

# Communications to the Editor

## (Indenyl)cobalt(I)-Catalyzed Cocyclization of Alkyne, Alkene, and Carbon Monoxide to Cyclopentenones<sup>1</sup>

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The development of simple and general methods for the preparation of cyclopentenones from readily available substrates is one of the major challenges of metal-promoted organic synthesis.<sup>2</sup> One of the most effective methods of synthesis of cyclopentenones is the Pauson-Khand reaction (PKR).<sup>3-5</sup> However, most PKRs are stoichiometric reactions. There have been many attempts<sup>6</sup> to catalyze the PKR, but the only truly catalytic reactions described so far are very limited.<sup>7,8</sup> A number of alternatives to the PKR have been reported that involve various transition metals as catalysts or promoters.<sup>2</sup> Herein we report the development of a new catalyst system that proceeds under mild reaction conditions to give cyclopentenones in excellent yields.

Our new process has been successfully achieved by introducing 1,5-cyclooctadiene(indenyl)cobalt(I) complex (**1**)<sup>9</sup> as a catalyst. Complex **1** is moderately stable and can be stored for a long time

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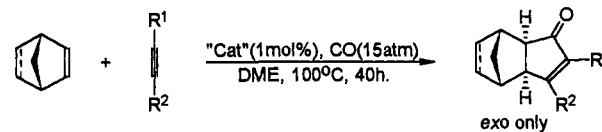
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Table 1. Intermolecular Reactions with Norbornadiene or Norbornene



entry no.	R <sup>1</sup>	R <sup>2</sup>	alkene	yield, %
1	Ph	H	norbornadiene	93
2	(CH <sub>2</sub> ) <sub>5</sub> CH <sub>3</sub>	H	norbornadiene	95
3	CH <sub>2</sub> OH	H	norbornadiene	96
4	CH(CH <sub>3</sub> )OH	H	norbornadiene	85 <sup>a</sup>
5	C(CH <sub>3</sub> ) <sub>2</sub> OH	H	norbornadiene	95
6	CH <sub>2</sub> CH <sub>2</sub> OH	H	norbornadiene	96
7	(CH <sub>2</sub> ) <sub>4</sub> OH	H	norbornadiene	97
8	Ph	Ph	norbornadiene	99 <sup>b</sup>
9	Ph	Me	norbornadiene	53 <sup>b</sup>
10	Ph	H	norbornene	82
11	(CH <sub>2</sub> ) <sub>5</sub> CH <sub>3</sub>	H	norbornene	95

<sup>a</sup> Both diastereomers were obtained (1:1, by <sup>13</sup>C NMR). <sup>b</sup> 5 mol % of catalyst was used, and unreacted alkynes were recovered.

under nitrogen in a freezer. To our knowledge, complex **1** is the first practically useful catalytic system for the formation of cyclopentenones from enynes and from alkynes with norbornadiene or norbornene.

A representative experimental procedure for the intermolecular cocyclization reaction of alkyne with norbornadiene is given as follows. When a mixture of alkyne (5.0 mmol), norbornadiene (25 mmol), and **1** (14 mg, 0.05 mmol) in 10 mL of DME was heated under carbon monoxide (15 atm at room temperature) at 100 °C for 40 h, the corresponding cyclopentenone derivative was obtained in high yield after column chromatography. Several representative results obtained under standard conditions are summarized in Table 1.

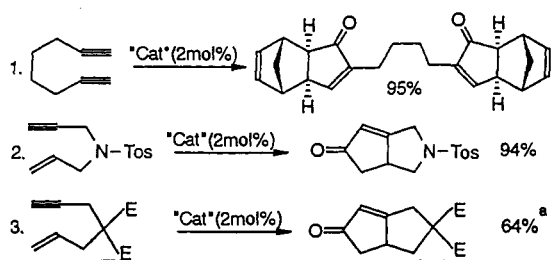
The efficiency of **1** was checked in the reaction of propargyl alcohol with norbornadiene. The maximum turnover number was 500.<sup>10</sup> However, for convenience, we used 1 mol % of catalyst for studying other reactions.

The following features deserve comment. (1) The intermolecular cyclocarbonylation of norbornadiene or norbornene with various terminal alkynes was achieved in high yields (Table 1). (2) Propargyl alcohol (entry 3 in Table 1) and 1,7-octadiyne (entry 1 in Scheme 1), which have been known as poor substrates<sup>11</sup>

(9) Salzer, A.; Taschler, C. *J. Organomet. Chem.* **1985**, *294*, 261. Jablonski, C. R.; Zhou, Z.; Bridson, J. N. *J. Organomet. Chem.* **1992**, *429*, 379. Complex **1** was synthesized according to the procedure published in Yamazaki, H.; Wakasuki, Y. *Organometallic Synthesis* **1988**; Vol 14, p 278. Indene (0.82 mL, 7.0 mmol) was dissolved in THF (14 mL), and the resulting solution was cooled to -78 °C. *n*-BuLi (3 mL in 2.5 M hexane solution) was added to the indene solution, and the solution was allowed to warm room temperature. Toluene (20 mL), COD (2.0 mL), and Co(PPh<sub>3</sub>)<sub>3</sub>Cl (4.4 g, 10.5 mmol) were added. The resulting solution was heated at 80 °C for 2 h and then cooled to room temperature. The solution was passed through neutral alumina. The remaining compounds on the alumina were eluted by using hexane. After evaporation of the solvent, the residue was redissolved in hexane. Most of PPh<sub>3</sub> was removed by recrystallization from the solution. The remaining solution was column chromatographed on neutral alumina (100-125 mesh, Fluka) by eluting with a mixture of hexane and ether (v/v, 100:1). After evaporation of the solvent, orange-red solids were obtained in 43% yield (0.85 g). Complex **1** was checked by <sup>1</sup>H NMR and HRMS. The (ind)Co(COD) is stable enough to be weighed and handled in air in a short time.

(10) To check the maximum turnover number, the following reaction conditions were applied: a mixture of propargyl alcohol (3.0 mL, 50 mmol), norbornadiene (16 mL, 150 mmol), and **1** (14 mg, 0.1 mol %) in 30 mL of DME was heated under carbon monoxide (60 atm at room temperature) at 100 °C for 2 days. After chromatographic separation, the product was obtained in 50% yield.

(11) Jaffer, H. J. Ph.D. Thesis, Strathclyde University, Glasgow G1 1XL, Scotland, 1982.

Scheme 1<sup>a</sup>

<sup>a</sup> 30% of starting material was recovered.

for PKR, generated cyclopentenones in high yields. Particularly in the case of 1,7-octadiyne, we did not observe any [2 + 2 + 2] cycloaddition products. (3) With disubstituted alkynes, e.g., diphenylacetylene (entry 8 in Table 1) and methylphenylacetylene (entry 9 in Table 1), the reaction proceeds less effectively. However, when the reaction temperature was increased to 140 °C, the turnover number increased to ca. 20.<sup>12</sup> Thus, we expect that by using more catalysts and/or high reaction temperatures, the reaction may proceed to completion. (4) Only the *exo* isomer was observed.<sup>13</sup> (5) Intramolecular reaction (entries 2 and 3 in Scheme 1) gave the corresponding products in good yields. It should also be noted that the required substrates are readily available in most cases.

Attempts to obtain cyclopentenones with less strained or less reactive alkenes, e.g., ethylene, cyclopentene, allyl alcohol, and methyl acrylate, were not successful yet. We are struggling to

(12) The following reaction conditions were used: catalyst, 1 mol%; reaction time, 40 h; reaction medium, DME; reaction temperature, 140 °C.

(13) Khand, I. U.; Murphy, E.; Pauson, P. L. *J. Chem. Res. (S)* 1978, 350.

achieve the formation of cyclopentenones from less reactive alkenes by changing the reaction conditions.

When the cyclization was done with  $\text{CpCo}(\text{CO})_2$  or  $\text{CpCo}(\text{COD})$  under the same conditions as in Table 1, the reaction was negligible. Thus, the indenyl ligand is essential for this cocyclization reaction.<sup>14</sup> However, we do not have any direct evidence of which step in the catalytic cycle would be assisted by the indenyl group.

In conclusion, we have found the first practically useful catalytic system for the formation of cyclopentenones from alkyne, alkene, and carbon monoxide. Table 1 holds that the method shows considerable promise as a synthetic tool. The demonstrated process can be potentially useful in large scale synthesis of the cyclopentenones. Examination of the ways to extend this process to less strained or less reactive alkenes is under investigation.

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**Supplementary Material Available:** Spectroscopic characterization of the new products listed in Table 1 and Scheme 1 (3 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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