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Hydrogenative Cyclopropanation and Hydrogenative Metathesis

Sebastian Peil, Alexandre Guthertz, Tobias Biberger, and Alois Fürstner*

Abstract: The unusual geminal hydrogenation of a propargyl alcohol derivative with [Cp^{X}RuCl] as the catalyst entails formation of pianostool ruthenium carbenes in the first place; these reactive intermediates can be intercepted with tethered alkenes to give either cyclopropanes or cyclic olefins as the result of a formal metathesis event. The course of the reaction is critically dependent on the substitution pattern of the alkene trap.

Recent investigations into the *trans*-hydrogenation of internal alkynes with the aid of [Cp*Ru]-based catalysts (Cp* = pentamethylcyclopentadienyl) showed that the perplexing stereochemical outcome of this reaction can be reached along two competing pathways (Scheme 1).[1,2,3,4] The routes bifurcate at the stage of the metallacyclopropene **B** that is initially formed by transfer of an H-atom to the triple bond activated by coordination to the metal fragment. **B** then either evolves via a concerted process to the *E*-alkene **C** or converts into a discrete ruthenium carbene complex **D** by a formal *gem*-hydrogenation of the triple bond; **D** transforms into **C** via an associative mechanism in which a second H_2 molecule needs to be ligated to the metal center to lower the barriers.[2,4] The concerted path plays a prominent role for unbiased alkyne substrates and is fostered by electron rich Cp^X ligands on the metal (Cp^X = substituted cyclopentadienyl).[5] In contrast, propargylic alcohol derivatives **A** (largely) prefer the stepwise process via carbene intermediates. In this case, the –OR group exerts a notable directing effect in that an unprotected propargyl alcohol (R = H) can engage in hydrogen bonding with the catalyst and usually instigates carbene formation at the proximal alkyne C-atom,[6,7] whereas non-protic –OR substituents (R ≠ H) prompt complexation at the distal site; only this latter scenario is depicted in Scheme 1 for clarity. Favorable cases lead to the essentially quantitative and

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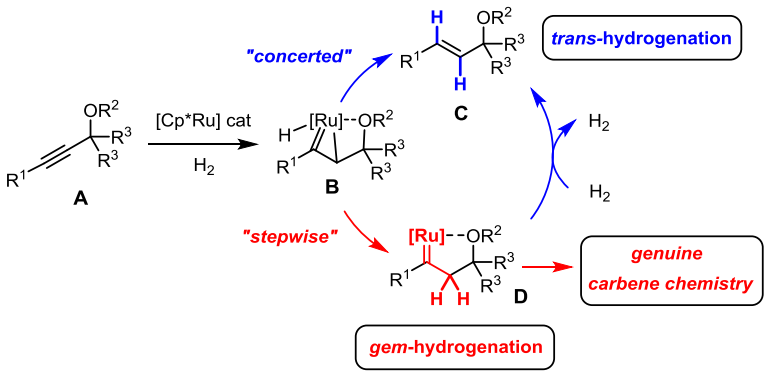
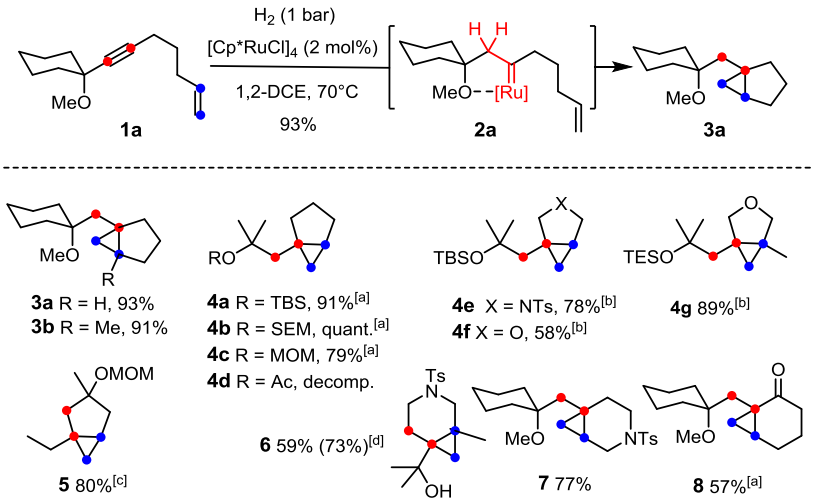
regioselective formation of well-defined pianostool ruthenium carbene complexes such as **D**.[2,4] Therefore it was deemed promising to explore whether this non-canonical *gem*-hydrogenation mechanism allows genuine metal carbene reactivity to be harnessed.



Scheme 1. Gross features of the two pathways that can lead to alkyne *trans*-hydrogenation



Scheme 2. Hydrogenative cyclopropanation; the reacting sites of the enyne substrates are color-coded; [a] at RT; [b] at 90°C; [c] dr = 1.1:1; [d] NMR yield in brackets; Cp* = pentamethylcyclopentadienyl; 1,2-DCE = 1,2-dichloroethane; MOM = methoxymethyl; SEM = (2-trimethylsilyl)ethoxymethyl; TBS = *tert*-butyldimethylsilyl; TES = triethylsilyl; Ts = *p*-toluenesulfonyl

Enyne **1a** was chosen as a model substrate to test whether it is feasible to trap the transient carbene **2a** formed by *gem*-hydrogenation. Upon stirring of a solution of this compound in 1,2-dichloroethane under an atmosphere of H_2 in the presence of $[Cp^*RuCl]_4$ (2 mol%), cyclopropane **3a** was formed in

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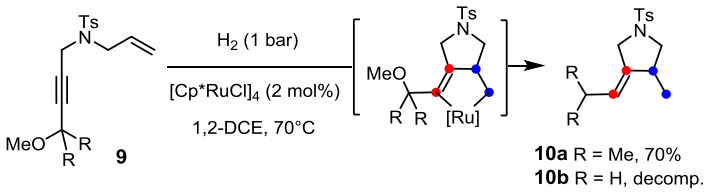
excellent yield; the reaction worked best at 70°C (Scheme 2).[4] This result confirms that the regioselective *gem*-hydrogenation entailed carbene formation distal to the steering –OMe group, and shows that the subsequent intramolecular reaction with the tethered alkene is fast enough to outperform simple reduction to the *E*-alkene. Moreover, this remarkable transformation illuminates the electrophilic Fischer-carbene-like behavior of pianostool ruthenium complexes of type **2** as one trait of their multifaceted character.[8] This outcome accords well with previous findings which showed that [Cp*Ru]-carbene complexes – generated by entirely different routes – readily engage, *inter alia*, in cyclopropanation.[9,10,11,12,13,14] In conceptual terms, the "hydrogenative cyclopropanation" manifest in this example stands in striking contrast to the practice of cyclopropane ring cleavage by hydrogenolysis, as widely exercised in organic synthesis.[15]



Scheme 3. Cycloisomerization/reduction as a competing process

Scheme 2 also illustrates the current scope of this new transformation. Propargylic ethers, silyl ethers and acetal substituents turned out to be suitable directing groups, all of which lead to carbene formation at the distal site. Not unexpectedly, a propargylic acetate precursor was decomposed. In line with our previous studies, use of an unprotected propargyl alcohol redirected carbene formation to the proximal C-atom of the triple bond as illustrated by product **6**.[4] Although kinetically more challenging, annulated six-membered rings can also be formed by hydrogenative cyclopropanation (**6**-**8**). Moreover, the successful synthesis of the cyclopropyl ketone **8** is noteworthy, since such products are usually made from α-diazo ketone precursors;[16] *gem*-hydrogenation of a simple ynone constitutes a safe alternative that deserves more detailed study.[17] In contrast, the closely related substrate **9a** failed to undergo hydrogenative cyclopropanation (Scheme 3). The constitution of the resulting product **10a** suggests that metallacycle formation by oxidative enyne cyclization[18,19] is faster than *gem*-hydrogenation, even though the exact mechanism that results in concomitant loss of MeOH is unknown. The analogous primary ether **10b** gave a rather complex mixture.

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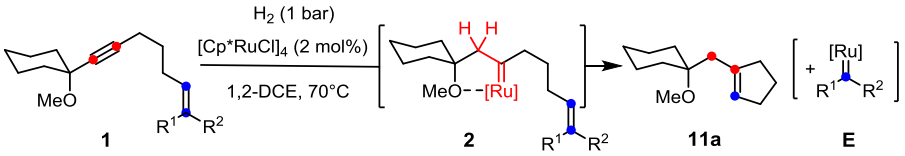
Table 1. Hydrogenative metathesis: Influence of the olefin terminus



Entry	Substrate	R^1	R^2	11a (Yield, %)[a]
1	**1a**	H	H	--- [**3a**: 93%]
2	**1b**	H	Me	49
3	**1c**	Me	H	40
4	**1d**	H	Et	60
5	**1e**	H	*i*Pr	93[b]
6	**1f**	Me	Me	93[b]

[a] NMR yield, unless stated otherwise; [b] yield of isolated pure material

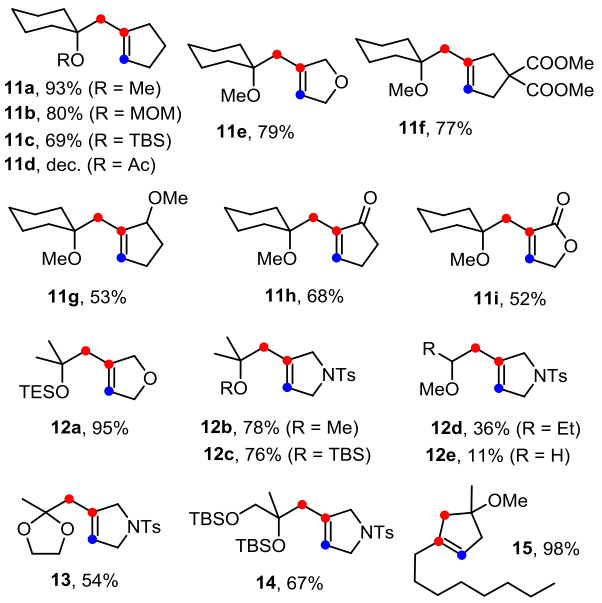


Chart 1. Hydrogenative metathesis of enyne substrates (isolated yields, color code as shown in Table 2); unless stated otherwise, all reactions were carried out using $[Cp^*RuCl]_4$ (2 mol%) in 1,2-dichloroethane under an atmosphere of H_2 at 70°C; variable amounts of products formed by alkyne *trans*-hydrogenation were detected in the crude reaction mixtures

In our initial foray, we had deliberately chosen enyne **1a** comprising a terminal and sterically unhindered alkene in an attempt to maximize the likelihood that intramolecular cyclopropanation outcompetes alkyne *trans*-reduction (Scheme 2). This prudence proved somewhat unnecessary since terminal disubstituted olefins also reacted well (cf. **3b**, **4g**, **6**). Substrates comprising an internal

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olefin, in contrast, led to an entirely different outcome (Table 1): metathesis eventually becomes the major path. This result is striking since earlier work had shown that putative [Cp*Ru(Cl)(=CR_2)] complexes, which were formed by an entirely different method, are highly competent in cyclopropanation but basically failed to engage in metathesis.[9,20,21] Although various competing processes (*trans*-hydrogenation with or without positional olefin isomerization, enyne cycloisomerization,[18,19] cyclopropanation) were observed for **1b**-**d**, the formation of the five-membered ring eventually is selective and fast enough to give product **11a** in good to excellent yields. The fact that the efficiency of cyclization is innately correlated with the substitution pattern of the alkene site of the substrate must have a mechanistic bearing (see below);[22,23,24] for the time being, dimethylated enyne derivatives such as **1f** are the best compromise between accessibility and the efficiency of the ring closing metathesis event.[25]

Substrates of this exact type allowed a number of hydrogenative metathesis reactions to be accomplished (Chart 1). The yields are high as long as the steering substituent is a tertiary *e*ther, silyl ether or acetal. The formation of such trisubstituted cycloalkene products is not necessarily trivial even with the aid of (first generation) Grubbs catalysts;[26] this is particularly true for cyclopentenones and butenolides such as **11h,i** respectively,[27,28] which can be reached by the new hydrogenative metathesis in respectable yields. As expected for a ruthenium-based catalyst system, the functional group compatibility is promising.

In order to address all relevant preparative issues in a more rational way and increase the scope of the reaction in the future, several mechanistic aspects need to be clarified at first. Of prime importance is the question as to how the catalytic cycle of a hydrogenative metathesis reaction is actually closed because the “secondary” ruthenium carbene **E** itself, formed upon release of cycloalkene **4**, cannot be the propagating species; if it were, its carbene entity would get incorporated into the product and the overall process would transmute to an ordinary enyne metathesis reaction delivering a 1,3-diene rather than the observed cycloalkene (Scheme 4).[29] That a secondary carbene of type **E** is initially generated, however, is highly likely in view of a stoichiometric control experiment which furnished the bridging carbene complex **16** (δ_C = 252.8 ppm) as the only detectable Cp*-containing product; its formation is best explained by assuming that incipient **E** is instantly trapped by unreacted [Cp*RuCl] to give **16**. The structure of this complex was assigned by

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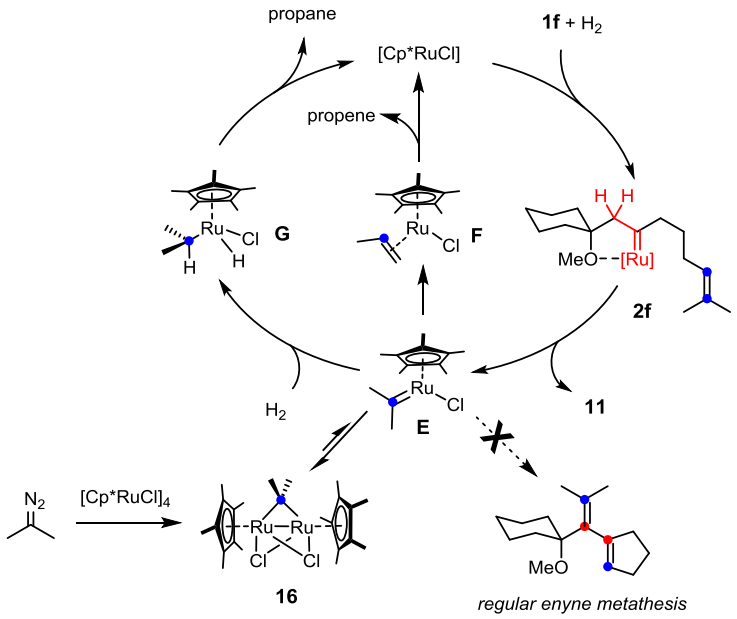
extensive NMR spectroscopy and comparison with a closely related complex known in the literature.[30] To avoid any ambiguity, **16** was also made by an independent route by decomposition of 2-diazopropane with $[Cp^*RuCl]_4$ at low temperature (for further details, see the SI).



Scheme 4. Mechanistic proposal

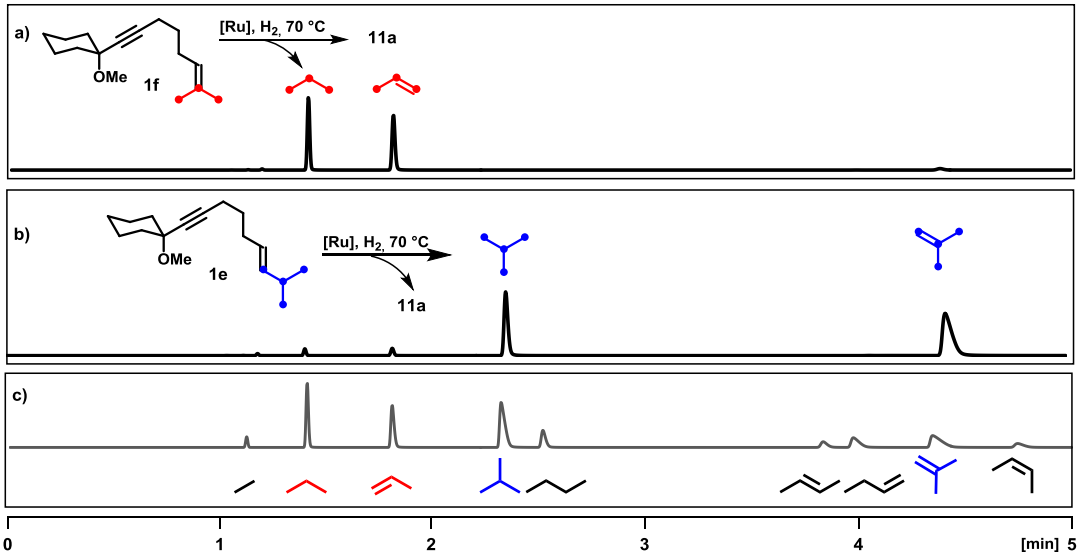


Figure 1. a) and b): GC-based headspace analysis of two different hydrogenative metathesis reactions showing the release of alkene and alkane products derived from the olefinic terminus of the particular enyne substrate; c) reference library of light hydrocarbons

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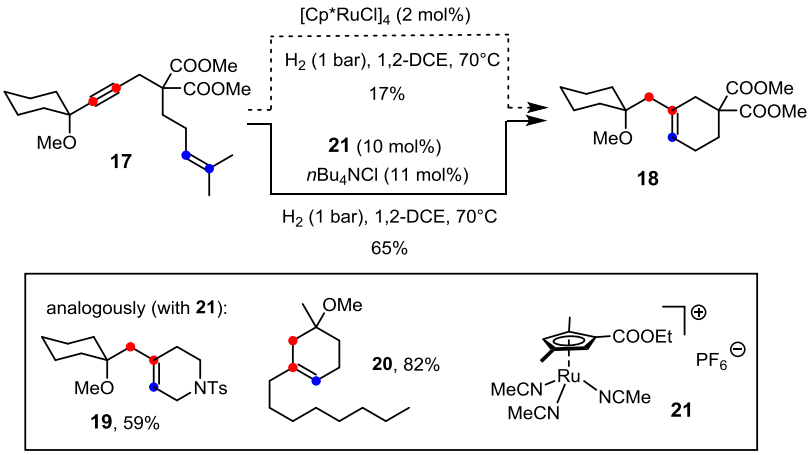
The stoichiometric reaction of **1f** with $[Cp^*RuCl]_4$ under H_2 atmosphere furnishing cycloalkene **11** and complex **16** proceeds rapidly at or below ambient temperature (Scheme 4), whereas the catalytic hydrogenative metathesis of the very same substrate requires heating to ≈70°C to ensure reasonable rates (Table 1, entry 6). This comparison suggests that the dinuclear complex **16** is a dormant rather than active species and the turnover-limiting step of the catalytic cycle must come after its formation.[31] Headspace analyses of several independent catalytic runs at 70°C provided further insights: hydrogenative metathesis of substrate **1f** releases propane and propene, whereas substrate **1e** gave isobutane and isobutene; all of these volatile components were unambiguously identified by GC/MS and comparison with authentic samples (Figure 1). Hence, the initially formed secondary ruthenium carbene complex **E** likely succumbs to competing formation of alkene and/or reduction by H_2 via **F** and **G**, respectively; these are nothing but the regular steps that the primary carbene **2** would take during alkyne *trans*-reduction.[3,4] It is important to note that either route regenerates [Cp*RuCl] which therefore constitutes the actual catalyst.



Scheme 5. More electrophilic carbenes enhance the efficiency of metathesis

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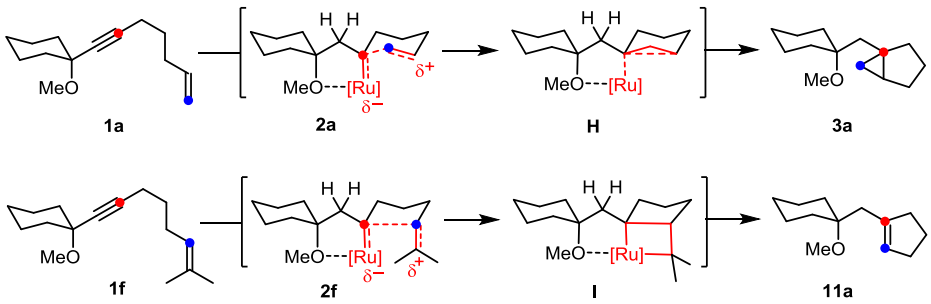

Scheme 6. Tentative rationale for the role of the alkene substitution pattern on the reaction outcome; the prime sites of interactions are color-coded

Additional experiments provide preliminary insights into why the alkene substitution pattern of a given enyne determines whether cyclopropanation or metathesis will take place. The carbene intermediates **2a** and **2f** derived from **1a** and **2f**, respectively, differ from each other only in the presence or absence of two methyl groups *five* bonds away from the reactive site (Scheme 6). Such a peripheral change does not entail a sudden switch from a presumed Fischer carbene character to reactivity seemingly more befitting a Schrock alkylidene.[32] This notion is corroborated by preliminary results concerning ligand tuning (Scheme 5): While the reaction of enyne **17** in the presence of [Cp*RuCl] largely failed to deliver the six-membered trisubstitued cycloalkene **18** (≤ 17%), the use of the less electron rich analogue prepared in situ from **21** and *n*Bu_4NCl afforded this compound (as well as **19** and **20**) in respectable yield. As shown in the accompanying paper, **21** leads to a carbene of *increased* electrophilicity which one does not expect to bolster metathesis.[33] This rather perplexing correlation[34] suggests that attack of the electrophilic carbene by the more nucleophilic site of the alkene partner might be selectivity-determining, which happens to be the terminus if R^1 = R^2 = H, but the internal positon if R^1 = R^2 = Me ("Markovnikov's rule").[35,36] Under this premise, **2a** could evolve via a 6-*endo-trig* transition state **H** into the cyclopropane **3a** by an outersphere process, whereas **2f** is geometrically poised for metallacycle formation (**I**) and hence metathesis to furnish cycloalkene **11a**.[37]

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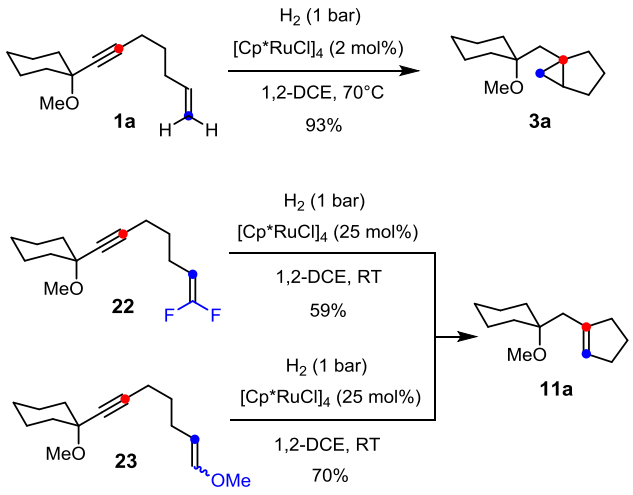

Scheme 7. Additional control experiments; the primarily interacting sites are color-coded

This tentative mechanistic interpretation is in accord with additional stoichiometric control experiments (Scheme 7), which indicate that the course of the reaction responds to the polarization of the alkene bond in a give substrate. Specifically, **1a** provides cyclopropane **3a**, whereas enyne **22** containing a difluoroolfinic site gave the metathesis product **11a**; since hydrogen and fluorine are isosteric, this divergent outcome implies that the product-determining step is (largely) governed by electronic rather than steric factors. Equally instructive is the comparison of difluoroolefin **22** and enol ether **23**: although the electronic character of their double bonds is very different, it is the internal position in both substrates that is more electron rich; in accordance with the proposed rationale, attack at this site should entail metathesis, which is indeed the case; no trace of the corresponding cyclopropane was detected in the crude reaction mixtures.[37]

We appreciate that the mechanistic information gathered at this point provides only indirect evidence; combined experimental and computational efforts will be necessary to corroborate or disprove the proposed scenario and draw a more detailed and accurate picture. Most notably, the proposition that cyclopropanation might bypass a metallacyclic intermediate needs further scrutiny.[35,38] These and other open aspects notwithstanding, the present study shows that *gem*-hydrogenation is an intriguing new entry into transition metal carbene chemistry that allows hazardous carbene sources such as diazoalkanes or cyclopropenes to be replaced by internal alkynes. The ability to form cyclopropanes via catalytic hydrogenation is remarkable as it violates the established logic of organic synthesis which resort to hydrogenolysis for the cleavage of three-

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membered rings. Perhaps even more striking in conceptual terms is “hydrogenative metathesis” which represents an entirely novel manifold within the realm of metathesis in general:[26] it shares the substrate basis with traditional enyne metathesis but delivers cyclic olefins rather than 1,3-dienes.[29] Although the scope of the new transformations described herein is currently limited and far from the cosmic coverage of metathesis by Grubbs-type ruthenium carbene complexes,[26,39] the new strategy provides an orthogonal starting point for discovery that we consider worth pursuing.

Acknowledgements

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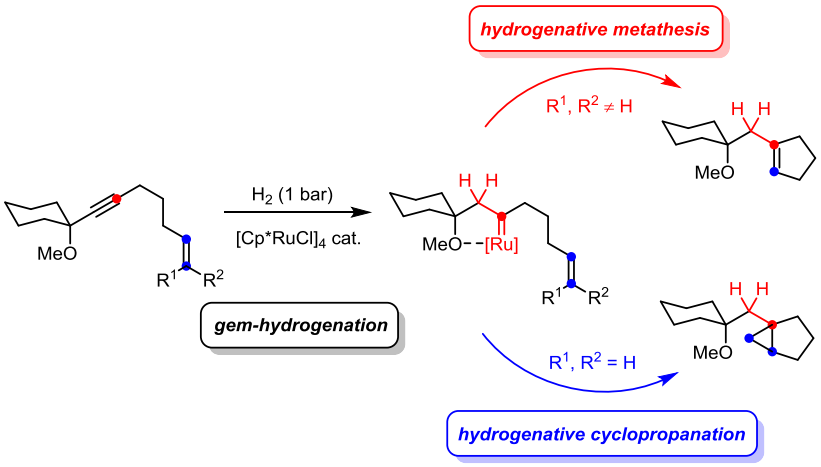

Janus Character: *gem*-Hydrogenation of propargyl alcohol derivatives provides a conceptually novel entry into metal carbene complexes. Specifically, the use of $[Cp^*RuCl]_4$ as catalyst affords pianostool ruthenium carbenes which engage in either cyclopropanation or metathetic ring closure; the outcome of the reaction is largely dictated by the substitution pattern of the chosen olefinic trap.

Keywords: Carbene Complexes · Cyclopropanation · Enynes · Hydrogenation · Metathesis · Ruthenium

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[23] For a singular example of catalytic diazoacetate decomposition with $[Ru_2(OAc)_4]$ in the presence of net styrene/norbornene mixtures entailed cyclopropanation and ring opening cross metathesis, see: A. F. Noels, A. Demonceau, E. Calier, A. J. Hubert, R.-L. Márquez-Silva, R. A. Sánchez-Delgado, *J. Chem. Soc., Chem. Commun*. **1988**, 783-784.

[24] We are aware of a single example in which a classical Grubbs ruthenium carbene complex engaged an enyne into metathesis as well as cyclopropanation, see: a) B. P. Peppers, S. T. Diver, *J. Am. Chem. Soc*. **2004**, *126*, 9524-9525; furthermore, examples are known in which Grubbs catalysts react with diazo derivatives to give new carbene complexes which trigger cyclopropanation/metathesis cascades; for a review see: B. Alcaide, P. Almendros, A. Luna, *Chem. Rev*. **2009**, *109*, 3817-3858.

[25] Prenyl groups are good acceptor olefins in RCM reactions even for 1,1-disubstituted Grubbs-type ruthenium carbenes, see: K. A. Bahou, D. C. Braddock, A. G. Meyer, G. P. Savage, *Org. Lett*. **2017**, *19*, 5332-5353.

[26] R. H. Grubbs, D. J. O'Leary (Eds.), *Handbook of Metathesis*, 2nd Ed., Wiley-VCH, Weinheim, 2015.

[27] For early work from this laboratory, see: A. Fürstner, O. R. Thiel, L. Ackermann, H.-J. Schanz, S. P. Nolan, *J. Org. Chem*. **2000**, *65*, 2204-2207.

[28] A. Fürstner, *Angew. Chem. Int. Ed*. **2000**, *39*, 3012-3043; *Angew. Chem*. **2000**, *112*, 3140-3172.

[29] S. T. Diver, A. J. Giessert, *Chem. Rev*. **2004**, *104*, 1317-1382.

[30] M. R. Gagné, R. H. Grubbs, J. Feldman, J. W. Ziller, *Organometallics* **1992**, *11*, 3933-3935.

[31] This is also in line with the observation that a closely related complex reported in ref. 30 was found to be a poor ROMP initiator even for the strained substrate norbornene.

[32] R. R. Schrock, *Angew. Chem. Int. Ed*. **2006**, *45*, 3748-3759; *Angew. Chem*. **2006**, *118*, 3632-3844.

[33] It is important to note, however, that **21** also facilitates *gem*-hydrogenation and kinetically stabilizes the resulting carbene complex, see the accompanying paper

[34] **21** was the most efficient catalyst for the cyclopropanation of norbornene with propargyl alcohol as the "carbene" source; ROMP, though inherently facile for this strained olefin, has not been observed, see: a) H. Kikuchi, M. Uno, S. Takahashi, *Chem. Lett*. **1997**, 1273-1274; b) Y. Matsushima, H. Kikuchi, M. Uno, S. Takahashi, *Bull. Chem. Soc. Jpn*. **1999**, *72*, 2475-2482.

[35] Ample literature shows that the attack of an electrophilic carbene onto an appropriately substituted alkene can generate reactive intermediates of largely carbenium ion character; for representative cases, see: a) M. Brookhart, G. O. Nelson, *Organometallics* **1984**, *3*, 650-652; b) A. Fürstner, L. Morency, *Angew. Chem. Int. Ed*. **2008**, *47*, 5030-5033; *Angew. Chem*. **2008**, *120*, 5108-5111; c) A. G. Tskhovrebov, J. B. Lingnau, A. Fürstner, *Angew. Chem. Int. Ed*. **2019** (doi: 10.1002/anie.201903957)

[36] For an insightful discussion, which includes addition of free carbenes to olefins and allows ^{13}C NMR shifts to be used as predictive tool (that we found valid in the present case), see: W. F. K. Schnatter, D. W. Rogers, A. A. Zavitsas, *Chem. Eur. J*. **2015**, *21*, 10348-10361.

[37] In ref. 22c it was suggested that the stability of the secondary carbene released during metathesis might play a role in determining whether metathesis of cyclopropanation is favored; this seems unlikely in the present case because substrates **1f**, **22** and **23** invariably undergo metathesis even though they release secondary carbenes of greatly different stability.

[38] Based on DFT data, the cyclopropanation reactions observed on treatment of an enyne with a diazoalkane and [Cp*RuCl(cod)] (cat.) was proposed to proceed via ruthenacyclobutane intermediates, cf. ref. 9

[39] R. H. Grubbs, *Angew. Chem. Int. Ed*. **2006**, *45*, 3760-3765; *Angew. Chem*. **2006**, *118*, 3845-3850.