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Ruthenium catalyzed enyne cycloisomerizations and hydroxycyclizations with skeletal rearrangement

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Abstract

A neutral arene-tethered ruthenium complex was found to be a catalyst precursor for enyne cycloisomerizations and hydroxycyclizations. The observed products were the result of a skeletal rearrangement process, and include an unusual cyclization to form a six-membered ring. Labeling studies on the six-membered ring product are in accord with an electrophilic activation mechanism that proceeds via cationic cyclopropyl carbene intermediates.

Keywords: Carbene; Cycloisomerization; Enyne

1. Introduction

Transition-metal catalyzed cycloisomerizations of 1,6-enynes have received much attention in recent years, and there are now a wide range of catalysts that can mediate these reactions [1–3]. Most involve the formation of a metallacycle, a π-allyl complex, or a vinyl–metal complex, and generally tend to produce five-membered rings of various types (I–III) as shown in Fig. 1 [1].

Products of type IV, although they have been observed occasionally, are much less common [4–7]. In addition, there are several catalysts which, in the presence of water or alcohol, give rise to products of type V [8–10].

We have found that the planar chiral arene-tethered ruthenium complex that has been recently synthesized and resolved in our laboratory is a catalyst precursor for the cycloisomerization of 1,6-enynes [11,12]. Addition of two molar equivalents of $AgSbF_6$ results in the active species, which was observed to yield products of types III, IV, and V depending on the substrate and reaction conditions as shown in Fig. 2.

2. Results and discussion

When the cyclizations were performed in anhydrous CH_2Cl_2, two classes of compounds were produced: five-membered ring skeletally rearranged products (type III) and six-membered rings (type IV). When undried THF was used as the solvent, hydroxycyclized products were observed (type V), presumably owing to the incorporation of adventitious water in the solvent (see Table 1).

Terminal alkyl substitution on the olefin moiety favored the cyclization to form the six-membered ring under anhydrous conditions (entries 1 and 2). Enyne substrates with di- and trialkyl-substituted olefins both selectively formed **4a** and **4b**, respectively, although the trisubstituted enyne was cyclized more selectively. The reaction of **2a** in undried THF resulted in the selective formation of the hydroxylated product **5a**, and no traces of **3a** or **4a** were observed. Instead, a small amount (4%) of the common Alder-ene product (type I) was observed. The use of enantiopure catalyst resulted in an enantioenriched product, although the selectivity was low (23% ee) [13]. Generally the desired products in these reactions are not chiral and enantiopure catalysts would not be needed. In this case, however, the observation of non-racemic products serves to demonstrate that the chiral ruthenium complex is involved in the catal-

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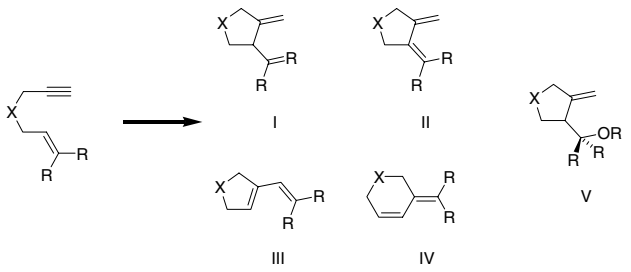


Fig. 1. Cycloisomerization of 1,6-enynes.

ysis rather than another acid produced by hydrolysis or decomposition of the complex.

The reaction was sluggish when the olefin was terminally substituted with an aryl group, though the five-membered ring was produced with modest conversion. In undried THF the hydroxylated product **5c** was formed, albeit in lower yield than with the alkyl-substituted enyne **2a**, and once again the enantioselectivity was low (9% ee) when enantiopure catalyst was used. The reaction of enyne **2d**, which contains a monosubstituted olefin, only proceeded to 12% of **3d**. Enyne **2e**, which is dialkyl-substituted though not terminally substituted, was cyclized selectively to **3e**. No trace of the hydroxylated product was observed when the reaction was performed in undried THF.

The incorporation of water from the solvent into the cyclic products was seen to be very sensitive to reactant concentrations. Specifically, changes in the concentrations of catalyst and substrate resulted in varying product distributions. Table 2 shows the effect of changing concentrations on the reaction. The optimal substrate concentration in terms of conversion to **5a** was 0.03 M; concentrations lower than this resulted in lower yields of **5a** and increased yields of **6** although the net conversion to cyclized product was lower. Catalyst decomposition is also favored by higher water concentrations, as addition of 10 equiv. (with respect to catalyst) of water resulted in no conversion to cyclized product. These results illustrate the dramatic effect of concentration on the cyclization reactions. The concentration dependency is perhaps best viewed as a kinetic effect owing to the relative concentration of water in comparison to the substrate and catalyst concentrations. That is, the relative rates of the various reactions (hydroxycyclization, Alderene cyclization, and catalyst decomposition) are affected to very different extents by the various concentration

Table 1
Catalytic results

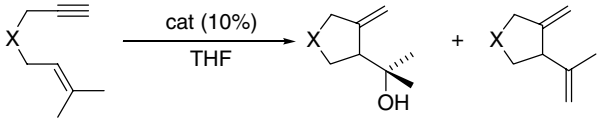
Entry	Enyne	Conc. (M)	Solvent	Major product	Yield (%)
1	**2a**	0.02	CH_2Cl_2	**4a**	89
2	**2b**	0.02	CH_2Cl_2	**4b**	75[a]
3	**2a**	0.03	THF	**5a**	82
4	**2c**	0.02	CH_2Cl_2	**3c**	37
5	**2c**	0.04	THF	**5c**	30
6	**2d**	0.02	CH_2Cl_2	**3d**	12[b]
7	**2e**	0.03	THF	**3e**	93

The concentration values correspond to the substrate concentration. All reactions were done at room temperature, stirring for 16 h. Yields are isolated yields, except where otherwise indicated.

[a] Enyne **2b** had an *E*:*Z* ratio of 9:1. The major product could not be isolated in pure form, due to the presence of several minor isomers. In this case, the conversion was determined by ^{1}H NMR with the addition of mesitylene as a standard.

[b] Yield determined by ^{1}H NMR.

Table 2
Effect of concentration on product distribution



Entry	Conc. (M)	Products (%)	
		5a	**6**
1	0.03	82	4
2	0.02	32	23
3	0.005	14	8

Percent conversion was determined by ^{1}H NMR.

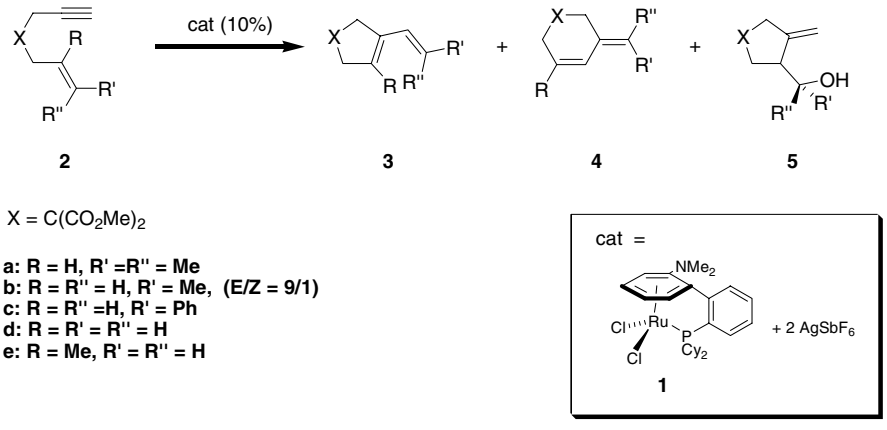


Fig. 2. Cycloisomerization of enynes by **1**/$AgSbF_6$.

changes of the reagents. The lower conversions at lower catalyst concentrations, for example, could be a result of the faster decomposition of the catalyst relative to the product forming reactions.

The five-membered ring products **3c–e** are the result of a skeletal rearrangement of the substrate during the catalytic cycle, which involves the breaking of the C–C bonds in the olefin. $PtCl_2$ [14–16], $GaCl_3$ [17], $[RuCl_2(CO)_3]_2$ [18], $[Au(PPh_3)]^+$ [4], and Grubbs' catalyst $Cl_2RuL(PCy_3)$=CHPh [6,19,20] are all effective at eliciting this type of cyclization. In order to determine whether the six-membered ring products were the result of a similar rearrangement process, ^2H and ^{13}C labeling experiments were performed as shown in Figs. 3 and 4.

The labeling studies are consistent with a ring-closing metathesis process that leads to the six-membered ring formation [6,20]. Alternatively, the position of the labels is suggestive of an electrophilic activation mechanism that has been proposed which proceeds via non-stabilized cyclopropyl metal carbene intermediates [4,14,16,21–26]. This mechanism, in contrast to enyne metathesis, can also give rise to the observed hydroxycyclization.

This latter process has been postulated for other electrophilic transition metal centers, mainly $PtCl_2$ and cationic Au complexes, which activate the triple bond through η^2-coordination of the alkyne toward nucleophilic attack by the pendant olefin. The six-membered rings **4a–b** would be a result of a 6-*endo* attack, followed by a rearrangement sequence that has only been observed in one other instance [4]. The preference for this pathway, as opposed to the more commonly observed pathway involving 5-*exo* attack, has been attributed to the relative activation energies of the two transition states. Theoretical studies have focused on such factors as the propargylic substituents [27] and the effect of heteroatoms within the substrate [25] on controlling the regiochemistry of the nucleophilic attack. It has also been noted that the electronegativity of the substituents on the substrate can have an influence on the outcome of these reactions [15,22]. This present study suggests that the steric environment of the metal catalyst can also play an important role in determining the regioselectivity. For example, in Echavarren's report [4], substrates **2a** and **2b**

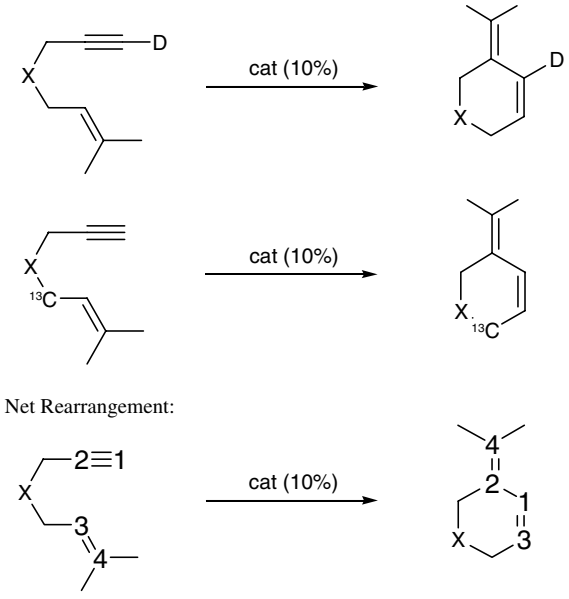


Fig. 4. Labeling experiments.

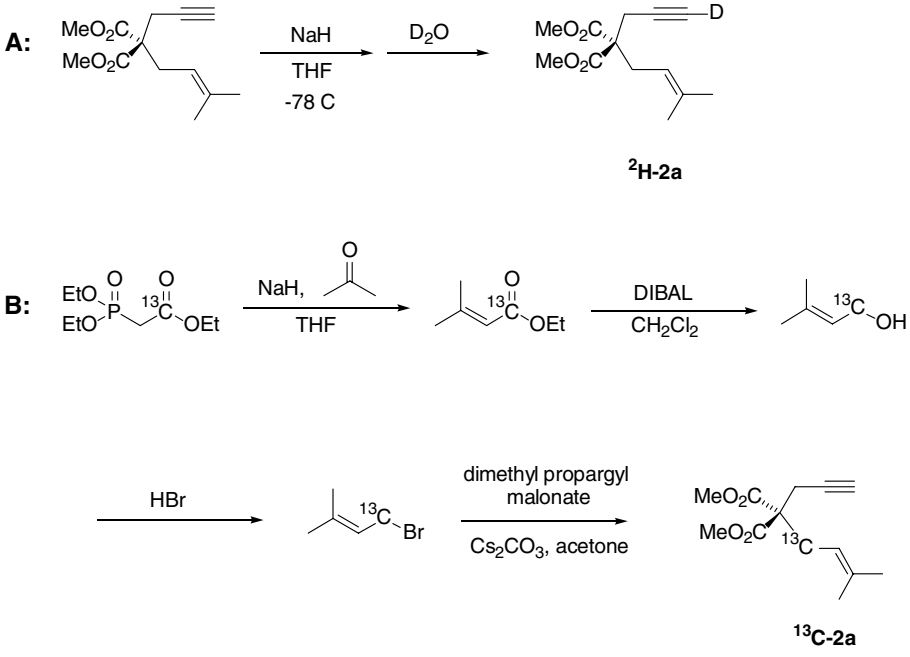


Fig. 3. Preparation of isotopically labeled enynes. (A) ^2H-labeled **2a**. (B) ^{13}C-labeled **2a**.

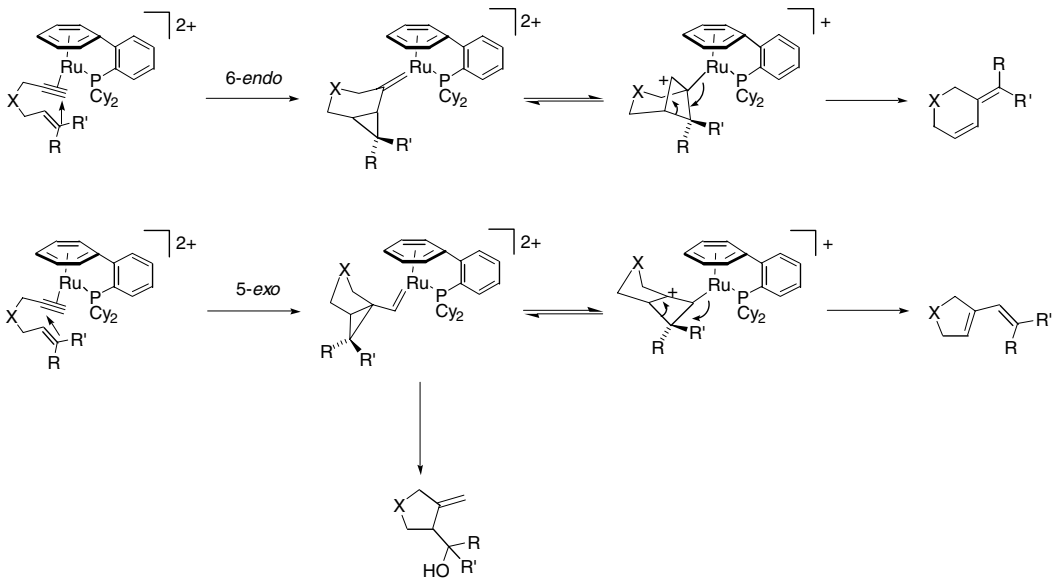


Fig. 5. Possible mechanism for skeletal rearrangement.

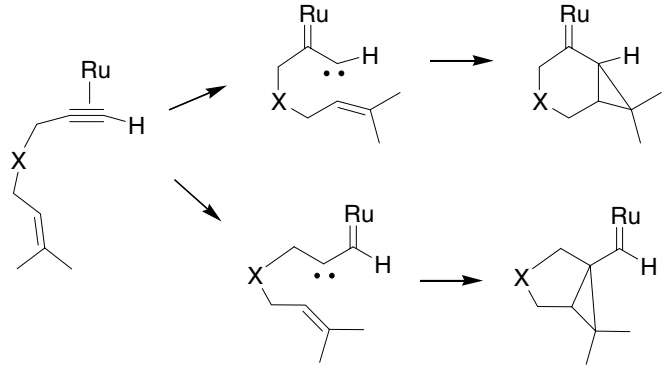


Fig. 6. Initial step viewed as a metal–carbene and carbene attack on the olefin.

were seen to react via the 5-*exo* pathway (see Fig. 5). Since in our case the 6-*endo* pathway was observed for the identical substrates, it is reasonable to assume that the unique steric environment of our catalyst plays a major role in controlling the regioselectivity. This can be viewed as favoring the initial formation of a more-substituted metal carbene while the other carbon of the alkyne assumes carbene-like reactivity as shown in Fig. 6.

3. Conclusions

In conclusion, the arene-tethered ruthenium complex **1** has been shown to be a catalyst precursor for enyne cycloisomerizations and hydroxycyclizations. The observed products are the result of a skeletal rearrangement process, and a rare cyclization to produce a six-membered ring has been observed. Thus, this catalyst complements the existing platinum and gold catalysts in that it may offer the potential of accessing different rearrangement pathways for a given substrate. Applications are currently being investigated which will probe the scope of this catalyst system for alkyne activation in different substrates, as well as in areas that could better exploit the chirality of the catalyst, such as desymmetrization reactions.

4. Experimental

4.1. General methods

All synthetic manipulations were done under nitrogen atmosphere using standard Schlenk techniques. CH_2Cl_2 and THF were dried by distillation over the appropriate drying agents prior to use, except when indicated otherwise. $AgSbF_6$ (Strem), crotyl alcohol, dimethyl propargylmalonate (Fluka), $CsCO_3$, NaH, allylic halides, DIBAL, and triethyl phosphonoacetate-1-^{13}C (Aldrich) were all used as received. NMR spectra were recorded on Bruker 400 and 500 MHz instruments, and chemical shifts are reported in ppm relative to solvent peaks. Enantiomeric excesses were determined with the use of europium tris[3-heptafluoro-propylhydroxymethylene-(+)-camphorate] as a chiral shift agent. The chiral shift experiments were done in C_6D_6, and it was observed that a resonance corresponding to the protons on one of the methoxy groups would begin to split after a downfield shift of ~0.5 ppm.

The following compounds have been previously described: **2a** [10], **2b** [28], **2c** [29], **2d** [30], **2e** [9], **3e** [31], **5a** [8] and **5c** [8].

4.2. Synthesis of 1,6-enynes

Enynes **2a**–**e** were synthesized according to a previously reported protocol [28].

4.2.1. 2-(3-Methyl-but-2-enyl)-2-prop-2-ynyl-malonic acid dimethyl ester (**2a**)

Dimethyl propargylmalonate (0.40 mL, 2.6 mmol) and Cs_2CO_3 (1.26 g, 3.9 mmol) were added to a flask containing acetone (10 mL) under a stream of nitrogen. To this was added 3,3-dimethylallyl bromide (0.60 mL, 5.3 mmol), and the mixture was heated under reflux for 16 h. Filtration, and drying of the crude mix under vacuum, followed by chromatography over silica gel eluting with 6:1 petroleum ether:diethyl ether yielded the desired product. Isolated yield: 886 mg (93%).

4.2.2. 2-But-2-enyl-2-prop-2-ynyl-malonic acid dimethyl ester (**2b**)

A flask was charged with crotyl alcohol (4.25 mL, $E/Z = 9.0{:}1$) and hexachloroacetone (15 mL), and was cooled to 0 °C. Triphenylphosphine (13.6 mg) was added slowly over 30 min, and then the mixture was allowed to warm to room temperature. After 1 h, the crotyl chloride was vacuum distilled into a cold trap (2.2 g, 28%). The E/Z ratio of 9.0:1 was retained. A portion of the crotyl chloride (0.65 mL) obtained in this manner was reacted directly without further purification with dimethyl propargylmalonate (0.50 mL, 3.3 mmol) and Cs_2CO_3 (1.64 g, 5.0 mmol) in analogous fashion to that described in the synthesis of **2a**. Isolated yield: 651 mg (88%).

4.2.3. 2-(3-Phenyl-allyl)-2-prop-2-ynyl-malonic acid dimethyl ester (**2c**)

Prepared analogously to **2a** with dimethyl propargylmalonate (0.30 mL, 2.0 mmol), cinnamyl bromide (0.60 mL, 4.0 mmol), and Cs_2CO_3 (0.97 g, 3.0 mmol). Isolated yield: 560 mg (99%).

4.2.4. 2-Allyl-2-prop-2-ynyl-malonic acid dimethyl ester (**2d**)

Prepared analogously to **2a** with dimethyl propargylmalonate (0.50 mL, 3.3 mmol), allyl bromide (0.60 mL, 6.9 mmol) and Cs_2CO_3 (1.64 g, 5.0 mmol). Isolated yield: 675 mg (97%).

4.2.5. 2-(2-Methyl-allyl)-2-prop-2-ynyl-malonic acid dimethyl ester (**2e**)

Prepared analogously to **2a** with dimethyl propargylmalonate (0.50 mL, 3.3 mmol), 3-bromo-2-methyl-propene (0.67 mL, 6.6 mmol) and Cs_2CO_3 (1.64 g, 5.0 mmol). Isolated yield: 670 mg (91%).

4.3. Synthesis of isotopically labeled enynes

4.3.1. Synthesis of ^2H labeled **2a**

A flame-dried flask equipped with an addition funnel and under a nitrogen atmosphere was charged with NaH (10 mg, 0.42 mmol) and THF (10 mL). The solution was cooled to −78 °C, and **2a** (90 mg, 0.38 mmol) was added dropwise via addition funnel. The mixture was stirred for 10 min at −78 °C, and then warmed to room temperature and stirred for 90 min. Quenching was done with D_2O (3 mL) at 0 °C. The THF was removed under vacuum on a rotary-evaporator, and the aqueous solution was extracted three times with Et_2O (3 × 5 mL). The combined organic extracts were dried with $MgSO_4$. Removal of solvent under vacuum resulted in quantitative recovery of ^2H-labeled **2a**. ^1H NMR ($CDCl_3$, 400 MHz): 4.89 (t, 1H, $J = 8.0$ Hz), 3.73 (s, 6H), 2.78 (br s, 2H), 2.77 (br s, 2H), 1.69 (s, 3H), 1.65 (s, 3H). ^{13}C NMR ($CDCl_3$, 100.6 MHz): 169.5, 136.0, 115.9, 77.8 (t, $J = 7.4$ Hz), 70.0 (t, $J = 38.2$ Hz), 56.1, 51.7, 29.8, 25.1, 21.4, 17.0.

4.3.2. Synthesis of ^{13}C labeled **2a**

Each of the intermediate ^{13}C labeled species (ethyl-3,3-dimethylacrylate, 3-methyl-2-buten-1-ol, and 3,3-dimethylallylbromide) have been previously synthesized and characterized [32].

A flask equipped with an addition funnel and under a nitrogen atmosphere was charged with NaH (108 mg, 4.5 mmol) and THF (7 mL). Triethyl phosphonoacetate (997 mg, 4.4 mmol) was added dropwise by addition funnel in THF (3 mL). The resulting mixture was stirred at room temperature for 45 min, before cooling to 0 °C, at which point acetone (0.5 mL) was added dropwise by addition funnel in THF (3 mL). Subsequent to this addition, the solution was allowed to warm to room temperature and was stirred overnight. A saturated aqueous NH_4Cl solution (6 mL) was added to quench the reaction. The organic layer was separated, and the aqueous layer was extracted twice more with Et_2O (2 × 5 mL). The combined organic extracts were dried with $MgSO_4$, and purified by column chromatography over silica gel with 1:9 EtOAc/hexanes as eluent. Isolated yield of ethyl-3,3-dimethylacrylate: 473 mg (83%).

A flask equipped with an addition funnel and under a nitrogen atmosphere was charged with DIBAL (6 mL, 1 M in CH_2Cl_2) and was cooled to −78 °C. Ethyl-3,3-dimethylacrylate (327 mg 2.55 mmol) was added dropwise by addition funnel in CH_2Cl_2 (8 mL). The mixture was allowed to warm to room temperature, and was stirred overnight, at which point it was quenched with EtOAc (5 mL), and then water (5 mL). The solution was filtered through Celite, and the organic layer was separated. The aqueous portion was extracted twice more with Et_2O (2 × 5 mL), and the combined organic extracts were dried with $MgSO_4$. Isolated yield of 3-methyl-2-buten-1-ol: 200 mg (91%).

A flask was charged with 3-methyl-2-buten-1-ol (200 mg, 2.32 mmol) and CH_2Cl_2 (7.5 mL), and was cooled to 0 °C. HBr (48%, 3 mL) was added, and the mixture was vigorously stirred with the exclusion of light for 90 min. $MgSO_4$ (800 mg), and 5 mL of additional CH_2Cl_2 were then added, and the solution was warmed to room temperature. The organic portion was separated, and the aqueous portion was extracted twice more with CH_2Cl_2 (2 × 5 mL). The combined organic extracts were dried with $MgSO_4$. Isolated yield of 3,3-dimethylallylbromide was 262 mg (76%).

The ^{13}C labeled 3,3-dimethylallylbromide was then subjected to analogous conditions as was described for the preparation of **2a**. ^1H NMR ($CDCl_3$, 400 MHz): 4.86 (m, 1H), 3.70 (s, 6H), 2.75 (dd, 2H, $J_{CH} = 132.0$ Hz, $J = 8.0$ Hz), 2.73 (dd, 2H, $J = 4.0$ Hz, 3.0 Hz), 1.98 (t, 1H, $J = 3.0$ Hz), 1.66 (s, 3H), 1.62 (s, 3H). ^{13}C NMR ($CDCl_3$, 100.6 MHz): 170.4, 136.8, 117.0 (d, $J = 45$ Hz), 79.2, 57.1 (d, $J = 34$ Hz), 52.6, 30.7, 26.0 (d, $J = 5$ Hz), 22.5, 17.8.

4.4. General method for ruthenium catalyzed enyne cycloisomerization

A flame-dried flask was charged with **1** (6 mg, 0.010 mmol) under a stream of nitrogen. The appropriate amount of solvent was then added by syringe, and to this solution was added the 1,6-enyne (0.10 mmol), and then $AgSbF_6$ (7 mg, 0.020 mmol) under a stream of nitrogen. The resulting mixture was allowed to stir with the exclusion of light overnight for 16 h, at which point it was dried under vacuum. The residue was passed through a small silica plug in Et_2O in order to remove the inorganic species. Purification of the organic portion was done by column chromatography over silica gel eluting with 1:9 EtOAc:hexanes.

4.5. Spectral characterization for new products

4.5.1. 5-Isopropylidene-cyclohex-3-ene-1,1-dicarboxylic acid dimethyl ester (*4a*)

^1H NMR ($CDCl_3$, 400 MHz): 6.45 (dt, 1H, $J = 10.1$ Hz, $J = 1.8$ Hz), 5.64 (dt, 1H, $J = 10.1$ Hz, $J = 4.0$ Hz), 3.72 (s, 6H), 2.87 (br s, 2H), 2.67 (m, 2H), 1.80 (s, 3H, Me), 1.79 (s, 3H, Me). ^{13}C NMR ($CDCl_3$, 100.6 MHz): 172.2, 130.1, 126.0, 124.1, 122.9, 54.5, 53.0, 32.5, 31.4, 20.9, 20.4.

4.5.2. 5-Ethylidene-cyclohex-3-ene-1,1-dicarboxylic acid dimethyl ester (*4b*)

^1H NMR ($CDCl_3$, 400 MHz): 6.43 (dt, 1H, $J = 10.4$ Hz, $J = 2$ Hz), 5.77 (dt, 1H, $J = 10.4$ Hz, $J = 4.8$ Hz), 5.35 (q, 1H, $J = 7.2$ Hz), 3.71 (s, 6H, OMe), 2.80 (m, 2H), 2.70 (m, 2H), 1.70 (d, 3H, $J = 7.2$ Hz). ^{13}C NMR ($CDCl_3$, 125.8 MHz): 170.5, 128.8, 124.2, 122.7, 121.9, 53.0, 51.9, 36.2, 30.7, 11.8. The stereochemistry was determined by an NOE difference experiment in which irradiation of the *exo* olefinic proton resonance resulted in an NOE enhancement to the methyl protons as well as a CH_2 resonance at 2.80 ppm.

4.5.3. 3-Styryl-cyclopent-3-ene-1,1-dicarboxylic acid dimethyl ester (*3c*)

^1H NMR ($CDCl_3$, 400 MHz): 7.42 (d, 2H, $J = 7.2$ Hz), 7.33 (t, 2H, $J = 7.2$ Hz), 7.25 (d, 1H, $J = 7.2$ Hz), 6.92 (d, 1H, $J = 16.0$ Hz), 6.47 (d, 1H, $J = 16.0$ Hz), 5.72 (br s, 1H), 3.79 (s, 6H), 3.29 (br s, 2H), 3.19 (br s, 2H). ^{13}C NMR ($CDCl_3$, 125.8 MHz): 172.9, 140.1, 137.6, 130.4, 129.0, 128.0, 127.8, 126.8, 124.7, 59.3, 53.4, 41.4, 40.1.

4.5.4. ^2H-labeled *4a*

^1H NMR ($CDCl_3$, 400 MHz): 5.55 (br t, 1H), 3.64 (s, 6H), 2.77 (br s, 2H), 2.60 (m, 2H), 1.71 (s, 3H, Me), 1.70 (s, 3H, Me). ^{13}C NMR ($CDCl_3$, 100.6 MHz): 172.2, 130.0, 125.8 (t, $J = 24$ Hz), 124.1, 122.7, 54.5, 53.0, 32.5, 31.4, 20.9, 20.4.

4.5.5. ^{13}C-labeled *4a*

^1H NMR ($CDCl_3$, 400 MHz): 6.47 (m, 1H), 5.65 (m, 1H), 3.73 (s, 6H), 2.86 (m, 2H), 2.69 (dm, 2H, $J_{CH} = 131.6$ Hz), 1.80 (s, 3H, Me), 1.79 (s, 3H, Me). ^{13}C NMR ($CDCl_3$, 125.8 MHz): 171.8, 129.7, 125.7, 123.8, 122.5 (d, $J = 40$ Hz), 53.1 (d, $J = 41$ Hz), 52.6, 32.1, 31.1, 20.5, 20.0. A COSY spectrum showed coupling between the CH_2 resonance corresponding to the protons on the ^{13}C atom and the olefin resonance at 5.65 ppm. Also, an NOE difference spectrum showed contacts between these same resonances (at 2.69 and 5.65 ppm).

Appendix A. Supporting information

Selected ^{13}C and ^1H NMR of new compounds. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2006.01.009.

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