Ruthenium-Catalyzed One-Pot Double Allylation/Cycloisomerization of 1,3-Dicarbonyl Compounds Leading to *exo*-Methylenecyclopentanes

Yoshihiko Yamamoto,*[a, b] Yu-ichiro Nakagai,[a] and Kenji Itoh[a]

Abstract: The ruthenium-catalyzed one-pot double allylation/cycloisomerization of 1,3-diketones and methyl acetoacetate gave *exo*-methylenecyclopentanes in moderate to good yields with high isomer selectivity. The double allylation step effectively proceeded in the presence of a Ru^{II} precatalyst, [Cp*RuCl(cod)], in 1,2-dichloroethane at 90 °C. The subsequent cycloisomerization was carried out upon addition of triethylsilane as a hydride source without purification of a 1,6-diene intermediate. Detailed inspections of the reaction by ^{1}H NMR spectroscopy disclosed that triethylsilyl methyl ether plays an important role for the conversion of a ruthenium(IV) allyl complex formed in the double allylation step into a ruthenium(II) species required for the cycloisomerization.

Keywords: alkenes · allylation · cycloisomerization · homogeneous catalysis · ruthenium

Introduction

Transition-metal-catalyzed multicomponent coupling cyclizations are powerful methods to synthesize complex cyclic molecules from inexpensive acyclic starting materials.[1] Especially, a one-pot sequential catalytic system that promotes multiple reactions in a single pot is highly desirable, because it would reduce the amount of waste produced from the separation and purification of intermediates.[2] Toward this end, two different strategies have been developed: a *multimetallic* catalysis that uses different some catalysts effective for a specific transformation, and a *multifunctional* catalysis, in which a single metal component catalyzes some transformations. For example, Jeong and co-workers reported that the Pd^0-catalyzed allylic substitution giving rise to enyne intermediates followed by the Rh^I-catalyzed Pauson–Khand reaction effectively afforded bicycloalkenones.[3] Such a bimetallic system is successful only when one of the two catalysts never interferes with the other one. Accordingly, a correct choice of the catalyst combination plays a critical role in the *multimetallic* catalysis. On the other hand, Evans and Robinson found that a similar one-pot annulation of bicycloalkenones was accomplished using only a single Rh^I precatalyst which proved to be effective for both allylic substitution and the Pauson–Khand reaction.[4] From the viewpoint of metal-atom economy,[5] this type of *multifunctional* catalysis is advantageous compared with the *multimetallic* systems, although they are still confined to a limited number of examples.[6]

To extend the scope of the *multifunctional* catalysis, we carried out our study on the ruthenium-catalyzed one-pot synthesis of *exo*-methylenecyclopentanes by means of sequential double allylation of 1,3-dicarbonyl compounds and cycloisomerization of 1,6-dienes. Catalytic cycloisomerization is a highly atom-economical method to convert 1,6-diene precursors into cyclopentane products without additional reagents except for an appropriate catalyst.[7,8] In turn, some 1,6-dienes can be obtained by catalytic double allylation of suitable 1,3-dicarbonyl compounds. Therefore, a new efficient protocol to construct a synthetically useful cyclopentane framework could be realized by combining these two catalytic transformations into a one-pot sequential process (Figure 1). Among a wide variety of transition-metal elements effective for cycloisomerization and/or allylic substitution, we chose ruthenium because we have already found and reported that the ruthenium(II)-catalyzed cycloisomeri-

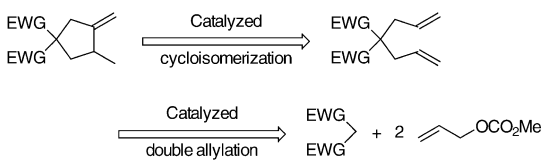

Figure 1. Retrosynthesis of *exo*-methylenecyclopentanes.

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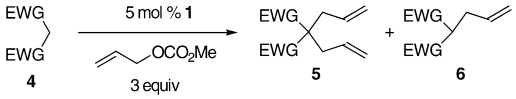
zation is quite tolerant for a wide range of functional groups and selectively produces *exo*-methylene isomers.[9] Although ruthenium-catalyzed allylations of 1,3-dicarbonyl compounds have been also reported,[10] re-optimization of the reaction conditions was required to selectively obtain doubly allylated products rather than monoallylation counterparts. In addition, we had to elaborate an efficient method to convert an allylruthenium complex which is formed by the first allylation step into a ruthenium(hydride) species active toward the second cycloisomerization. Herein, we wish to report on our endeavor to realize the one-pot double allylation/cycloisomerization leading to the *exo*-methylenecyclopentane derivatives by means of the ruthenium catalysis.

Table 1. Ru-catalyzed allylation of **4a** and **4b**.



Run	EWG	Solvent	T [°C]	t [h]	**5**/**6**[a]	**5**	Yield [%]
1	CO_2Me	NMP	90	6	99/1	**5a**	83
2	CO_2Me	DCE	90	24	13/87	–	
3	CO_2Me	neat	90	24	34/66	–	
4	CO_2Me	THF	70	24	6/94[b]	–	
5[c]	COMe	DCE	90	6	95/5	**5b**	89

[a] Determined by GC. [b] 46% conversion. [c] 10 mol% **1** was used.

Table 1 summarizes the results of the ruthenium-catalyzed allylation of 1,3-dicarbonyl substrates. In accordance with previous reports,[10b,12] dimethyl malonate **4a** underwent allylation in the presence of NMP and 5 mol% **1** to give rise to the desired diallylmalonate **5a** almost exclusively in 83% isolated yield (run 1). However, the strongly coordinated solvent such as NMP even in a trace amount might have a deteriorative effect on the next cycloisomerization step (see below). With this in mind, further examinations were carried out with respect to the solvent. In 1,2-dichloroethane (DCE), **4a** was completely consumed within 24 h at the same temperature, but monoallylated **6a** was the major product (run 2). The ratio of **5a** over **6a** was slightly increased without solvent (run 3). The reaction in refluxing THF resulted in a low conversion of 46%, probably due to lower reaction temperature (run 4). In contrast to **4a**, acetylacetone **4b** possessing more acidic methylene protons efficiently underwent allylation even without NMP (run 5). In the presence of 10 mol% **1**, **4b** was completely consumed at 90°C for 6 h to afford the desired doubly allylated product **5b** in 89% isolated yield.

Results and Discussion

Ruthenium-catalyzed double allylation of 1,3-dicarbonyl compounds: Previously, the efficient double allylation of acetylacetone with allyl methyl carbonate was achieved using [Ru(cod)(cot)] (cod = 1,5-cyclooctadiene, cot = 1,3,5-cyclooctatriene) as a precatalyst.[10b] The allylation proceeded at 50°C in the presence of *N*-methylpiperidine (NMP) and 4 mol% of the precatalyst to selectively afford a doubly allylated product in high yield. Later, a π-allylruthenium complex **2b** relevant to catalytic allylation was synthesized from [Cp*RuCl(cod)] (**1**) (Cp* = pentamethylcyclopentadienyl)[11] and cinnamyl chloride (Figure 2).[12] The isolated **2b** was treated with excess acetylacetone at room temperature in the presence of COD and NMP to produce a monoallylated product as a single regioisomer in high yield.[12] Moreover, **1** also proved to be effective for the catalytic allylation of piperidine with allyl carbonates. On the basis of these reports, we decided to use **1** as a precatalyst for the double allylation, because the same complex also effective for the catalytic cycloisomerization of dimethyl diallylmalonate in refluxing *i*PrOH, and, thus, the anticipated one-pot sequential procedure would be realized, if the allylruthenium complex formed in the first step could be converted into a hydride active species as generated from **1** in refluxing *i*PrOH.

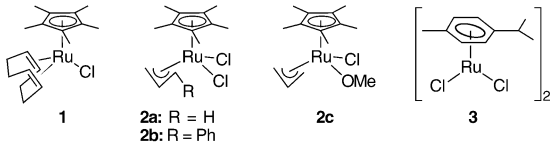
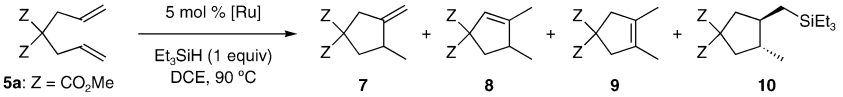


Figure 2. Ruthenium complexes relevant to this work.

Ruthenium-catalyzed cycloisomerization of 1,6-dienes using hydrosilane as hydride source: With the ruthenium-catalyzed double allylation of the 1,3-dicarbonyl substrates **4a** and **4b** secured, we then explored the cycloisomerization of the 1,6-dienes using the allyl complex **2a**[13] as a catalyst precursor. According to our previously reported protocol,[9] the diene **5a** was heated in refluxing *i*PrOH containing 5 mol% **2a** for 24 h. No reaction, however, took place and **5a** was recovered. This is in sharp contrast to the reaction using **1** giving rise to the desired *exo*-methylenecyclopentane **7a** in high yield under similar reaction conditions.[9] This incompatibility of *i*PrOH toward **2a** as a hydride source forced us to search for an alternative hydride donor. Recently, Widenhoefer et al. reported the novel cycloisomerization protocol utilizing the combination of a cationic π-allylpalladium complex and a hydrosilane.[14] With its relevance to our catalytic system in mind, hydrosilanes were examined as hydride donors. As summarized in Table 2, the combinations of several ruthenium complexes and triethylsilane were examined with respect to the cycloisomerization of **5a**. Heating of a DCE solution containing **5a**, 5 mol% **1**, and 1 equiv triethylsilane at 90°C for 10 h afforded a mixture of several cycliza-

Table 2. Ru-catalyzed cyclization of **5a** using Et_3SiH.



Run	[Ru]	t [h]	Product ratio [%][a]			
			7	**8**	**9**	**10**
1	**1**	10	69.6	23.1	–	7.3
2	**1**	24	48.4	40.3	–	11.3
3	**3**	17	20.5	36.3	19.5	23.7
4	**2a**	24	52.5	42.7	–	4.8
5	**2a**	14[b]	89.7	6.2	–	4.1

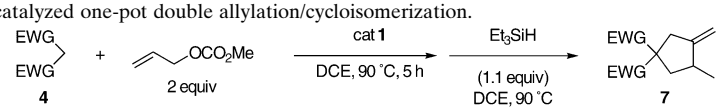
[a] Determined by GC analysis of crude product. [b] Triethylsilane (1 equiv) was added in eight portions at 2 h intervals.

tion products (run 1). The GC analysis of the crude reaction mixture revealed that the desired *exo*-methylenecyclopentane **7a** was the major product. Together with **7a**, a cyclopentene **8a** and a silylative cyclization product **10a**[15] were also detected by GC and ^{1}H NMR analyses. Prolonged reaction time of 24 h increased the amount of **8a** (run 2). This observation indicated that **8a** was formed via the isomerization of **7a** under the reaction conditions.[9] A dimeric arene complex **3**, $[\{RuCl_2(p\text{-cymene})\}_2]$,[16] exhibited a higher cyclization activity, but the product selectivity was lower than **1a** (run 4).[17] Other ruthenium complexes, [Ru(cod)(cot)][18] and $[(Cp^*RuCl_2)_2]$,[11] were less effective than the above precatalysts, and a phosphine complex, $[RuCl_2(PPh_3)_3]$,[19] was totally ineffective. With respect to hydrosilanes, an arylsilane, $PhMe_2SiH$, and an alkoxysilane, $(MeO)_3SiH$, were less effective than Et_3SiH.

Encouraged by these results, we further examined the catalytic activity of the π-allyl complex **2a** in the presence of the hydrosilane. The treatment of **5a** with 5 mol % **2a** and 1 equiv Et_3SiH at 90 °C in DCE gave rise to a nearly equal amount of **7a** and its isomer **8a** (Table 2, run 4). The controlled addition of the silane (1 equiv in eight portions at 2 h interval) improved the isomer selectivity up to around 90 % (run 5). Purification by silica gel chromatography afforded the desired *exo*-methylenecyclopentane **7a** in 75 % yield with 89 % isomeric purity. However, the reaction was completely suppressed in the presence of NMP as anticipated above.

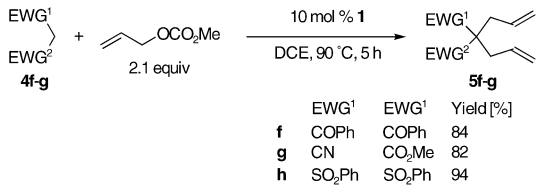
One-pot double allylation/cycloisomerization: Finally, the one-pot double allylation/cycloisomerization of some 1,3-dicarbonyl compounds was explored as summarized in Table 3. As a typical substrate, acetylacetone **4b** was first employed, because the double allylation of a 1,3-diester such as **4a** required a strongly coordinating solvent NMP, which would poison the catalyst in the second cycloisomerization step. Thus, **4b** was treated with 2 equiv allyl methyl carbonate in the presence of 10 mol % **1** in refluxing DCE for 5 h. Subsequently, 1.1 equiv triethylsilane was slowly added to the refluxing solution by syringe pump during 12 h, and additional refluxing for 8 h to give the desired *exo*-methylenecyclopentane **7b** in 67 % overall isolated yield with 94 % isomeric purity (run 1). In the same manner, cyclic 1,3-diketones, cyclohexane-1,3-dione **4c** and indane-1,3-dione **4d**, were subjected to the one-pot sequential reaction to furnish the corresponding spirocyclic products **7c** and **7d** in 76 and 47 % respective yields with excellent isomeric purity (runs 3 and 5). In addition to these 1,3-diketones, a 1,3-ketoester, methyl acetoacetate **4e**, also underwent the sequential reaction to give the expected cyclopentane as a 1:1 diastereomer mixture in 71 % yield (run 7). In contrast, dimethyl malonate (**4a**), 1,3-diphenylpropane-1,3-dione (**4f**), methyl cyanoacetate (**4g**), and bis(phenylsulfonyl)methane (**4h**) failed to undergo one-pot cyclization under the same reaction conditions. As mentioned above, **4a** is incompatible with the double allylation step without NMP, while other substrates **4f–h** gave doubly allylated products **5f–h** under the modified NMP-free conditions (Scheme 1). These facts show that **5f–h** were incompatible substrates for the present cycloisomerization protocol using triethylsilane as a hydride source. This is in contrast to the previously reported catalyst system,

Table 3. Ru-catalyzed one-pot double allylation/cycloisomerization.



Run	**4**	Method[a]	2nd step t [h]	**7**	Yield[b] [%]	Purity[c] [%]
1		A	20		67	94
2	**4b**	B	20	**7b**	75	89
3		A	20		76	99
4	**4c**	B	40	**7c**	60	99
5		A	20		47	99
6	**4d**	B	40	**7d**	57	93
7		A	20		71	90
8	**4e**	B	20	**7e**[d]	83	90

[a] Methods: A, 10 mol % **1** was used. B, 5 mol % **1** was used and each 20 mol % of Et_3SiH and COD were added in the 2nd step. [b] Overall isolated yield. [c] Determined by GC analysis of the isolated products. [d] 1:1 Diastereomeric mixture.

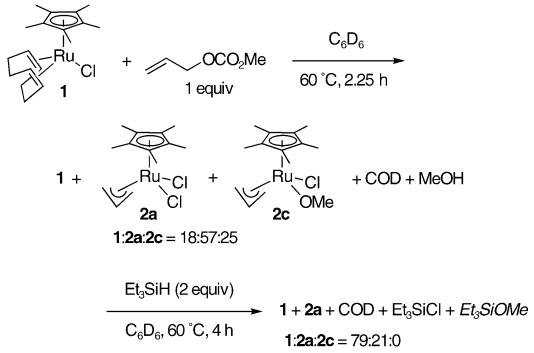


	EWG^1	EWG^1	Yield [%]
f	COPh	COPh	84
g	CN	CO_2Me	82
h	SO_2Ph	SO_2Ph	94

Scheme 1. Double allylation of active methylene compounds.

[{$RuCl_2$(cod)}$_n$]/*i*PrOH, converted **5g** and **5h** into the desired *exo*-methylenecyclopentanes without difficulty.[9]

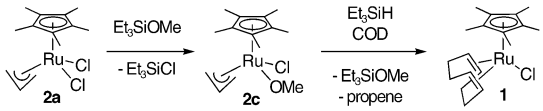
Influence of additives on one-pot process: To improve the efficiency of the present one-pot process, we carried out the careful inspections of the stoichiometric reaction of the precatalyst **1** with the allyl carbonate using ^{1}H NMR (500 MHz, C_6D_6) (Scheme 2, Figure 3). At the outset, **1** was treated



Scheme 2. Reaction of **1** with allyl methyl carbonate and Et_3SiH.

with 1 equiv allyl methyl carbonate in dry degassed C_6D_6 and the reaction mixture was heated at 60 °C. As the singlet peak corresponding to the Cp* ligand of **1** at δ 1.31 ppm decreased, two new singlet peaks appeared at δ 1.11 and 1.05 ppm and gradually increased. The former can be easily assigned to the Cp* ligand of the known π-ally complex **2a**. The latter was tentatively assigned to a methoxo complex **2c**, which was expected to be formed directly from **1** and allyl methyl carbonate, because the Cp* signal (δ 1.05 (s, 15H)) was observed together with absorptions due to the π-allyl ligand (δ 4.18–4.23 (m, 1H), 3.63 (d, J = 6.5 Hz, 2H), and 1.60 (dd, J = 11.5, 1.5 Hz, 2H)). However, the signal for the methoxo ligand cannot be differentiated from that of the concomitantly formed methoxide at δ 3.04 ppm (brs). After heating for 2.25 h, the ratio of **1**:**2a**:**2c** became 18:57:25. To this solution, 2 equiv Et_3SiH was added and the reaction mixture was further heated at 60 °C. Consequently, the amount of **1** was gradually increased, while the consumption of **2a** and **2c** was observed as shown in Figure 3. These observations show that the Ru^{IV} π-allyl complexes **2a** and **2c** were reduced by the hydrosilane to regenerate a [Cp*Ru^{II}Cl] fragment, which was further trapped with coexistent COD to give rise to **1**. It is noteworthy that the immediate decrease of the methoxo complex **2c** after the addition of Et_3SiH was followed by the slow conversion of the dichloro complex **2a**. The ^{1}H NMR spectra also showed the formation of Et_3SiCl and *Et_3SiOMe*.

In striking contrast to the above results, **1** was never restored from the *isolated* **2a** and COD upon treatment with Et_3SiH under similar conditions. After examining the influence of some by-products, we found that the *isolated* **2a** was converted into **1** albeit with 25% conversion in the presence of each 1 equiv Et_3SiH, COD, and *Et_3SiOMe* in dry degassed C_6D_6 at 80 °C for 7 h. On the contrary, the reduction of **2a** failed completely when MeOH or NaOMe was added in place of Et_3SiOMe. Although the exact role of Et_3SiOMe is not clear in this stage, we assumed that Et_3SiOMe is required to convert **2a** into **2c**, that is, in turn, reduced by Et_3SiH to give rise to **1** as depicted in Scheme 3.



Scheme 3. Transformation of **2a** into **1** via **2c**.

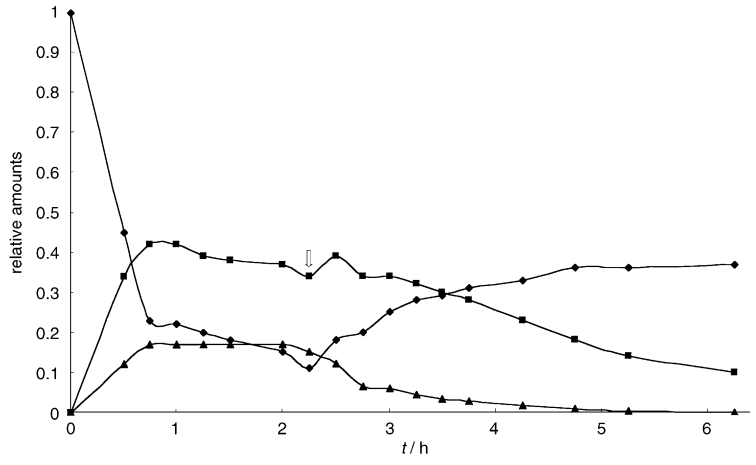


Figure 3. Time course of conversions of **1** (◆), **2a** (■), and **2c** (▲); the arrow indicates where Et_3SiH (2 equiv) was added.

On the basis of these results, the one-pot procedure was modified by employing each 20 mol% COD and Et_3SiOMe as additives at the cycloisomerization step (method B in Table 3). As a consequence, the *exo*-methylenecyclopentanes **7b**–**e** were obtained in similar or higher yields even with less amounts of catalyst loading (runs 2, 4, 6, and 8).

Reaction mechanisms: Figure 4 outlines the plausible mechanisms of the present one-pot double allylation/cycloisomerization. In the allylation step, the coordinatively unsaturated

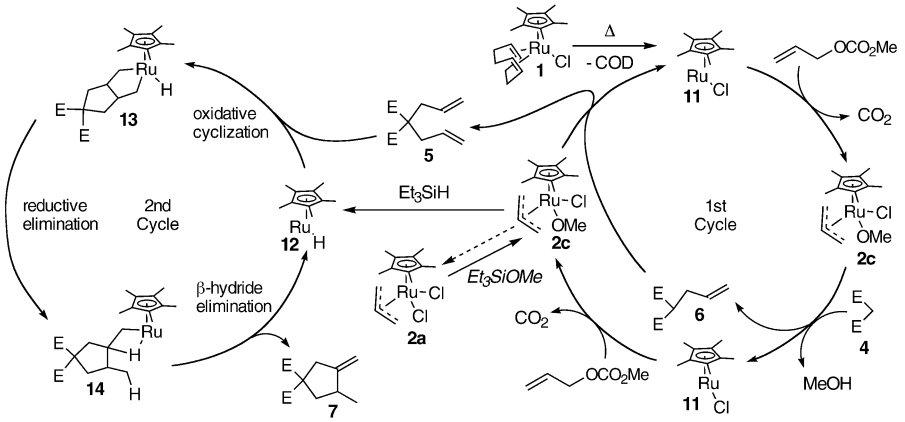


Figure 4. Possible mechanism for one-pot double allylation/cycloisomerization.

[Cp*Ru^{II}Cl] fragment **11** reacted with allyl methyl carbonate to initially generate the [Cp*Ru^{IV}(allyl)(methoxo)] complex **2c**, which reacted with an active methylene compound to give allylated products **5** and **6**. Under the reaction conditions, the dichloro complex **2a** was also formed probably from **2c**, although the mechanism of the formation is unclear. Upon addition of Et_3SiH, **2c** is considered to give rise to a Ru^{II}-hydrido complex **12** via **11**, whereas the (hydrido)ruthenium species could not be detected by ^{1}H NMR spectroscopy. On the contrary, **2a** proved to be inert toward Et_3SiH, but in the presence of Et_3SiOMe, **2a** was indirectly reduced to give **11** via **2c**.

Extensive mechanistic studies disclosed that the Pd-catalyzed cycloisomerizations of 1,6-dienes proceeds via sequential insertion/β-hydride elimination mechanism.[14b,20] On the other hand, we and others believe that the oxidative cyclization/β-hydride elimination/reductive elimination sequence is involved in the Ru-catalyzed cycloisomerization as shown in Figure 4.[9,21] Strongly coordinating molecules such as NMP and PPh_3 are considered to prevent the oxidative cyclization key step in the cycloisomerization cycle.

Conclusion

In summary, we successfully developed the novel protocol to synthesize *exo*-methylenecyclopentanes from 1,3-diketones and a ketoester by means of the ruthenium-catalyzed one-pot double allylation/cycloisomerization. A pentamethylcyclopentadienyl complex, [Cp*RuCl(cod)], proved to be an appropriate precatalyst for double allylation of active methylene compounds using allyl methyl carbonate without NMP. The subsequent cycloisomerization also effectively proceeded in the presence of triethylsilane as a hydride source, although the substrate was confined to the 1,3-diketones and the ketoester. The detailed inspection of the reaction conditions disclosed that Et_3SiOMe plays an important role for the regeneration of [Cp*Ru^{II}Cl] fragment from Ru^{IV} π-allyl species formed in the first allylation step.

Experimental Section

General: ^{1}H and ^{13}C NMR spectra were measured on a Varian Mercury 300 or a Varian Inova 500 NMR spectrometer as $CDCl_3$ or C_6D_6 solutions. Chemical shifts (δ) are given in ppm relative to $CDCl_3$ or C_6D_6, and coupling constants (J) in Hz. Mass spectra were recorded on a JEOL JMS-AX 505 HA mass spectrometer. Elemental analyses were performed at the Microanalytical Center of Kyoto University. Melting points were obtained by a Büchi Melting Point B-540 apparatus and are uncorrected. Flash chromatography was performed with a silica gel column (Merck silica gel 60) eluted with solvents [hexane/AcOEt]. THF and 1,2-dichloroethane were dried over CaH_2 and Na/benzophenone, respectively, and distilled. [Cp*RuCl(cod)] (**1**),[11] [(Cp*RuCl)$_2$],[11] [Cp*RuCl$_2$(η-allyl)] (**2a**),[13] [{RuCl$_2$(*p*-cymene)}$_2$],[16] [Ru(cod)(cot)],[18] and [RuCl$_2$(PPh$_3$)$_3$][19] were prepared according to the literature procedures. 1,6-Dienes and *exo*-methylenecyclopentanes **7a**–**c**, **e** are known compounds.[9]

Representative procedure for [Cp*RuCl(cod)]-catalyzed double allylations—Synthesis of 1,6-diene 5b from acetylacetone 4b and allyl methyl carbonate: A solution of acetylacetone (**4b**) (101 mg, 1.0 mmol), allyl methyl carbonate (239 mg, 2.1 mmol) and [Cp*RuCl(cod)] **1** (37.9 mg, 0.1 mmol) in dry 1,2-dichloroethane (0.6 mL) was degassed and heated at 90 °C for 5 h under Ar atmosphere. The solvent was evaporated and the crude product was purified by silica gel flash column chromatography (hexane/AcOEt 10:1) to give a 1,6-diene **5b** (161 mg, 89 %) as colorless oil.

Representative procedure for Ru-catalyzed cycloisomerization using hydrosilane—Synthesis of *exo*-methylenecyclopentane 7a from 1,6-diene 5a: A solution of 1,6-diene (**5a**) (219 mg, 1.0 mmol) and [Cp*RuCl$_2$(allyl)] (**2a**) (15.6 mg, 0.05 mmol) in dry 1,2-dichloroethane (2 mL) was degassed and heated at 90 °C under Ar atmosphere. To this solution, triethylsilane (116 mg, 1.0 mmol) was added in eight portions at 2 h interval. The solvent was evaporated and the crude product was purified by silica gel flash column chromatography (hexane/AcOEt 30:1) to give an *exo*-methylenecyclopentane **7a** (164 mg, 75 %) as colorless oil.

Representative procedure for one-pot double allylation/cycloisomerization—Synthesis of *exo*-methylenecyclopentane 7b from acetylacetone 4b: A solution of acetylacetone (**4b**) (101 mg, 1.0 mmol), methyl allyl carbonate (248 mg, 2.0 mmol) and [Cp*RuCl(cod)] (**1a**) (19 mg, 0.05 mmol) in dry 1,2-dichloroethane (0.6 mL) was degassed and stirred at 90 °C under Ar for 5 h. After addition of 1,5-cyclooctadiene (61 μL, 0.50 mmol) and Et_3SiOMe (36 μL, 0.20 mmol), a solution of Et_3SiH (160 μL, 1 mmol) in dry degassed 1,2-dichloroethane (0.8 mL) was added to the refluxing reaction mixture over 12 h by syringe pump. The reaction mixture was stirred at 90 °C for an additional 8 h. The solvent was then evaporated and the crude product was purified by silica gel flash column chromatography (hexane/AcOEt 40:1) to give an *exo*-methylenecyclopentane **7b** (136 mg, 75 %) as colorless oil. Analytical data for **7b** has been reported in ref. [7g].

Analytical data for 7d: m.p. 73–75 °C; IR ($CHCl_3$): $\tilde{\nu}$ = 1706, 1598 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 1.17 (d, J = 6.6 Hz, 3H), 1.72 (dd, J = 12.6, 11.4 Hz, 1H), 2.10 (dd, J = 12.6, 7.8 Hz, 1H), 2.70 (dq, J = 16.5, 1.2 Hz, 1H), 2.76 (dq, J = 16.5, 2.1 Hz, 1H), 3.04 (m, 1H), 4.89 (dd, J = 4.5, 2.4 Hz, 1H), 4.94 (dd, J = 4.5, 2.4 Hz, 1H), 7.81–7.87 (m, 2H), 7.93–7.99 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 17.47, 38.51, 39.70, 42.95, 57.81, 105.23, 123.18, 123.39, 135.47, 135.59, 140.98, 141.38, 153.88, 203.19, 203.71; MS (FAB): m/z (%): 227 (40) [M+H$^+$], 147 (100); elemental analysis calcd (%) for $C_{15}H_{14}O_2$ (226.27): C 79.62, H 6.24; found: C 79.54, H 6.32.

Stoichiometric reaction of [Cp*RuCl(cod)] (1) with allyl methyl carbonate and Et_3SiH: In a standard NMR tube, a dry degassed C_6D_6 solution

of [Cp*RuCl(cod)] (1.9 mg, 0.005 mmol), allyl methyl carbonate (0.57 μL, 0.005 mmol), and $(Me_3Si)_2O$ (1.06 μL, 0.005 mmol) as a internal standard was heated at 60 °C. After heating for 2.25 h, Et_3SiH (1.6 μL, 0.01 mmol) was added to the solution and continued heating at 60 °C. The progress of the reaction was monitored by ^1H NMR (500 MHz).

Spectral data: ^1H NMR (500 MHz, C_6D_6, 25 °C): [**1**] δ = 1.31 (s, 15H), 1.76–1.79 (m, 4H), 1.86–1.88 (m, 2H), 2.92–2.95 (m, 2H), 3.73–3.75 (m, 2H), 3.96–4.20 (m, 2H); [**2a**] δ = 1.11 (s, 15H), 1.81 (d, J = 10 Hz, 2H), 4.00 (d, J = 5.5 Hz, 2H), 5.26–5.32 (m, 1H); [**2c** (tentative)] δ = 1.05 (s, 15H), 1.60 (dd, J = 11.5, 1.5 Hz, 2H), 3.63 (d, J = 6.5 Hz, 2H), 4.18–4.32 (m, 1H) (methoxo peak obscured).

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