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Methylidynetricobalt nonacarbonyl catalyzed cyclotrimerization of alkynes

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A cobalt carbonyl cluster, methylidynetricobalt nonacarbonyl, catalyzed inter- and intramolecular cyclotrimerization of alkynes producing substituted benzene derivatives in good to excellent yields.

Alkylidynetricobalt nonacarbonyl clusters[1,2] are easily prepared by reaction of dicobalt octacarbonyl with trihaloalkanes and are more stable against auto-oxidation than the parent dicobalt octacarbonyl. Since the clusters can be also synthesized by heating a solution of terminal alkyne-dicobalt hexacarbonyls,[3,4] the clusters are more thermally stable than the structurally similar alkyne-dicobalt hexacarbonyls. We recently reported that one of the clusters, methylidynetricobalt nonacarbonyl (**1a**), catalyzed the Pauson–Khand reaction of phenylacetylene (**2**) with norbornene to give **3**.[5,6] When the reaction with allyl ether **4** was carried out, the desired cyclopentenone **6** was not obtained, but 1,2,4-triphenylbenzene (**5**) was produced in good yield even under 7 atm of CO atmosphere (Scheme 1).

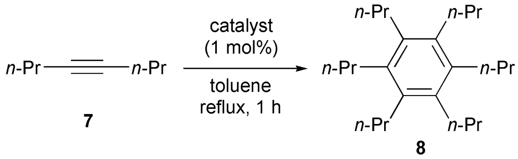
Whereas some of the clusters, benzylidyne- and ethylidynetricobalt nonacarbonyl, were known to catalyze the [2 + 2 + 2]-cyclotrimerization of alkynes producing substituted benzenes,[4,7] the reaction conditions were vigorous and the turnover number was not satisfactory compared with the result shown in Scheme 1. The present results suggest that the alkylidyne unit of the clusters might greatly influence the catalytic activity in the reaction. To confirm this, oct-4-yne (**7**) was chosen as the substrate and we investigated the catalytic activity of various alkylidynetricobalt nonacarbonyls (**1**). The results are shown in Table 1.

When methylidynetricobalt nonacarbonyl (**1a**)[8] was used as a catalyst, the cyclization proceeded smoothly to give hexa(*n*-propyl)benzene (**8**) in an excellent yield (Entry 1). In the presence of ethylidyne-, benzylidyne-, and ethoxycarbonyl-methylidynetricobalt nonacarbonyl (**1b**), (**1c**), and (**1d**), the cyclization was slow and the yield of **8** was moderate as reported in the literature (Entries 2–4).[4] Whereas the cyclization did not proceed smoothly in the presence of **1e** (Entry 5), the cluster with a bromomethylidyne-unit (**1f**) catalyzed the cyclization (Entry 6). While it is known that treatment of **1f** in refluxing toluene gave **1g**,[9] **1g** itself also catalyzed the cyclization (Entry 7). The catalytic activity of the clusters was greatly influenced by the nature of the substituent on the carbon unit. The thermally stable clusters, such as **1b–e** were not good catalysts, and the structurally simple **1a** was the most efficient among the thermally unstable ones, such as **1a**, **1f**, and **1g**. Binary cobalt carbonyl complexes, such as dicobalt octacarbonyl **9** and tetracobalt dodecacarbonyl **10**, also catalyzed the cyclization (Entries 8 and 9), although the catalytic activity was much less than **1a**.

An interesting feature of the present method was that the cyclization could be carried out at a lower temperature and the catalyst **1a** was recovered (Scheme 2). The result suggested that not the decomposition products but the cluster **1a** itself was transformed into the active catalysts, such as the coordinatively unsaturated complexes, under the conditions and also that **1a** was the catalyst resting state.

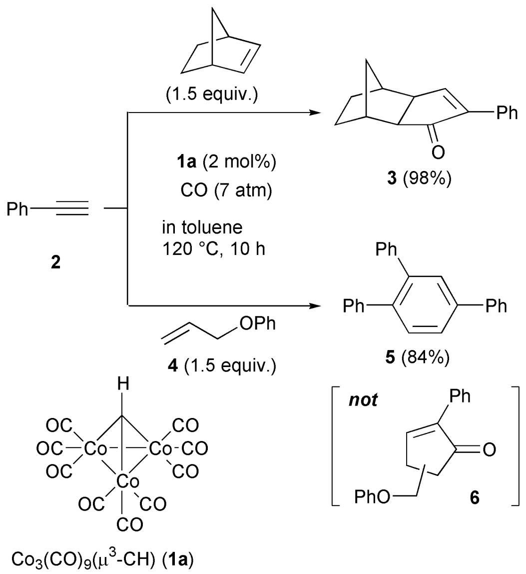
The method was also applied to various substrates (Scheme 3). When conjugated diyne **11** was used as the substrate,

Table 1 Cyclization of oct-4-yne (**7**) catalyzed by various cobalt carbonyl complexes.[a]

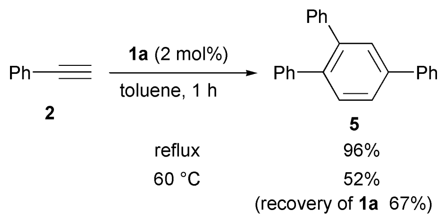


Entry	Catalyst		Yield of **8** (%)
1	$Co_3(CO)_9(\mu^3\text{-CH})$	**1a**	92
2	$Co_3(CO)_9(\mu^3\text{-CMe})$	**1b**	13
3	$Co_3(CO)_9(\mu^3\text{-CPh})$	**1c**	21
4	$Co_3(CO)_9(\mu^3\text{-CCOOEt})$	**1d**	19
5	$Co_3(CO)_9(\mu^3\text{-CCl})$	**1e**	11
6	$Co_3(CO)_9(\mu^3\text{-CBr})$	**1f**	42
7	$[Co_3(CO)_9(\mu^3\text{-C})]_2$	**1g**	38
8	$Co_2(CO)_8$	**9**	8
9	$Co_4(CO)_{12}$	**10**	47

[a] All reactions were carried out in 0.3 M solution in toluene under argon atmosphere.



Scheme 1



Scheme 2

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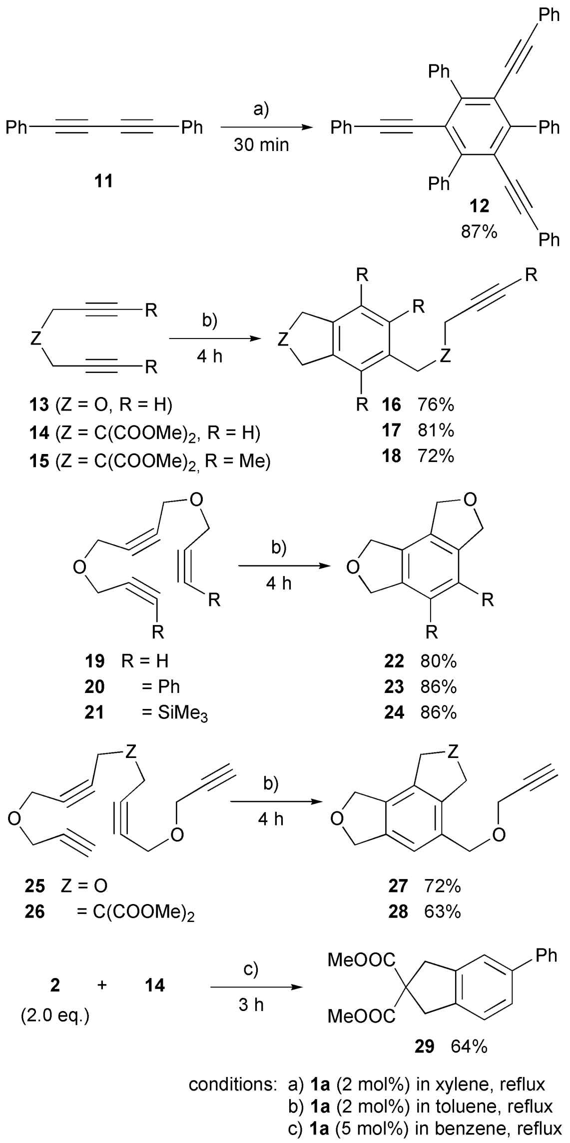
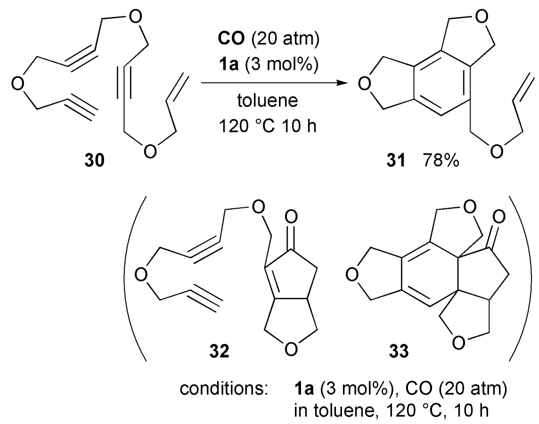


Scheme 3

1,3,5-triphenyl substituted benzene derivative **12** was produced and the 1,2,4-triphenyl substituted one was not detected at all. The regioselectivity in the cyclization seemed to be controlled by both electronic and steric factors of the substituents. Diynes **13–15**, triynes **19–21**, and tetraynes **25** and **26**, were also cyclized in the presence of 2 mol% of **1a**, although a longer reaction time was required. Cocyclization between diyne **14** and phenylacetylene (**2**) also proceeded nicely to give the desired **29** in a good yield.

As we reported previously, methylidynetricobalt nonacarbonyl (**1a**) also nicely catalyzed the intramolecular Pauson–Khand reaction under CO atmosphere.[5,6] When the substrate has the possibility to proceed both the cyclotrimerization of alkynes and the Pauson–Khand reaction, which process is favorable? The answer is shown in Scheme 4. The cyclization of **30** under 20 atm of CO atmosphere, which was suitable for the Pauson–Khand reaction, gave neither the cyclopentenone **32** nor the pentacyclic compound **33**, but the substituted benzene derivative **31**. This result suggested that the intramolecular cyclotrimerization of alkynes was much faster than the intramolecular Pauson–Khand reaction and the intermolecular



Scheme 4

cyclotrimerization of alkynes. Polynuclear organotransition metal complexes are considered to have a tendency to accept coordination of an alkyne more preferably than that of an alkene.[10] The present results may support this consideration.

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8 Methylidynetricobalt nonacarbonyl (**1a**) was easily prepared by reaction of dicobalt octacarbonyl (cheap transition metal complex) with bromoform in 80% yield and was purified by silica gel column chromatography (eluted with *n*-hexane; open-air). The cluster was quite stable at ambient temperatures and could be used as a catalyst with no problems after storing for more than four years at 0 °C. See also ref. 2.

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