Cobalt/rhodium heterobimetallic nanoparticle-catalyzed carbonylative [2 + 2 + 1] cycloaddition of allenes and bisallenes to Pauson–Khand-type reaction products†‡

Ji Hoon Park, Eunha Kim, Hyeong-Mook Kim, Soo Young Choi and Young Keun Chung*

The first catalytic intra- and intermolecular [2 + 2 + 1] cocyclization reactions of allenes and carbon monoxide have been developed. In the Co_2Rh_2 heterobimetallic nanoparticle-catalyzed carbonylative [2 + 2 + 1] cycloaddition of allenes and carbon monoxide, the allenes formally serve both as an excellent alkene- and alkyne-like moiety within a Pauson–Khand-type process.

Recently, the chemistry of allenes has attracted a lot of attention, presumably due to their high reactivity.[1] In particular, they are being increasingly used in metal-catalyzed annulation reactions[2] due to their unique reactivity and special manipulation possibilities. However, if the reactivity of allenes is not controlled properly, the reactions of such substrates tend to be complex and useless. In this respect, the allenic Pauson–Khand reaction is a very useful process.[3]
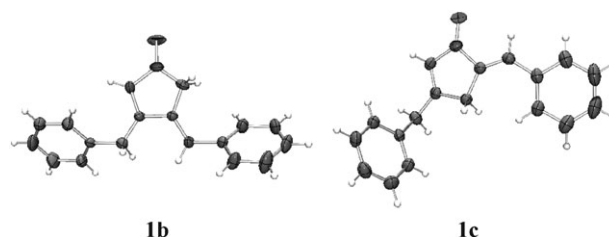
In the exploration of the use of Co/Rh nanoparticles as a catalyst,[4] we recently studied a Co/Rh nanoparticle-catalyzed allenic Pauson–Khand reaction.[5] The catalytic system was quite effective to give a Pauson–Khand reaction product. As an extension of the previous study, we recently tested an intermolecular allenic Pauson–Khand reaction. When an intermolecular Pauson–Khand reaction of phenylallene with 1-phenylpropyne was examined, two unknown compounds were isolated instead of the allenic Pauson–Khand reaction product (Scheme 1). According to the ^{1}H NMR, the reaction product did not seem to have incorporated the 1-phenyl propyne moiety. Instead, carbonylative cycloaddition products were obtained. An X-ray diffraction analysis (Fig. 1) showed that the products had been constructed from two allene units and carbon monoxide. Although many transition metal-catalyzed cycloaddition of allenes have been disclosed,[2,6] there has been no report on the catalytic formation of cyclopentenones via a [2 + 2 + 1] cycloaddition of two allenes and carbon monoxide. Encouraged by this observation, we examined the reaction more closely. Here we communicate our preliminary results.

Intelligent Textile System Research Center, Department of Chemistry, College of Natural Sciences, Seoul National University, Seoul 151-747, Korea. E-mail: ykchung@snu.ac.kr; Fax: +82-2-889-0310; Tel: +82-2-880-6662
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Scheme 1 Co/Rh nanoparticle catalyzed carbonylation reaction of phenylallene with 1-phenylpropyne.

When phenylallene was reacted with 2 atm of CO in the presence of a catalytic amount (5 mol%) of Co_2Rh_2 at 130 °C for 18 h, two carbonylated products, **1b** and **1c**, were isolated in 59% and 3% yield, respectively (Scheme 2). The product was found to be a cyclic enone bearing two phenyl groups. Thus, the allenes formally serve both as an excellent alkene and alkyne-type moiety in Co_2Rh_2-catalyzed [2 + 2 + 1] cycloaddition with carbon monoxide when compared to the classical Pauson–Khand process. About two decades ago, Pasto et al. reported[7] the formation of **1b** in the stoichiometric carbonylative reaction of phenylallene with tris(triphenylphosphine)nickel(0). However, they obtained **1c** in 4.8% yield as one of eight major by-products.

Using phenylallene as a substrate, we screened the reaction conditions including the reaction temperature, the reaction time, and the CO pressure (Table 1). The reaction solvent (toluene) was adopted from the previous study.[5] The reaction was highly sensitive to and dependent upon the reaction temperature and the reaction time. The yield was higher at 130 °C as opposed to 100 °C. However, when the reaction time was lengthened, the yield decreased. Thus, the best yield (80%) was obtained when the temperature was 130 °C and the reaction time was 6 h. As shown in Table 1, the reaction of **1a** in the presence of [Rh(CO)$_2$Cl]$_2$ at 130 °C for 6 h gave a mixture of **1b** and **1c** in 32% and 25% yields, respectively.
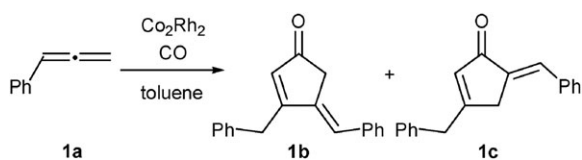

Fig. 1 X-Ray structures of **1b** and **1c** with 30% probability thermal ellipsoids.

Scheme 2 Carbonylative cycloaddition of allene **1a**.

Encouraged by the above results, we screened other allenes under the optimized reaction conditions (Table 2).§ In all cases except entry 5, compounds **b** and **c** are easily separated by chromatography and show characteristic ¹H NMR patterns. Thus we can easily differentiate them by ¹H NMR study: for example, the benzylic proton in **b** is shifted up-field with respect to the corresponding proton in **c**. When 4-tolylallene (**2a**) was used as a substrate, **2b** was obtained in 70% yield, with concomitant formation of **2c** in 14%. In the case of 1,3-dimethyl-5-(1,2-propadienyl)benzene (**3a**), the yields of **3b** and **3c** were 71% and 13%, respectively. Treatment of (naphthalen-1-yl)allene (**4a**) under the same reaction conditions led to the isolation of **4b** isomer in 72% yield, with isomer **4c** in 20% yield. Interestingly, a reaction of *p*-anisylallene (**5a**) under the same reaction conditions gave **5b** in 61% yield as the sole product. When 4′-acetylphenylallene (**6a**) was used as a substrate, **6b** and **6c** were obtained in 64% and 20% yields, respectively. In the same way, reaction of *p*-chlorophenylallene (**7a**) gave **7b** and **7c** in 68% and 8% yields, respectively, and reaction of 1,2-nonadiene (**8a**) gave **8b** and **8c** in 52% and 7% yields, respectively. The yield of the minor isomer (**c**) was somewhat dependent upon the substituent on the allene. The overall yields of carbonylative cycloaddition reactions, apart from entries 4 and 7, were quite high (76–92%).

We next investigated the use of bisallenes as substrates in a Co₂Rh₂-catalyzed carbonylative cycloaddition reaction. Compared to the use of allenes as substrates, the use of bisallenes is rather uncommon, as seen from the fact that only a handful of reactions have been reported.[8] We screened the reaction conditions including the amount of the catalyst, the CO pressure, the reaction temperature, and the reaction time (Table 3). Treatment of **9a** led to the isolation of bicyclic enone **9b**. We have provisionally established a set of optimum reaction conditions to be as follows: 5 mol% Co₂Rh₂, toluene, 2 atm CO, 100 °C, and 4 h.
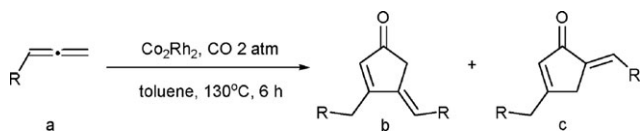
We investigated the carbonylative cycloaddition of other bisallenes under the optimized reaction conditions (Table 4). For entries 1–3, it is possible for two regioisomeric products to

Table 2 Co₂Rh₂-Catalyzed [2 + 2 + 1] cycloaddition of allenes[a]

| Entry	R		Product	Yield (%) (**b**/**c**)[b]
1	4-Tolyl	**2a**	**2b** + **2c**	84(70/14)
2	3,5-Dimethylphenyl	**3a**	**3b** + **3c**	84(71/13)
3	1-Naphthyl	**4a**	**4b** + **4c**	92(72/20)
4	4-Anisyl	**5a**	**5b**	61(61/0)
5	4-Acetylphenyl	**6a**	**6b** + **6c**	84(64/20)[c]
6	4-Chlorophenyl	**7a**	**7b** + **7c**	76(68/8)
7	*n*-Hexyl	**8a**	**8b** + **8c**	59(52/7)

[a] Reaction condition: 1.0 mmol allene, 5 mol% Co₂Rh₂ catalyst, 5 mL toluene, 130 °C, CO (2 atm), and 6 h. [b] Isolated yield. [c] Yields of **6b** and **6c** were determined by ¹H NMR.

result from these annulation processes. However, only one regioisomer was isolated. The isolated regioisomer was easily characterized by ¹H NMR peak of the vinyl proton (see ESI†). Introduction of a methyl to the position between the allene and *N*-Ts did not alter the yield of the reaction (**10b**, entry 1). However, introduction of a phenyl group onto the allene (**11b**, entry 2) slightly enhanced the yield to 74%. In contrast, introduction of a methyl group onto the allene at the same position (**12b**, entry 3) slightly decreased the yield to 53%. Reaction of a bisallene (**13a**) with an oxygen tether gave **13b** in 45% yield.

Interestingly, introduction of substitutents on the terminal positions of an allene (**14a**) led to the isolation of a monocyclic seven-membered triene, **14b**, as the sole product (Scheme 3). In the absence of carbon monoxide, no reaction was observed. Thus, the presence of carbon monoxide was indispensable. Very recently, Lu and Ma have reported[9] the [RhClL₂]₂ (L = CO, COD)-catalyzed conversion of 1,5-bisallenes to seven-membered trienes.

Considering the results obtained above, we postulated a mechanism for this newly developed intramolecular [2 + 2 + 1] cocyclization of allenes and CO, as shown in Scheme 4. Coordination of carbon monoxide to the nanoparticles generates **I** as an active metal species. Then, the next step involves

**Table 3** Reaction of **9a** under various reaction conditions[a]
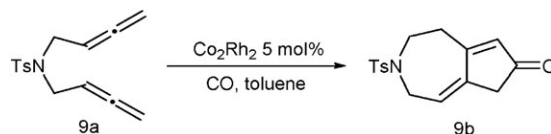
Entry	CO/atm	Temp/°C	Time/h	Yield (%)[b]
1	1	100	12	33
2	2	100	12	66
3	2	80	12	n.r.[c]
4	2	110	12	55
5	3	100	4	70
6	2	100	4	68

[a] 0.3 mmol of **9a** and 5 mol% Co₂Rh₂ were used. [b] Isolated yield. [c] The reactant was recovered.

Table 1 Reaction of **1a** under various reaction conditions[a]

Entry	Catalyst	CO/ atm	Temp/°C	Time/h	Yield (**1b**/**1c**)[b]
1	Co₂Rh₂ 5 mol%	1	130	18	53(45/8)
2	Co₂Rh₂ 5 mol%	2	130	18	62(59/3)
3	Co₂Rh₂ 5 mol%	3	130	18	60(55/5)
4	Co₂Rh₂ 5 mol%	2	130	12	72(62/10)
5	Co₂Rh₂ 5 mol%	2	130	6	80(68/12)
6	Co₂Rh₂ 5 mol%	2	100	12	51(45/6)
7	[Rh(Co)₂Cl]₂ 5 mol%	2	130	6	57(32/25)
8	[Rh(Co)₂Cl]₂ 5 mol%	2	100	6	39(39/0)

[a] 1.0 mmol of **1a** and 5 mL toluene were used. [b] Isolated yield.

Table 4 Co_2Rh_2-Catalyzed [2 + 2 + 1] cycloaddtion of bisallenes[a]

Entry	Bisallene	Product	Yield (%)[b]
1	R_1 = Me, R_2 = H **10a**	**10b**	67
2	R_1 = H, R_2 = Ph **11a**	**11b**	74
3	R_1 = H, R_2 = Me **12a**	**12b**	53
4	**13a**	**13b**	45

[a] Reaction condition: 0.3 mmol allene, 5 mol% Co_2Rh_2 catalyst, 3 mL toluene, 100 °C, and 4 h. [b] Isolated yield.
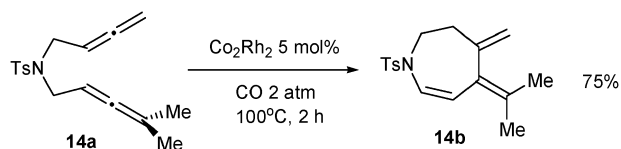
Scheme 3 Co_2Rh_2 catalyzed cycloisomerization of **14a**.
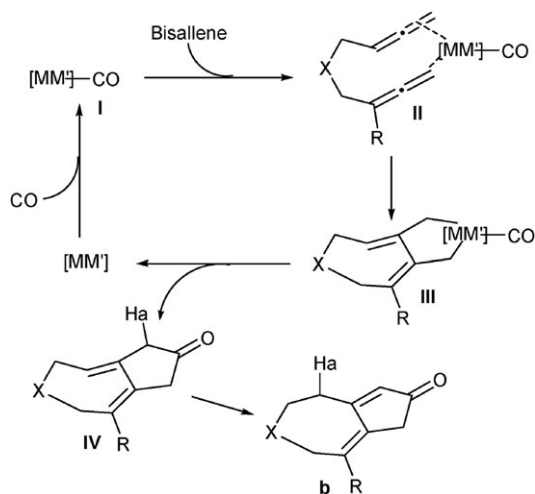
Scheme 4 Proposed mechanism.

formation of a bis-π-complex **II** in which π-bond formation occurs around the unsubstituted double bonds of the allenes. Coupling in **II** occurs to produce apparently only **III**. Carbonylation of **III** produces **IV** which undergoes a 1,3-hydrogen shift to produce the product, **b**. The hydrogen shift occurs to the carbon with less substituents, since a substituent on the carbon is believed to restrict the shift of a hydrogen. Having stated this, it is acknowledged that this rationalisation does not explain the regioselectivity observed in the formation of **10b** from substrate **10a**, where the hydrogen shift in both possible directions would be to a carbon with only an

H. Nonetheless, it is believed that the 1,3-hydrogen shift is catalyzed by some Lewis acidic or basic species present within the reaction mixture after carbonylation. The drive for isomerization of **IV** to create the product is the relief of strain in the twisted diene chromophore.

In conclusion, we have developed the first catalytic inter- and intramolecular [2 + 2 + 1] cocyclization of allenes and CO. This process provides a rapid and atom-economical method for the synthesis of a variety of cyclopentenones with an exocyclic double bond, or [5.3]bicyclic enones in one step. The process developed in this study will enrich the chemistry of Pauson–Khand-type transformations and related reactions.

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