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Catalytic Pauson–Khand-Type Reaction Using Aldehydes as a CO Source

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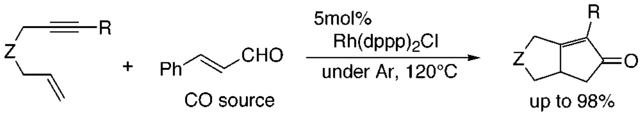
ABSTRACT



Rhodium complex-catalyzed carbonylative alkene–alkyne coupling proceeds using aldehydes as a CO source. Cinnamaldehyde is the best CO donor, and various cyclopentenones were provided in high isolated yields by a solvent-free system.

The decarbonylation of carbonyl compounds mediated by transition metal complexes is an important and fundamental reaction in organometallic chemistry, and it has been thoroughly examined, including the mechanism.[1] Rhodium and iridium complexes are well-known to be effective catalysts,[2] and catalytic decarbonylation under mild reaction conditions is still an intriguing topic.[3] Recently, decarbonylation has attracted much attention as a key step in metal-catalyzed carbon−carbon bond cleavage.[4] However, the synthetic utilization of the carbon monoxide generated from decarbonylation has been neglected.[5] We considered that, if CO was promptly captured by metal-catalyzed carbonylative coupling, both the decarbonylation and coupling could be facilitated, and an efficient tandem process would be realized.

We report here the first catalytic Pauson−Khand-type reaction[6] using aldehyde as a CO source as far as we know. Moreover, the reaction proceeds effectively and cleanly even under solvent-free conditions, and various bicyclic enones can be obtained in high yield.

We examined intramolecular alkene−alkyne coupling using Rh(dppp)$_2$Cl[7] (dppp: 1,3-bis(diphenylphosphino)-propane) as a catalyst with cinnamaldehyde (20 equiv) without any solvent. Enyne **1** was readily consumed (2 h), and cyclopentenone **2** was obtained in almost quantitative yield (Table 1, entry 1).[8,9] When only one-fourth of the amount of aldehyde was used, the yield decreased slightly (entry 2). Even with almost an equivalent amount of aldehyde, the reaction proceeded smoothly to provide **2** in

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[1] Alyea, E. C.; Meek, D. W. In *Catalytic Aspects of Metal Phosphine Complexes*; American Chemical Society: Washington, DC, 1980; Chapter 4, pp 65−83. Doughty, D. H.; Pignolet, L. H. In *Homogeneous Catalysis with Metal Phosphine Complexes*; Pignolet, L. H., Ed.; Plenum: New York, 1983; Chapter 11, pp 343−375. Jardine, F. H. In *Carbonylations*; Colquhoun, H. M., Thompson, D. J., Twigg, M. V., Eds.; Plenum: New York, 1991; Chapter 11, pp 407−469.

[2] Ohno, K.; Tsuji, J. *J. Am. Chem. Soc.* **1968**, *90*, 99−107. Blum, J.; Oppenheimer, E.; Bergmann, E. D. *J. Am. Chem. Soc.* **1967**, *89*, 2338−2341.

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[5] Decarbonylated CO from formic acid is utilized in metal-catalyzed hydroxycarbonylation: Simonato, J.-P.; Walter, T.; Métivier, P. *J. Mol. Catal. A* **2001**, *171*, 91−94 and references therein.

[6] Recent reviews of the Pauson−Khand(-type) reaction: (a) Schore, N. E. In *Comprehensive Organometallic Chemistry II*; Hegedus, L. S., Ed.; Pergamon: Oxford, 1995; Vol. 12, pp 703−739. (b) Geis, O.; Schmalz, H. G. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 911−914. (c) Jeong, N. In *Transition Metals In Organic Synthesis*; Beller, M., Bolm, C., Eds.; Wiley-VCH: Weinheim, Germany, 1998; Vol. 1, pp 560−577.

[7] Rhodium complex-catalyzed Pauson−Khand-type reactions: (a) Koga, Y.; Kobayashi, T.; Narasaka, K. *Chem. Lett.* **1998**, 249−250. (b) Kobayashi, T.; Koga, Y.; Narasaka, K. *J. Organomet. Chem.* **2001**, *624*, 73−87. (c) Jeong, N.; Lee, S.; Sung, B. K. *Organometallics* **1998**, *17*, 3642−3644. (d) Jeong, N.; Sung, B. K.; Choi, Y. K. *J. Am. Chem. Soc.* **2000**, *122*, 6771−6772. (e) Evans, P. A.; Robinson, J. E. *J. Am. Chem. Soc.* **2001**, *123*, 4609−4610.

[8] In solvent-free conditions under an atmospheric pressure of CO, it took 24 h to consume enyne **1** and the reaction gave a complex mixture that included enone **2** (33%).

[9] Iridium complex (IrCl(CO)(PPh$_3$)$_2$) also catalyzes the present reaction under the same reaction conditions but in an unsatisfactory yield of 35%. Iridium complex can catalyze Pauson−Khand-type reaction: Shibata, T.; Takagi, K. *J. Am. Chem. Soc.* **2000**, *122*, 9852−9853.

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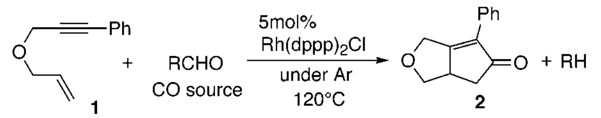
Table 1. Carbonylative Coupling of **1** Using Various Aldehydes as a CO Source[a]



entry	aldehyde (equiv)	time/h	yield/%
1	cinnamaldehyde (20)	2	98
2	cinnamaldehyde (5)	3	93
3	cinnamaldehyde (1.2)	3	83
4[b]	cinnamaldehyde (1.2)	3	80
5[c]	cinnamaldehyde (20)	24	54
6	benzaldehyde (20)	3	87
7	benzaldehyde (1.2)	4	12
8	2-hexenal (20)	2	68
9	hexanal (20)	2	30

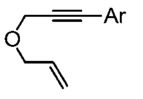
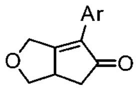
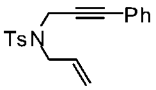
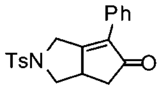
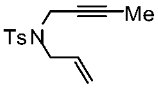
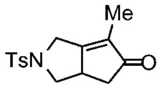
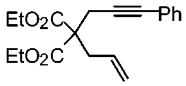
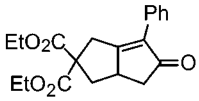
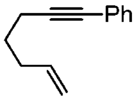
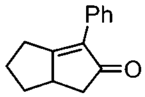
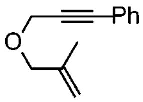
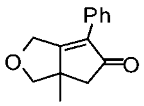
[a] Reaction was employed in a 0.3 mmol scale, and enone **2** was purified using preparative TLC, except entry 4. [b] Reaction was employed in a 2.1 mmol scale, and enone **2** was purified by bulb-to-bulb distillation. [c] Reaction was employed at 60 °C.

high yield (entry 3). Carbonylative coupling proceeded at a larger reaction scale within the same reaction time, and the product was isolated by simple distillation in almost the same yield, which means that all of these procedures can be performed in a completely solvent-free system (entry 4).[10] It is noteworthy that this reaction, including both catalytic decarbonylation and alkene−alkyne coupling, proceeded with a moderate yield even at a temperature as low as 60 °C (entry 5). The yield depended on the aldehydes used. Benzaldehyde is a good CO source, but when 1.2 equiv of benzaldehyde was used, the reaction gave a complex mixture and enone **2** was obtained in very low yield (entries 6 and 7). An aliphatic α,β-unsaturated aldehyde gave **2** in moderate yield, but an alkyl aldehyde was a poor CO donor (entries 8 and 9). These results imply that cinnamaldehyde is the best CO source among these four aldehydes and that a phenyl group and carbon−carbon double bond are important components of the CO donor.

Under solvent-free conditions using cinnamaldehyde as a CO source, Rh(cod)(dppp)Cl, which was prepared in situ from $[Rh(cod)Cl]_2$ and 2 equiv of dppp, was also a good catalyst, and enone **2** was obtained in 75% yield. Other rhodium complexes, including phosphine-free and cationic complexes, were also examined. In each reaction, enyne **1** was readily consumed, but the yield of **2** was very poor ($[Rh(cod)Cl]_2$, 7%; $[Rh(CO)_2Cl]_2$, 13%; $[Rh(dppp)_2]$ BF_4, <5%).

Various enynes were subjected to the above reaction conditions (catalyst, $Rh(dppp)_2Cl$; CO source, cinnamaldehyde; 120 °C) (Table 2). Another allyl propargyl ether, 4-methoxyphenyl-substituted enyne, was also transformed into the bicyclic enone in good yield (entry 1). Allyl propargylamine is also a good substrate for the present system to give the enone in an almost quantitative yield (entry 2). Enyne with an alkyl substituent on alkyne was also appropriate for obtaining the corresponding product in high yield (entry 3). The carbonylative coupling of enynes bridged by a carbon chain, allylpropargylmalonate and 1-hepten-6-yne, took slightly longer than that of enynes bridged by heteroatoms, but enones were obtained in acceptable yields (entries 4 and 5). 1,1-Disubstituted olefin is a rather inactive substrate in the Pauson−Khand-type reaction, but coupling proceeded with a good yield (entry 6).

Table 2. Solvent-Free Catalytic Carbonylative Coupling of Various Enynes[a]

entry	enyne	cyclopentenone	time/h	yield/%
1	 Ar=4-MeOPh		2	88
2			2	98
3			2	90
4			5	56
5			4	65
6			24	75

[a] Molar ratio of $Rh(dppp)_2Cl$:enyne:cinnamaldehyde = 0.05:1.0:20. Reaction was employed at 120 °C under an atmospheric pressure of argon.

An elucidation of the precise mechanism of this reaction will require further investigation, but we can consider here the possibility that the two catalytic cycles, decarbonylation and carbonylative coupling, operate in concert (Scheme 1).[11] The facile transfer of CO from the metal−carbonyl complex to the metallacycle intermediate of Pauson−Khand-type reaction enables effective coupling: dissociation of CO facilitates catalysis of the decarbonylative supply of CO[12] and the gradual supply of CO by decarbonylation from aldehyde is an appropriate condition for carbonylative coupling.[13] It is unclear, but the coordination of the carbon−

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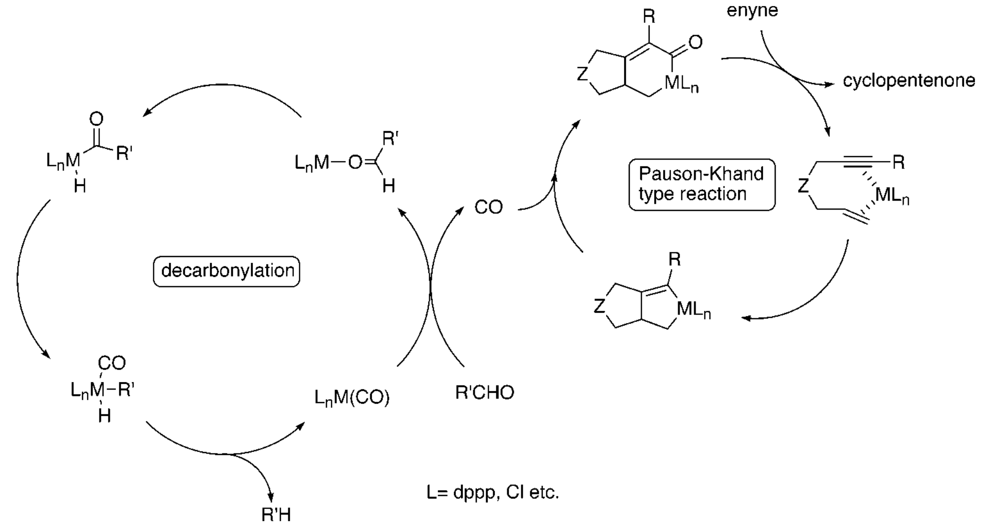
[10] Experimental procedures: $Rh(dppp)_2Cl$ (101 mg, 0.105 mmol), enyne **1** (362 mg, 2.10 mmol), and cinnamaldehyde (333 mg, 2.52 mmol) were placed in a flask, and the mixture was stirred at 120 °C for 3 h under argon. The flask was then attached to a bulb-to-bulb distillation apparatus. After removal of styrene and a small amount of cinnamaldehyde, the pure product **2** was distilled (334 mg, 1.67 mmol, 80% yield).

[11] Rh(cod)(dppp)Cl is also an efficient catalyst, and therefore the coordination of one bidentate phosphine ligand is fundamentally sufficient for the present catalytic cycles.

[12] O'Connor, J. M.; Ma, J. *J. Org. Chem.* **1992**, *57*, 5075−5077.

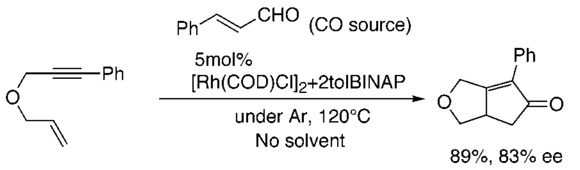
[13] Reduction of the partial pressure of carbon monoxide has been reported to accelerate the Pauson−Khand-type reaction (ref 7b).

Scheme 1



carbon double bond of cinnamaldehyde would make possible decarbonylation under these mild conditions (Table 1, entry 5).

This protocol was examined in the asymmetric reaction. As a preliminary experiment, chiral bicyclic enone **2** was obtained using tolBINAP ligand (eq 1). It is noteworthy that a neutral, not cationic, chiral rhodium complex achieved good enantioselectivity in Pauson−Khand-type reaction.[7d]



(1)

To establish the environmentally friendly process, the waste of large amounts of organic solvents is one of the serious problems to be resolved. Recently, several reaction media, including water,[14] ionic liquids,[15] and supercritical liquids[16] have been reported to be promising alternatives to organic solvents. While the simplest solution is to develop a solvent-free system, the solvent plays a pivotal role in achieving efficient and selective synthesis in metal-catalyzed reactions.[17,18] In this study, we realized a completely solvent-free system in catalytic carbonylative alkene−alkyne coupling using an aldehyde as a CO source. This could pave the way for a new environmentally benign process for preparing various cyclopentenones.

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(14) *Organic Synthesis in Water*; Grieco, P. A., Ed.; Blackie Academic & Professional: London, 1998.

(15) Welton, T. *Chem. Rev.* **1999**, *99*, 2071−2083.

(16) Jessop, P. G.; Ikariya, T.; Noyori, R. *Chem. Rev.* **1999**, *99*, 475−493.

(17) A recent example of solvent-free catalytic syntheses using organometallic compounds: Sato, I.; Saito, T.; Soai, K. *Chem. Commun.* **2000**, 2471−2472.

(18) Recent reviews: Metzger, J. O. *Angew. Chem., Int. Ed.* **1998**, *37*, 2975−2978. Tanaka, K.; Toda, F. *Chem. Rev.* **2000**, *100*, 1025−1074.