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PII: S0040-4039(18)31332-7
DOI: https://doi.org/10.1016/j.tetlet.2018.11.016
Reference: TETL 50401

To appear in: *Tetrahedron Letters*

Received Date: 20 September 2018
Revised Date: 2 November 2018
Accepted Date: 5 November 2018

Please cite this article as: Dolan, M.A., Dixon, A.D.C., Chisholm, J.D., Clark, D.A., Ruthenium Dihydride Complexes as Enyne Metathesis Catalysts, *Tetrahedron Letters* (2018), doi: https://doi.org/10.1016/j.tetlet.2018.11.016

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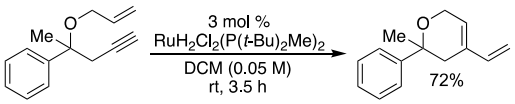

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ARTICLE INFO

Article history:
Received
Received in revised form
Accepted
Available online

Keywords:
Metathesis
Enyne
Alkyne
1,3-Diene
Ruthenium
Dihydride

ABSTRACT

Ruthenium–catalyzed enyne metathesis is a reliable and efficient method for the formation of 1,3-dienes, a common structural motif in synthetic organic chemistry. The development of new transition-metal complexes competent to catalyze enyne metathesis reactions remains an important research area. This report describes the use of ruthenium (IV) dihydride complexes with the general structure $RuH_2Cl_2(PR_3)_2$ as new catalysts for enyne metathesis. These ruthenium (IV) dihydrides have been largely unexplored as catalysts in metathesis-based transformations. The reactivity of these complexes with 1,6 and 1,7-enynes was investigated. The observed reaction products are consistent with the metathesis activity occurring through a ruthenium vinylidene intermediate.

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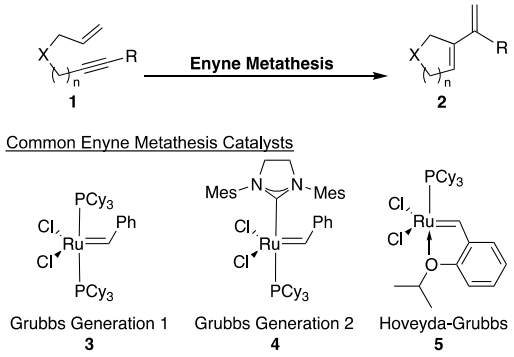
The synthesis of substituted 1,3-dienes remains an active research area, as these motifs are commonly encountered in natural products[1] and have applications in materials science.[2] A number of palladium-catalyzed cross coupling approaches to 1,3-dienes have been developed to facilitate the synthesis of these systems.[3] In most of these cases the formation of the 1,3-diene is accomplished by the coupling of vinyl halides and vinyl metal intermediates. Installation of a diene with these methods is accompanied by significant waste generation, with loss of stoichiometric amounts of both a halogen (or pseudohalogen) and metal (or metalloid) being responsible for the poor atom economy.[4] Many of the precursors for the vinyl starting materials are generated from alkyne precursors, so it is unsurprising that methods are continuously being developed to circumvent the need for the formation of the vinyl halide or vinyl metal intermediates; they instead focus on proceeding directly from an alkyne to a 1,3-diene product.[5]

Enyne metathesis,[6] where a ruthenium carbene complex catalyzes an addition reaction between an alkene and an alkyne, is one example of the direct formation of a 1,3-diene from unactivated precursors (Scheme 1). Unlike palladium catalyzed cross couplings, enyne metathesis both creates a new carbon-carbon bond and provides a new arrangement of unsaturated functionality, arriving at the conjugated 1,3-diene with complete atom-economy. Intermolecular enyne metathesis may be performed with nearly equal amounts of alkyne and alkene to provide the 1,3-diene product, demonstrating high efficiency of the process.[7] Enyne metathesis may be performed in an intramolecular or intermolecular fashion, providing both cyclic and acyclic products respectively. Typically ruthenium alkylidene catalysts like the ones developed by Grubbs (**3** and **4**)[8,9] or Hoveyda (**5**)[10] are used to execute these transformations.



Scheme 1. Overview of enyne metathesis transformation and commonly used catalysts

The development of new transition metal complexes competent to catalyze enyne metathesis reactions with high turnover, useful regio- and stereocontrol, and which allow access to diverse substitution patterns on the diene product is still an active research area. As an extension of our work on ruthenium hydrides,[11] the reactivity of the ruthenium dihydride **7** with 1,7-enyne **6** was evaluated (Scheme 2). Our intent was to provide a new route to the exocyclic 1,3-diene **9**, however careful consideration of the ^{1}H and ^{13}C NMR of the reaction product indicated clean conversion to the endocyclic diene **8** in moderate yield. Diene **8** is more commonly accessed from traditional ring closing enyne metathesis (RCEYM). To further verify formation of the RCEYM product, the use of Grubbs-I catalyst under Mori's conditions (3 mol % Grubbs-I, 0.01 M DCM, 1 atm ethylene)[12] was performed and provided **8** which was identical in all respects to the product obtained in Scheme 2. Ruthenium dihydrides have been utilized as catalysts in carbon-carbon bond

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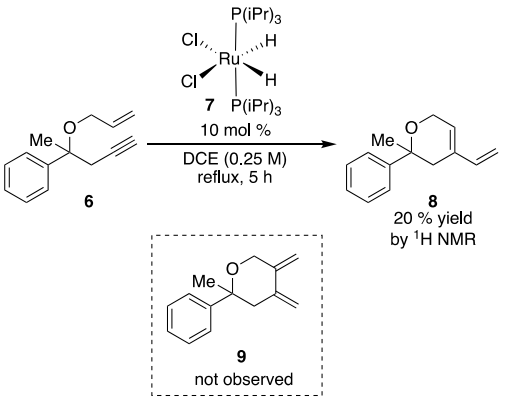
forming reactions previously[13] and this subject has been reviewed.[14]

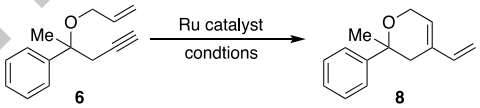


Scheme 2. Enyne metathesis by ruthenium dihydride **7**

We set out to optimize the reaction conditions to determine if comparable yields could be obtained compared to the more common ruthenium alkylidenes (**3**-**5**, Scheme 1). Initially a solvent screen was conducted (Table 1). Chlorinated solvents were first examined, as these were used to good effect by Mascarenas and co-workers in their intramolecular cycloadditions of allenes utilizing dihydride **7**.[13c] Reaction in DCM at room temperature provided RCEYM product **8** in 19% yield after 24 hours (entry 1). Increasing the temperature and switching to 1,2-dichloroethane (DCE) gave a similar yield of 20% in a shorter reaction time (5 hours) (entry 3). Other solvents were also examined, with toluene proving to be the most effective with catalyst **7** (entry 5). The effect of concentration was then explored, with a small improvement in yield (42%) being observed upon dilution to 0.10 M (entry 6). Other ruthenium complexes were examined to improve the transformation, with $RuH_2Cl_2(P(t\text{-}Bu)_2Me)_2$ (**10**) providing a 68% yield (entry 7). Given the better performance from complex **10**, the reaction parameters were re-examined. Performing the transformation in toluene at room temperature (0.05 M) gave diene **8** in 73% yield (entry 8). Interestingly, dichloromethane under similar conditions with complex **10** also gave a good yield of **8** (entry 9). This concentration was utilized throughout later experiments, as further dilution to 0.025 M did not show improvement. Decreasing the amount of complex **10** led to increased yield of **8** (entries 11-13), with 3 mol % loading being optimal. Evaluation of the previously unreported ruthenium dihydride $RuH_2Cl_2(P(t\text{-}Bu_2)Cy)_2$ **11** under similar reaction conditions showed no metathesis activity, presumably due to the increased steric bulk of the di-*tert*-butylcyclohexylphosphine (entry 15).

The mechanism of the enyne metathesis with these dihydride catalysts was also considered (Scheme 3). Previously, ruthenium dihydrides have been utilized as intermediates in the formation of other ruthenium complexes,[15] including vinylidene type complexes analogous to **13** which formed upon addition of terminal alkynes or propargylic alcohols.[16] These vinylidenes strongly resemble proposed intermediates within the commonly invoked enyne metathesis catalytic cycle.[17] Entry into an enyne metathesis catalytic cycle commences with [2+2] cycloaddition of ruthenium vinylidene **13** and alkyne **12**. Previous NMR studies in the literature support the hypothesis that the enyne metathesis with ruthenium catalysts usually occurs via the ene-then-yne pathway.[18] A retro [2+2] (as shown in **15**) then provides formation of the vinyl ruthenium carbene species **17** which is the key intermediate for enyne metathesis.[6a,6c,6e] Vinyl ruthenium **17** then proceeds to ruthenacyclobutene **18**, which upon cycloreversion gives the alternate complex **19**. Cycloaddition of **19** with enyne **12** then leads to ruthenacyclobutane **20**, which upon cycloreversion extrudes the diene product **21** and regenerates the key intermediate alkylidene **17**, allowing for catalyst turnover.

Table 1. Optimization of Reaction Conditions[a]



Entry	Catalyst	Catalyst Loading	Solvent	Temperature (°C)	Concentration [M]	Time (h)	Yield[b]
1	$RuH_2Cl_2(P(i\text{-}Pr)_3)_2$ (**7**)	10 mol %	DCM	rt	0.25	24	19
2	$RuH_2Cl_2(P(i\text{-}Pr)_3)_2$ (**7**)	10 mol %	THF	66	0.25	24	27
3	$RuH_2Cl_2(P(i\text{-}Pr)_3)_2$ (**7**)	10 mol %	DCE	86	0.25	5	20
4	$RuH_2Cl_2(P(i\text{-}Pr)_3)_2$ (**7**)	10 mol %	CPME	110	0.25	2	32
5	$RuH_2Cl_2(P(i\text{-}Pr)_3)_2$ (**7**)	10 mol %	toluene	110	0.25	1.5	38
6	$RuH_2Cl_2(P(i\text{-}Pr)_3)_2$ (**7**)	10 mol %	toluene	110	0.10	4.5	42
7	$RuH_2Cl_2(P(t\text{-}Bu)_2Me)_2$ (**10**)	10 mol %	toluene	110	0.10	5	68
8	$RuH_2Cl_2(P(t\text{-}Bu)_2Me)_2$ (**10**)	10 mol %	toluene	rt	0.05	1.5	73
9	$RuH_2Cl_2(P(t\text{-}Bu)_2Me)_2$ (**10**)	10 mol %	DCM	rt	0.05	0.5	66
10	$RuH_2Cl_2(P(t\text{-}Bu)_2Me)_2$ (**10**)	10 mol %	toluene	rt	0.025	1.5	73
11	$RuH_2Cl_2(P(t\text{-}Bu)_2Me)_2$ (**10**)	5 mol %	toluene	rt	0.05	1	76
12	$RuH_2Cl_2(P(t\text{-}Bu)_2Me)_2$ (**10**)	5 mol %	DCM	rt	0.05	2.5	82
13	$RuH_2Cl_2(P(t\text{-}Bu)_2Me)_2$ (**10**)	3 mol %	DCM	rt	0.05	3.5	84 (72)
14	$RuH_2Cl_2(P(t\text{-}Bu)_2Me)_2$ (**10**)	1 mol %	DCM	rt	0.05	24	18
15	$RuH_2Cl_2(P(t\text{-}Bu)_2Cy)_2$ (**11**)	5 mol %	DCM	rt	0.05	1	0

[a]Trials performed on a 0.20 mmol scale under Ar atmosphere.

[b]Yields were determined from ^{1}H NMR using mesitylene as an internal standard, isolated yields are reported in parentheses.

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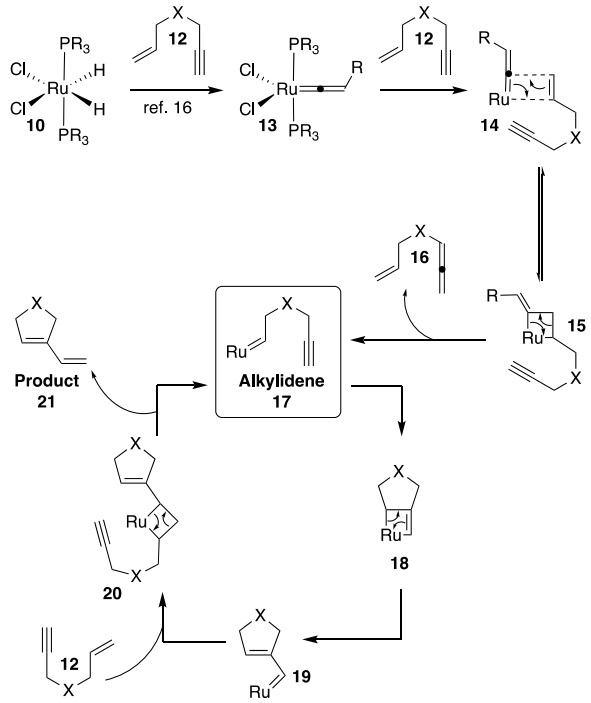
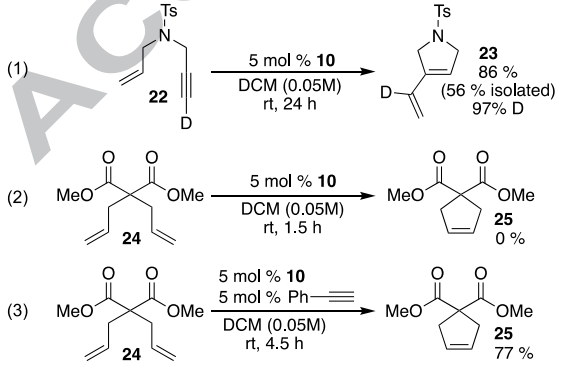


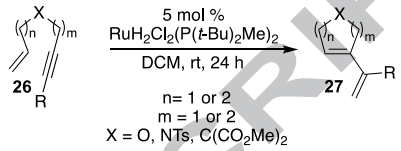
Scheme 3. Proposed mechanism for ruthenium dihydride catalyzed enyne metathesis

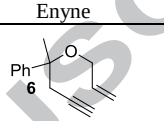
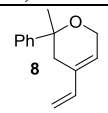
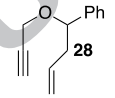
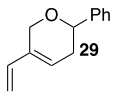
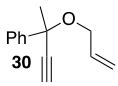
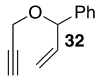
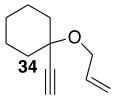
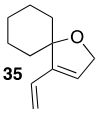
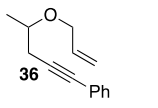
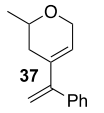
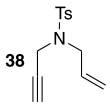
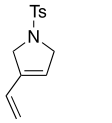
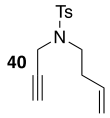
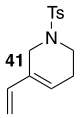
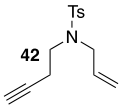
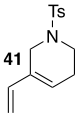
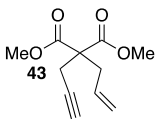
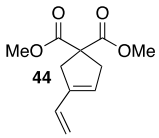
Efforts were also made to provide experimental evidence to support this mechanistic proposal. First, deuterated alkyne **22** was employed to verify the fate of the alkynyl hydrogen (equation 1). Exposing enyne **22** to the reaction conditions gave the expected deuterated 1,3-diene **23** in 86% yield as determined by ^{1}H NMR (56% isolated yield). This material retained the deuterium label (~97% D) originally included from the enyne, supporting the mechanism shown in Scheme 3. Additionally, the formation of the vinylidene intermediate from an alkyne was explored with the use of alkyne additives. Using diallyl dimethylmalonate **24**, two reactions were conducted with and without the use of the alkyne additive phenylacetylene (equations 2 and 3). With no added phenylacetylene, ring closing metathesis was not observed. Addition of (5 mol %) phenylacetylene to the dihydride complex **10** afforded cyclopentene **25** in 77% yield. This further suggests the formation of a metathesis active vinylidene species.



The scope of complex **10** in RCEYM reactions was also briefly evaluated (Table 2). Metathesis was amenable to homopropargyl ether **6**, as diene **8** was isolated in 72% yield (entry 1). The method was also successfully applied to propargyl ethers to afford 5- and 6-membered rings (entries 2-5). Dienes **29** and **31** were isolated in 58% and 72% yield, respectively. Diene **33** and spirocyclic diene **35** also participated in the RCEYM, providing yields of 42% and 40% respectively. While the method was widely applicable to propargyl and homopropargyl terminal alkynes, metathesis was not observed with an internal alkyne (entry 6, substrate **36**). RCEYM of sulfonamides was also demonstrated, accessing dihydropyrrole **39** in 78% yield. Piperidine **41** was also furnished in excellent yield, accessed from one of two sulfonamides, **40** or **42**. Metathesis was also demonstrably effective with the malonate substituted enyne **43**, resulting in the synthesis of cyclopentene **44**.

Table 2. Scope of the New Enyne Metathesis Catalyst



Entry	Enyne	1,3-Diene	Yield[a]
1[b]			84 (72)
2			61 (58)
3[c]			85 (72)
4			42
5			40
6			0
7			88 (78)
8			83 (56)
9[d]			78
10			62

[a]Yields were determined from ^{1}H NMR using mesitylene as an internal standard, isolated yields are reported in parentheses.

[c] Reaction was complete in 6.5 h.

[b]3 Mol % of the catalyst was used and the reaction was complete in 3.5 h.

[d]7.5 Mol % of the catalyst was used.

Overall the yields in Table 2 are somewhat lower than those reported by Mori and co-workers for the same substrates.[12] This may be due to some catalyst decomposition (the ruthenium

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dihydrides are quite air-sensitive). The precatalyst also requires a sacrificial alkyne in the same quantity as the catalyst loading to form the active vinylidene, which limits the overall yield (the reported yields are not adjusted for the loss of alkyne to form the vinylidene). Additionally, in many cases it was difficult to isolate the pure diene products due to contamination by ruthenium catalyst decomposition side products (difficulties in removal of metal catalyst decomposition side-products from metathesis reactions have been reported[19]), which required careful chromatography to remove. This was especially problematic with the more polar dienes (like **39** and **41**), and accounts for the significant differences in the NMR yields and the isolated yields. Mori and co-workers did have to employ an atmosphere of ethylene to achieve their higher yields, however, which was not required for the ruthenium dihydride based catalysts. Attempts to improve the yield of enyne metathesis for catalyst **10** by performing the reaction under an ethylene atmosphere did not result in an improved yield.

In summary, a new enyne metathesis catalyst system has been developed based on a ruthenium dihydride precursor. This catalyst system has been shown to be active in ring closing enyne metathesis and was also capable of performing ring closing olefin metathesis through use of a sacrificial alkyne. Experimental evidence suggests that ruthenium vinylidene intermediate is the active catalyst in this reaction. This hypothesis is further supported by deuterium labeling experiments and olefin metathesis activity in the presence of a terminal alkyne. This work demonstrates that ruthenium dihydrides may access a RCEYM mode of reactivity.

Supplementary Material

Supplementary data associated with this article can be found, in the online version, at (insert web address). This material includes detailed experimental procedures and NMR data (^{1}H and ^{13}C spectra).

Acknowledgments

Support for the Syracuse University NMR facility was provided by the National Science Foundation (CHE-1229345).

References and notes

1. a) *The Chemistry of Dienes and Polyenes* (Ed.: Rappoport, Z.), Wiley, Chichester, **1997**; b) *1,3-Dienes* (Eds.: Rawal, V. H., Kozmin, S. A.), Science of Synthesis Vol.46; Georg Thieme Verlag KG: Stuttgart, **2009**; c) K. C. Nicolaou, S. A. Snyder, *Classics in Total Synthesis II: More Targets, Strategies*, Wiley-VCH, Weinheim, **2003**; d) Woerly, E. M.; Roy, J.; Burke, M. D. *Nat. Chem.* **2014**, *6*, 484. e) Ananikov, V. P.; Hazipov, O. V.; Beletskaya, I. P. *Chem. Asian J.* **2011**, *6*, 306.
2. a) Handbook of Conducting Polymers, 3rd ed., (Eds.: Skotheim, T. A., Reynolds, J. R.), CRC Press: Boca Raton, FL, **2007**; b) Facchetti, A. *Chem. Mater.* **2011**, *23*, 733-758; c) Xu, S.; Kim, E. H.; Wei, A.; Negishi, E.-i. *Sci. Technol. Adv. Mater.* **2014**, *15*, 44201/1; d) Dini, D.; Calvete, M. J. F.; Hanack, M. *Chem. Rev.* **2016**, *116*, 13043; e) Calvete, M. J. F. *Int. Rev. Phys. Chem.* **2012**, *31*, 319; f) Cheng, Y.-J.; Yang, S.-H.; Hsu, C.-S. *Chem. Rev.* **2009**, *109*, 5868-5923.
3. a) *Metal-Catalyzed Cross-Coupling Reactions* (Eds.: A. de Meijere, F. Diederich), Wiley-VCH, Weinheim, **2004**; b) *Cross-Coupling Reactions: A Practical Guide* (Ed.: N. Miyaura), *Topics in Current Chemistry, Vol.219*, Springer, Heidelberg, **2002**; c) *Metal Complexes as Catalysts for C-C Cross-Coupling Reactions*, I. P. Beletskaya, A. V. Cheprakov in *Comprehensive Coordination Chemistry II, Vol. 9* (Eds.: J. A. McCleverty, T. J. Meyer), Elsevier Ltd., Oxford, **2004**, pp. 305–368; d) Johansson Seechurn, C. C. C.; Kitching, M. O.; Colacot, T. J.; Snieckus, V. *Angew. Chem., Int. Ed.* **2012**, *51*, 5062; e) Miyaura, N.; Suzuki, A. *Chem. Rev.* **1995**, *95*, 2457.
4. a) Trost, B. M. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 259; b) Trost, B. M. *Science* **1991**, *254*, 1471.
5. a) Gallenkamp, D.; Fürstner, A. *J. Am. Chem. Soc.* **2011**, *133*, 9232; b) Saito, N.; Saito, K.; Shiro, M.; Sato, Y. *Org. Lett.* **2011**, *13*, 2718; c) Perez, L. J.; Shimp, H. L.; Micalizio, G. C. *J. Org. Chem.* **2009**, *74*, 7211; d) Neisius, N. M.; Plietker, B. *Angew. Chem., Int. Ed.* **2009**, *48*, 5752; e) Mori, M.; Tanaka, D.; Saito, N.; Sato, Y. *Organometallics* **2008**, *27*, 6313; f) Nishimura, T.; Washitake, Y.; Uemura, S. *Adv. Synth. Catal.* **2007**, *349*, 2563.
6. a) Fischmeister, C.; Bruneau, C. *Beilstein J. Org. Chem.* **2011**, *7*, 156; b) Li, J.; Lee, D. *Eur. J. Org. Chem.* **2011**, *2011*, 4269; c) Diver, S. T. *Coord. Chem. Rev.* **2007**, *251*, 671; d) Diver, S. T. *Sci. Synth.* **2009**, *46*, 97; e) Diver, S. T.; Giessert, A. J. *Chem. Rev.* **2004**, *104*, 1317.
7. Clark, J. R.; Diver, S. T. *Org. Lett.* **2011**, *13*, 2896.
8. Grubbs, R. H. *Tetrahedron* **2004**, *60*, 7117.
9. Fu, G. C.; Nguyen, S. T.; Grubbs, R. H. *J. Am. Chem. Soc.* **1993**, *115*, 9856.
10. Hoveyda, A. H. *J. Org. Chem.* **2014**, *79*, 4763.
11. a) Kaminsky, L.; Wilson, R. J.; Clark, D. A. *Org. Lett.* **2015**, *17*, 3126; b) Kaminsky, L.; Clark, D. A. *Org. Lett.* **2014**, *16*, 5450; c) Liu, S.; Zhao, J.; Kaminsky, L.; Wilson, R. J.; Marino, N.; Clark, D. A. *Org. Lett.* **2014**, *16*, 4456; d) Zhao, J.; Liu, S.; Marino, N.; Clark, D. A. *Chem. Sci.* **2013**, *4*, 1547; e) Dixon, A. D. C.; Wilson, R. J.; Nguyen, D. D.; Clark, D. A. *Tetrahedron Lett.* **2017**, *58*, 4054.
12. Mori, M.; Sakakibara, N.; Kinoshita, A. *J. Org. Chem.* **1998**, *63*, 6082.
13. a) Hirasawa, D.; Watanabe, Y.; Yamahara, T.; Tanaka, K.; Sato, K.; Yamagishi, T. *Mol. Catal.* **2018**, *452*, 184; b) Ogiwara, Y.; Miyake, M.; Kochi, T.; Kakiuchi, F. *Organometallics* **2017**, *36*, 159; c) Gulias, M.; Collado, A.; Trillo, B.; Lopez, F.; Onate, E.; Esteruelas, M. A.; Mascarenas, J. L. *J. Am. Chem. Soc.* **2011**, *133*, 7660; d) Kitazawa, K.; Kochi, T.; Kakiuchi, F. *Org. Synth.* **2010**, *87*, 209; e) Mitsudo, T.; Naruse, H.; Kondo, T.; Ozaki, Y.; Watanabe, Y. *Angew. Chem.* **1994**, *106*, 595; f) Warrener, R. N.; Abbenante, G.; Kennard, C. H. L. *J. Am. Chem. Soc.* **1994**, *116*, 3645; g) Yamaguchi, M.; Kido, Y.; Omata, K.; Hirama, M. *Synlett* **1995**, 1181; h) Wakatsuki, Y.; Yamazaki, H.; Kumegawa, N.; Satoh, T.; Satoh, J. Y. *J. Am. Chem. Soc.* **1991**, *113*, 9604; i) Mitsudo, T.; Nakagawa, Y.; Watanabe, K.; Hori, Y.; Misawa, H.; Watanabe, H.; Watanabe, Y. *J. Org. Chem.* **1985**, *50*, 565.
14. Trost, B. M.; Toste, F. D.; Pinkerton, A. B. *Chem. Rev.* **2001**, *101*, 2067.
15. a) Lozano-Vila, A. M.; Monsaert, S.; Bajek, A.; Verpoort, F. *Chem. Rev.* **2010**, *110*, 4865; b) deLosRios, I.; Tenorio, M. J.; Puerta, M. C.; Valerga, P. *J. Am. Chem. Soc.* **1997**, *119*, 6529; c) Wakatsuki, Y.; Koga, N.; Yamazaki, H.; Morokuma, K. *J. Am. Chem. Soc.* **1994**, *116*, 8105; d) Nolan, S. P.; Belderrain, T. R.; Grubbs, R. H. *Organometallics* **1997**, *16*, 5569.
16. a) Wolf, J.; Stuer, W.; Grunwald, C.; Gevert, O.; Laubender, M.; Werner, H. *Eur. J. Inorg. Chem.* **1998**, 1827; b) Belderrain, T. R.; Grubbs, R. H. *Organometallics* **1997**, *16*, 4001; c) Wilhelm, T. E.; Belderrain, T. R.; Brown, S. N.; Grubbs, R. H. *Organometallics* **1997**, *16*, 3867.
17. Galan, B. R.; Giessert, A. J.; Keister, J. B.; Diver, S. T. *J Am Chem Soc* **2005**, *127*, 5762.
18. Grotevendt, A. G. D.; Lummiss, J. A. M.; Mastronardi, M. L.; Fogg, D. E. *J. Am. Chem. Soc.* **2011**, *133*, 15918.
19. a) Maynard, H. D.; Grubbs, R. H. *Tetrahedron Lett.* **1999**, *40*, 4137; b) Paquette, L. A.; Schloss, J. D.; Efremov, I.; Fabris, F.; Gallou, F.; Mendez-Andino, J.; Yang, J. *Org. Lett.* **2000**, *2*, 1259; c) Ahn, Y. M.; Yang, K.; Georg, G. I. *Org. Lett.* **2001**, *3*, 1411; d) Knight, D. W.; Morgan, I. R.; Proctor, A. J. *Tetrahedron Lett.* **2010**, *51*, 638; e) French, J. M.; Caras, C. A.; Diver, S. T. *Org. Lett.* **2013**, *15*, 5416.

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Ruthenium Dihydride Complexes as Enyne Metathesis Catalysts

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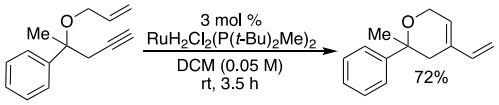
Martin A. Dolan, Alexandre D. C. Dixon, John D. Chisholm* and Daniel A. Clark*



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Highlights

• $RuH_2Cl_2(PR_3)_2$ complexes act as catalysts for enyne metathesis.

• Mechanistic studies implicate a ruthenium vinylidene as the active catalyst.

• Many good yields are obtained with 1,6 and 1,7-enynes using these catalysts.

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