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LETTERS

Hexacarbonyldicobalt-Alkyne Complexes as Convenient $Co_2(CO)_8$ Surrogates in the Catalytic Pauson-Khand Reaction

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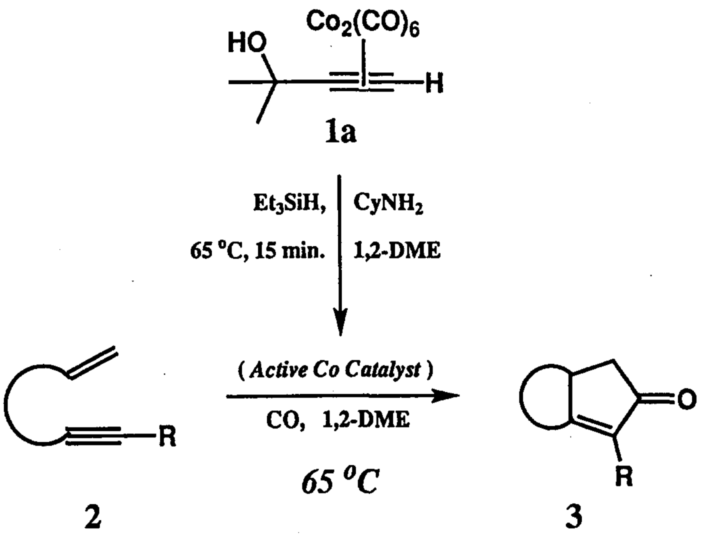
Abstract: Selected hexacarbonyldicobalt-alkyne complexes have been found to serve as convenient substitutes for the labile $Co_2(CO)_8$ in thermal, *catalytic* Pauson-Khand reactions.

In the preceding Letter, we described a convenient, thermally driven Pauson-Khand reaction catalyzed by $Co_2(CO)_8$. The need for $Co_2(CO)_8$, which is labile to both heat and O_2, in a very high state of purity constitutes an experimental disadvantage inherent to this procedure. The identification of alternatives to this dinuclear complex that are chemically robust should greatly enhance the practical attractiveness of the Co catalyzed PKR. Herein we show that selected, *shelf stable*, $Co_2(CO)_6$-alkyne complexes can serve as sources of an active catalyst for carbonylative enyne cyclizations. Very recently, Isobe reported that Et_3SiH is a useful reagent for the conversion of $Co_2(CO)_6$-alkyne complexes into vinylsilanes via reductive decomplexation.[2] In view of the possibility that the (carbonyl)cobalt byproduct generated in these reactions might exhibit catalytic activity, a series of $Co_2(CO)_6$-alkyne complexes (e.g., complexes of: $HO(CH_3)_2CC{\equiv}CH$, $PhC{\equiv}CH$, $PhC{\equiv}CPh$, $TMSC{\equiv}CTMS$, $HOCH_2C{\equiv}CH$, $HOCH_2C{\equiv}CCH_2OH$ and $MeO_2CC{\equiv}CCO_2Me$) were screened in combination with Et_3SiH[3] as $Co_2(CO)_8$ surrogates in the catalytic PKR involving enyne **2a**.



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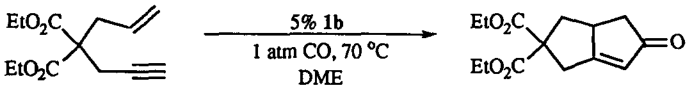
Of the various alkyne derivatives examined, the $Co_2(CO)_6$ complexes of 2-methyl-3-butyn-2-ol, **1a**[4] and phenylethyne **1b** proved most satisfactory and were virtually identical as sources of a highly active catalyst. In addition, with the exception of $(EtO)_3SiH$, several alternative reagents proved less effective than Et_3SiH for catalyst generation via reductive decomplexation (**Table I**). Since **1a** is an easily prepared, *crystalline* substance, it was selected for examination as a precatalyst in a series of representative intramolecular Pauson-Khand cyclizations.

Table I. Effect of Additives on the Thermal PKR with Catalytic 1b



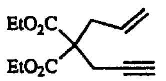
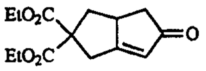
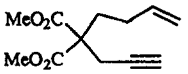
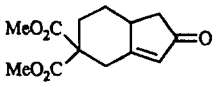
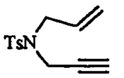
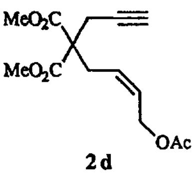
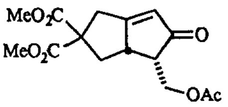
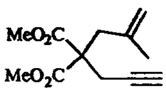
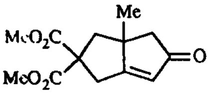
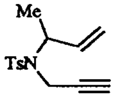
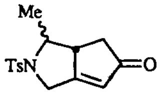
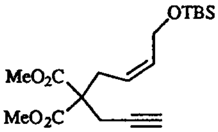
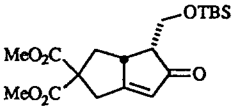
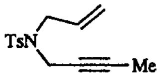
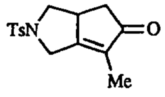
Entry	Additive^a	Time (h)	Yield (%)^b
1	none	8	61
2	Et_3SiH	4	69
3	PMHS^d	1.5	18^c
4	HBPin^e	1.5	6^c
5	$(EtO)_3SiH$	4	68
6	Bu_3SnH	2	18^c

a. 1 equiv/complex **1b**. b. isolated yield, unless noted otherwise. c. % conversion, as determined by GC. d. Polymethylhydrosiloxane. e. Pinacolborane

In a typical example, a solution of **1a** (0.025 mmol, 5 mol%) in 1,2-DME (5 mL) under a CO atmosphere was treated with Et_3SiH[3] (0.025 mmol) and cyclohexylamine (0.075 mmol).[5] The resulting solution was heated at 65 °C for 15 min to generate the active cobalt catalyst. Subsequent addition of the enyne substrate **2a-h** followed by stirring at 65 °C under 1 atm of CO for the designated time furnished the corresponding cyclopentenones **3a-h** in the indicated yield.[6] A summary of results obtained for the cyclization of a range of representative enynes appears in **Table II.**

The beneficial effect of the auxiliary ligands cyclohexylamine or thiophene on reaction efficiency and yield enhancement deserves comment. Although significant rate increases were not apparent under the conditions used for these cyclizations,[5] measurable improvements in product yield were obtained in many instances. Accordingly, carbonylative cyclization of the enynes **2a**,[7a] **2b**[7b] and **2c**[7b] to cyclopentenones **3a**, **3b** and **3c** proceeded in only 71%, 64% and 65% yield respectively in the absence of $CyNH_2$.

Table II. Thermally Promoted Pauson-Khand Cyclizations Catalyzed by Complex 1a/Et$_3$SiH

Entry	Substrate	Time (h)	Product	Yield (%)[a]
1	 2a	6	 3a	92[b]
2	 2b	12	 3b	86[b,c]
3	 2c	12	 3c	77[b,c]
4	 2d	12	 3d	81[d,f]
5	 2e	12	 3e	95
6	 2f	12	 3f	85[e]
7	 2g	12	 3g	90[d,g]
8	 2h	15	 3h	92[d]

a. All reactions were performed using substrate concentrations of 0.1M with 5 mol% Et$_3$SiH, 15% CyNH$_2$ and 5 mol% alkyne-cobalt complex at 65 °C, unless stated otherwise. b. average of two experiments. c. 7.5 mol% alkyne-cobalt complex. d. 10 mol% alkyne-cobalt complex e. 1.3/1.0 ratio of diastereomers. f. Thiophene was used (30 mol%) instead of CyNH$_2$. g. >20/1 cis/trans by ^{1}H NMR spectroscopy.

In conclusion, selected $Co_2(CO)_6$-alkyne complexes have been shown to serve as exceptionally convenient substitutes for the relatively labile $Co_2(CO)_8$ in the catalytic, thermal PKR. Of these, **1a** is noteworthy due to its shelf stability,[8] ready preparation, crystallinity and high decomplexation rate in the presence of Et_3SiH.

Acknowledgements. Generous financial support for this research by a grant from the National Science Foundation is gratefully acknowledged.

Literature Cited and Footnotes

1. Recipient of a Japan Society for the Promotion of Science Fellowship, 1997.
2. Hosokawa, S.; Isobe, M. *Tetrahedron Lett.* **1998**, *39*, 2609-2612.
3. By way of comparison, a control experiment in which **2a** was heated at 65 °C in the presence of **1a** (5 mol%) and $CyNH_2$ (15 mol%) for 4h proceeded to only **15%** conversion in the absence of Et_3SiH.
4. To a solution of $Co_2(CO)_8$ (1.8 g, 5.3 mmol, 1.00 equiv) in diethyl ether (25 mL) under argon was added 2-methyl-3-butyn-2-ol (485 μL, 5.0 mmol, 0.95 equiv) dropwise. The resulting solution was allowed to stir for 5 h at rt, then the solvent was removed under reduced pressure. Flash chromatography using a 5 x 9 cm silica gel column (100% hexanes for nonpolar material elution, then 15% EtOAc/hexanes for product elution) and subsequent evaporation of solvent afforded 1.57 g (85%) of complex **1a** as a deep red microcrystalline solid.
5. Sugihara has shown that selected primary amines induce a rate enhancement of the stoichiometric PKR. Sugihara, T.; Yamada, M.; Ban, H.; Yamaguchi, M.; Kaneko, C. *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 2801-2804.
6. Representative Procedure: To a solution of 2-methyl-3-butyn-2-ol hexacarbonyldicobalt (9.2 mg, 0.025 mmol, 5 mol%) in 1,2-DME (5 mL) under a CO atmosphere was sequentially added Et_3SiH (50μL of a 0.5 M *p*-xylene solution, 0.025 mmol) and cyclohexylamine (9 μL, 0.075 mmol). The resulting solution was heated at 65 °C for 15 min at which time 2-allyl-2-prop-2-ynyl malonic acid diethyl ester **2a** (119 mg, 0.5 mmol) was added via a gastight syringe. The resulting solution was maintained at 65 °C for 6 h. After cooling to room temperature, brine and ethyl acetate were added (1 mL each) and the biphasic mixture was stirred open to air for 30 min. Workup with EtOAc (50mL), brine (25 mL) and drying (Na_2SO_4) followed by evaporation of solvent and final purification by flash chromatography (SiO_2, 15% ethyl acetate in hexanes to 30% ethyl acetate in hexanes gradient for elution) afforded 125 mg of 5-oxo-3,3a,4,5-tetrahydro-1*H* - pentalene-2,2-dicarboxylic acid diethyl ester **2b** (93% yield) as a colorless oil.
7. (a) Conducted at 65 °C. (b) Conducted at 70 °C.
8. A sample of **1a** that was deliberately exposed to air at room temperature for 24 h showed no loss of activity as a precatalyst.