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

Alkylidyne(tricobalt nonacarbonyl) clusters 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 alkylidyne-dicobalt hexacarbonyls, the clusters are more thermally stable than the structurally similar alkylidyne-dicobalt hexacarbonyls. We recently reported that one of the clusters, methylidyne(tricobalt nonacarbonyl) (1a), catalyzed the Pauson–Khand reaction of phenylacetylene with norbornene to give 3. 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).

When methylidyne(tricobalt nonacarbonyl) (1a) was used as a catalyst, the cyclization proceeded smoothly to give hexa(propyl)benzene (8) in an excellent yield (Entry 1). In the presence of ethylidyne-, benzylidyne-, and ethoxycarbonyl-methylidyne(tricobalt nonacarbonyl) (1b), (1c), and (1d), the cyclization was slow and the yield of 8 was moderate as reported in the literature (Entries 2–4). 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, 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 tetracarbonyldodecacarbonyl 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,
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 31 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 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.7,8 The present results may support this consideration.

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.