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HYDROGEN-ACTIVATED BENZYLIDYNETRICOBALT NONACARBONYL: CARBONYLATIVE CYCLIZATION OF ENYNES IN SYNTHESIS GAS WITHOUT REDUCING SUBSTRATES AND PRODUCTS

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This manuscript is dedicated to Professor Dr. Albert Eschenmoser on the occasion of his 85th birthday.

Abstract – Benzylidynetricobalt nonacarbonyl was activated by hydrogen and catalyzed the carbonylative cyclization of enynes without reducing substrates and products.

The use of organotransition-metal complexes in carbon-carbon-bond-forming reactions was initiated by the discovery of hydroformylation of alkenes.[1] Since then, a number of complexes that catalyze various types of organic transformation have been discovered. However, their catalytic activity is usually moderate except in hydroformylation. One major reason for the higher catalytic activity in hydroformylation was considered to be the long lifetime of actual catalytic species with lower oxidation states under reductive conditions.[2] As seen in catalytic hydrogenation, once a reaction is carried out in the presence of hydrogen, metal hydride complexes are produced and the hydride transfer reaction from a metal to coordinated organic substrates proceeds smoothly to give reduced products. Thus, the role of a hydride ligand in the higher catalytic activity remains unclear. We report herein the novel results that hydrogen present in synthesis gas activated metal complexes and that the resulting active complexes catalyzed the carbonylative cyclization of enynes to produce cyclopentenones without reducing substrates and products.

Alkylidynetricobalt nonacarbonyls are easily prepared by the reaction of dicobalt octacarbonyl with trihaloalkane and more stable against auto-oxidation than their parent complex.[3] One of the most stable clusters in air is benzylidynetricobalt nonacarbonyl. Although one of the clusters, methylidynetricobalt nonacarbonyl, catalyzes the carbonylative cyclization of enynes to produce cyclopentenones, most of the other clusters, specifically benzylidynetricobalt nonacarbonyl, does not show any catalytic activity even at elevated temperatures.[4,5] On the other hand, benzylidynetricobalt nonacarbonyl catalyzes the hydroformylation of simple alkenes in synthesis gas.[6] One major difference between the two reactions is the presence or absence of hydrogen. The hydrogen may activate inert benzylidynetricobalt nonacarbonyl. To confirm this, the enyne **2** was chosen as the substrate and cyclization catalyzed by benzylidynetricobalt nonacarbonyl **1** in synthesis gasses of various compositions was examined. The results are shown in Table 1.

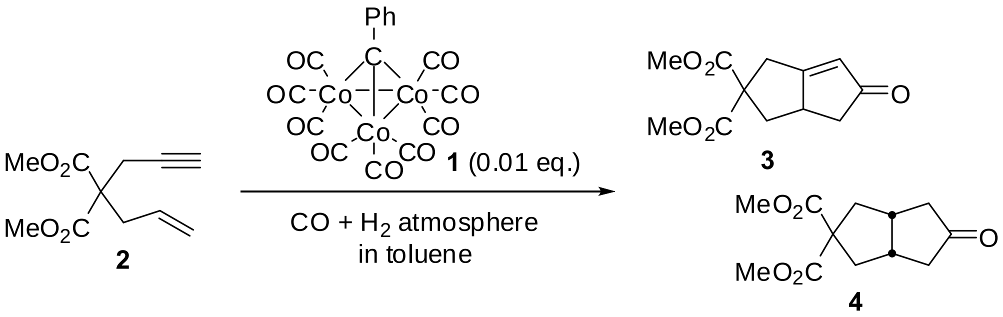
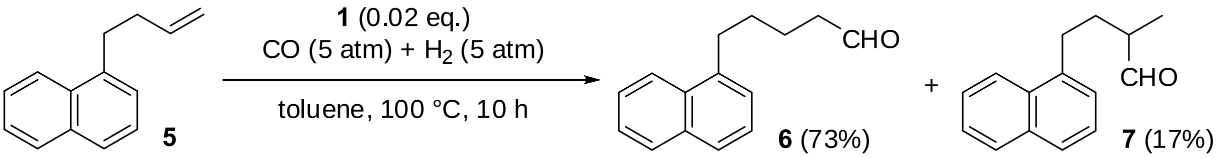


Table 1. Benzylidynetricobalt nonacarbonyl **1** catalyzed the cyclization of **2** under various conditions.[a]

Entry	*P* (atm) CO	H_2	*Temp.* (°C)	*Time* (h)	*Yield (%)* **2**	**3**	**4**
1	10	0	100	10	99	-	-
2	9	1	100	10	82	9	-
3	8	2	100	10	45	53	-
4	7	3	100	10	-	97	-
5	5	5	100	10	-	99	-
6	3	7	100	5	-	98	-
7	2	8	100	3	-	96	-
8	5	15	100	6	-	99	-
9	5	25	100	4	-	97	-
10	5	35	100	2	-	98	-
11	5	35	80	5	-	94	-
12	5	35	60	10	10	85	-
13	5	35	45	10	97	-	-
14	5	35	100	20	-	3	93

[a] A 20.0 µmol of **1**, 2.00 mmol of **2**, and 5.0 mL of toluene were used for the reaction.

When a mixture of enyne **2** and 0.01 equiv. of the benzylidynetricobalt nonacarbonyl **1** in toluene was stirred in 10 atm of carbon monoxide at 100 °C for 10 h, nothing happened to recover the starting enyne **2** in an almost quantitative yield (Entry 1).[4] The presence of hydrogen initiated the production of the desired cyclopentenone **3** (Entry 2). An increase in the partial pressure of hydrogen markedly changed the ratio of the remaining enyne **2** to the desired cyclopentenone **3** and shortened the reaction time (Entries 3-7). These results suggested that hydrogen activated benzylidynetricobalt nonacarbonyl and that the resulting active complexes catalyzed the carbonylative cyclization. Although an increase in total pressure also shortened the reaction time and lowered the reaction temperature (Entries 8-12), no reaction was obsereved below 60 °C even in the mixed atmosphere of 40 atm (Entry 13). This meant that a high energy process was involved in the carbonylative cyclization. Noteworthy is that the catalyst **1** was recovered in approximately 85% average yield and successfully reused for the second and third cycles in most cases. In addition, the prolonged reaction time resulted in formation of a reduced product, cyclopentanone **4** (Entry 14).[6] When the simple alkene **5** was treated under the similar conditions with Entry 5, hydroformylation proceeded to give the aldehydes **6** and **7** in 73% and 17% yields, respectively (Eq. 1).[7,8] Therefore, the carbonylative cyclization of the enyne was much faster than the hydroformylation and the reduction of the alkene, alkyne, and products.

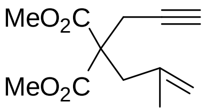
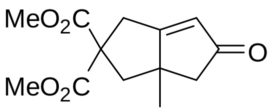
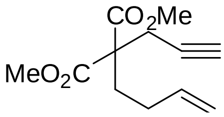
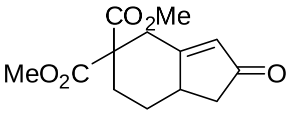
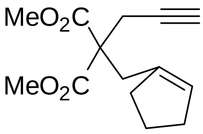
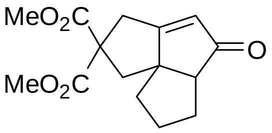
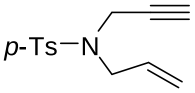
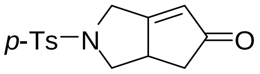
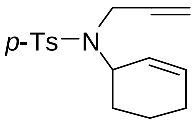
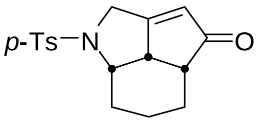
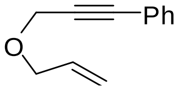
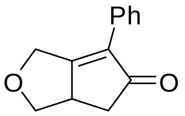
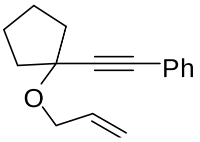
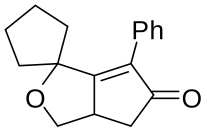
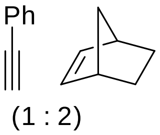
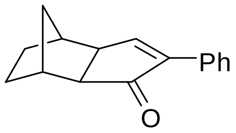


(Eq. 1)

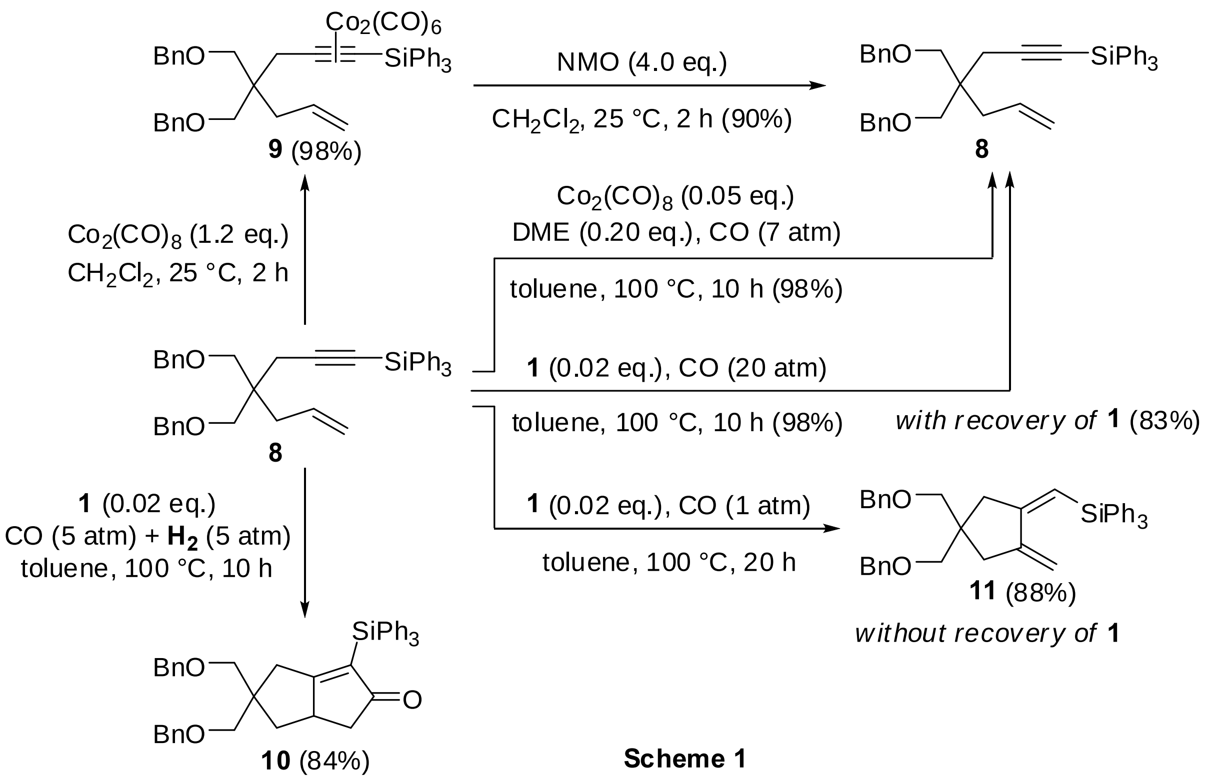
As shown in Table 2, the present method could be applied for various substrates including the intermolecular reaction with norbornene. Benzylidynetricobalt nonacarbonyl was decomposed by reaction with ‘hard’ Lewis bases, such as alcohols, ethers, and amines. When the method A was applied to the substrate shown in Entry 6, no reaction was occurred. Once again, an increase in the partial pressure of hydrogen markedly changed the reaction feature to give the desired cyclopentenone.

The most interesting feature of the present method was observed when the enyne had a bulky substituent (Scheme 1). Although the NMO-mediated stoichiometric cyclization[9] of **9** and the catalytic cyclization[10] of **8** were not successful, the catalytic cyclization in synthesis gas produced the desired product **10** in good yield. The stoichiometric version was usually superior to the catalytic version in this type of cyclization. This is one large advantage of the present method over conventional ones. In the absence of hydrogen, the starting **8** was recovered in 20 atm of carbon monoxide and the diene **11** was produced in an atmospheric pressure of carbon monoxide.[11] This is also clear that hydrogen present plays important role to carry out the carbonylative cyclization successfully.

Table 2. Carbonylative cyclization catalyzed by **1** in synthesis gas.

Entry	*Substrate*	*Method*[a]	*Time* (h)	*Product*	*Yield* (%)
1		A	5		100
2		A	10		89
3		A	10		82
4		A	5		96
5		A	5		78
6		B	5		95
7		B	5		93
8		A	3		100

[a]Reaction conditions for method A: **1** (0.02 equiv.), CO (5 atm) + H_2 (5 atm), toluene, 100 °C; for method B: **1** (0.02 equiv.), CO (5 atm) + H_2 (35 atm), toluene, 100 °C



Scheme 1

ACKNOWLEDGEMENTS

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