

Cyclohydrocarbonylation of substituted alkynes and tandem cyclohydrocarbonylation–CO insertion of α -keto alkynes catalyzed by immobilized Co–Rh heterobimetallic nanoparticles

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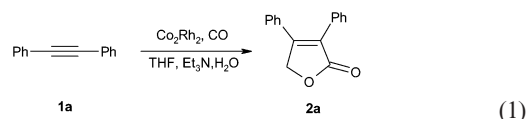
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The use of cobalt–rhodium (Co_2Rh_2) heterobimetallic nanoparticles in the cyclohydrocarbonylation of substituted alkynes and tandem cyclohydrocarbonylation–CO insertion of α -keto alkynes to give 2(3*H*)- or 2(5*H*)-furanones is described.

Transition metal complex-catalyzed carbonylation has been proven to be a useful method for the direct introduction of a carbonyl group into an organic molecule *via* the insertion of carbon monoxide into a carbon–metal bond.¹ Important variants of carbonylation are cyclocarbonylation and cyclohydrocarbonylation. Both reactions allow the introduction of a carbonyl group along with ring closure. Thus, they are expected to provide a novel tool for the construction of cyclic systems. Transition metal-catalyzed cyclocarbonylation reactions have been extensively studied and established as excellent methods for direct synthesis of cyclic carbonyl compounds such as ketones, aldehydes, acrylic acid, esters, lactones, furanones, indenones, and indanones.² However, transition metal-catalyzed cyclohydrocarbonylation reactions have been relatively undeveloped. Only a handful of studies have been reported by Takahashi,³ Ojima,⁴ and Alper⁵ and their coworkers in the syntheses of furanones and pyrrolinones.

Recently, the chemistry of transition-metal nanoparticles has developed rapidly⁶ and their use has widened to include many catalytic reactions such as oxidation,⁷ hydrogenation,⁸ coupling,⁹ and photocatalytic reactions.¹⁰ In the context of our studies on the use of transition metal nanoparticles in organic reactions, we have reported many useful catalytic reactions such as allylic alkylation, the Pauson–Khand reaction, and the reductive Pauson–Khand reaction.¹¹ Very recently, we found that cobalt–rhodium nanoparticles (Co_2Rh_2) derived from $\text{Co}_2\text{Rh}_2(\text{CO})_{12}$ were quite useful catalysts in Pauson–Khand-type reactions and silylcarbocyclization.¹² While we were investigating the use of Co_2Rh_2 , we found that Co_2Rh_2 catalyzed carbonylative coupling reactions. Here we report the use of immobilized cobalt–rhodium heterobimetallic nanoparticles in the presence of CO and H_2O for the cyclohydrocarbonylation of substituted acetylenes and the tandem cyclohydrocarbonylation–CO insertion reaction of α -keto alkynes to give 2(3*H*)- or 2(5*H*)-

furanones. In our catalytic system, neither phosphite nor hydrogen is needed for the catalysis and no hydrogenated byproducts are generated. Furthermore, the Co_2Rh_2 heterogeneous catalysts are easily recovered and reused without loss of catalytic activity.



Diphenylacetylene (**1a**) was reacted with carbon monoxide (10 atm) and water in the presence of triethylamine and a catalytic amount of Co_2Rh_2 in THF at 120 °C (eqn. 1). The reaction proceeded smoothly and gave 3,4-diphenylfuran-2(5*H*)-one (**2a**) in 26% yield; the products were identified by instrumental analytical techniques such as ¹H NMR, IR, and mass spectroscopy. Judging from the structure, furanone **2a** is constructed by the combination of **1a** with one molecule of hydrogen and two molecules of carbon monoxide. The hydrogen atoms were from water. The presence of the amine is necessary for the selective syntheses of furanone. In order to establish optimized reaction conditions, we screened the reaction temperature and pressure of CO (Table 1). As shown in Table 1, the yield was highly dependent upon the reaction temperature, the pressure of CO, and the reaction time. The best yield was 87% and the optimized reaction conditions were established as follows: 30 atm of CO, 100 °C, and 18 h. To check the recyclability, Co_2Rh_2 was separated and reused several times. The results shown in Table 1 confirm that the catalyst maintained its high activity even after being recycled five times. In order to recycle the catalyst, it was filtered from the reaction mixture and dried *in vacuo*. It could then be reused for further catalytic reactions.

Furanones have been of interest for many years due to their biological activity.¹³ Thus, a variety of transition metal-catalyzed methods have been utilized for the preparation of furanones.¹⁴ The first rhodium-catalyzed carbonylation of acetylenes under water–gas shift reaction conditions to furanones was reported by Takahashi *et al.*³ They used rhodium carbonyl clusters such as $\text{Rh}_4(\text{CO})_{12}$ and $\text{Rh}_6(\text{CO})_{16}$ as catalysts in the presence of water and triethylamine under 100 atm of CO. Recently,

Table 1 Optimization of the reaction conditions

Entry	Catalyst	Pressure/atm	Temp./°C	Time/h	Yield (%) ^a
1	Co_2Rh_2	10	120	18	26
2	Co_2Rh_2	20	120	18	53
3	Co_2Rh_2	20	100	18	19
4	Co_2Rh_2	30	100	6	12
5	Co_2Rh_2	30	100	18	87
6	Recovered from #6	30	100	18	88
7	Recovered from #7	30	100	18	85
8	Recovered from #8	30	100	18	86
9	Recovered from #9	30	100	18	87

^a Isolated yields, acetylene (0.864 g, 4.85 mmol), Co_2Rh_2 (0.01 g, 0.029 mmol), Et_3N (2 ml), H_2O (1 ml), THF (10 ml).

Table 2 Cyclohydrocarbonylation of acetylenes

Entry	Compound	Substrate		Yield(%)	
		R ¹	R ²	2	3
1	1a	Ph	Ph	87	
2	1b	Et	Et	89	
3	1c	H	Ph	40	53
4	1d	Me	Ph	61	31
5	1e	Et	Ph	72	18
6	1f	EtO ₂ C	Ph	23	14
7	1g	EtO ₂ C	Me	30	54
8	1h	EtO ₂ C	H	17	68

^a Isolated yields. Reaction conditions: acetylene (0.864 g, 4.85 mmol), Co₂Rh₂ (0.01 g, 0.029 mmol), Et₃N (2 ml), H₂O (1 ml), THF (10 ml), 30 atm CO, 100 °C, and 18 h.

Alper *et al.*^{5c} reported a zwitterionic rhodium complex (η^6 -C₆H₅BPh₃)Rh(cod) (2 mol%) catalyzed formation of furanones using α -keto alkynes in the presence of a considerable amount (32 mol%) of P(OPh)₃ under 38.5 atm CO and 3.5 atm H₂ at 90 °C for 24 h. In addition to furanones, a hydrogenated alkyne was obtained as a byproduct.

In order to examine the scope of the present reaction and to obtain further information on the reaction mechanism, cyclohydrocarbonylation of various acetylenes was carried out. The results are summarized in Table 2, which shows that furan-2-(5*H*)-ones, **2** and **3**, were obtained in satisfactory yields for internal acetylenes bearing alkyl, aryl, and ester aryl substituents.

For monosubstituted acetylenes such as phenylacetylene, two structural isomeric furanones **2** and **3** were obtained in 72% and 18% yields, respectively, under the adopted reaction conditions. The two isomers were easily separated. When Rh₄(CO)₁₂ was used as a catalyst, the ratio of **2** to **3** was approximately 1 : 1.^{3f}

Asymmetrically substituted acetylenes afforded two structural isomers **2** and **3**, the ratio of which varied depending on the steric and electronic nature of the substituents of the acetylenes. Takahashi *et al.*^{3d} obtained a similar isomer ratio (73 : 27) to that obtained by us (72 : 18) for **2d** and **3d**. However, the same authors^{3f} reported that the ratio of **2** : **3** was *ca.* 1 : 1 for phenylacetylene derivatives independent of the electronic and steric nature of the substituents on the phenyl ring of aromatic acetylenes. As

the isomers were easily separated by column chromatography, the isomer ratio was based on the isolated yields. Table 2 shows that the isomer ratio is affected by both the steric and electronic nature of the substituents of the acetylenes. In the case of R² = a phenyl group, as the steric bulkiness of the R¹ increased, the yield of **2** decreased but the yield of **3** increased. In the case of R¹ = an ester group, as the steric bulkiness of R² decreased, the yield of **3** increased, but there was not an apparent tendency in the yield of **2**.

Next we investigated the use of α -keto alkynes as substrates instead of acetylenes. We screened the reaction conditions using 4-methyl-1-phenyl-1-pentyn-3-one (**4a**) as a substrate. Interestingly, the reaction pathway is highly dependent upon the reaction temperature and pressure. Thus, depending upon the reaction conditions, three distinctive pathways were found and four different cyclohydrocarbonylation products were obtained (Scheme 1). Surprisingly, this phenomenon was quite general. Thus, the reaction can be applied to other substrates (Table 3).

Under the same conditions (30 atm, 100 °C, and 18 h) as the cyclohydrocarbonylation of acetylene derivatives, the tandem cyclohydrocarbonylation–CO insertion reaction products, **5** and **6**, were obtained in various ratios depending upon the substituents. The total yields of **5** and **6** were also highly variable depending upon the substrates: high yields (83–85%) were obtained for substrates **4a–4c**, but poor to moderate yields (24–59%) were obtained for **4d–4f**. A similar reaction of α -iminio alkynes was reported by Alper *et al.*^{5b} They obtained the tandem cyclohydrocarbonylation–CO insertion reaction products of α -iminio alkynes by employing a total pressure of 21 atm to 42 atm of CO and H₂, catalytic quantities of zwitterionic rhodium complex (η^6 -C₆H₅BPh₃)Rh(1,5-COD)⁺, and P(OPh)₃. In our case, water was used as a hydrogen source instead of hydrogen gas and no additives such as triphenylphosphite were required.

When the pressure of CO was lowered to 1 atm, two different products were obtained in reasonable to high yields depending upon the reaction temperature: **7** at 60 °C and **8** at 100 °C, respectively. The yields were dependent upon the substituents. Compared to the alkyl substituent, a substrate containing a phenyl group gave a higher yield. Alper *et al.*^{5c} also observed the formation of **7** and **8** in their rhodium-catalyzed cyclohydrocarbon reaction of α -keto alkynes. They suggested that structural and electronic properties present in the starting materials mediate the chemo- and regioselectivity of the reaction. For example, having an aromatic ring adjacent to the triple bond appears to favor the formation of the unsaturated γ -lactones.

Takahashi *et al.*^{3f} proposed a mononuclear anionic rhodium complex species stabilized by coordination of an alkyne

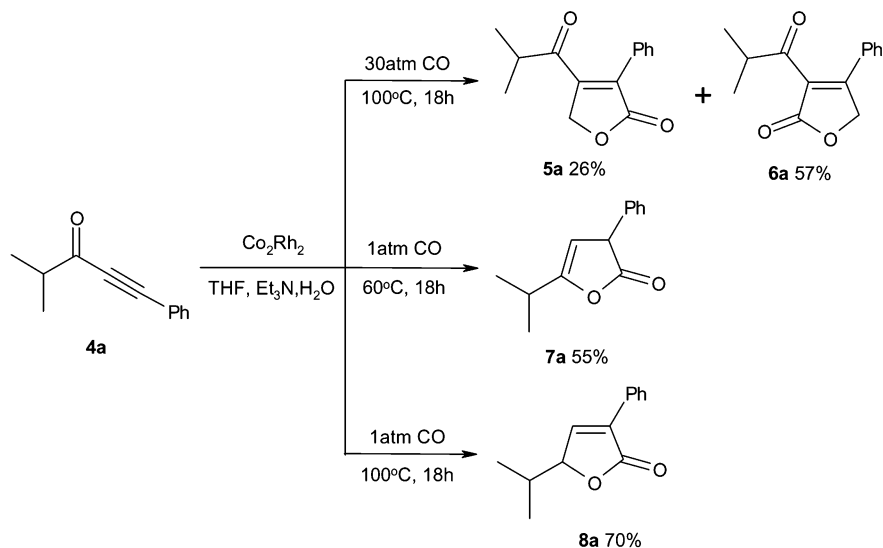
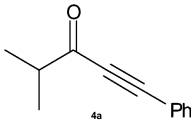
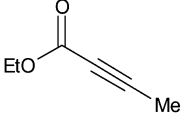
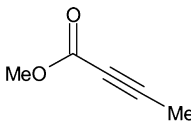
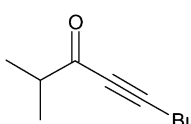
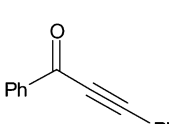
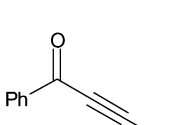
**Scheme 1**

Table 3 Cyclohydrocarbonylation of α -keto alkynes

Entry	Substrate	Yield (%) ^a			
		5	6	7	8
1		26	57	55 ^b	70
2		30	54	23	43
3		17	68	22	42
4		11	13	48	62 ^c
5		12	25	73	84
6		31	28	80	78

^a Isolated yields, α -keto alkynes (0.5 g, 2.42 mmol), Co_2Rh_2 (0.01 g, 0.029 mmol), Et_3N (2 ml), H_2O (1 ml), THF (10 ml). ^b 5-Isopropyl-3-phenyl-3H-furan-2-one (**7a**): ¹H NMR (CDCl_3 , 300 MHz): δ 7.54–7.50 (m, 2H), 7.40–7.30 (m, 3H), 5.19 (d, $J = 5.10$ Hz, 1H), 2.92–2.80 (m, 1H), 2.16–2.14 (m, 1H), 1.23 (d, $J = 2.11$ Hz, 3H), 1.19 (d, $J = 2.09$ Hz, 3H); ¹³C NMR (CDCl_3 , 75 MHz): δ 194.6, 133.3, 131.0, 128.9, 71.8, 53.1, 30.1, 21.7, 18.9, 17.9; HRMS for $\text{C}_{13}\text{H}_{14}\text{O}_2$: calcd. 202.0994, obsd. 202.0996. ^c 5-Isopropyl-3-phenyl-3H-furan-2-one (**7a**): ¹H NMR (CDCl_3 , 300 MHz): δ 7.54–7.50 (m, 2H), 7.40–7.30 (m, 3H), 5.19 (d, $J = 5.10$ Hz, 1H), 2.92–2.80 (m, 1H), 2.16–2.14 (m, 1H), 1.23 (d, $J = 2.11$ Hz, 3H), 1.19 (d, $J = 2.09$ Hz, 3H); ¹³C NMR (CDCl_3 , 75 MHz): δ 194.6, 133.3, 131.0, 128.9, 71.8, 53.1, 30.1, 21.7, 18.9, 17.9; HRMS for $\text{C}_{13}\text{H}_{14}\text{O}_2$: calcd. 202.0994, obsd. 202.0996.

molecule as the active species in the cyclohydrocarbonylation of acetylenes. In the cyclohydrocarbonylation of α -keto alkynes, Alper *et al.*^{5c} proposed a rhodium hydride as the active species. The reaction was initiated by the binding of the rhodium hydride complex to the triple bond of the alkynone with possible weak H-bonding interactions to the ketone functionality. However, the precise mechanism of Co_2Rh_2 catalysis has not yet been revealed, but it is likely to be distinct from those proposed by the Takahashi and Alper groups.

In conclusion, we have demonstrated that the cyclohydrocarbonylation of acetylenes was readily accomplished by Co_2Rh_2 heterobimetallic nanoparticles in the presence of CO, water, and triethylamine. Neither a toxic phosphite nor expensive hydrogen

was needed for our process. Good chemo- and regioselectivity were observed for a variety of α -keto alkynes to produce 2(3H)-, or 2(5H)-furanone as the dominant product. The three different reaction pathways can be controlled simply by variation of the reaction conditions, *i.e.*, the reaction temperature and the pressure of CO. Furthermore, the Co_2Rh_2 catalyst is recyclable and no hydrogenated byproduct was obtained. Current efforts in our laboratory are directed towards acquiring a deeper understanding of the mechanism responsible for this new type of reaction.

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