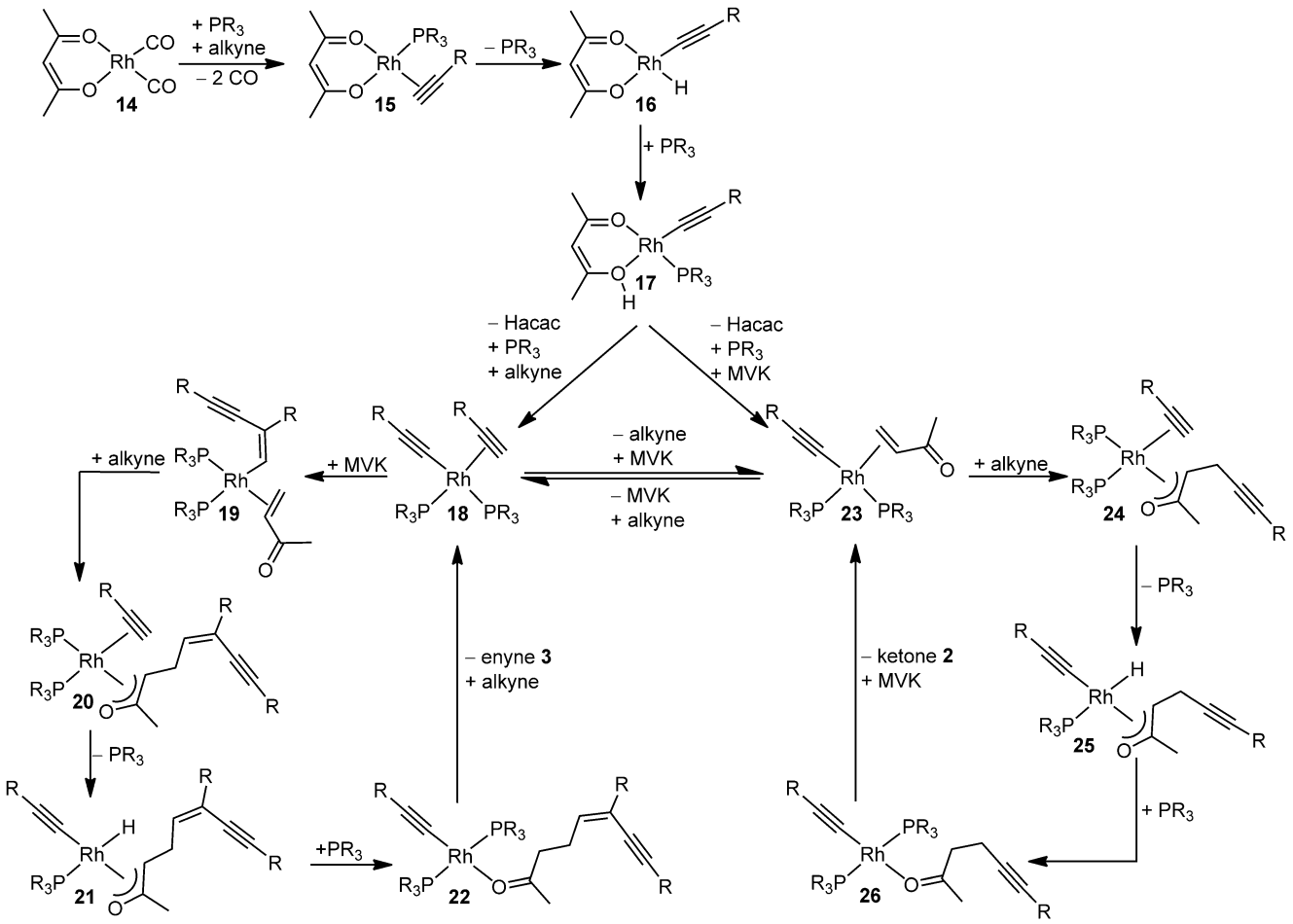


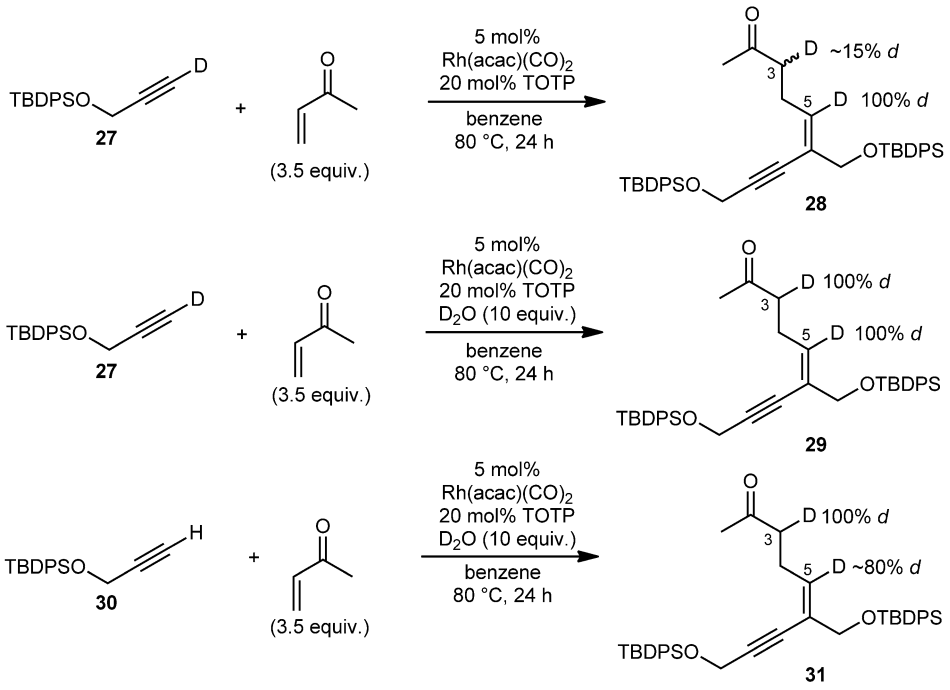

**Figure 3.** Proposed mechanism.

hypothesis using a smaller excess of acryloyloxazolidinone, as in this case volatility should not be an issue (acryloyloxazolidinone is a solid with a melting point of 80–81 °C). Using a smaller excess of alkene did provide a product ratio favoring product **3**, but the conversion was significantly lower, with ~25% starting alkyne being recovered in both entries 5 and 6 (Table 4). Ethyl acrylate and dimethylacrylamide proved to be inert under these conditions. Any substitution on the alkene also caused the reaction to shut down, and provided no dimerization/addition or 1,4-addition product.

Taking into account the stereochemistry of the dimerization/addition product (Figure 2) and the need for a phosphine ligand to promote the reaction we propose the following reaction mechanism for the dimerization/addition reaction (Figure 3). Rhodium complex **15** is generated *in situ* by the displacement of the CO ligands with a phosphine and chelation of the alkyne. Oxidative addition of the alkyne C–H bond and protonation of the acetylacetonate ligand then provides complex **17**.

Loss of the acetylacetonate ligand from **17** and coordination of a second equivalent of alkyne and a phosphine provides intermediate **18**, which then undergoes a regioselective head-to-tail dimerization of the alkynes to provide vinylrhodium **19**. A selective *syn* addition across the alkyne to generate **19** accounts for the observed alkene geometry in product **3**. The vinylrhodium then adds to MVK forming the oxa-π-allyl rhodium complex **20**. Coordination of another equivalent of alkyne and insertion into the alkyne C–H bond then provides complex **21**, which through reductive elimination releases the enyne product **3** and returns rhodium complex **18** to initiate another catalytic cycle. The formation of 1,4-addition product **2** can be explained by addition of MVK to complex **17** instead of the alkyne. The alkyne could then add directly to the MVK, providing the oxa-π-allyl rhodium complex **24**. Insertion of the rhodium into the alkyne C–H bond followed by protonation of the rhodium enolate leads to complex **26**, which can the release ketone **2**, regenerating complex **23** and beginning another cycle. Complexes **23** and **18** may also equilibrate

 © 2013 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim 




**Scheme 2.** Deuterium labeling studies.

through ligand exchange, so the initial formation of **23** or **18** may not determine the dominant pathway.

Deuterium-labeled terminal alkyne **27** was subjected to the dimerization/addition reaction conditions to gain additional insight into the mechanism of the reaction (Scheme 2). With alkyne **27** minimal deuterium incorporation (15%) was observed at C-3 while 100% incorporation was observed at C-5. The low incorporation of deuterium at C-3 was initially puzzling, but we hypothesized that the deuterium on the alkyne may exchange with adventitious water or the free acetylacetonate ligand leading to lowered deuterium incorporation in the product. When the reaction was repeated with the addition of $D_2O$ (10 equiv. with respect to alkyne) the $^1H$ NMR indicated quantitative inclusion of a single deuterium at the C-3 position. Given that the deuterium could be incorporated from a reductive elimination or a protonation of a rhodium allyl intermediate, alkyne **30** was also subjected to the above experiment with excess of $D_2O$. The enyne product was obtained with 100% *d*-incorporation (relative to one proton) at C-3 and with 80% *d*-incorporation at the olefinic position (C-5). Deuterium incorporated at the olefinic position when using alkyne **30** suggests that the C–H insertion of the rhodium complex into the terminal alkyne is reversible and that this proton exchanges rapidly with the excess $D_2O$.

In summary, a tandem rhodium-catalyzed dimerization/1,4-addition of terminal alkynes and enones is reported. This methodology provides a convenient entry into highly functionalized enyne systems. Two carbon-carbon bonds are formed in a single step in this tandem reaction, which is selective for a *Z* trisubstituted alkene. A number of alkynes (including some with unprotected alcohols) and electron-deficient alkenes were compatible with the reaction conditions. This multicomponent reaction provides rapid access to π-conjugated alkynes, which are important intermediates in transition metal-catalyzed cycloadditions and are also useful in molecular electronics.

## Experimental Section

### General Procedure for the Dimerization/1,4-Addition Reaction of Alkynes and Electron Deficient Alkenes

To dicarbonylacetylacetonatorhodium(I) (0.021 mmol, 5.4 mg) and the tris(*ortho*-tolylphosphine) (0.08 mmol, 26 mg) in benzene (1.1 mL) was added a solution of 10-undecyn-1-ol (0.42 mmol, 73 mg) and methyl vinyl ketone (1.47 mmol, 121 μL) dissolved in benzene (1.0 mL). The reaction was stirred for 24 h at 80 °C then pre-absorbed onto silica gel and purified by silica gel flash chromatography (gradient elution of 40%–80% ethyl acetate:hexanes) to give alkyne 1,4-addition product **2a** (yield: 24 mg, 24%) and dimerization/addition product **3a** (yield: 64 mg, 76%).

## Acknowledgements

*Acknowledgement is made to the Donors of the American Chemical Society Petroleum Research Fund and to Syracuse University for partial support of this research. J.E.M. thanks*

 © 2013 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim 

*the Syracuse University NSF-REU program for summer support.*

## References


[1] a) M. Gonzalez-Lopez, J. T. Shaw, *Chem. Rev.* **2009**, *109*, 164–189; b) B. B. Toure, D. G. Hall, *Chem. Rev.* **2009**, *109*, 4439–4486; c) B. Jiang, T. Rajale, W. Wever, S.-J. Tu, G. Li, *Chem. Asian J.* **2010**, *5*, 2318–2335; d) J. G. Hernandez, E. Juaristi, *Chem. Commun.* **2012**, *48*, 5396–5409.

[2] a) A. Ulaczyk-Lesanko, D. G. Hall, *Curr. Opin. Chem. Biol.* **2005**, *9*, 266–276; b) J. E. Biggs-Houck, A. Younai, J. T. Shaw, *Curr. Opin. Chem. Biol.* **2010**, *14*, 371–382; c) E. Ruijter, R. Scheffelaar, V. A. Orru Romano, *Angew. Chem.* **2011**, *123*, 6358–6371; *Angew. Chem. Int. Ed.* **2011**, *50*, 6234–6246; d) A. Domling, W. Wang, K. Wang, *Chem. Rev.* **2012**, *112*, 3083–3135.

[3] a) G. Balme, D. Bouyssi, N. Monteiro, in: *Multicomponent Reactions*, (Eds.: J. Zhu, H. Bienaymé), Wiley-VCH, Weinheim, **2005**, pp 224–276; b) D. M. D′Souza, T. J. J. Müller, *Chem. Soc. Rev.* **2007**, *36*, 1095–1108; c) B. A. Arndtsen, *Chem. Eur. J.* **2009**, *15*, 302–313; d) M. Zhang, *Adv. Synth. Catal.* **2009**, *351*, 2243–2270; e) M. J. Climent, A. Corma, S. Iborra, *RSC Adv.* **2012**, *2*, 16–58; f) H. Clavier, H. Pellissier, *Adv. Synth. Catal.* **2012**, *354*, 3347–3403; g) H. Pellissier, *Chem. Rev.* **2013**, *113*, 442–524; h) J. S. Quesnel, B. A. Arndtsen, *Pure Appl. Chem.* **2013**, *85*, 377–384; i) M. A. Fernandez-Rodriguez, P. Garcia-Garcia, E. Aguilar, *Chem. Commun.* **2010**, *46*, 7670–7687.

[4] R. V. Lerum, J. D. Chisholm, *Tetrahedron Lett.* **2004**, *45*, 6591–6594.

[5] a) B. M. Trost, C. Chan, G. Ruhter, *J. Am. Chem. Soc.* **1987**, *109*, 3486–3487; b) H.-D. Xu, R.-W. Zhang, X. Li, S. Huang, W. Tang, W.-H. Hu, *Org. Lett.* **2013**, *15*, 840–843; c) C. Jahier, O. V. Zatolochnaya, N. V. Zvyagintsev, V. P. Ananikov, V. Gevorgyan, *Org. Lett.* **2012**, *14*, 2846–2849.

[6] a) M. Charpenay, A. Boudhar, G. Blond, J. Suffert, *Angew. Chem.* **2012**, *124*, 4455–4458; *Angew. Chem. Int. Ed.* **2012**, *51*, 4379–4382; b) B. M. Trost, A. J. Frontier, *J. Am. Chem. Soc.* **2000**, *122*, 11727–11728; c) C. J. Brennan, J. M. Campagne, *Tetrahedron Lett.* **2001**, *42*, 5195–5197; d) X.-Y. Wu, X. She, Y. Shi, *J. Am. Chem. Soc.* **2002**, *124*, 8792–8793; e) J. R. Hanson, C. Uyanik, *J. Chem. Res. Synop.* **2003**, 426–427; f) A. Gopalarathnam, S. G. Nelson, *Org. Lett.* **2006**, *8*, 7–10; g) S. Lopez, J. Montenegro, C. Saa, *J. Org. Chem.* **2007**, *72*, 9572–9581; h) B. M. Trost, G. Dong, *J. Am. Chem. Soc.* **2010**, *132*, 16403–16416; i) B. M. Trost, J.-P. Lumb, J. M. Azzarelli, *J. Am. Chem. Soc.* **2011**, *133*, 740–743; j) B. M. Trost, B. R. Taft, J. T. Masters, J.-P. Lumb, *J. Am. Chem. Soc.* **2011**, *133*, 8502–8505; k) L. M. Geary, S. K. Woo, J. C. Leung, M. J. Krische, *Angew. Chem.* **2012**, *124*, 3026–3030; *Angew. Chem. Int. Ed.* **2012**, *51*, 2972–2976.

[7] L. Zhao, X. Lu, *Org. Lett.* **2002**, *4*, 3903–3906.

[8] Y. Hoshino, Y. Shibata, K. Tanaka, *Angew. Chem.* **2012**, *124*, 9541–9545; *Angew. Chem. Int. Ed.* **2012**, *51*, 9407–9411.

[9] a) S. Ikeda, K. Kondo, Y. Sato, *J. Org. Chem.* **1996**, *61*, 8248–8255; b) S. Ikeda, Y. Sato, *J. Am. Chem. Soc.* **1994**, *116*, 5975–5976.

[10] a) M. Rubina, M. Conley, V. Gevorgyan, *J. Am. Chem. Soc.* **2006**, *128*, 5818–5827; b) H. Kusama, Y. Onizawa, N. Iwasawa, *J. Am. Chem. Soc.* **2006**, *128*, 16500–16501; c) R. L. Danheiser, A. E. Gould, R. F. de La Pradilla, A. L. Helgason, *J. Org. Chem.* **1994**, *59*, 5514–5515; d) J. M. Robinson, S. F. Tlais, J. Fong, R. L. Danheiser, *Tetrahedron* **2011**, *67*, 9890–9898.

[11] a) Y. Liu, M. Nishiura, Y. Wang, Z. Hou, *J. Am. Chem. Soc.* **2006**, *128*, 5592–5593; b) N. K. Pahadi, D. H. Camacho, I. Nakamura, Y. Yamamoto, *J. Org. Chem.* **2006**, *71*, 1152–1155; c) K. Campbell, C. J. Kuehl, M. J. Ferguson, P. J. Stang, R. R. Tykwinski, *J. Am. Chem. Soc.* **2002**, *124*, 7266–7267; d) N. N. P. Moonen, C. Boudon, J.-P. Gisselbrecht, P. Seiler, M. Gross, F. Diederich, *Angew. Chem.* **2002**, *114*, 3170–3173; *Angew. Chem. Int. Ed.* **2002**, *41*, 3044–3047.

[12] I. P. Kovalev, Y. N. Kolmogorov, Y. A. Strelenko, A. V. Ignatenko, M. G. Vinogradov, G. I. Nikishin, *J. Oganomet. Chem.* **1991**, *420*, 125–133.

[13] J. D. McClure, *J. Org. Chem.* **1970**, *35*, 3045–3048.

[14] M. V. Farnworth, M. J. Cross, J. Louie, *Tetrahedron Lett.* **2004**, *45*, 7441–7443.

[15] H. Werner, *Chem. Commun.* **1997**, 903–910.

[16] T. Nishimura, X.-X. Guo, N. Uchiyama, T. Katoh, T. Hayashi, *J. Am. Chem. Soc.* **2008**, *130*, 1576–1577.

[17] a) G.-J. Ho, D. J. Mathre, *J. Org. Chem.* **1995**, *60*, 2271–2273; b) M. P. Sibi, H. Miyabe, *Org. Lett.* **2002**, *4*, 3435–3438.


 © 2013 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim 