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CO-Transfer Carbonylation Reactions. A Catalytic Pauson−Khand-Type Reaction of Enynes with Aldehydes as a Source of Carbon Monoxide

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Transition-metal-catalyzed carbonylation has been a subject of intense research in the area of organic synthesis and is recognized as a powerful tool for the direct synthesis of a wide variety of carbonyl compounds.[1] However, the use of highly poisonous carbon monoxide represents a drawback to this procedure. A carbonylation reaction without the use of carbon monoxide would make reactions such as these more desirable and further advance this area. Thus, we envisioned an approach to this problem in which metal carbonyl species, which are essential key intermediates in the reaction, could be generated without the use of carbon monoxide.

In transition-metal-catalyzed carbonylation reactions, the coordination of carbon monoxide to the metal center results in the generation of metal carbonyls. Decarbonylation of aldehydes, mediated by transition metals, also represents an alternative approach to the formation of metal carbonyls (Scheme 1a).[2] If the material to be carbonylated were introduced into the decarbonylation system of aldehydes, it would be expected that it would react with the metal−carbonyl species, formed by the decarbonylation, to afford the desired carbonylated products. Herein, we wish to report the verification of our working hypothesis. This study provides, to our knowledge, the first example of a CO-transfer carbonylation.[3]

To test our hypothesis, we targeted the Pauson−Khand-type reaction of enynes (Scheme 1b).[4] Although catalytic[4,5] and enantioselective[6] variants have been developed for this transformation, it continues to attract considerable attention due to its use in the preparation of bicyclic cyclopentenones. Most of the catalytic Pauson−Khand-type reactions of enynes have been conducted under a high pressure of carbon monoxide,[7] similar to other carbonylations. This encouraged us to develop a catalytic Pauson−Khand-type reaction of enynes using aldehydes as a carbon monoxide source without the need for gaseous carbon monoxide.

Our initial studies examined the feasibility of the Rh-catalyzed CO transfer from benzaldehyde to enyne **1a**, because Rh complexes are known not only to decarbonylate aldehydes[2] but also to catalyze the Pauson−Khand-type reaction of enynes.[5d,e,6e,7a,b] The reaction of **1a** and benzaldehyde in the presence of a catalytic amount of $[RhCl(cod)]_2$ and dppp in xylene at 130 °C for 24 h afforded the desired carbonylated product **2a** in 33% isolated yield, along with 65% of unreacted **1a** (Table 1, entry 1). This shows that benzaldehyde can be used as a carbon monoxide equivalent and that its CO moiety is incorporated into **2a**. Reactions with $RhCl(PPh_3)_3$, $RhCl(CO)(PPh_3)_2$, and $[RhCl(cod)]_2$/dppe resulted in lower yields of **2a**, while no carbonylated product was obtained when $[RhCl(cod)]_2$ and $[RhCl(cod)]_2$/dppb were used as catalysts.

To improve the efficiency of CO transfer, a variety of aldehydes were examined (Table 1, entries 1−6). All the aromatic aldehydes tested were able to serve as a carbon monoxide source (entries 1−4), and it was found that the electrochemical nature of aldehydes was responsible for the CO-transfer catalysis; aldehydes having electron-withdrawing substituents (entries 3 and 4) donated a CO moiety more effectively than one having electron-releasing substituents (entry 2). This is consistent with the general tendency for alkyl groups to migrate from acyl complexes leading to the formation of metal−carbonyls.[8] An α,β-unsaturated aldehyde could also be used as a carbon monoxide source; however, its reactivity was lower than that of C_6F_5CHO (entry 5). The reaction tolerated the use of an aldehyde having β-hydrogen, which could serve as a source of a formyl group[3] (entry 6). Interestingly, for all aldehydes tested, the catalyst abstracted a CO moiety from aldehydes and transferred them to the enyne, without hydroacylating the alkene and/or the alkyne portions of the enyne.[9] Ir and Ru complexes are also known to decarbonylate aldehydes[10] and to catalyze the Pauson−Khand-type reaction.[11] When they were used as catalysts, CO transfer from the aldehyde was observed, but the efficiency was inferior to that found for the Rh catalyst (entries 7 and 8).[12]

Scheme 1. Working Hypothesis for CO-Transfer Carbonylation

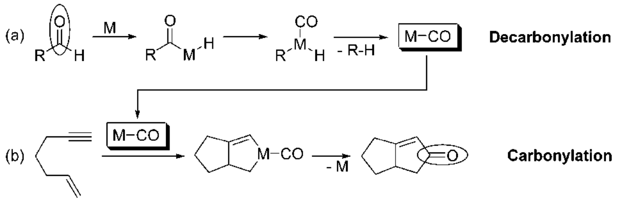
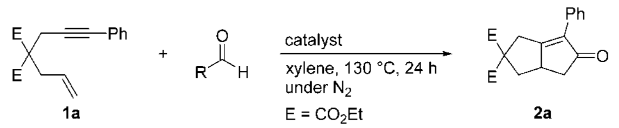


Table 1. Catalytic Pauson−Khand-Type Reaction of Enyne **1a** with Aldehydes as a Source of CO[a]



entry	R	catalyst	yield of **2a**[b]
1	Ph	$[RhCl(cod)]_2$/dppp[c]	33% (65%)
2	p-MeO-C_6H_4		35% (64%)
3	p-CF_3-C_6H_4		47% (49%)
4	C_6F_5		61% (38%)
5	(E)-Ph-CH═CH		33% (64%)
6	$PhCH_2CH_2$		62% (28%)
7	C_6F_5	$[IrCl(cod)]_2$/BINAP[d]	20% (78%)
8	C_6F_5	$Ru_3(CO)_{12}$[e]	22% (70%)

[a] Conditions: **1a** (0.25 mmol), aldehyde (0.50 mmol), and xylene (2 mL) at 130 °C for 24 h under N_2. [b] Values in parentheses are the yields of **1a** recovered. [c] 5 mol % $[RhCl(cod)]_2$ and 11 mol % dppp. [d] 5 mol % $[IrCl(cod)]_2$ and 11 mol % BINAP. [e] 3.3 mol % $Ru_3(CO)_{12}$.

Various enynes were converted to the corresponding cyclopentenones under the following conditions: enynes (0.50 mmol), C_6F_5-CHO (1.0 mmol), and xylene (2 mL) in the presence of $[RhCl(cod)]_2$ (0.025 mmol) and dppp (0.055 mmol) at 130 °C under N_2.[13]

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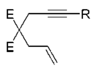
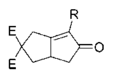
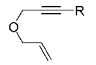
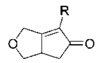
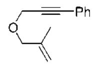
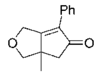
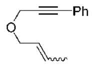
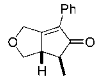
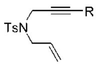
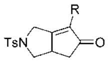
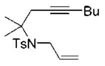
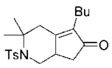
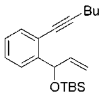
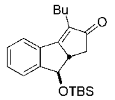
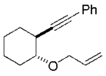
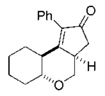
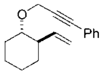
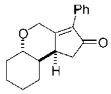
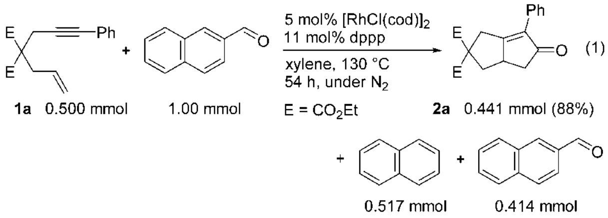
Table 2. Catalytic CO-Transfer Pauson−Khand-Type Reactions[a]

entry	enyne		time	product[b]	
1		**1a** R = Ph	60h		**2a** 97%
2[c]		**1a** R = Ph	57h		**2a** 91%
3		**1b** R = Bu	48h		**2b** 95%
4		**1c** R = Me	48h		**2c** 84%
5		**1d** R = H	24h		**2d** 71%
6		**3a** R = Ph	2h		**4a** 91%
7		**3b** R = Bu	72h		**4b** 74%
8		**5**	5h		**6** 92%
9		**7** (*E*/*Z* = 85/15)	30h		**8** 69% (13/1)[d]
10		**9a** R = Ph	4h		**10a** 95%
11		**9b** R = Bu	13h		**10b** 84%
12		**11**	100h		**12** 36% (52%)[e]
13		**13**	50h		**14** 88% (11/1)[d]
14		**15**	96h		**16** 77%[f]
15		**17**	4h		**18** 90%[f]

[a] Conditions: enyne (0.50 mmol), C_6F_5CHO (1.0 mmol), $[RhCl(cod)]_2$ (0.025 mmol), dppp (0.055 mmol), and xylene (2 mL) at 130 °C under N_2. [b] Isolated yield. [c] Benzaldehyde (5.0 mmol) was used in place of C_6F_5CHO. [d] Diastereomeric ratios were determined by GC. [e] The value in parentheses is the yield of the recovered enyne. [f] Single stereoisomers.

The present reaction is remarkably general and high-yielding (Table 2).[14] When the reaction time was prolonged (60 h) until all of **1a** was consumed, a quantitative yield of **2a** were obtained (entry 1). Use of a large excess (10 equiv) of benzaldehyde also resulted in the formation of **2a** in excellent yield (entry 2). The reaction of aryl-substituted acetylenes afforded the carbonylated products in higher yields than those of alkyl-substituted acetylenes (entries 1−7, 10, and 11). The reactions of enynes having tethered heteroatoms such as oxygen and nitrogen proceeded more smoothly than those of enynes in which the tether consisted of only carbon (entries 1, 6, and 11). Enynes having 1,1- and 1,2-disubstituted alkene portions reacted smoothly (entries 8 and 9). 1,7-Enynes also were applicable for this carbonylation and were converted to bicyclo[4.3.0]nonanone derivatives (entries 12, 14, and 15). For substrates where two groups were positioned on contiguous carbons of a ring system, the cyclocarbonylation proceeded diastereoselectively, resulting in the formation of tricyclic cyclopentenones (entries 13−15).

Last, the CO moiety on an aldehyde was found to transfer efficiently to an enyne. The reaction of enyne **1a** (0.500 mmol) with 2-naphthaldehyde (1.00 mmol) afforded the carbonylated product **2a** (0.441 mmol) in 88% yield, along with the decarbonylated product, naphthalene (0.517 mmol), and unreacted aldehyde (0.414 mmol) (eq 1). The majority of the CO moiety that had been abstracted from the aldehyde was utilized in the carbonylation step.[15] This indicates that, in the present carbonylation system, a cascade sequence involving decarbonylation and carbonylation proceeds with negligible loss of the CO moiety, as shown in Scheme 1.



In conclusion, we report on a successful transition metal-catalyzed Pauson−Khand-type reaction using aldehydes as the carbon monoxide source without the need for gaseous carbon monoxide. This represents the first reported example of a CO-transfer carbonylation. Further studies to address the scope of this new strategy for other carbonylations are also underway.

Acknowledgment. We thank Ms. Yoshiko Nishiura for assistance in obtaining HRMS.

Supporting Information Available: Experimental details and characterization data (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(11) For the Ir complex, see ref 6f. For the Ru complex, see: (a) Morimoto, T.; Chatani, N.; Fukumoto, Y.; Murai, S. *J. Org. Chem.* **1997**, *62*, 3762. (b) Kondo, T.; Suzuki, N.; Okada, T.; Mitsudo, T. *J. Am. Chem. Soc.* **1997**, *119*, 6187.

(12) A combination of $[IrCl(cod)]_2$ with other phosphines such as PPh_3, dppe, dppp, and dppb resulted in the formation of trace amounts of **2a**.

(13) The CO-transfer reaction proceeded even at lower temperature (110 °C) to give 33% of **1a** for 24 h.

(14) All new compounds were characterized by NMR, IR, and mass spectral data, as well as by high-resolution mass spectra. See Supporting Information.

(15) It is unclear whether the rest of the carbonyl moiety that is abstracted from the aldehyde is used for other transformations or removed from the reaction system. We postulate that a portion is present on the rhodium metal, in the form of a carbon monoxide ligand.

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