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Ruthenium- and Rhodium-Catalyzed Ring-Opening Coupling Reactions of Cyclopropenones with Alkenes or Alkynes

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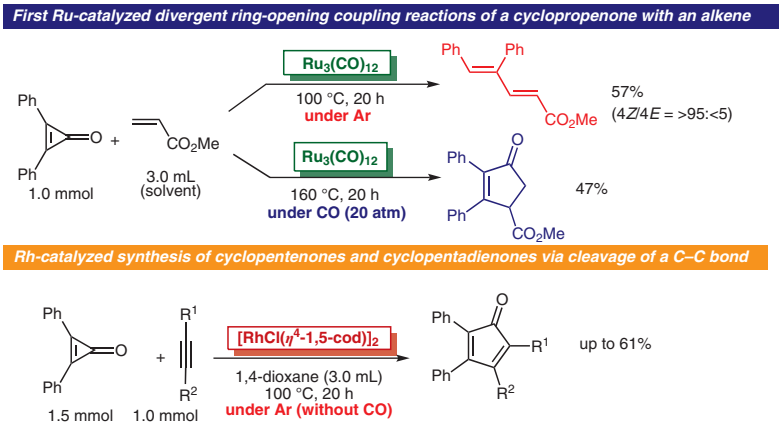

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Abstract $Ru_3(CO)_{12}$-catalyzed divergent ring-opening coupling reactions of a cyclopropenone with methyl acrylate (an electron-deficient alkene) are developed. Under an argon atmosphere, a decarbonylative linear codimer is obtained, while cyclopentenones are obtained under carbon monoxide (20 atm) without decarbonylation. While ruthenium complexes show no catalytic activity for the ring-opening cocyclization of cyclopropenones with ethylene (20 atm) or bicyclo[2.2.1]hept-2-ene (2-norbornene), rhodium complexes, especially $[RhCl(\eta^4\text{-}1,5\text{-cod})]_2$, show high catalytic activity for the desired cocyclization reactions to give the corresponding cyclopentenones in high yields and selectivities. In addition, $[RhCl(\eta^4\text{-}1,5\text{-cod})]_2$ realizes the catalytic ring-opening cocyclization of cyclopropenones with internal alkynes to give the corresponding cyclopentadienones. In all these reactions, ruthena- or rhodacyclobutenones are considered to be key intermediates, generated by strain-driven oxidative addition of a cyclopropenone C–C bond to an active ruthenium or rhodium species.

Key words C–C bond cleavage, cyclopropenone, ruthenium, rhodium, cyclopentenone, cyclopentadienone, metallacyclic intermediate

The development of catalytic cleavage of a C–C bond under mild reaction conditions is one of the most important, attractive, and challenging subjects in atom-economical organic, organometallic, and industrial chemistry, because novel functional organic molecules that cannot be obtained by the simple combination of traditional synthetic methods can be synthesized in one step. Over the last three decades, there have been significant advances in homogeneous transition-metal-complex-catalyzed cleavage and reconstruction of the C–C bond for the synthesis of fine chemicals.[1,2]

In particular, C–C bond cleavage of strained cyclic molecules is considerably facilitated by the release of ring-strain through metal insertion.[3] Ito and Murakami reported the first C–C bond cleavage of cyclobutanones with a Rh(I) catalyst in 1994.[4] Murakami and co-workers then developed a series of Rh(I)- as well as Pd(0)- and Ni(0)-catalyzed reactions cleaving a C–C bond in cyclobutanones, involving the intramolecular interception of metallacyclopentanone intermediates by tethered C–C unsaturated bonds.[5,6] More recently, Cramer reported the regiodivergent ring-opening of 3-(2-alkanoylphenyl)cyclobutanones by the appropriate choice of Lewis acid catalysts, $Cu(OTf)_2$ or $SnCl_4$, to give the corresponding indenylacetic acids and benzoxabicyclo[3.2.1]octane-3-ones in high yields, respectively.[7] Uemura and Nishimura reported a similar palladium-catalyzed β-carbon elimination[8] from *tert*-cyclobutanols. An enantioselective version of this process was also developed by Nishimura[9] and Cramer,[10] independently.

We have already developed a series of ruthenium- and rhodium-catalyzed strain-driven reactions cleaving a C–C bond in cyclopropenones,[11a,12] cyclobutenones,[11b,c] cyclobutenediones,[11d] and bicyclo[2.2.1]hepta-2,5-diene (2,5-norbornadiene),[11e] followed by the reconstruction of novel and valuable functional organic molecules. As a continuation of our study on the catalytic cleavage of a C–C bond in cyclopropenones, we succeeded in developing novel ruthenium- and rhodium-catalyzed ring-opening coupling reactions of cyclopropenones with alkenes or alkynes through the formation of ruthena- or rhodacyclic intermediates.

First, the reaction of 2,3-diphenylcycloprop-2-en-1-one (**1**) with methyl acrylate (**2**) (solvent) was examined in the presence of a catalytic amount of $Ru_3(CO)_{12}$ at 100 °C for 20 hours under an argon atmosphere to give the decarbonylated linear codimer, methyl (2*E*,4*Z*)-4,5-diphenylpenta-2,4-dienoate (**3**), in 57% yield with high stereoselectivity (4*Z*/4*E* = >95:<5) (the upper reaction in Scheme 1).

In sharp contrast, the same reaction of **1** with **2** gave a single regioisomeric cyclopentenone, methyl 4-oxo-2,3-diphenylcyclopent-2-ene-1-carboxylate (**4**), in 47% yield when the reaction was carried out with the same $Ru_3(CO)_{12}$ catalyst in toluene at 160 °C for 20 hours under carbon

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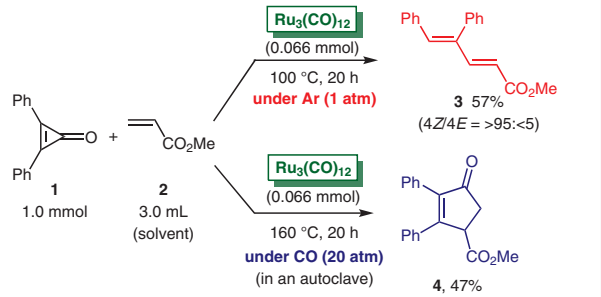
monoxide (20 atm) (the lower reaction in Scheme 1). External carbon monoxide could suppress the decarbonylation of **1** to 1,2-diphenylethyne and serve as an effective π-acidic ligand to promote reductive elimination to give **4**.[13]



Scheme 1 $Ru_3(CO)_{12}$-catalyzed divergent ring-opening coupling reactions of 2,3-diphenylcycloprop-2-en-1-one (**1**) with methyl acrylate (**2**)

The present $Ru_3(CO)_{12}$-catalyzed divergent reactions can be explained by assuming the same ruthenacyclobutenone intermediate, generated by the oxidative addition of cyclopropenone **1** to an active ruthenium species (Scheme 2).[14] Subsequent insertion of an electron-deficient alkene **2** occurred to give two regioisomeric ruthenacyclohexenone intermediates depending on the reaction conditions.[15] Under an argon atmosphere, the usual insertion of **2** would occur to give a ruthenacyclohexenone bearing a methoxycarbonyl group at an α-position with respect to ruthenium. Decarbonylation of the ruthenacyclohexenone proceeded predominantly prior to reductive elimination, followed by β-hydrogen elimination/reductive elimination to give a linear codimer **3**. In sharp contrast, under carbon monoxide (20 atm), the regioisomeric ruthenacyclohexenone bearing a methoxycarbonyl group at a β-position with respect to ruthenium formed, and subsequent reductive elimination gives an unusual cyclopentenone **4** without decarbonylation. The structure of **4** was confirmed by single-crystal X-ray structure determination (Figure 1).

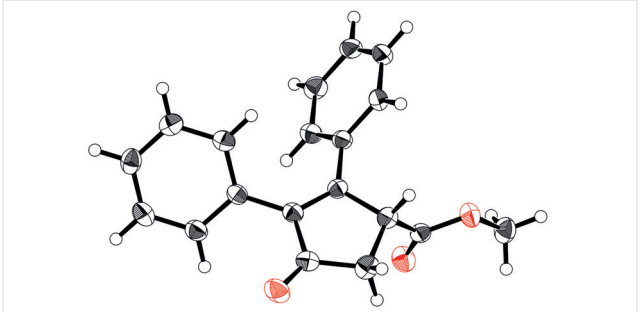
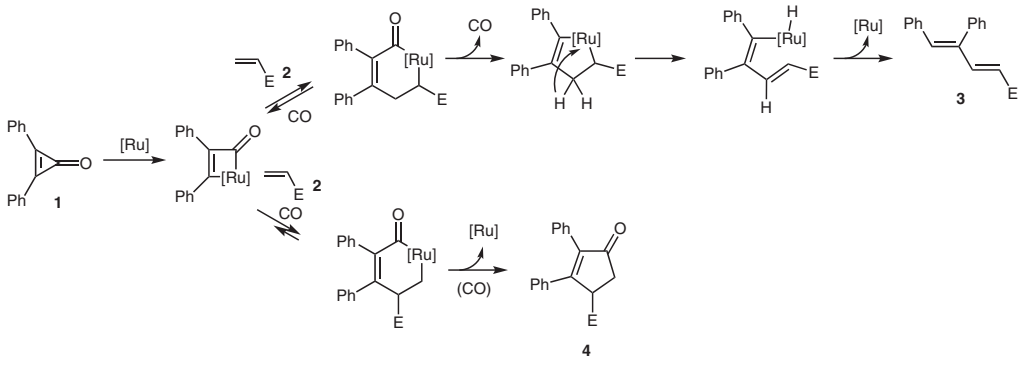


Figure 1 X-ray crystal structure of compound **4** (CCDC 1826244)

It is well known that an electron-withdrawing group at an α-position to a metal stabilizes many metallacycles, and the insertion of methyl acrylate (**2**) into a ruthenacyclobutenone stabilized by a phenyl group may occur to give two regioisomeric ruthenacyclohexenones. Under carbon monoxide, replacement of the strongly coordinated carbon monoxide ligand is required, and an alkene **2** should coordinate and insert into a ruthenacyclobutenone in a less-hindered direction to give another regioisomeric ruthenacyclohexanone, which gives an unusual cyclopentenone **4** with high selectivity in place of methyl 2-oxo-3,4-diphenylcyclopent-3-ene-1-carboxylate (**4′**).

To obtain other cyclopentenones, **1** was treated with a catalytic amount of several ruthenium complexes in 1,4-dioxane at 100 °C for 20 hours under ethylene (**5**) (40 atm). However, no reaction occurred with ruthenium catalysts such as $Ru_3(CO)_{12}$, Ru(η⁴-1,5-cod)(η⁶-1,3,5-cot) [1,3,5-cyclooctatriene], and $[RuCl_2(CO)_3]_2$.

Next, the catalytic activities of several rhodium complexes were investigated. As a result, $[RhCl(\eta^4\text{-}1,5\text{-cod})]_2$ (1,5-cod = 1,5-cyclooctadiene) showed the highest catalytic activity giving 2,3-diphenylcyclopent-2-en-1-one (**6**) in 82% yield (Scheme 3, a); $[RhCl(CO)_2]_2$: 25%, $[RhCl(\eta^2\text{-}C_2H_4)_2]_2$: 44%, $[RhCl(\eta^4\text{-}2,5\text{-norbornadiene})]_2$: 31%. Bicyclo[2.2.1]hept-2-ene (2-norbornene) (**7**) could also be used in the present reaction to give a tricyclic cyclopentenone,



Scheme 2 A possible mechanism

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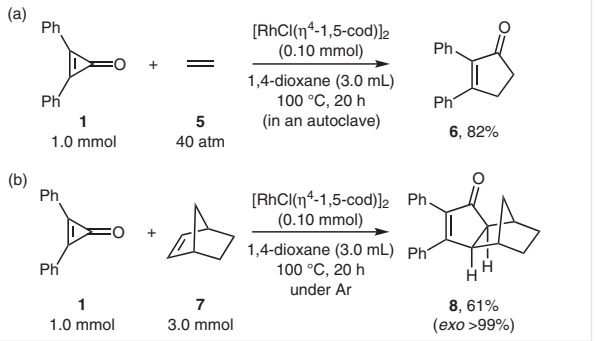
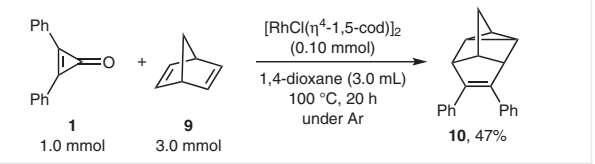


Scheme 3 [RhCl(η⁴-1,5-cod)]$_2$-catalyzed synthesis of cyclopentenones

exo-2,3-diphenyl-3a,4,5,6,7,7a-hexahydro-1*H*-4,7-methanoinden-1-one (**8**), in 61% yield with high *exo* selectivity (>99%) (Scheme 3, b). However, the reaction of **1** with bicyclo[2.2.1]hepta-2,5-diene (2,5-norbornadiene) (**9**) gave 5,6-diphenyl-1,2,3,3a,4,6a-hexahydro-1,2,4-(epimethanetriyl)pentalene (**10**) in 47% yield in place of the desired tricyclic cyclopentenone **10′**; compound **10** was obtained by a formal cycloaddition reaction of 1,4-diene **9** with 1,2-diphenylethyne derived from the decarbonylation of **1** (Scheme 4).



Scheme 4 The reaction of **1** with bicyclo[2.2.1]hepta-2,5-diene (2,5-norbornadiene) (**9**)

To optimize the reaction conditions for the synthesis of **6**, the effect of the solvent was examined: the present reaction proceeded smoothly in toluene (**6**, 85%), THF (**6**, 83%), 1,4-dioxane (**6**, 82%), and *N*,*N*-dimethylacetamide (**6**, 67%). Among the solvents examined, acetonitrile gave the best results, and **6** was obtained in 92% yield. However, triethylamine (**6**, 17% yield) and pyridine (**6**, trace) were unsuitable solvents, probably due to their high ability to coordinate to an active rhodium species.

The effects of both the ethylene pressure and the reaction temperature were examined in acetonitrile, and the results are shown in Figure 2. Product **6** was obtained in over 90% yield under an ethylene pressure over 40 atmospheres at a reaction temperature from 60 to 100 °C. Consequently, **6** was obtained in the best yield of 94% by the [RhCl(η⁴-1,5-cod)]$_2$-catalyzed ring-opening coupling reaction of **1** with **5** (50 atm) in acetonitrile at 100 °C for 20 hours. In addition, **6** was not obtained from the reaction of 1,2-diphenylethyne, ethylene, and carbon monoxide (40 atm) with [RhCl(η⁴-1,5-cod)]$_2$ catalyst under the above reaction conditions. This result clearly suggests that the successful formation of rhodacyclobutenones requires the use of cyclopropenones as starting materials.

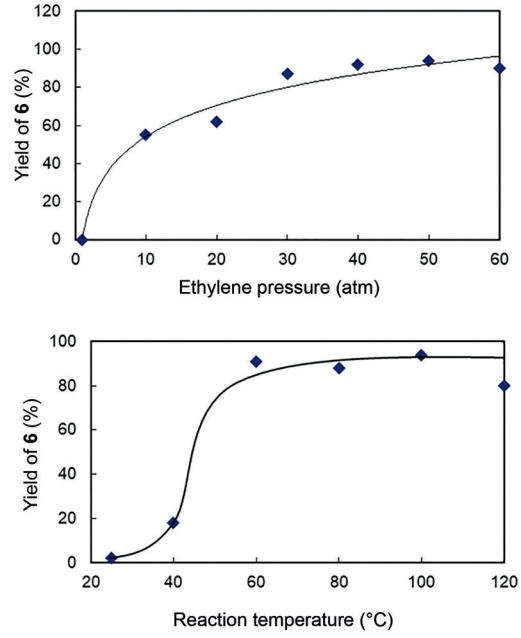
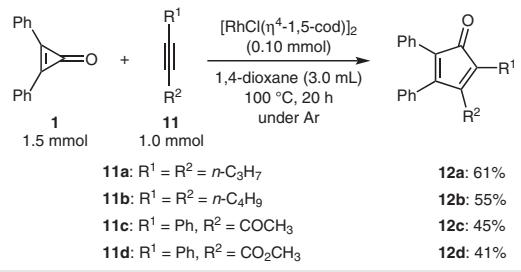


Figure 2 The effect of both the ethylene pressure (at 100 °C for 20 h) and the reaction temperature (under 40 atm of ethylene for 20 h)

Next, the reactions of **1** with symmetrically substituted internal alkynes such as oct-4-yne (**11a**) and dec-5-yne (**11b**) were carried out in the presence of a catalytic amount of [RhCl(η⁴-1,5-cod)]$_2$ in 1,4-dioxane at 100 °C for 20 hours under an argon atmosphere, which gave the expected cyclopentadienones, 2,3-diphenyl-4,5-dipropylcyclopenta-2,4-dien-1-one (**12a**) in 61% yield and 2,3-dibutyl-4,5-diphenylcyclopenta-2,4-dien-1-one (**12b**) in 55% yield, respectively (Scheme 5).



Scheme 5 [RhCl(η⁴-1,5-cod)]$_2$-catalyzed synthesis of cyclopentadienones

Unsymmetrically substituted alkynes such as 4-phenylbut-3-yn-2-one (**11c**) and methyl 3-phenylpropiolate (**11d**) could be used in this reaction, and single regioisomeric cyclopentadienones, 3-acetyl-2,4,5-triphenylcyclopenta-2,4-

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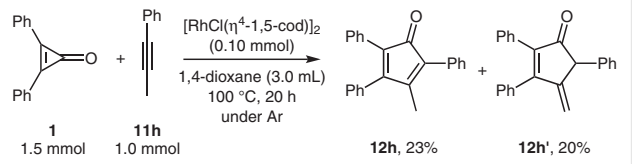
dien-1-one (**12c**) and methyl 3-oxo-2,4,5-triphenylcyclopenta-1,4-diene-1-carboxylate (**12d**), were obtained in respective yields of 45% and 41%, while no reaction occurred with 1,2-diphenylethyne (**11e**), dimethyl but-2-ynedioate (**11f**), and ethynylbenzene (**11g**).

Two isomeric products were obtained from the reaction of **1** with prop-1-yn-1-ylbenzene (**11h**). The single-crystal X-ray structure determination clearly showed that the two isomeric products were the expected cyclopentadienone, 3-methyl-2,4,5-triphenylcyclopenta-2,4-dien-1-one (**12h**) (23% yield), and the unexpected cyclopentenone, 4-methylene-2,3,5-triphenylcyclopent-2-en-1-one (**12h′**) (20% yield), respectively (Scheme 6).[16]



Scheme 6 $[RhCl(\eta^4\text{-}1,5\text{-cod})]_2$-catalyzed reaction of **1** with prop-1-yn-1-ylbenzene (**11h**)

ORTEP drawings of **12h** and **12h′** are shown in Figures 3 and 4. In **12h**, all of the carbon atoms in the five-membered ring exist within the same plane, and have an sp^2 configuration, while the carbon atom attached to the phenyl group at C-5 in **12h′** is outside the plane. Thus, this carbon atom has an sp^3 configuration. The C–C bond length between the carbon at the 3-position of cyclopentadienone and the methyl carbon in **12h** was 1.489 Å, while the equivalent bond in **12h′** was 1.336 Å.

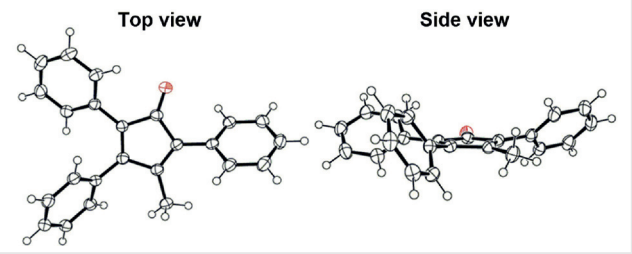


Figure 3 X-ray crystal structure of compound **12h** (CCDC 1826245)

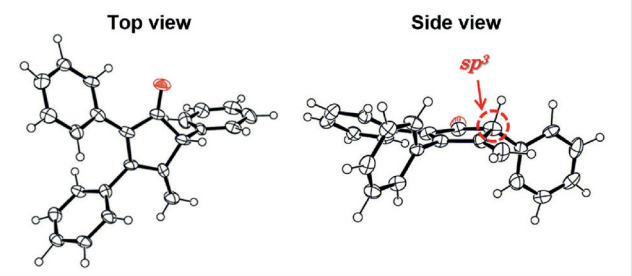
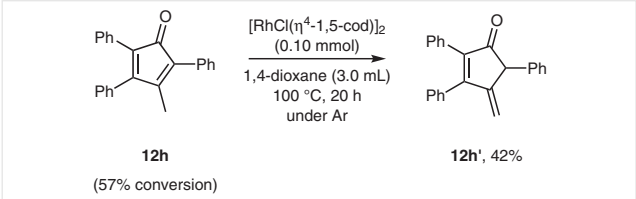
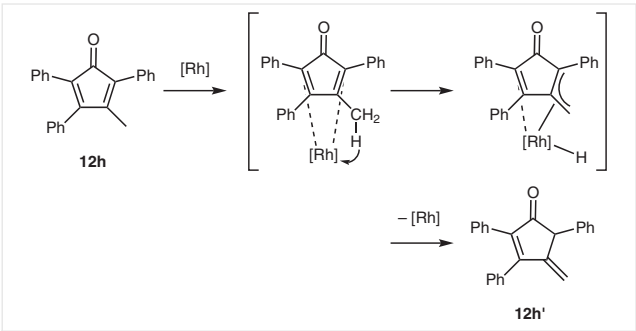


Figure 4 X-ray crystal structure of compound **12h′** (CCDC 1826246)

In addition, treatment of the isolated compound **12h** with $[RhCl(\eta^4\text{-}1,5\text{-cod})]_2$ catalyst in 1,4-dioxane at 100 °C for 20 hours gave **12h′** in 42% yield (conversion of **12h**, 57%) (Scheme 7). Accordingly, a possible mechanism for this isomerization is illustrated in Scheme 8. Coordination of **12h** to an active rhodium species, followed by activation of a C–H bond of the methyl group by rhodium proceeds to give an (η^3-allyl)rhodium complex, and subsequent reductive elimination gives isomeric methylenecyclopentenone **12h′**. Nishinaga and co-workers reported a similar isomerization of cyclopentadienones giving methylenecyclopentenones under basic reaction conditions.[17]



Scheme 7 $[RhCl(\eta^4\text{-}1,5\text{-cod})]_2$-catalyzed isomerization of **12h** into **12h′**



Scheme 8 A possible mechanism

Since rhodacyclobutenone is more stable than ruthenacyclobutenone, the subsequent insertion of alkenes or alkynes proceeded smoothly, and reductive elimination would give cyclopentenones or cyclopentadienones in high yields, respectively, without decarbonylation, even under an argon atmosphere.

In conclusion, we have succeeded in developing the first $Ru_3(CO)_{12}$-catalyzed divergent ring-opening coupling reactions of a cyclopropenone with an electron-deficient alkene to give the linear codimer, a dienoic ester (under an argon atmosphere) and the cocyclized cyclopentenone (under 20 atm of carbon monoxide), depending on the reaction conditions. On the other hand, $[RhCl(\eta^4\text{-}1,5\text{-cod})]_2$ effectively catalyzed the ring-opening cocyclization of a cyclopropenone with alkenes or alkynes to give the corresponding cyclopentenones or cyclopentadienones in high yields and with high selectivities.[18]

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Supporting Information

Supporting information for this article is available online at https://doi.org/10.1055/s-0037-1609339.

References and Notes

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(13) The reactions using other cyclopropenones such as 2,3-dipropylcycloprop-2-en-1-one and bicyclo[6.1.0]non-1(8)-en-9-one competed with decarbonylation of cyclopropenones, and the corresponding alkynes were formed as the main products. Accordingly, a careful tuning of the reaction conditions for each cyclopropenone is apparently required. As shown in Scheme 1, compounds **3** and **4** were obtained in moderate yields due to the decarbonylation of **1** to give 1,2-diphenylethyne. However, no other by-products which disturb analysis and isolation of the desired compounds **3** and **4** were obtained at all.

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(15) The free energy profiles of ruthenacycles such as ruthenacyclobutenone, ruthenacyclopentene, and (maleoyl)ruthenium complexes as well as the orbital interactions in the insertion of ethylene or bicyclo[2.2.1]hept-2-ene were calculated by the BP86 density functional theory (DFT) method, see Ref. 19. The 6-31G* basis set was used for C, H, and O atoms, and Stuttgart/Dresden's pseudopotential SDD basis set (see Ref. 20) was used for the Ru atom. See: Wang C., Wu Y.-D. *Organometallics*. **2008**, *27*, 6152.

(16) Wender and co-workers also reported a similar $[RhCl(CO)]_2$-catalyzed ring-opening cocyclization of cyclopropenones with alkynes to give cyclopentadienones; however, the reaction of 1 with **11h** gave **12h** selectively without **12h'**, see: Wender, P. A.; Paxton, T. J.; Williams, T. J. *J. Am. Chem. Soc.* **2006**, *128*, 14814.

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(18) **Ruthenium-Catalyzed Divergent Ring-Opening Coupling Reactions of 2,3-Diphenylcycloprop-2-en-1-one (1) with Methyl Acrylate (2); General Procedure**

A mixture of 2,3-diphenylcycloprop-2-en-1-one (**1**) (1.0 mmol), methyl acrylate (**2**) (3.0 mL), and $Ru_3(CO)_{12}$ (0.066 mmol) was placed in a two-necked 20-mL Pyrex flask equipped with a magnetic stir bar and a reflux condenser under a flow of argon. The reactor was connected to a balloon (1 L) and the reaction was carried out at 100 °C for 20 hours with stirring. After the reaction mixture had been cooled, the products were analyzed by GC and GC/MS, and isolated by medium-pressure column chromatography (SiO_2 60 µm, eluent: EtOAc/hexane). The reactions under carbon monoxide pressure were carried out in a 50-mL stainless steel autoclave at 160 °C for 20 hours.

Rhodium-Catalyzed Ring-Opening Cocyclization of 2,3-Diphenylcycloprop-2-en-1-one (1) with Alkenes/Alkynes; General Procedure

A mixture of 2,3-diphenylcycloprop-2-en-1-one (**1**) (1.0–1.5 mmol), $[RhCl(\eta^4\text{-}1,5\text{-cod})]_2$ (0.10 mmol), solvent (3.0 mL), and an alkene (3.0 mmol) or an alkyne (1.0 mmol) was placed in a two-necked 20-mL Pyrex flask equipped with a magnetic stir bar and a reflux condenser under a flow of argon. The reactor was connected to a balloon (1 L) and the reaction was carried out at 100 °C for 20 hours with stirring. After the reaction mixture had been cooled, the products were analyzed by GC and GC/MS, and isolated by medium-pressure column chromatography (SiO_2 60 µm, eluent: EtOAc/hexane). The reactions under ethylene were carried out in a 50-mL stainless steel autoclave.

The MS and NMR data of the representative new compounds, **4**, **8**, **12h**, and **12h'** are reported below. See also the Supporting Information.

Methyl 4-Oxo-2,3-diphenylcyclopent-2-ene-1-carboxylate (4)

Yield: 137.2 mg (47%); pale yellow solid; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.75–2.93 (dd, *J* = 16.0, 18.5 Hz 1 H), 2.76–2.95 (dd, *J* = 20.0, 18.5 Hz, 1 H), 3.50 (s, 3 H), 4.25–4.28 (dd, *J* = 4.2, 3.0 Hz, 1 H), 7.11–7.25 (m, 10 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 39.26, 46.76, 52.42, 128.18, 128.23, 128.35, 128.45, 129.45, 129.87, 131.13, 133.99, 141.07, 164.94, 172.62, 204.60; MS (EI): *m*/*z* = 292 (M^+).

***exo*-2,3-Diphenyl-3a,4,5,6,7,7a-hexahydro-1*H*-4,7-methanoinden-1-one (8)**

Yield: 183.0 mg (61%); orange solid; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.98–1.04 (m, 1 H), 1.21–1.27 (m, 1 H), 1.38–1.44 (m, 2 H), 1.62–1.68 (m, 2 H), 2.10–2.36 (m, 1 H), 2.50 (d, *J* = 5.4 Hz, 1 H), 2.59–2.62 (m, 1 H), 3.20 (d, *J* = 5.4 Hz, 1 H), 7.17–7.33 (m, 10 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 28.77, 28.91, 31.52, 38.23, 39.43, 50.65, 53.99, 127.66, 128.25, 128.31, 128.47, 129.24, 129.39, 132.11, 135.03, 142.54, 169.85, 208.50; MS (EI): *m*/*z* = 300 (M^+).

3-Methyl-2,4,5-triphenylcyclopenta-2,4-dien-1-one (12h)

Yield: 74.1 mg (23%); dark purple solid; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.07 (s, 3 H), 7.11–7.45 (m, 15 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.52, 124.61, 125.64, 127.27, 127.30, 127.93, 128.21, 128.49, 128.59, 128.62, 129.54, 129.82, 130.68, 131.34, 133.73, 154.12, 154.46, 200.42; MS (EI): *m*/*z* = 322 (M^+).

4-Methylene-2,3,5-triphenylcyclopent-2-en-1-one (12h')

Yield: 64.4 mg (20%); light purple solid; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.34 (s, 1 H), 5.30 (s, 1 H), 5.44 (s, 1 H), 7.20–7.41 (m, 15 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 56.05, 114.81, 127.20, 127.92, 128.09, 128.50, 128.58, 128.77, 128.94, 129.77, 130.66, 133.16, 137.69, 139.68, 148.91, 164.47, 202.67; MS (EI): *m*/*z* = 322 (M^+).

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