Advances in the Pauson–Khand Reaction: Development of Reactive Cobalt Complexes

Takumichi Sugihara,*[a] Masahiko Yamaguchi,[b] and Mugio Nishizawa[a]

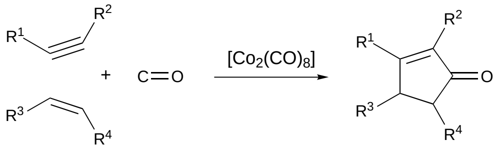
Dedicated to Professor Peter L. Pauson and late Dr. Ihsan U. Khand.

Abstract: Three conceptually new methods employing reactive cobalt carbonyl complexes have been developed for the Pauson–Khand reaction. The first method involves activation of alkyne-dicobalt hexacarbonyls with "hard" Lewis bases. Primary amines dramatically promote the *stoichiometric* Pauson–Khand reaction. The active cobalt complexes produced in the system exhibit high reducing ability. The second method involves activation of dicobalt octacarbonyl with less electron-donating "hard" Lewis bases such as 1,2-dimethoxyethane and water. These Lewis bases were successfully utilized as a promoter for the *catalytic* Pauson–Khand reaction. The third method employs methylidynetricobalt nonacarbonyl cluster, which exhibits high reactivity in the *catalytic* Pauson–Khand reaction in the *absence* of activator. This may be due to facile coordination of the substrate to the metal center through dissociative and associative mechanisms and/or cleavage of one of the cobalt–cobalt bonds.

Keywords: alkyne ligands • carbonyl ligands • cluster compounds • cobalt • cyclization

Introduction

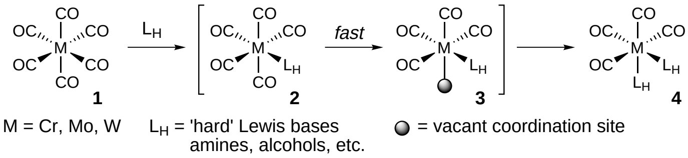
Since Pauson and Khand et al. found a fascinating cocyclization of an alkyne, an alkene, and carbon monoxide mediated by dicobalt octacarbonyl (Scheme 1),[1] the reaction has been widely utilized for construction of a variety of cyclopentenones[2] including natural products.[3]



Scheme 1.

The reaction was originally carried out by simply heating a mixture of $[Co_2(CO)_6(alkyne)]$ and alkene in hydrocarbon solvent.[1] In most cases, however, a prolonged reaction time was required and the yields of the products were moderate. Several modifications to improve its efficiency have been explored.[4] Among them, tertiary amine oxides have been considered as the best promoter in the *stoichiometric* intramolecular Pauson–Khand reaction.[4a,b] Not only the Pauson–Khand reaction, but also a variety of reactions mediated by low-valent organotransition-metal complexes start from the formation of a vacant coordination site on the metal followed by coordination of a substrate. The efficiency of this step is often critical for the overall reaction. Therefore, oxidative removal of coordinated carbon monoxide[5] from $[Co_2(CO)_6(alkyne)]$ complexes by reaction with tertiary amine oxides is effective for the promotion of the *stoichiometric* Pauson–Khand reaction.

"Hard" Lewis bases, such as amines and alcohols, on low-valent organotransition metal carbonyls are known to make the coordinated CO ligands labile and promote the ligand liberation. A representative example is found in the reaction of the Group 6 metal carbonyls with "hard" Lewis bases (Scheme 2).[6]



Scheme 2.

Reaction of **1** with excess "hard" Lewis bases gives **2**. Then, the electron-donating ability of the "hard" Lewis base

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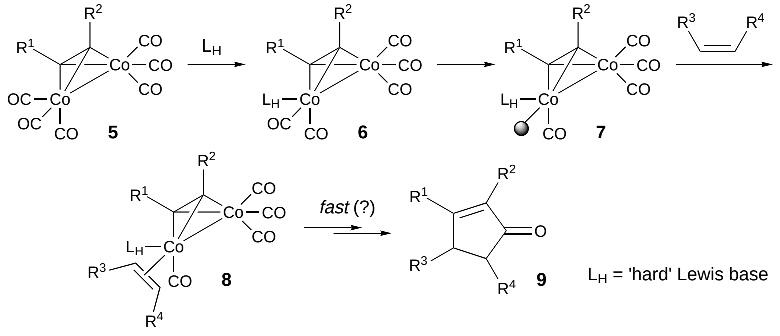
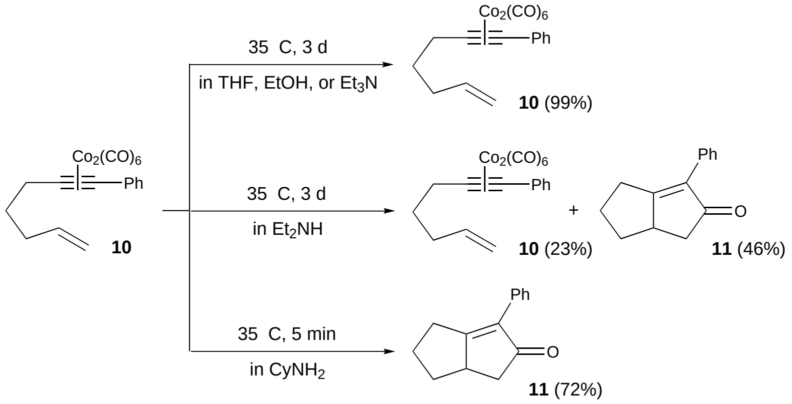
increases the electron density on the metal and the M–CO σ-bond is weakened. In addition, the "hard" Lewis base can stabilize the coordinatively unsaturated species **3**, which is formed by liberation of the CO. Overall, these two effects enhance the rate of the formation of **3** and finally the *cis*-disubstituted complex **4**. If [Co$_2$(CO)$_6$(alkyne)] complexes (**5**) react with "hard" Lewis bases, what will happen? As seen in from Scheme 2, one of the CO ligands on the cobalt will be displaced by the "hard" Lewis base to give **6** in the first step (Scheme 3); this will probably lead to the formation of the coordinatively unsaturated complex **7**. An alkene, if present, can coordinate to the vacant site on **7**, to give **8**. Since the "hard" ligand makes the coordinated alkyne and alkene reactive, the cyclization of **8**, to give **9**, may be promoted further. This was the starting point of our study to develop and utilize new active cobalt complexes for the Pauson–Khand reaction.



Scheme 3.

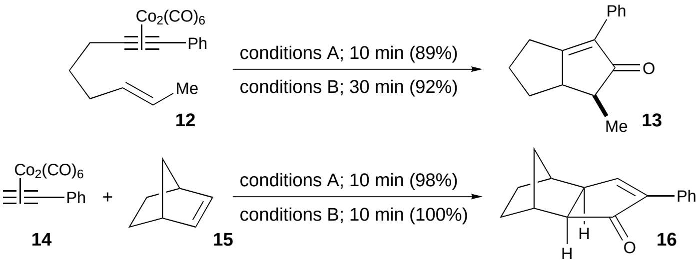


Scheme 4.

Discussion

Activation of [Co$_2$(CO)$_6$(alkyne)] complexes with primary amines: As we mentioned before, when "hard" Lewis bases react with [Co$_2$(CO)$_6$(alkyne)] complexes, a coordinatively unsaturated complex may be produced. Since the electron density on the cobalt increases by coordination of the "hard" Lewis base, the ligands are made labile and reactive. When an alkene coordinates to the cobalt complex, insertion of the alkene and carbon monoxide may be enhanced, and, therefore, the Pauson–Khand reaction may be promoted. To confirm our hypothesis, compound **10** was chosen as the substrate and treated with an excess amount of various "hard" Lewis bases (Scheme 4).[7]

When ethers, alcohols, or tertiary amines were used as a solvent, compound **10** was recovered quantitatively even after three days at 35 °C. Whereas the cyclization proceeded slowly in diethylamine, it was completed within five minutes in cyclohexylamine (CyNH$_2$) to give **11** in a good yield. Since the Pauson–Khand reaction under the original conditions, that is, heating under reflux in hydrocarbon solvent, took more than 38 h and the yield of **11** was low (23 %), this result suggests that primary amines could activate [Co$_2$(CO)$_6$(alkyne)] complexes and promote the *stoichiometric* Pauson–Khand reaction. After much experimentation, two conditions, namely 3.5 equivalents of cyclohexylamine in 1,2-dichloroethane at 83 °C (conditions A) and a 1:3 mixture (v/v) of 1,4-dioxane and 2 M aqueous solution of ammonium hydroxide at 100 °C (conditions B), were found to be practical. Typical examples of the amine-promoted Pauson–Khand reaction are shown in Scheme 5.[7]



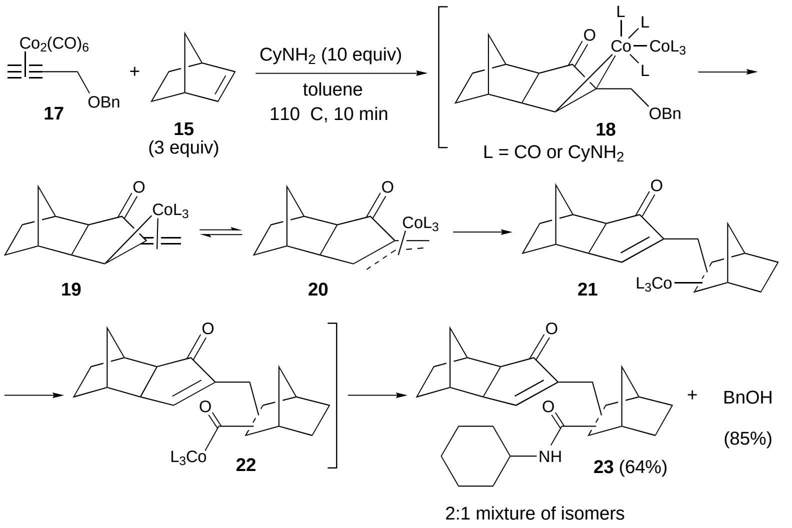
Scheme 5.

Abstract in Japanese:

本論文では，１）アミン類やアルコール類，エーテル類のようなハードなルイス塩基の配位による低原子価コバルトカルボニル錯体の活性化と，２）炭素核を有するコバルトカルボニルクラスター錯体が，安定かつ活性な触媒として機能するという二つの知見を，化学量論的あるいは触媒的な Pauson-Khand 反応に適用し，反応の効率性が飛躍的に向上したという最近の研究結果について述べる．

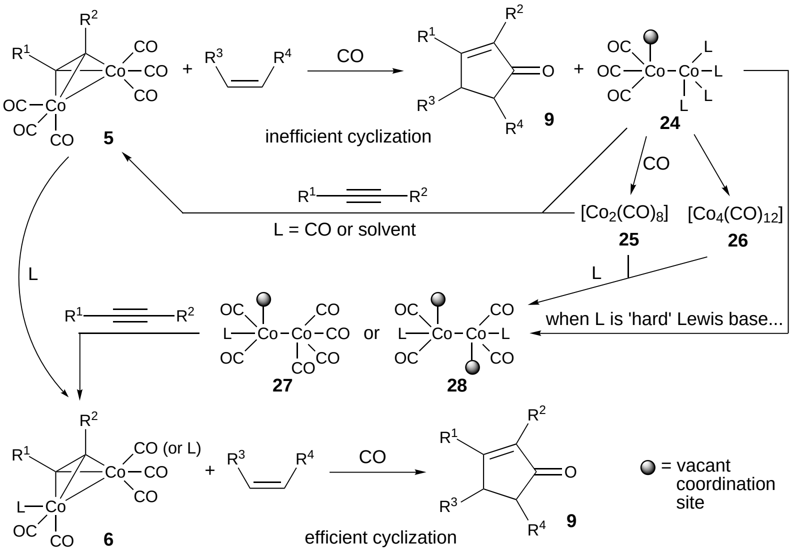
Although a variety of promoters for the Pauson – Khand reaction have already been reported,[4] the present methods, that is, primary amine promoters, have proven to be convenient and economical.

Notably it was found that the active cobalt complexes with high reducing ability were formed in this reagent system. When 1,2-dichloroethane was used as a solvent, a blue complex was produced as the co-product derived from cobalt. Although the structure of the complex has not been elucidated yet, the elemental analysis indicated that chlorine was in its composition. Since 1,2-dichloroethane does not readily react with amines, the result suggests that some reactive low-valent cobalt complex is produced in this reaction system and reacts with 1,2-dichloroethane to give cobalt chloride derivatives. The formation of active cobalt complexes with reducing ability has also been suggested by the reaction of **17** with **15** in the presence of cyclohexylamine to produce **23** (Scheme 6).[8] This novel tandem reaction probably proceeds as follows: i) the amine-promoted Pauson – Khand reaction gives **18**, ii) the elimination of the benzyloxy group at the allylic position, iii) the metallo "*ene*" reaction with a second norbornene (**15**), iv) the CO insertion into the C_{sp^3}–Co bond, and v) trapping of the acyl cobalt species **22** by the amine. Involvement of the reductive cleavage of benzyloxy group at the α position of **18**, step (ii), suggested that the cobalt with the coordinated amine should be electron rich and exhibit reducing ability.



Scheme 6.

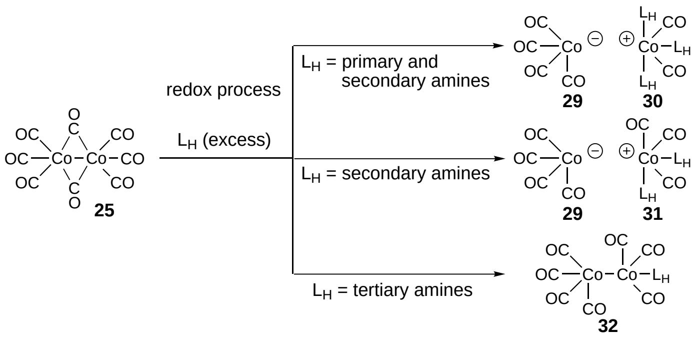
This is another interesting aspect of the cobalt complexes activated by primary amines.



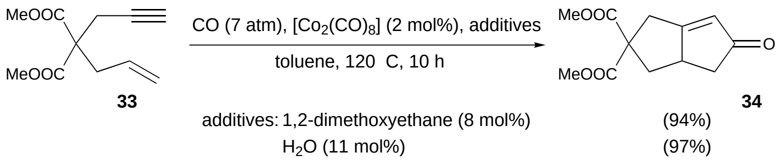
Scheme 7.

The catalytic Pauson – Khand reaction promoted by "hard" Lewis bases: Under the original conditions,[1] coordinatively unsaturated cobalt carbonyl complex **24** is produced after the cyclization (Scheme 7). When the reaction is carried out under CO atmosphere, the complexes **24** may transform into the parent dicobalt octacarbonyl (**25**) or, in the presence of alkyne, $[Co_2(CO)_6(alkyne)]$ complexes (**5**); therefore, a catalytic amount of dicobalt octacarbonyl (**25**) is theoretically required to complete the cyclization. Although an attempt to carry out the catalytic reaction has been made from the beginning, the turnover number was not satisfactory.[1b, 9] The reasons are considered as follows: i) feasibility in transformation of the coordinatively unsaturated dicobalt carbonyl complex **24** into tetracobalt dodecacarbonyl (**26**), which is considered as inactive in the catalytic Pauson – Khand reaction,[9b,c, 10] ii) retardation of re-formation of $[Co_2(CO)_6(alkyne)]$ complexes (**5**) and coordination of an alkene to $[Co_2(CO)_6(alkyne)]$ complexes under CO atmosphere, and iii) inefficiency of the Pauson – Khand reaction under the original conditions. When the reaction is carried out in the presence of "hard" Lewis bases, what will happen (Scheme 7)? Tetracobalt dodecacarbonyl (**26**) may be transformed into dicobalt octacarbonyl (**25**) or the coordinatively unsaturated cobalt complexes **27** and **28** by reacting with "hard" Lewis bases.[11] The electron-donating effect of "hard" Lewis bases may stabilize the coordinatively unsaturated cobalt complexes **27** and **28**. In addition, once **6** is produced, the cyclization may be facilitated as seen in the primary-amine-promoted Pauson – Khand reaction discussed before. Therefore, the presence of “hard” Lewis bases also anticipates promotion of the *catalytic* Pauson–Khand reaction.

It is known that reaction of dicobalt octacarbonyl (**25**) with an excess amount of primary and secondary amines gave anionic and cationic complexes **29**, **30**, and **31** by redox process (Scheme 8).[12] These complexes do not mediate the Pauson–Khand reaction. Thus, inhibition of the redox process is necessary to carry out the catalytic Pauson–Khand reaction[9, 13, 14] promoted by Lewis bases.



Scheme 8.

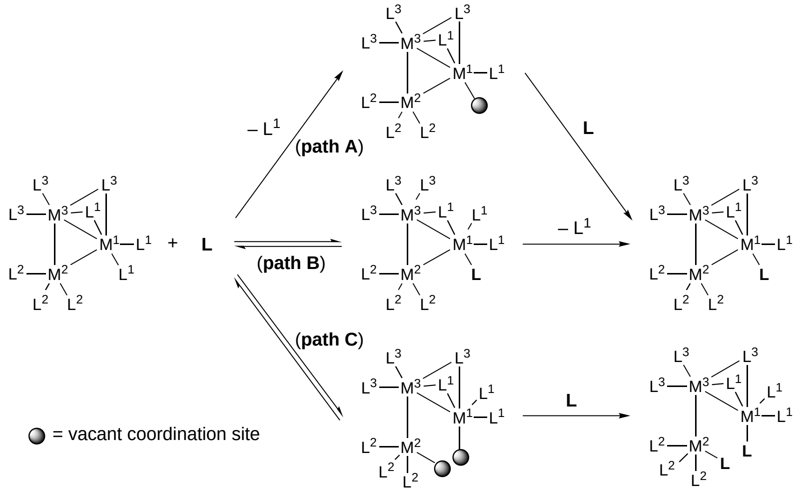


Scheme 9.

A tertiary amine, triethylamine, has been reported to react with dicobalt octacarbonyl (**25**) to give monosubstituted complex **32** instead of **29**, **30**, and **31**.[12c] This implies that the tertiary amine does not promote the redox process. Probably, the steric hindrance of the nitrogen substituents made the cobalt–nitrogen bond length longer. The coordination, therefore, did not increase the electron density on the cobalt so much as in the case of the primary amines. Alternatively, the steric bulkiness of the coordinated tertiary amine prevented the access of the second amine molecule, which could induce the unfavorable redox process. Whatever the mechanism is, this appeared to show that sterically bulky or less electron-donating “hard” Lewis base can activate dicobalt octacarbonyl without decomposition and stabilize coordinatively unsaturated active cobalt complexes, such as **27** and **28**. We were, therefore, pleased to find that the Lewis bases such as diisopropylethylamine, benzyl alcohol, 1,4-dioxane, 1,2-dimethoxyethane (DME), and water catalyzed the cyclization of **33** in good yields.[15] Among these activators, DME seems to be the most effective and water the most economical. The amount of the Lewis base used was also important and use of a large excess of the Lewis base was detrimental to catalysis at higher temperature. It has been reported that the intramolecular Pauson–Khand reaction catalyzed by dicobalt octacarbonyl could be carried out in DME in a temperature range of 60–80 °C.[13d] This result and together with those from our experiments suggest that the DME can act as the activator for dicobalt octacarbonyl in a tight range of the temperature without decomposing the active catalyst. In the same sense, cyclohexylamine could promote the catalytic cyclization in DME in the temperature range 60–70 °C,[13e,i] while the catalyst, dicobalt octacarbonyl, was killed by the amine in toluene at 120 °C for the same type of reactions shown in Scheme 8.[15] Typical examples of the catalytic Pauson–Khand reaction promoted by 1,2-dimethoxyethane or water are shown in Scheme 9.[15]

Sterically bulky or less electron-donating “hard” Lewis bases activate dicobalt octacarbonyl and promote the *catalytic* Pauson–Khand reaction. Suppression of the redox process, which decomposes dicobalt octacarbonyl, is a key to bring about a fruitful result. In this sense, most of the known methods for the catalytic Pauson–Khand reaction by the addition of a Lewis base, such as phosphites,[13a] ethers,[13b, d] amines,[13e, i] and phosphane sulfides,[13g] may activate dicobalt octacarbonyl and stabilize the active catalysts sterically and electronically by their coordination.

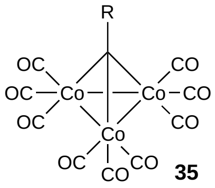
Use of methylidynetricobalt nonacarbonyl as a catalyst: Organotransition-metal clusters sometimes exhibit higher reactivity than the monomeric complexes in organic transformations.[16] One of the major reasons may be the ease of coordination of the substrate to the clusters. Since the ligands rapidly exchange positions within the clusters, ligand substitution can occur more readily than in monomeric complexes through dissociative (Scheme 10, path A) or associative



Scheme 10.

mechanisms (path B). Cleavage of one of the metal–metal bonds can also generate vacant sites (path C), at which the substrate is able to coordinate. The cleavage of the metal–metal bond, however, is often accompanied by decomposition of the clusters. A possible methodology to stabilize the clusters in the activated state, in which one of the metal–metal bonds is cleaved, is introduction of a carbon unit, since a metal–carbon bond is generally stronger than a metal–metal bond.[17]

Alkylidynetricobalt nonacarbonyls (**35**) are clusters that consist of one carbon and three cobalt units. The clusters are easily prepared by the reaction of dicobalt octacarbonyl with trihaloalkanes and are more stable against auto-oxidation than the parent dicobalt octacarbonyl.[18, 19]



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There is a report that benzylidynetricobalt nonacarbonyl catalyzes hydroformylation of alkenes under mild conditions compared with dicobalt octacarbonyl.[20] Since dicobalt octacarbonyl mediates the Pauson–Khand reaction, it was expected that such tetranuclear clusters might also effectively promote the reaction (Table 1).[21]

Table 1. Cyclization of **33** catalyzed by alkylidynetricobalt nonacarbonyls.[a]

Entry	Catalyst		Yield [%][b]	
			34	**33**
1	$[Co_2(CO)_8]$	**25**	12	82
2	$[Co_3(CO)_9(\mu_3\text{-CH})]$	**35a**	78	22
3	$[Co_3(CO)_9(\mu_3\text{-CCH}_3)]$	**35b**	31	66
4	$[Co_3(CO)_9(\mu_3\text{-CCOOC}_2H_5)]$	**35c**	31	65
5	$[Co_3(CO)_9(\mu_3\text{-CCl})]$	**35d**	2	95
6	$[Co_3(CO)_9(\mu_3\text{-CC}_6H_5)]$	**35e**	–	99
7	$[Co_3(CO)_9(\mu_3\text{-CC}_6H_4\text{-}p\text{-CH}_3)]$	**35f**	–	96

[a] A mixture of **33** (1.00 mmol) and catalyst (0.01 mmol) in toluene (2.5 mL) was stirred at 120 °C under CO atmosphere. [b] All yields given in this table are isolated yields.

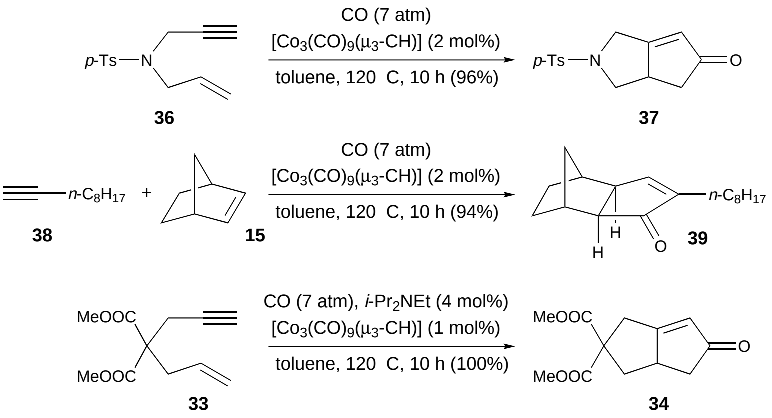
When dicobalt octacarbonyl (**25**) was used as a catalyst in the absence of activator, only a low conversion was obtained (Entry 1). As mentioned above, the catalytic cyclization generally proceeded in the presence of **25** and activators such as 1,2-dimethoxyethane or water.[13, 15] In contrast, methylidynetricobalt nonacarbonyl (**35a**) itself efficiently catalyzed the reaction (Entry 2). It is therefore an interesting aspect of the cluster reaction that no activator is required. Clusters with a relatively small substituent on the carbon unit, such as **35a**, **35b**, and **35c**, catalyzed the desired cyclization (Entries 2–4), while ones with aromatic substituents **35e** and **35f** were detrimental to catalysis (Entries 6 and 7). Not only steric but also electronic factors appear to affect the catalytic activity of the cluster. Since the substituent on the cluster greatly affects the catalytic activity, it may be reasonable to assume that the cluster itself catalyzed the Pauson–Khand reaction, but not the dissociated dicobalt hexacarbonyl species. The best results were obtained by using the parent cluster, methylidynetricobalt nonacarbonyl (**35a**). The cluster **35a** is quite stable against auto-oxidation, and this is another advantage of the present method. Typical examples of the Pauson–Khand reaction catalyzed by methylidynetricobalt nonacarbonyl are shown in Scheme 11.[21, 22]

In the presence of diisopropylethylamine, methylidynetricobalt nonacarbonyl (**35a**) showed the highest catalytic activity in the Pauson–Khand reaction.[22] Coordination of bulky “hard” Lewis bases to the cobalt in the cluster or deprotonation of the methylidyne unit may promote the cleavage of one of the cobalt–cobalt bond without decomposition[11] and, therefore, promote the cyclization.

It is known that thermal decomposition of dicobalt octacarbonyl (**25**) produced tetracobalt dodecacarbonyl (**26**), which itself is inactive in the catalytic Pauson–Khand reactions.[9b,c, 10] When $[Co_2(CO)_6(\text{alkyne})]$ complexes (**5**) were used as a catalyst, an activator, such as cyclohexylamine, was required.[14c] It is, therefore, interesting that exchanging one cobalt tricarbonyl unit of tetracobalt dodecacarbonyl with a methylidyne or exchanging one alkylidyne unit of $[Co_2(CO)_6(\text{alkyne})]$ with cobalt tricarbonyl brings about excellent results. We presume that the following two properties of the cluster plays an important role; i) the substrate can easily coordinate to the metal center of the clusters by dissociative or associative mechanisms, or cleavage of one of the cobalt–cobalt bonds; ii) a carbon unit of alkylidynetricobalt nonacarbonyl makes the active clusters thermally stable. Use of cobalt clusters is an interesting approach for the development of a highly active catalyst system.

Conclusion

One method for the stoichiometric Pauson–Khand reaction and two methods for the catalytic reactions have been



Scheme 11.

developed. The stoichiometric Pauson–Khand reaction promoted by primary amines is based on the concept that "hard" Lewis bases in low-valent organotransition-metal complexes make the existing ligands labile and produce the reactive complexes. This concept can also be employed in the catalytic Pauson–Khand reaction mediated by dicobalt octacarbonyl. Sterically bulky or less electron-donating "hard" Lewis bases such as 1,2-dimethoxyethane or water turned out to be the best promoters. Another method for the catalytic Pauson–Khand reaction uses methylidynetricobalt nonacarbonyl cluster. The cluster itself exhibited high catalytic activity in the Pauson–Khand reaction without any activator. These three methods to produce active cobalt complexes provide new advances in the Pauson–Khand reaction. We hope that these concepts might bring the new direction for future researches.

Acknowledgement

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