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The Pauson−Khand Reaction Catalyzed by the Methylidynetricobalt Nonacarbonyl Cluster

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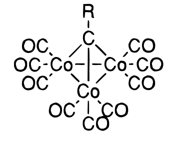
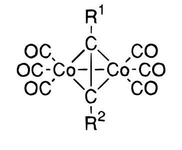
Cyclic cotrimerization of an alkyne, an alkene, and carbon monoxide mediated by dicobalt octacarbonyl was first discovered by Pauson et al.[2] and has been widely utilized for the construction of a variety of cyclopentenones[3] including natural products.[4] Catalytic versions of this cyclization have been recently developed using early and late transition metals.[5]

Alkylidynetricobalt nonacarbonyl clusters (**1**) are easily prepared by the reaction of dicobalt octacarbonyl with trihaloalkanes.[6] They are more stable against autooxidation than the parent dicobalt octacarbonyl.[7] These clusters have a similar structure with alkyne−$Co_2(CO)_6$ complexes (**2**) in which one carbon edge of the tetrahedron is replaced with the $Co(CO)_3$ unit. Thus, we started to examine the use of the clusters **1** as catalyst precursors for the Pauson−Khand reaction.

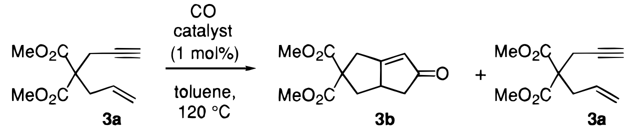


$Co_3(CO)_9(\mu^3\text{-}CR)$ (**1**)



$Co_2(CO)_6(\mu^2\text{-}R^1C{\equiv}CR^2)$ (**2**)

Table 1. Cyclization of Enyne **3a** Catalyzed by Alkylidynetricobalt Nonacarbonyls[a]



entry	catalyst	pressure of CO (atm)	time (h)	yield[b] (%) 3b	yield[b] (%) 3a
1	$Co_2(CO)_8$	7	10	12	82
2	$Co_3(CO)_9(\mu^3\text{-}CH)$	7	10	78	22
3	$Co_3(CO)_9(\mu^3\text{-}CH)$	1	10		97
4	$Co_3(CO)_9(\mu^3\text{-}CH)$	3	10	63	29
5	$Co_3(CO)_9(\mu^3\text{-}CH)$	10	10	80	17
6	$Co_3(CO)_9(\mu^3\text{-}CH)$	20	10	82	15
7	$Co_3(CO)_9(\mu^3\text{-}CCl)$	7	10	2	95
8	$Co_3(CO)_9(\mu^3\text{-}CCH_3)$	7	10	31	66
9	$Co_3(CO)_9(\mu^3\text{-}CCOOC_2H_5)$	7	10	31	65
10	$Co_3(CO)_9(\mu^3\text{-}CC_6H_5)$	7	10		99
11	$Co_3(CO)_9(\mu^3\text{-}CC_6H_5\text{-}p\text{-}CH_3)$	7	10		96

[a] A mixture of 1.00 mmol of **3a** and 0.01 mmol of catalyst in 2.5 mL of toluene was stirred at 120 °C under CO atmosphere. [b] All yields given in this table are isolated yields.

Various clusters were prepared by known methods.[6,7] Since the Lewis bases can affect the course of the Pauson−Khand reaction,[8] an inert solvent, toluene, was chosen in the reaction. A mixture of **3a** and an alkylidynetricobalt nonacarbonyl cluster (1 mol %) in toluene was stirred at 120 °C under various pressures of CO and the results are summarized in Table 1.

When dicobalt octacarbonyl was used, only a low conversion was obtained (Entry 1). In contrast, methylidynetricobalt nonacarbonyl efficiently catalyzed the cyclization (Entry 2). The CO pressures had influence on its catalytic activity and those greater than 3 atm led to the desired cyclization in good yield (Entries 2−6). The cluster turned out to be more effective for the catalytic Pauson−Khand reaction than the parent $Co_2(CO)_8$. Furthermore, while the use of $Co_2(CO)_8$ as the catalyst precursor usually requires additional promoters, such as $P(OPh)_3$[5b] or Q-beam,[5c] to allow the cyclization efficiently, the cluster alone smoothly catalyzed the cyclization.

Among the clusters investigated, the ones having a relatively small substituent on the bridging carbon, such as $Co_3(CO)_9(\mu^3\text{-}CCl)$, $Co_3(CO)_9(\mu^3\text{-}CCH_3)$, and $Co_3(CO)_9(\mu^3\text{-}CCOOC_2H_5)$, catalyzed the desired cyclization, albeit in low yields (Entries 7−9). In contrast, the ones having aromatic substituents were detrimental to catalysis (Entries 10 and 11). No product in which the carbon unit of the cluster was incorporated has been detected even when 0.2 molar equiv of the cluster was used. The best results were obtained by using the parent cluster, *i.e.* methylidynetricobalt nonacarbonyl. It is known that thermal decomposition of $Co_2(CO)_8$ produced tetracobalt dodecacarbonyl, which is inactive in the catalytic Pauson−Khand reactions.[5b] Although Rautenstrauch et al. reported the catalytic Pauson−Khand reaction using alkyne−$Co_2(CO)_6$ complexes, it could not be reproduced by the authors.[5a] It is, therefore, interesting that changing one $Co(CO)_3$ unit of $Co_4(CO)_{12}$ with a methylidyne or one alkylidyne unit of alkyne−

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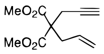
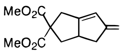
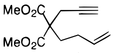
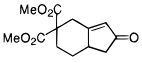
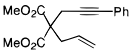
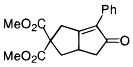
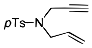
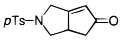
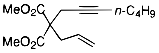
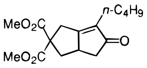
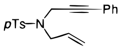
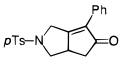
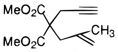
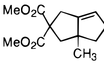
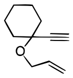
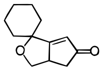
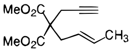
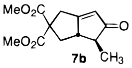
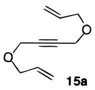
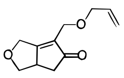
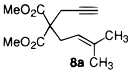
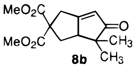
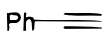
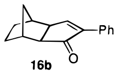
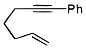
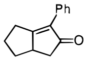
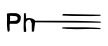
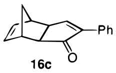
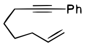
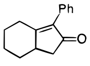
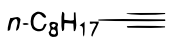
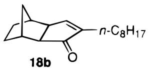
Table 2. The Pauson−Khand Reaction Catalyzed by Methylidynetricobalt Nonacarbonyl[a]

Entry	Substrate	Time (h)	Product	Yield (%)[b]	Entry	Substrate	Time (h)	Product	Yield (%)[b]
1	 **3a**	10	 **3b**	98	9	 **11a**	10	 **11b**	97
2	 **4a**	10	 **4b**	91	10	 **12a**	10	 **12b**	96
3	 **5a**	20	 **5b**	89	11	 **13a**	10	 **13b**	91
4	 **6a**	10	 **6b**	89	12	 **14a**	20	 **14b**	78[e]
5	 **7a**	15	 **7b**	83	13	 **15a**	10	 **15b**	89
6	 **8a**	20	 **8b**	N. R.[c]	14[f]	 **16a** +  **17a**	10	 **16b**	98
7	 **9a**	10	 **9b**	98	15[f]	 **16a** +  **17b**	10	 **16c**	89
8	 **10a**	20	 **10b**	23[d]	16[f]	 **18a** +  **17a**	10	 **18b**	94

[a] A mixture of 1.00 mmol of the substrate and 0.02 mmol of $Co_3(CO)_9(\mu^3\text{-CH})$ in 2.5 mL of toluene was stirred at 120 °C under 7 atm of CO. [b] All yields given in this table are isolated yields. [c] The substrate **8a** was recovered in a 98% yield. [d] The substrate **10a** was recovered in a 70% yield. [e] The substrate **14a** was recovered in a 10% yield. [f] 1.5 mmol of norbornene (**17a**) and norbornadiene (**17b**) were used for the reaction.

$Co_2(CO)_6$ complexes with $Co(CO)_3$ brings about excellent results for this catalytic cyclization.

We then continued to investigate the scope of this reaction using 2 mol % of methylidynetricobalt nonacarbonyl under 7 atm of CO. The results are summarized in Table 2. Independent of the nature of the substituents on the alkyne moiety, [3.3.0]-bicyclic systems were formed in good yields (Entries 1−3). On the other hand, the number of substituents on the alkene is rather important. While 1,1- and 1,2-disubstituted alkene gave a high yield of their corresponding cyclized compounds (Entries 4 and 5), trisubstituted **8a** was unchanged under the same conditions (Entry 6). Additionally, an increase in the tether length was detrimental to cyclization leading to low conversions (Entries 7 and 8), but the addition of an assisting group for cyclization, such as *gem*-disubsituents, resulted in clean reaction (Entry 9). This effect, however, did not appear when the reaction was applied to larger ring systems such as [5.3.0]-bicyclic ones. Heteroatoms containing compounds such as tosylamides or ethers also cyclized effectively (Entries 10−13). Finally, the intermolecular Pauson−Khand reaction was also possible in the presence of norbornene (**17a**) and norbornadiene (**17b**) in combination with a terminal alkyne (Entries 14−16).[9]

In conclusion, we have shown that the easily prepared and air-stable methylidynetricobalt nonacarbonyl cluster can be used as a catalyst precursor for the Pauson−Khand reaction. We are currently investigating its catalytic activity for other organic transformations.

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Supporting Information Available: Listings of ^{1}H and ^{13}C NMR, IR, and HRMS or elemental composition data for all compounds (6 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

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(9) Alkylidynetricobalt nonacarbonyl clusters are known to catalyze the [2+2+2]-cyclization of alkynes to produce the aromatic derivatives. However, the intermolecular Pauson−Khand reactions of phenyl acetylene with **17a** and **17b** were much faster than the formation of aromatic derivatives. See, also: Dickson, R. S.; Taliby, G. R. *Aust. J. Chem.* **1970**, *23*, 229.