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Transition metal alkyne complexes: the Pauson–Khand reaction

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Contents

Abstract

The Pauson–Khand reaction (PKR) is a cocyclization of alkynes with alkenes and carbon monoxide by dicobalt octacarbonyl leading to cyclopentenones and has become one of the most useful methods for the synthesis of cyclopentenone. However, most of the known PKRs were stoichiometric and slow reactions. Thus, several promoters were reported to promote the PKR. Recently the catalytic version of PKR has been revealed. A number of variation with different transition-metals appeared. Most of the reactions studied are not asymmetric. However, asymmetric PKRs appeared. The utilization of the PKR in organic chemistry is quite general. Recently, the utilization of the PKR products in the synthesis of

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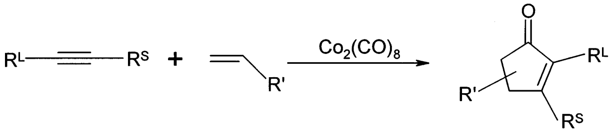
various cyclopentadienyl complexes has been published.

Keywords: Cycloaddition reaction; Cobalt carbonyls; Promotion; Catalytic

1. Introduction

Dicobalt hexacarbonyl complexes of alkynes are quite stable to a wide variety of electrophilic and nucleophilic reagents. However, when they are heated in the presence of an alkene, an interesting and useful cycloaddition occurs producing cyclopentenone (known as the Pauson–Khand reaction (PKR)) [1] (Eq. (1)).

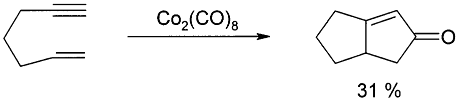
(1)



The overall process is a formal three-component, [2 + 2 + 1] cycloaddition, incorporating the alkene π-bond, an alkyne π-bond, and the carbon atom of CO into the new five-membered ring. The reaction joins an alkyne, an alkene, and carbon monoxide in a regioselective manner, tending to place a large alkyne substituent adjacent to the CO.

Early work focused on the scope and limitations of the intermolecular version of the process [2]. In 1981, the first example of intramolecular Pauson–Khand cycloadditions was reported [3] (Eq. (2)).

(2)

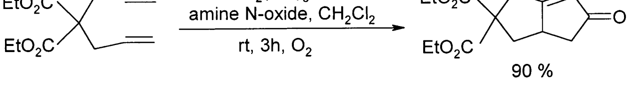


Now the reaction has been recognized as an important methodological approach to the challenging cyclopentenone ring system and has been used in many synthetic applications [4].

Despite its versatility and tolerance of a number of reactive functional groups, the PKR often has encountered some limitations because of its intrinsic problems in reaction conditions such as requiring high temperature (usually 60–120°C) and long reaction time (6 h–4 days).

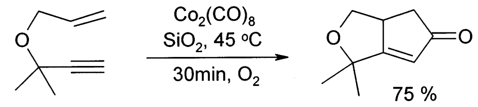
Initially, the synthetic utility of the process was compromised by the necessity of the severe conditions and the resulting low yields. However, the addition of a number of additives or promoters enhances the reaction [5–9] (Eq. (3)).

(3)



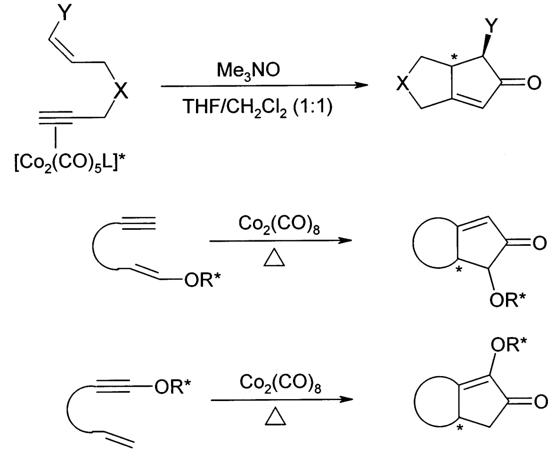
Smit et al. [6] reported the remarkable discovery that adsorption of the cobalt-complexed enynes onto any of a variety of chromatographic supports (silica gel, alumina, zeolites, etc.) facilitates enormously the intramolecular Pauson–Khand cycloaddition (Eq. (4)).

(4)



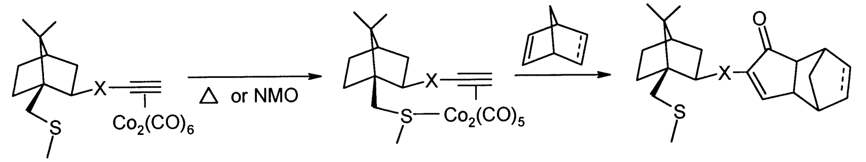
Efforts have been devoted to the development of the enantioselective PKR. Two main approaches have been studied to induce asymmetry, e.g., the generation of complexes possessing a disymmetric C_2Co_2 core [10] (Eq. (5)) and use of chiral auxiliary bound to either of the reacting fragment [11,12] (Eqs. (6 and 7)).

(5, 6, 7)



Recently, Pericàs et al. [13] introduced a new concept which combines the main advantages of the two aforementioned approaches (Eq. (8)):

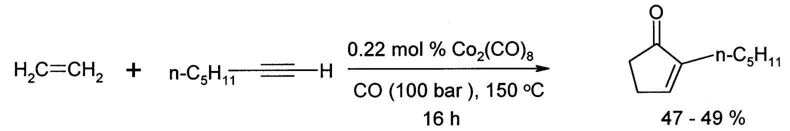
(8)



The use of a chiral auxiliary with chelating capability could allow an efficient transfer of chirality to the C_2Co_2 core. However, all approaches mentioned are based on the stoichiometric reactions.

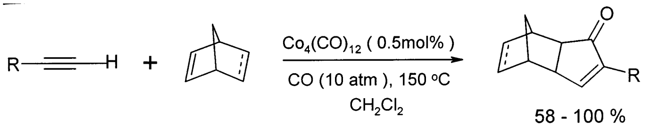
Very recently, the catalytic versions of the Pauson–Khand have been reported by several groups [14,15]. Early work suggested that the process could be carried out in a catalytic fashion by stirring a mixture of alkene and 10 mol% $Co_2(CO)_8$ in an inert solvent under 1:1 alkyne/CO atmosphere [16]. The success of these attempts depended upon the continuous supply of excess alkyne and recycle reactive cobalt-containing fragments. However, the turnover numbers were very low. Recently Rautenstrauch et al. [14] has found a catalytic PKR by employing a high pressure of CO and alkene in an autoclave (Eq. (9)).

(9)



However, the method appears to be limited to the use of ethene as the alkene reaction partner. More recent work by Chung and Kim [15] critically examined the thermal Pauson–Khand reaction employing a catalytic amount of cobalt carbonyls, e.g. $Co_2(CO)_8$ and $Co_4(CO)_{12}$ (Eq. (10)).

(10)



They found that most known PKR can be catalytic under high pressures of CO and high temperature in an autoclave. The method appears to be limited to the use of strained alkenes such as norbornadiene and norbornene as an alkene substrate.

The variants of the Pauson–Khand reaction, e.g., the synthesis of cyclopentenones employing other transition metal complexes such as titanium, zirconium, iron, molybdenum, tungsten, nickel, rhodium, ruthenium and palladium complexes, have been reported by several groups [17]. Now, the transition metal-mediated carbocyclization quite popular in organic synthesis [18]. However, many studies, especially the use of transition metals other than cobalt, have some limitation in their reactivities toward the intermolecular reactions.

The development of efficient approaches to the generation of highly functionalized cyclopentadienyl ligands is of continuing importance [19]. One of the strategies to synthesize cyclopentadienyl ligands is to use cyclopentenone as a starting material. The PKR is one of the most effective methods in the syntheses of cyclopentenones. Recently, the use of cyclopentenones in the synthesis of cyclopentadienyl compounds has developed [20], but the application of the PKR to the synthesis of cyclopentadienyl ligands has not attracted much attention yet. Chung's group reported the use of the Pauson–Khand chemistry in the synthesis of cyclopentadienyl and fulvalenyl organometallic compounds [21].

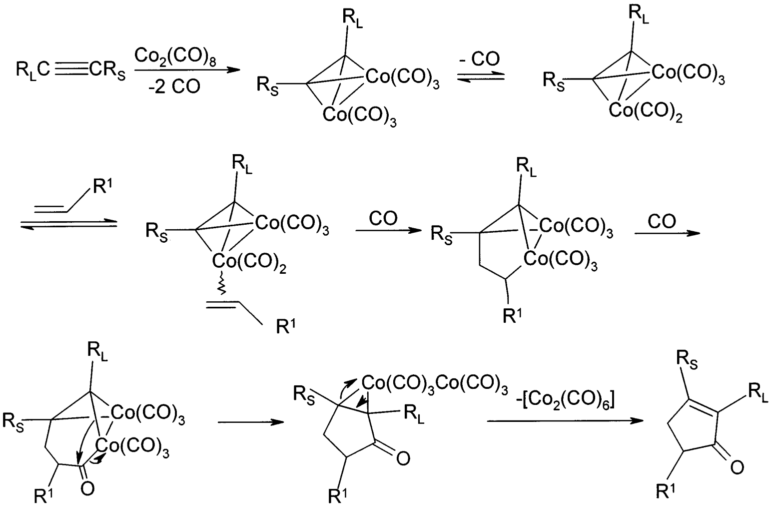
Coverage in this review will focus on the promotion, catalytic version, stereoselectivity, variations, and application of PKR. It excludes the application of the PKR to the syntheses of complex organic compounds including natural products. Excellent reviews on the Pauson–Khand reaction have been published by Pauson [2c,4a] and Schore [4c,e].

2. Mechanism

While a detailed mechanism has not been established, a plausible mechanism can be made based on the products obtained. The current level of mechanistic understanding is inferred from observations of regio- and stereochemistry in large number of examples, and is illustrated schematically in Scheme 1 [22]. It is usually assumed that complexation of the alkene to one cobalt atom takes place via a dissociative mechanism involving initial loss of CO. This process is almost certainly reversible. In the amine *N*-oxide promoted reaction, CO_2 should be liberated in the first step and the first step becomes irreversible. Subsequently, irreversible insertion of the complexed face of the alkene π-bond into one of the formal cobalt–carbon bonds of the alkyne complex occurs, in the step that is probably both rate- and product-determining and is followed by addition of CO to the coordinatively unsaturated cobalt atom. The metallocycle that forms may proceed to product by a standard sequence of steps beginning with migratory insertion of a cobalt–bound CO, addition of a ligand, and reductive elimination of the $Co(CO)_3$ moiety. The structure obtained is simply the $Co_2(CO)_6$ complex of the final enone; loss of the $Co_2(CO)_6$ fragment, either before or after attachment of an additional ligand, completes the process.

The only evidence that bears on the mechanism of the Pauson–Khand reaction is the unambiguous observation that the alkyne complex $Co_2(CO)_6(RC{\equiv}CR)$ is involved in the first stage of the process. No intermediates have been detected beyond this alkyne complex.

Regiochemistry with respect to both alkyne and alkene is determined during the insertion into the cobalt–carbon bond. The incipient carbon–carbon bond is most susceptible to steric crowding. If the alkyne is unsymmetrical, insertion and carbon–carbon bond formation proceed exclusively at the alkyne carbon possessing the smaller substituent. Alkene regiochemistry is less readily predicted.



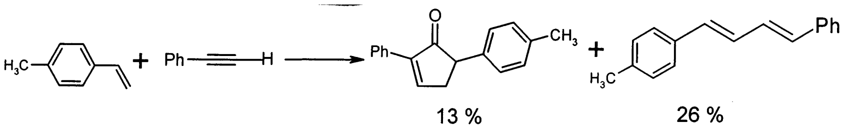
Scheme 1.

3. Scope of the reaction

All simple alkynes are good substrates although the yields are quite dependent upon the degree of substitution and bulkiness of substituents. Especially, ethyne and simple terminal alkynes are the most satisfactory substrates. Internal alkynes usually give lower yields of cyclopentenones. In general, polar groups remote from the triple bond have little effect, but those in close proximity are commonly detrimental. However, using acetonitrile as the reaction medium, conjugated alkynones can be successfully employed [25]. Compounds known as poor substrates [23] such as derivatives of propargyl alcohol and electron-deficient alkynes can be good substrates in the presence of amine *N*-oxide [3b,c] or employing $Co(acac)_2$ [24] as a cobalt source instead of cobalt carbonyls.

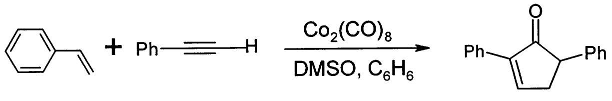
Strained cyclic alkenes such as norbornadiene, norbornene, and cyclobutene are the best substrates and cyclopentenes, cyclohexenes, and simple acyclic alkenes are suitable substrates. Steric hindrance around the double bond exerts significant deleterious effect on the cycloaddition. As the number of alkene substituents or steric bulk of the substituents at the carbon atom of attachment increases, carbon–cobalt bond insertion becomes more difficult. When the alkene is not suitable, aromatics produced by alkyne trimerization are usually observed [26]. Alkenes bearing strongly electron-withdrawing groups are not good substrates. As an alkene becomes more electron deficient, formation of diene by alkene–alkyne coupling without carbon monoxide insertion becomes competitive [27]. For example, 4-methylstyrene-phenylacetylene coupling affords mixtures of cyclopentenones (13%) and dienes (26%) [1d,2c] (Eq. (11)).

(11)



However, in the presence of a promoter such as DMSO the cycloaddition reaction is dominant to give cyclopentenones as a major product [8] (Eq. (12)).

(12)



The Pauson–Khand reaction is highly tolerant of the common organic functional groups such as ethers, alcohols, tertiary amines, thioethers, ketones, ketals, esters, amides, alkyl and aryl halides, vinyl ethers and esters, aromatic rings including benzene, furan, and thiophene, and even Fischer carbene complexes [28].

Modification of cobalt complexes by replacement of one or two carbonyl ligands by phosphines or phosphites has been tried to limited success due to the reduced yield or the reduced reaction rate of the reaction [7,12a]. However, in the presence of a promoter such as Me_3NO, compound (alkyne)$Co_2(CO)_5P(OMe)_3$ in CH_2Cl_2 and THF (v/v, 1:1) displays high reactivities [12d].

4. Promotion of the reaction

The Pauson–Khand reaction often encountered some limitations because of its intrinsic problems in reaction conditions such as requiring high temperature and long reaction time. In early studies, several modifications of reaction condition have been devised but with limited success [7].

Smit et al. [6] unexpectedly discovered that the intramolecular Pauson–Khand reaction accelerates if it is carried out not in solution, but in adsorbed state on the surface of some adsorbent in an oxygen atmosphere (Eq. (4)). The procedure can be applicable to an entire series of allylpropargyl ethers containing substituents in various positions in both the allyl and propargyl moieties as shown in Chart 1. Under essentially the same conditions, but in an argon atmosphere, the reactant was converted into monocyclic product (Eq. (13)).

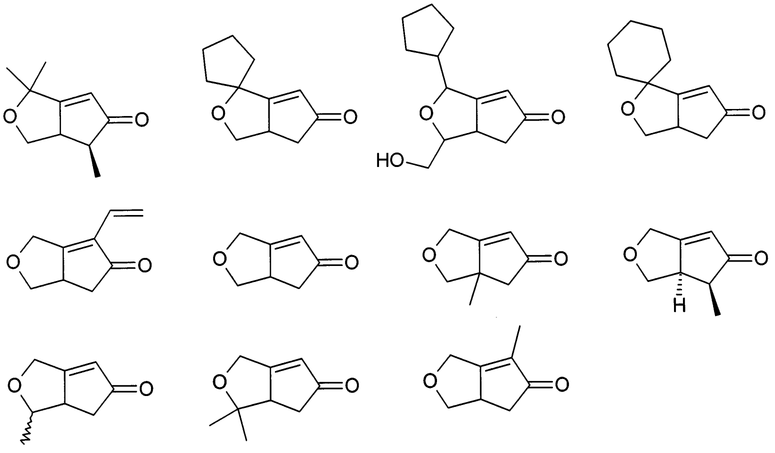
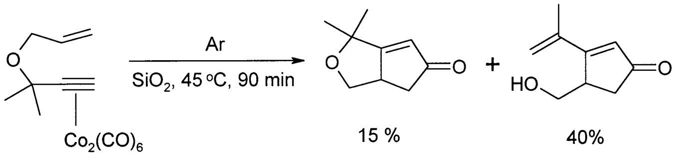
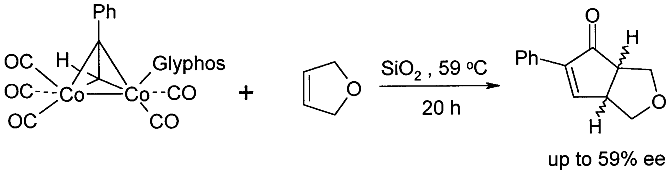


Chart 1

(13)



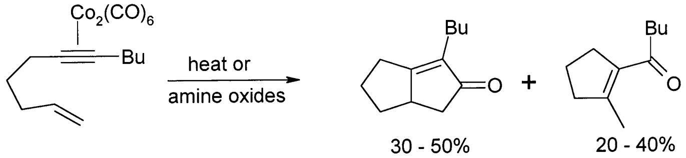
According to their studies; (1) various silica gels produce comparable rate enhancement effects; (2) alumina may also be used as an active support in this reaction, the effect being insensitive to the pH of the adsorbent, and 3) silica gels containing about 30% water or dried up 5% are rather inactive as media for the reaction and the optimum water contents lies between 10 and 20%. They explained this phenomenon as the possible influence of the adsorption on the conformation of the reactant (precursor). The adsorption of precursor on the SiO_2 surface is governed mainly by the interaction of the hydrophilic adsorbent centers with the ether center of the precursor. This effect, together with the repulsive interaction of the surface with the hydrophobic ends of precursor, would assist in the formation of the cyclic transition state leading to bicyclic product. This surface promoted Pauson–Khand cyclization has been used to synthesize many useful organic compounds [29] and has also been applied to the enantioselective synthesis of 3-oxabicyclo[3.3.0]oct-7-en-7-phenyl-6-on [30] (Eq. (14))



(14)

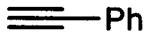
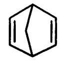
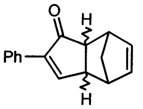
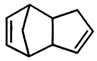
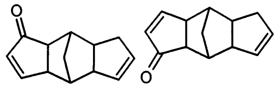
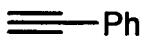
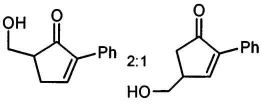
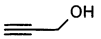
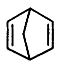
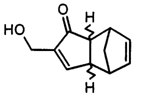
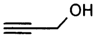
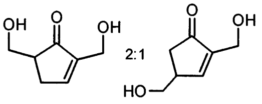
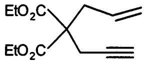
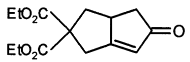
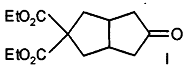
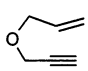
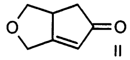
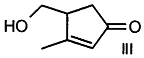
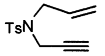
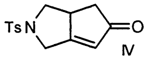
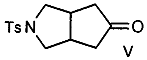
One of the primary reasons for the harsh reaction conditions, is presumably, associated with the initial step of decarbonylation to generate a vacancy for the incoming alkenes. It has been known that tertiary amine *N*-oxide such as *N*-methylmorpholine *N*-oxide (NMO) and trimethylamine *N*-oxide (TMO) could readily remove CO from the transition metals oxidatively as carbon dioxide [31]. Schreiber et al. [5a] used NMO to remove metal as an oxidized cluster for easy work-up after the usual thermal Pauson–Khand reaction. This reagent seems to serve as a promoter to generate a vacancy for incoming olefins and accelerate the overall reaction. TMO also has been used as a promoter [5b]. TMO provided a better chemical yield under milder reaction conditions and also a faster reaction and the resulting trimethylamine was easily removed by evaporation after the reaction. The scope of the promotion by TMO has been examined with a number of substrates either in intermolecular or in intramolecular fashion. As summarized in Table 1, TMO procedure is quite successful. One notable thing is that for entries 7 and 8 the presence of O_2 during the reaction is quite crucial. Otherwise, the ring opened products for oxygen containing substrates and the saturated ketones for nitrogen containing substrates were obtained, respectively, along with the desired products. This result is quite contradictory to the results reported by Krafft et al. [32]. They reported the interrupted Pauson–Khand reaction. Thermolysis of enyne **1** under a nitrogen atmosphere yielded not only the bicyclic enone **2** but also enone **3** in 20–40% yields (Eq. (15)).

(15)



1 **2** **3**

Table 1. The Pauson-Khand Reaction Promoted by TMO

	substrate	product	yield(%)
1	 	 exo:endo = 83:17	80
2	 		99
3	 		64
4	 	 exo:endo = 80:20	62
5	 		64
6		  I	81
7		 II  III	70 (II) [a] 27 (II), 23 (III)[b]
8		 IV  V	99 (IV)[a] 82 (IV:V = 4:1)[b]

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[a] Under O_2. [b]Under N_2.

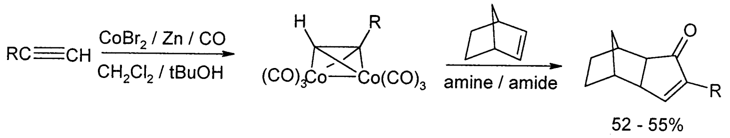
Thermal cycloaddition of **1** at 70°C in an open flask yielded enone **3** as the major product along with small amounts of Pauson–Khand enone **2**. The actual role of molecular oxygen in interrupting the normal Pauson–Khand reaction is not yet clear.

Phosphine oxides are poor oxidants and can not act in the way as the amine oxides; carbonyl ligand can be substituted by a weaker, more easily replaceable ligand, phosphine oxide. As expected, addition of phosphine oxide to the reaction mixture did not significantly increase yields in most cases [7]. The ultrasonic irradiation of the reaction mixture allows the reaction to proceed considerably faster at low temperatures, but has little effect on the yields. Addition of tributylphosphine oxide to the reaction mixture under ultrasonic irradiation did not enhance yields.

The use of dimethyl sulfoxide (DMSO) is more efficient than phosphine oxides [8]. It would not be expected to cause the oxidative destruction of the cobalt complexes induced by DMSO. The use of DMSO for the intermolecular and intramolecular cyclization has been established in Table 2. The quantity of DMSO used is not critical in the reaction. However, the choice of reaction medium is rather important. In dichloromethane, the yield was poor and a small amount of saturated ketone was obtained as a side product for the intramolecular reaction. In benzene, the reaction was rather slow but no saturated ketones were obtained. In addition to DMSO, other polar solvents such as acetonitrile and methanol, while requiring longer reaction times, give comparable or slightly better yields, but neither ethyl formate nor acetate matched DMSO in the yield attained. When DMSO is replaced by (−)-methyl-p-tolylsulfoxide, no asymmetric induction is observed.

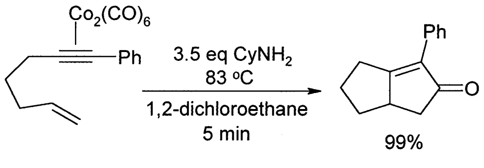
Recently, the amine induced Pauson–Khand reaction has been reported by Periasamy et al. [9a] (Eq. (16)).

(16)



According to their report, tetramethylenediamine, α-methylbenzylamine, and dimethylformamide promote the Pauson–Khand reaction of the alkyne–cobalt complexes prepared in situ in dichloromethane/*t*-BuOH using $CoBr_2/Zn/CO$ (1 atm). The amine induced reaction is not comparable to other promoters such as amine *N*-oxide and DMSO. They suggested that the amine may form a weak complex which could facilitate the PKR. The use of primary amine in the rate enhancement of the PKR has been reported by Sugihara et al. [9b] (Eqs. (17 and 18)).

(17)



(18)

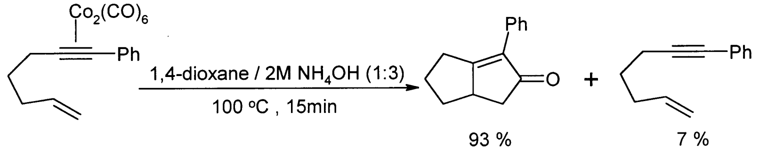
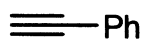
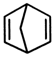
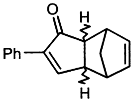
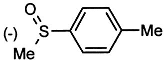
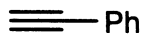
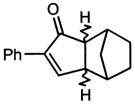
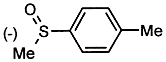
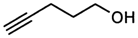
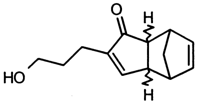
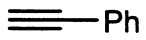
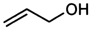
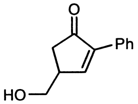
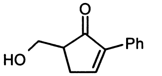
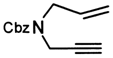
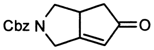
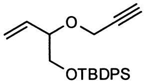
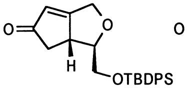
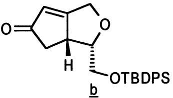


Table 2. The Pauson-Khand Reaction Promoted by Sulfoxide

entry	substrate	reagent	solvent	temp.(°C)	time(hr)	products	yield(%)[a]
1	 	DMSO(3 eq.)	C_6H_6	40	48		94 (exo 93 : endo 7)
2			C_6H_6	40	24		90 (exo 86 : endo 14)
3	 	DMSO(3 eq.)	C_6H_6	40	24		93(exo only)
4			C_6H_6	40	24		100(exo only, 0%ee)
5	 	DMSO(3 eq.)	C_6H_6	40	36		90(exo 94 : endo 6)
6	 	DMSO(3 eq.)	CH_2Cl_2	40	5	 	30(3- : 2- = 72 : 28)
7		DMSO(3 eq.)	C_6H_6	60	24		63(3- : 2- = 54 : 46)
8		DMSO(3 eq.)	C_6H_6	40	36		64
9		Me_3NO(4 eq.),O_2	CH_2Cl_2	rt	4	 a  b	73(a : b = 4 : 1)
10		silica gel,O_2		50	3		28(a only)
11		DMSO(3 eq.)	CH_2Cl_2	40	12		37(a : b = 1.5 : 1)
12		DMSO(3 eq.)	C_6H_6	45	72		67(a : b = 5 : 1)

[a] Yields based on starting alkynes or enynes.

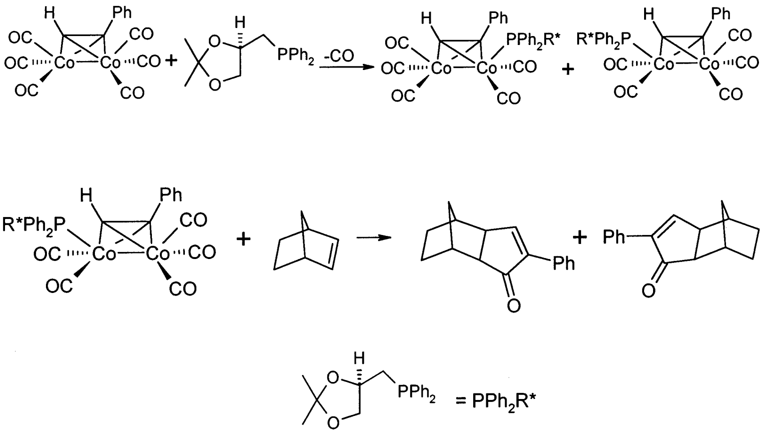
According to their study, the alkyl group on the primary amines has a great influence on the course of the reaction. The moderately hindered primary amines, such as the ones containing secondary alkyl groups, seem to promote the PKR most effectively. Especially they reported the use of ammonia in a biphasic system in which an aqueous solution of ammonium hydroxide would be the source of ammonia. They have established two sets of reaction conditions: 3.5 equivalents of cyclohexylamine in 1,2-dichloroethane at 83°C and a 1:3 mixture (v/v) of 1,4-dioxane and 2 M aqueous solution of ammonium hydroxide at 100°C. The two methods gave comparable results in terms of the rates and yields. In all cases they studied, the reaction was complete in a short time (10–135 min) and afforded the desired cyclopentenones in good yields (45–100%).

5. Stereoselective Pauson–Khand reaction

The cobalt-mediated Pauson–Khand cyclization is a powerful synthetic tool in organic synthesis. However, examples of asymmetric versions of the Pauson–Khand reaction have been few in number and have been utilized with a limited range of substrates. One of the diastereoselective approaches involves the chirality transfer from another ligand, e.g. the optically active phosphorus donor, to the metal core to generate complexes possessing a disymmetric C_2Co_2 core [10] and the other is based on the use of conventional chiral auxiliaries [11,12] directly bound to either of the reacting fragments. Recently, Pericàs et al. [13] introduced a new concept which combines the main advantages of the two aforementioned approaches. Greene et al. have greatly advanced the understanding of the stereoselective PKR. A selection is presented.

The first asymmetric induction study was carried out by Pauson et al. [10a] using a chiral phosphine ligand. Instead of attaching the chiral auxiliary on an organic group, an optically active phosphine, glyphos, substitutes one of carbonyl ligands and the reaction with a chiral cobalt cluster had been tested (Eqs. (19 and 20)).

(19,20)

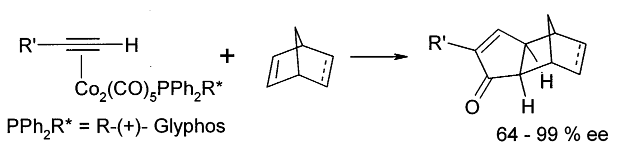


]

When the glyphos reacted with $Co_2(CO)_6$(alkyne), two diastereomers were obtained. Both diastereomers can be separated by preparative liquid chromatography. Thus the optically pure diastereomer would give the enantiomerically pure cyclopentenone derivative. However, the replacement of carbonyl by phosphine or phosphite ligands reduced the final yields (22–31%) or reduced the reaction rate. In addition, the diastereomer was epimerized at high reaction temperatures and a poor e.e. value was obtained. Thus it is crucial to use reaction conditions under which the epimerization is slow. The use of promoter [10b,d] may solve the problems of low yields and epimerization. Brunner and Niedernhuber [30] used the surface promoted Pauson–Khand to reduce the possibility of epimerization.

Kerr et al. [10b] reported the synthesis and separation of diastereomeric (alkyne)pentacarbonyldicobalt complexes containing the chiral phosphine ligand (R)-(+)-glyphos and their use in the enantioselective intermolecular Pauson–Khand reaction using anhydrous NMO as a reaction promoter (Eq. (21)).

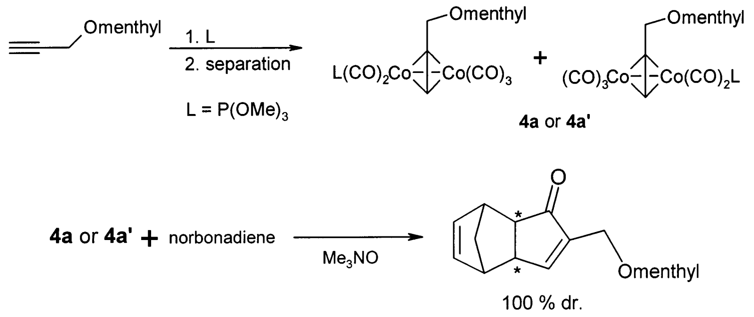
(21)



They also concluded that the enantioselection does not arise from the influence of the chiral glyphos ligand but from the chiral C_2Co_2 core.

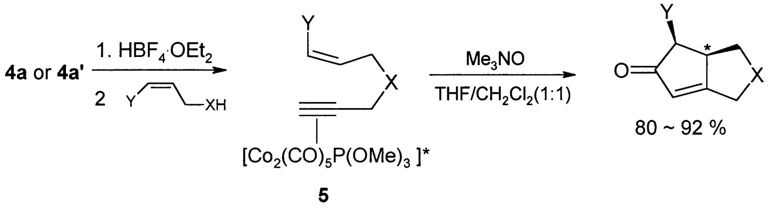
Chung et al. [10d] reported the synthesis of a diastereomeric mixture of (alkyne)pentacarbonyldicobalt complexes **4** by the reaction of $Co_2(CO)_8$ with (−)menthyl propargyl ether followed by replacement of carbonyl by phosphite (Eqs. (22 and 23)).

(22,23)



Chromatography of **4** gave the two diastereomers **4a** and **4a**′ in equal amounts. Treatment of the diastereomer **4a** or **4a**′ norbornene in the presence of Me_3NO gave the product in 85–98% yield with the 100% diastereomeric excess. In comparison, when ((−)menthyl propargyl ether)$Co_2(CO)_6$ was treated with norbornadiene in thepresence of Me_3NO, the diastereomeric mixtures of *exo* and *endo* product was obtained in 67% and 19% yields, respectively. The diastereoselection arises mainly from the presence of a chiral cluster core. For the intramolecular Pauson–Khand reaction, enyne complexes **5** were treated with Me_3NO in CH_2Cl_2/THF (v/v, 1:1), the corresponding products after the reaction were obtained in high yields with high diastereoselectivities (Eq. (24)).

(24)



The use of chiral auxiliaries directly bound to the reacting fragments has been studied by many groups, especially Greene et al. At first, the asymmetric intramolecular PKR of alkoxy enynes derived from chiral alcohols had been studied. Chart 2 shows some chiral auxiliaries used in the asymmetric intramolecular PKR. For the intramolecular PKR of 7-alkoxy-1-hepten-6-ynes derived from chiral alcohols **2-a**, **2-b**, and **2-c** in Chart 2, the yields were poor (24–38%) and the best diastereomeric ratio was 3.2:1 [12a]. The stereochemical outcome of the reaction was explained by the intermediacy of a *cis*-cobaltbicyclooctane. When acetylenic *O*-alkyl enol ethers derived from chiral alcohol **2-b** in Chart 2 were used as a substrate, the best diastereomeric ratio was 10:1 and the *E* isomer proved much more effective in this reaction than the *Z* isomer [11a]. The stereochemical outcome of the reaction was explained based on chiral auxiliary-directed π-face discrimination. When alkynyl-substituted enol ethers derived from camphor-derived neopentyl ether **2-d** or **2-e** in Chart 2 were used as a substrate, the yields were improved up to 53% and the best diastereomeric ratio was 9:1 [12b] (Eq. (24)). The stereochemical outcome of the reaction was dependent upon the conformational preference of the enol ether, e.g. the diastereofacial selectivity in the interaction between the enol ether moity and the dicobalt cluster. When alkenyl-substituted ynol ethers derived from camphor-derived neopentyl ether **2-d** or **2-e** in Chart 2 were used as a substrate, the yields were improved up to 65% and the best diastereomeric ratio was 94:6 under very mild reaction conditions [12b] (Eq. (26)). The stereochemical outcome of the reaction was explained by the conformational preference of the vinyl group.

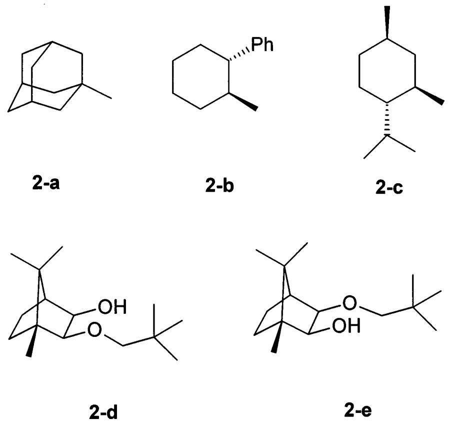
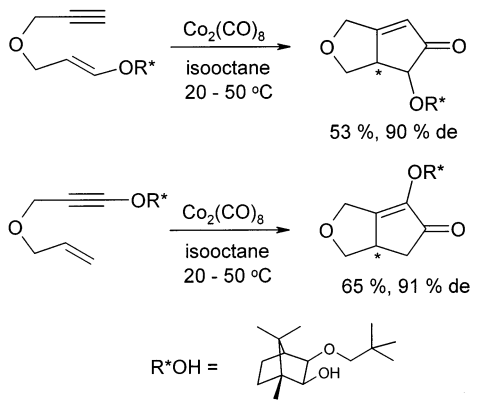


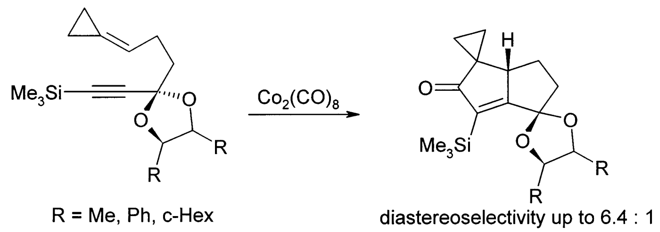
chart 2

(25, 26)



De Meijere et al. [33] studied the intramolecular Pauson–Khand reaction using a chiral acetal adjacent to the triple bond in 1.6-enyne. They obtained diastereoselectivity up to 6.4:1 (Eq. (27)).

(27)



The first practical asymmetric intermolecular PKR based was reported by Greene et al. in 1994 [12c]. This reaction was based on a chiral alkoxy acetylene dicobalt hexacarbonyl complexes (Eq. (28)).

(28)

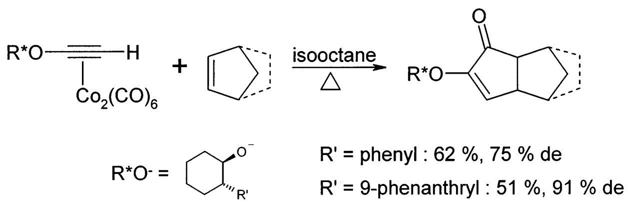


Chart 3 shows the chiral alcohols used in this study. The phenanthrylhexanol derivatives afforded the best diastereoselection of 10:1. However, due to the difficulty in the preparation of phenanthrylhexanol in enantiopure form, the authors used *trans*-2-phenylcyclohexanol as the chiral auxiliary of choice.

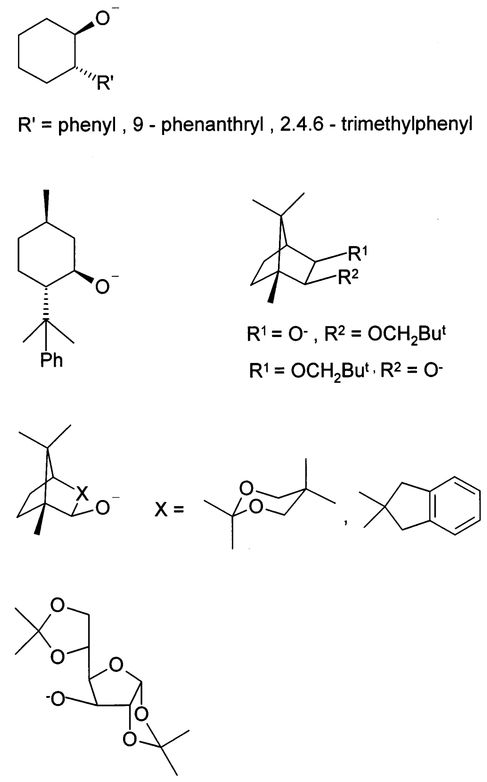
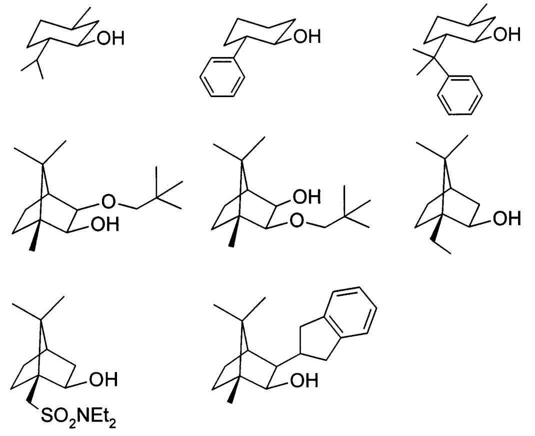


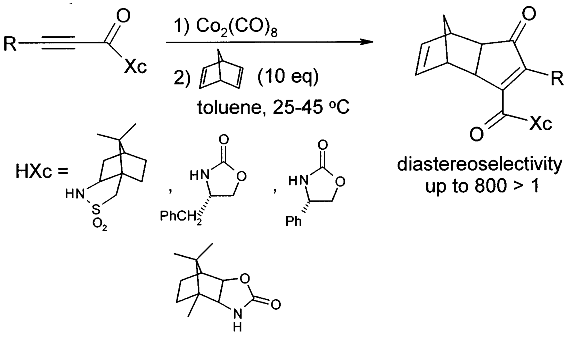
chart 3

Moyano et al. [34] reported the diastereoselectivity in the intermolecular PKR of chiral 2-alkynoates ($R\equiv CO_2R^*$). Chart 4 shows chiral alcohols used in this study. The stereoselectivities obtained were not great, but moderate. The stereochemical outcome was explained by the restricted conformational mobility of the carboxyl group in the dicobalt hexacarbonyl complexes. Replacing the ester linkage in chiral 2-alkynoates ($R\equiv CO_2R^*$) by a less-mobile amide bond gave higher degrees of stereoselectivity [12f] (Eq. (29)).



(29)

Chart 4

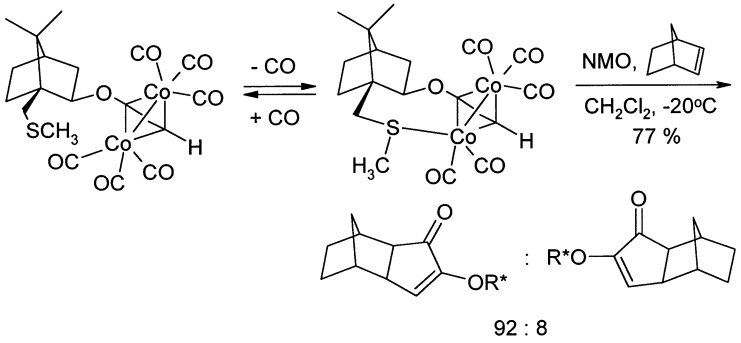


(29)

A series of 2-alkynol derivatives of the homochiral 2-oxazolidinones and of (+)-10,2-camphorsultam had been tested. Independent of the substitution of the alkyne, *Oppolzer* bornane-10,2-sultam leads to the totally stereocontrolled formation of the 3-carbamoyl cyclopentenone. The intermolecular PKR of 2-alkynol derivatives of 2-oxazolidinone and bornanesultams with norbornadiene or norbornene proceeds in a highly stereocontrolled manner, with excellent yields and under mild and simple experimental conditions.

Greene et al. [13] have examined 10-methylthioisoborneol as a chiral controller which bears an appropriately positioned group able to interact with the metal center along the reaction pathway and thus potentially improve the diastereoselection of the reaction (Eq. (30)).

(30)



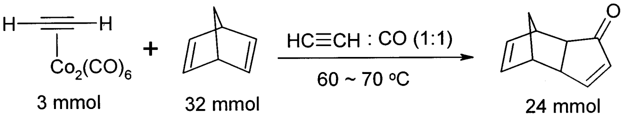
They used a chiral auxiliary with chelating capability which could allow an efficient transfer of chirality to the C_2Co_2 core and found that the internally chelated, dicobalt pentacarbonyl complex was reactive at unusually low temperature to give enones in high yields and with high diastereomeric ratio. For the reaction with norbornene, the best result (77% yield; d.r. 92:8) was obtained when the reaction was carried out in dichloromethane at − 20°C. They developed a conceptually new and very efficient chiral controller for the intermolecular PKR.

Due to the availability of alkynes and alkenes and to the variety of conditions for the removal of the chiral auxiliaries, the resulting Pauson–Khand adducts offer considerable interest for the efficient enantioselective construction of chiral synthetic intermediates or ligands. Due to the practical reason, the methodologies based on the chiral auxiliary approach have been found wide application such as the synthesis of complex natural products e.g. (+)-hirsutene, (+)-β-cuparenone, brefeldin A, and nor-pentalene [11a,c,d].

6. The catalytic version of the Pauson–Khand reaction

Until the early 1990s, a catalytic version of this cyclization was a dream of many chemists involved in this area. Pauson [16] tried a catalytic reaction with octacarbonyldicobalt in the early stage of the Pauson–Khand reaction (Eq. (31)).

(31)



Early work with gaseous alkynes suggested that the process could be carried out in a catalytic fashion by stirring a mixture of alkene and ca. 10 mol.% $Co_2(CO)_8$ in an inert solvent under a 1:1 alkyne/CO atmosphere. The success of these attempts depended upon the continuous supply of excess alkyne being able to trap and recycle reactive cobalt-containing fragments. Several chemists in the 1970–1980s attempted the catalytic reaction using hexacarbonyldicobalt, but they did not obtain better results than Pauson.

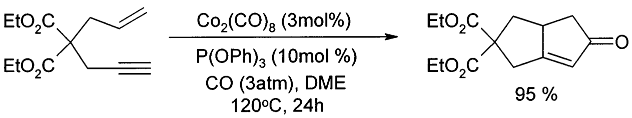
In this respect, recent developments [14,15,25,35–37] in catalytic PKR, especially in the 1990s, have been quite impressive. Nowadays the catalytic PKR was successful in intermolecular reactions involving ethylene and the strained, reactive alkenes such as norbornadiene and norbornene with 1-alkyne or acetylene, and CO. Intramolecular reaction using various enynes have also been reported.

Rautenstrauch et al. [14] reported the preparation of 2-pentylcyclopent-2-en-1-one (Eq. (9)), a precursor of an important perfumery chemical *trans*-dihydrojasmonate, from hept-1-yne, ethylene and CO, by a catalytic PKR.

Cyclopentenone was synthesized in 47–49% yield, whose turnover number is ca. 220. However, the scope of this reaction was very narrow.

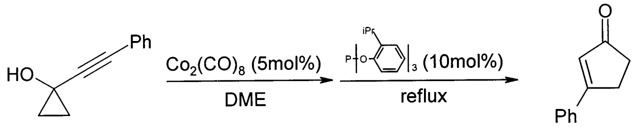
It has been suggested [16c,38] that the main impediment to catalysis in the thermal PKR is the formation of either metal clusters or inactive cobalt carbonyl species. For example, at 50°C, $Co_2(CO)_8$ is converted $Co_4(CO)_{12}$, which is inactive toward alkyne substrates. For this reason, phosphite and phosphine ligands have been added to inhibit the formation of inactive cobalt species. A catalytic conversion of enynes into cyclopentenones employing phosphites as coligands has been reported by Jeong and Chung et al. [35] (Eq. (32)).

(32)



The addition of phosphite was quite useful for the intramolecular PKR. The corresponding products were obtained with turnover numbers of 5–30. However, they could not find the catalytic reactivity in the intermolecular PKR. Very recently, Iwasawa et al. [36] reported the catalytic conversion of 1-(1-alkynyl)cyclopropanols to 2-cyclopentenones employing $Co_2(CO)_8$ with triphenylphosphite as a coligand (Eq. (33)).

(33)



An alternative way to prevent the formation of $Co_4(CO)_{12}$ is to use a high pressure of CO. The kinetics and thermodynamics of an equilibrium between $Co_2(CO)_8$ and $Co_4(CO)_{12}$ in hexane under CO pressure have been investigated by Bor et al. [39]. They scanned the equilibrium constant of $Co_4(CO)_{12}$, $Co_2(CO)_8$, and CO partial pressure at various temperatures. The equilibrium constant was defined as follows:

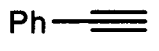
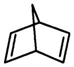
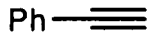
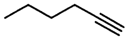
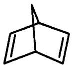
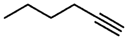
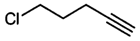
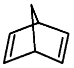
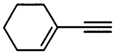
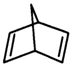
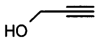
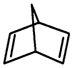
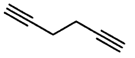
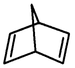
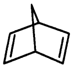
$$K_p = [Co_4(CO)_{12}]PCO^4/[Co_2(CO)_8]^2$$

The temperature dependence of K_p was determined by a linear least squares fit yielding an empirical equation as follows:

$$\log K_p = 21.84 - 6455/T \ (K_p \text{ in bar}^4 \text{ dm}^3 \text{ mol}^{-1})$$

From these two equations, it is expected that the molarity of $Co_2(CO)_8$ will increase as the CO partial pressure increases (when the temperature remains constant), and that equilibrium constant will increase as the temperature increases, then the molarity of $Co_4(CO)_{12}$ will also increase. Therefore, when the pressure of CO is high enough, $Co_2(CO)_8$ should be the predominant species even at high temperatures, preventing the formation of $Co_4(CO)_{12}$ and allowing the PKR to be catalytic. Chung's group has examined [15] some simple experiments using cobalt carbonyls in 100 ml stainless autoclaves. Treatment of a CH_2Cl_2 solution of $Co_2(CO)_8$ with 40 atm of CO at 80°C for 13 h afforded a small amount of $Co_4(CO)_{12}$ with most $Co_2(CO)_8$ remaining unchanged. Conversely, treatment of a CH_2Cl_2 solution of $Co_4(CO)_{12}$ with 40 atm of CO at 80°C for 12 h led to the conversion of $Co_4(CO)_{12}$ into $Co_2(CO)_8$. Thus, under high pressure of CO and at high temperature, most of cobalt carbonyls exist as $Co_2(CO)_8$ instead of $Co_4(CO)_{12}$. Being encouraged with these results, Chung's group carried out the PKR using $Co_2(CO)_8$ and $Co_4(CO)_{12}$ under the conditions of high pressure of CO and high temperature [15]. The reaction was catalytic and the optimum condition was a reaction at 150°C under 10 atm of CO. The practical lower limit of the reaction temperature seems to be about 60–79°C, although they did not search the upper limit because in most cases the temperature of 150°C was sufficient to make the reaction fast enough. The lower limit of the CO pressure seems to be dependent upon the substrate, but in general at less than 5 atm of CO the reaction did not

Table 3. Intermolecular Pauson-Khand Reaction Catalyed by $Co_4(CO)_{12}$ (0.005 equiv.)

	Alkyne	Alkene	Reaction Time (h)	Yield[a](%)	Turnovers
1			1.5	97	194
2			23	93	186
3			1	98	196
4			22	100	200
5			23	71	142
6			6	75	150
7			22	80	160
8			22	58	216
9	 [b]		72	3803	38

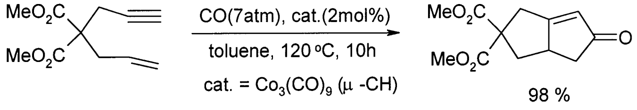
[a] All yields are isolated yields based on substrates except acetylene. All products are known compounds. The formation of each product was conformed by checking their spectral data (IR, NMR, MS). [b]Reaction Conditions: 80°C, 5 atm.of acetylene and 40 atm.of CO. The yield is based on $Co_4(CO)_{12}$.

proceed well. A notable exception is the reaction of phenylacetylene with norbornadiene in the presence of 2 mol% of $Co_2(CO)_8$ at 1–2 atm of CO for 3 days giving the product in 58% yield. The scope of this reaction has been examined with a number of substrates either in intermolecular or intramolecular fashion. Tables 3 and 4 show the intermolecular and intramolecular catalytic PKR using the cobalt cluster $Co_4(CO)_{12}$. The catalytic system is quite effective for terminal alkynes having aryl, alkyl, alkylchloride, alcohol, and alkenes as a substituent. With a terminal diyne, the reaction proceeded to give the expected dicyclopentenone derivative. The catalytic system is quite effective with norbornadiene and/or norbornene, but not with cyclopentene. In a case of norbornene, longer reaction times were needed for complete reaction, probably because of the better reactivity of norbonadiene owing to the π-orbital interactions between two double bonds. The reaction time was highly dependent upon the substrate and inversely dependent upon the reaction temperature. Within 24 h, most reactions went to completion with high turnover numbers. Acetylene reacted readily with norbornadiene, but was not reactive at low pressure of CO (10 atm). The maximum turnover number for the reaction between phenylacetylene and norbornadiene in the presence of $Co_4(CO)_{12}$ was ca. 1000.

Compared to the intermolecular reactions, the intramolecular reactions need more $Co_4(CO)_{12}$ and take longer reaction times, and the turnover numbers are not great as in the intermolecular reaction. However, the catalytic system is also quite effective for intramolecular reactions.

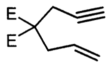
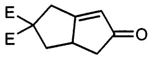
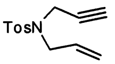
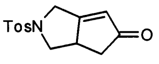
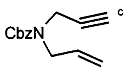
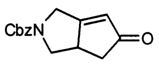
Most reaction have been carried out in dichloromethane because cobalt carbonyls and almost all products are readily soluble in this solvent. It has been known that for the stoichiometric intramolecular PKR promoted by $NMO \cdot H_2O$ the influence of solvent is evident [40]. However, the catalytic PKR reactions are not influenced much by the solvent.

Very recently, Livinghouse et al. [41] reported the thermal promotion of intramolecular PKR catalyzed by high purity $Co_2(CO)_8$ (Eq. (34)). The turnover numbers are not high.



(34)

Table 4. Intramolecular Pauson-Khand Reaction Catalyzed by $Co_4(CO)_{12}$(0.01equiv.)[a]

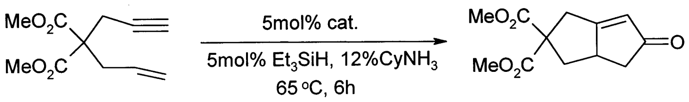
Enyne	Bicyclopentenone	Yield[b](%)	Turnovers
		92	92
		87	87
		81	81

[a] Reaction time: 1 day. [b] Isolated yields based on substrates. E=EtOC(O). [c] Cbz=PhOC(O).

Note that the reaction proceeds at the relatively low reaction temperature 60–70°C under one atmosphere of CO pressure. The need for $Co_2(CO)_8$ in high purity can be an experimental disadvantage.

Livinghouse and Belanger [42] found that some $Co_2(CO)_6$-alkyne complexes can serve as sources of an active catalyst for carbonylative enyne cyclations. They screened a series of $Co_2(CO)_6$-alkyne complexes in combination with Et_3SiH as surrogates in the catalytic PKR (Eq. (35)).

(35)



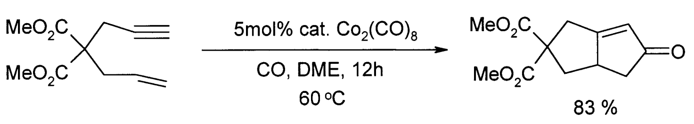
cat. = $[HO(CH_3)_2CC{\equiv}CH]Co_2(CO)_6$

Chung et al. [24,37] reported two cobalt complexes which showed their catalytic reactivity toward both intramolecular and intermolecular fashions. Their new process has been successfully achieved by introducing $Co(acac)_2$ with/without $NaBH_4$ [24] or 1,5-cyclooctadiene(indenyl)cobalt(I) complex [37] as a new catalyst system under mild conditions to afford cyclopentenones in good yields and high turnover numbers. In comparison to the (indenyl)Co(COD) system, $Co(acac)_2$ with/without $NaBH_4$ tolerates functionalities such as halide and ester and is applicable to the reaction employing acetylene. Both systems will be discussed in detail in the Variations of the Pauson–Khand Reaction. These studies suggested that a system could be catalytic provided it leads to the in situ generation of low valent cobalt, which could then react with available CO to afford cobalt carbonyls and the catalytic precursor would be $Co_2(CO)_8$ and that system which could generate $Co_2(CO)_8$ in situ could be a catalyst.

Earlier reported methods [43] for preparation of $Co_2(CO)_8$ involve reduction of various cobalt salts such as $CoCO_3$, CoO, $Co(NO_3)_2$, $Co(OAc)_2$ with high pressure (150–300 atm) mixture of hydrogen and carbon monoxide at elevated temperature (80–200°C). The reduction of CoI_2 in *t*-BuOH/toluene mixture by Zn metal in presence of CO at atmospheric pressure gives $Co_2(CO)_8$ in 38% yield after 24 h [44]. Recently, Periasamy et al. [45] reported that (alkyne)$Co_2(CO)_6$ was readily available through reduction of $CoBr_2$ with Zn in THF or CH_2Cl_2/*t*-BuOH in the presence of alkynes while bubbling carbon monoxide at room temperature. They understood that the in situ generation of $Co_2(CO)_8$ from cobalt salt by the reduction in the presence of CO was crucial to the formation of (alkyne)$Co_2(CO)_6$. However, they did not realize that at high pressure of CO $Co_2(CO)_8$ can be continuously generated and the reaction can be catalytic. Various cobalt sources, even cobalt clusters and cobalt metal known as the main obstacles of the catalytic PKR, can be used to generate $Co_2(CO)_8$. Cobalt slurry, made by reduction of anhydrous cobalt chloride with lithium naphthalenide, could be used to make $Co_2(CO)_8$ and was quite reactive toward the PKR under a high pressure of CO [46].

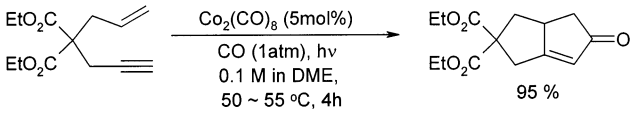
Sugihara and Yamaguchi [47] used methylidynetricobalt nonacarbonyl cluster as active sources of active catalyst in the intramolecular and intermolecular PKR (Eq. (36)).

(36)



Livinghouse and Pagenkopf [48] reported the photochemical promotion of the intramolecular PKR (Eq. (37)): high-intensity visible light effectively promoted an intramolecular catalytic PKR at 50–55°C and 1 atm of CO.

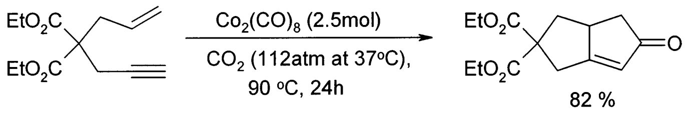
(37)



As we have already mentioned in the promotion of the PKR, TMO and DMSO markedly accelerate stoichiometric Pauson–Khand reactions. These reagents have been proposed to function via the oxidative removal of CO, thereby providing an empty coordination site for alkene complexation. In the same way, Livinghouse realized that various metal carbonyl complexes undergo the photoinduced CO dissociation and pursued this simple expedient in connection with facilitating a catalytic Pauson–Khand reaction. They found that the purity of $Co_2(CO)_8$, the choice of an appropriate light source, and reaction temperature (ca. 50°C) were critically important for successful catalytic reactions. This photochemical promotion is limited to the intramolecular reaction and the turnover numbers were not high (max. 60).

Recently, catalytic PKR in supercritical CO_2 fluid was reported by Jeong et al. [49] (Eq. (38)).

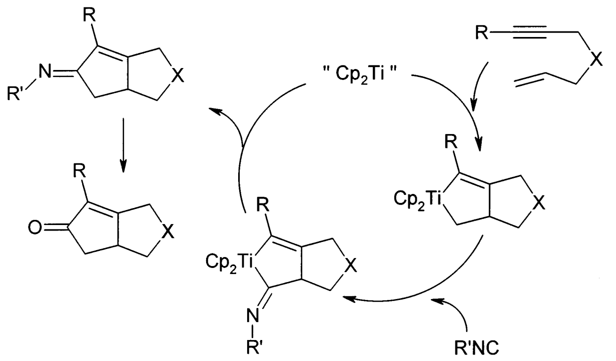
(38)



Catalytic Pauson–Khand reactions were performed in supercritical CO_2 by charging a cylindrical stainless steel reactor with a catalyst and enynes followed by pressurizing properly with carbon monoxide and carbon dioxide. According to their study, high reaction temperature (90–100°C) and high carbon monoxide pressure (15–30 atm) were required and the turnover numbers were not high (max. 34). They presented only four intramolecular reactions and two intermolecular reactions. Thus, decision about the usefulness of the PKR in supercritical fluids has to wait until more thorough studies have been done.

7. Variations of the Pauson–Khand reaction

Cocyclization of alkynes with alkenes and carbon monoxide by transition metals has become one of the most popular reactions for the preparation of cyclopen-

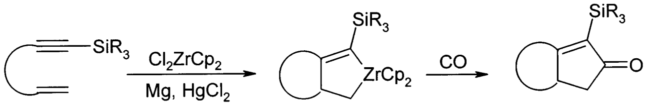


Scheme 2.

tenones. Since the first success of the synthesis of cyclopentenones from alkynes and alkenes employing dicobalt octacarbonyl, a number of variations with other cobalt complexes [25,35] and with different metals including zirconium [50], titanium [51], nickel [52], palladium [53], iron [54], molybdenum and tungsten [55], rhodium [56], and ruthenium [57] have appeared in the literature.

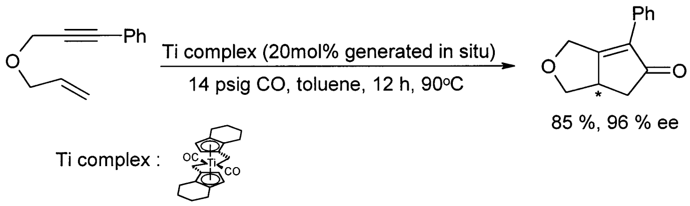
Metallocene equivalents generated from Cp_2ZrCl_2 and Cp_2TiCl_2 in combination with CO can be utilized to effect the transformation of enyne to bicyclic enone [50,51]. The initially formed metallacycles are converted to enone by carbonylation. This method provides an easy way to prepare cyclopentenone skeletons from simple starting materials. However, functional group tolerance may not be good due to the basic, highly reducing conditions. Terminal alkynes are incompatible with the cyclization; blocking is required. Negishi et al. reported [50a] that the reaction of ω-vinyl-1-silyl-1-alkynes with a $Zr(II)Cp_2$ reagent produces, in excellent yields, a zirconabicyclic derivative, which can be treated in situ with CO to produce the corresponding α-silylcyclopentenones in good yield (Eq. (39)).

(39)



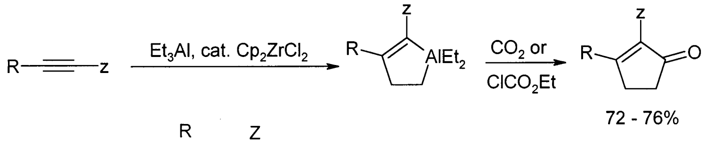
When an isocyanide is used instead of CO, the reaction gives an iminocyclopentene which can be converted to a bicyclic enone. Buchwald et al. [51b] found that $Cp_2Ti(PMe_3)_2$ (10 mol%) would catalytically convert enynes and a slight excess of Me_3SiCN to the corresponding iminocyclopentene (Scheme 2). Mild hydrolysis afforded bicyclic cylopentenones. This system was also applied to an enantioselective catalytic Pauson–Khand type reaction [51d] (Eq. (40)).

(40)

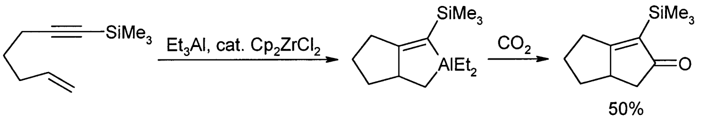


Recently, Negishi et al. [50e] reported zirconium–catalyzed carboalumination of alkynes and enynes as a route to aluminacycles and their conversion to cyclic enones (Eqs. (41 and 42)).

(41, 42)



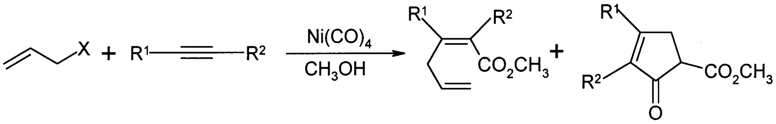
R	Z
nBu	nBu
nPr	nPr
Me	Ph



Superficially, the reaction is similar to other Pauson–Khand type reactions, but is mechanically quite different from those of other transition metal complexes.

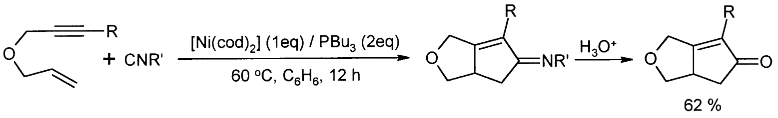
Another superficially similar, but mechanically quite different cyclopentenone formation was derived from the work of Chiusoli [52a–f] (Eq. (43)).

(43)



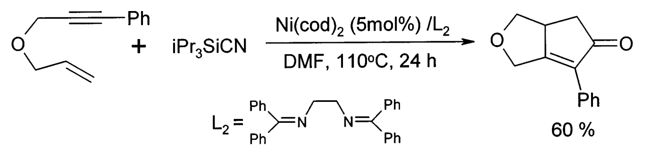
In this process, $Ni(CO)_4$ acts as a catalyst precursor and a double bond of an allylic halide serves as an alkene component of a formal [2 + 2 + 1] cycloaddition. Tamao et al. [52h,i] reported the nickel(0)-promoted cyclization of enynes with isocyanides to form 1-imino-2-cyclopentenes which can hydrolyzed to the corresponding cyclopentenones (Eq. (44)).

(44)



They used a stoichiometric amount of bis(1,5-cyclooactadiene)nickel(0), $[Ni(cod)_2]$ with 2 equivalents of PBu_3. Alternatively, nickel(0) species generated in situ from air-stable $[Ni(acac)_2]$ and two equivalents of diisobutylaluminum hydride exhibit essentially the same activity. While this reaction proceeds in good yields, a separate hydrolysis step is required to yield the corresponding enones. Recently, a catalytic transformation of enynes to bicyclic enones employing a Ni(0) complex generated in situ from $Ni(cod)_2$ and a bulky bisketimine ligand was reported [52j] (Eq. (45)).

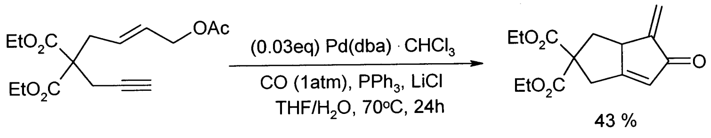
(45)



This method is tolerant of a variety of functional groups including esters, ketones, nitriles, ethers, and amines.

Heathcock et al. [53] reported a method for the construction of (α-methylenecyclopentenone fused to five membered ring employing palladium as a catalyst (Eq. (46)).

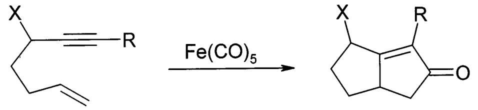
(46)



They proposed the formation of a π-allylpalladium intermediate which undergoes sequential intramolecular alkyne insertion, CO insertion, intramolecular alkene insertion, and β-hydride elimination.

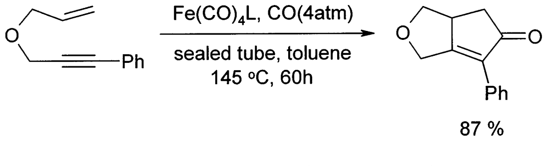
Metal carbonyl systems such as $Fe(CO)_4L$ (L = CO, NMe_3, acetone, and CH_3CN) [54], $Cp_2Mo_2(CO)_4$ [55a], $M(CO)_6$ (M = Mo, W) [55b], $W(CO)_5(THF)$ [55c], $[RhCl(CO)_2]_2$ [56a], *trans*-$[RhCl(CO)(dppp)]_2$ [56b], and $Ru_3(CO)_{12}$ [57] can convert enynes to bicyclic enones. The *in situ* generated $Fe(CO)_4$ has been used in the cycloaddition of alkynes, alkenes, and CO to give completely regioselective 4-methylene-cyclopentenone [54a] (Eq. (47)).

(47)



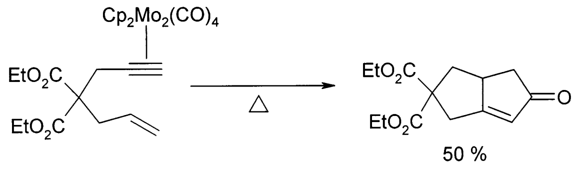
High yielding intramolecular carbonylative coupling of alkyne with alkene can be carried out employing iron carbonyls. The pre-generation of $Fe(CO)_4L$ (L = acetone or acetonitrile) allows cyclocarbonylation in high yields, but the reaction requires a high reaction temperature and involves the synthesis and handling of air-sensitive intermediates [54b–d] (Eq. (48)).

(48)



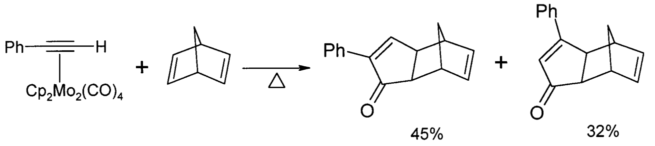
Compounds $(alkyne)Mo_2Cp_2(CO)_4$ are isoelectronic compounds of (alkyne) $Co_2(CO)_6$. Interestingly, heating $(alkyne)Mo_2Cp_2(CO)_4$ with norbornadiene or norbornene afforded the corresponding 2-substituted and 3-substituted cyclopentenone derivatives [55a] (Eq. (49)).

(49)



The molybdenum-alkyne complex was also found to be effective for intermolecular cycloaddition (Eq. (50)).

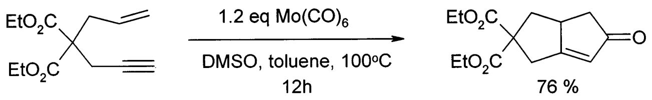
(50)



When alkyne was phenylacetylene, the corresponding 2-substituted and 3-substituted cyclopentenones were obtained at 45 and 32%, respectively.

$M(CO)_6$ (M = Mo and W) has been used in the presence of excess DMSO [55b] (Eq. (51)).

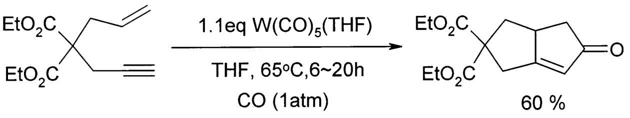
(51)



Due to the competition favored to alkyne over alkene for the second ligation, the intermolecular reaction was not carried out efficiently.

Hoye and Surigano [55c] reported that $W(CO)_5(THF)$ promoted a Pauson–Khand like cyclization of a variety of substrates including those containing electron-deficient alkene or alkyne (Eq. (52)).

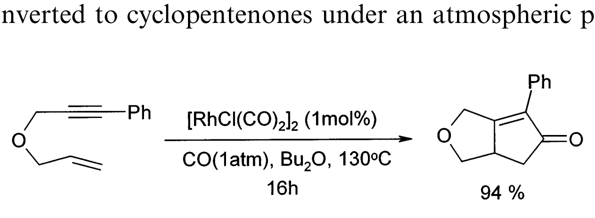
(52)



They found the reaction from the study of cyclization reaction of enynes with Fischer carbene. The in situ generated $W(CO)_5(THF)$ (by irradiation of $W(CO)_6$ in THF) was reacted with enyne substrate and then bubbled with CO. After reaction, $W(CO)_6$ (total recovery of ca. 95%) and enyne-derived product were isolated. Thus, the process is batch-catalytic with regard to the metal species. Attempts to make the reaction truly catalytic through the use of substoichiometric amount of $W(CO)_5(THF)$ in the presence of CO have been marginally successful.

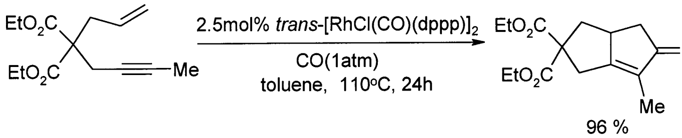
$[RhCl(CO)_2]_2$ serves as a catalyst for the intramolecular cycloaddition reaction. 1,6-Enynes are converted to cyclopentenones under an atmospheric pressure of CO [56a] (Eq. (53)).

(53)



Jeong et al. reported [56b] the catalytic intramolecular PKR using $RhCl(PPh_3)_3$, *trans*-$RhCl(CO)(PPh_3)_2$, RhCl(CO)(dppe), or *trans*-$[RhCl(CO)(dppp)]_2$ as a Rh(I) catalyst under 1 atm of carbon monoxide (Eq. (54)).

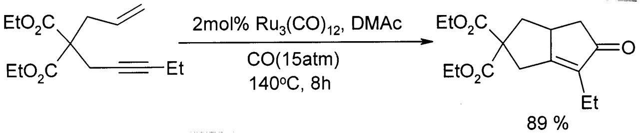
(54)



When $RhCl(PPh_3)_3$ or *trans*-$RhCl(CO)(PPh_3)_2$ was used as a catalyst, the addition of additive AgOTf was required for the initial activation. When RhCl(CO)(dppe) was employed as a catalyst, the addition of additive was not required, but was quite helpful for the completion of the reaction. However, when *trans*-$[RhCl(CO)(dppp)]_2$ was used as a catalyst, no additive was required.

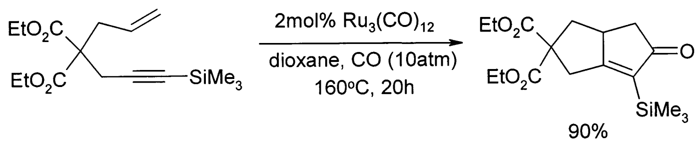
Mitsudo et al. [55a] reported the ruthenium-catalyzed intramolecular cycloaddition reaction of enynes in DMAc (*N*,*N*-dimethylacetamide) under 15 atm of CO (Eq. (55)).

(55)



Almost at the same time, Murai et al. [57b] reported the $Ru_3(CO)_{12}$-catalyzed cyclocarbonylation of enynes to bicyclic enones (Eq. (56)).

(56)



Dioxane and acetonitrile were the solvents of choice, when the reaction was run at 160°C under 10 atm of CO for 20 h. The reaction shows a high level of functional group compatibility, e.g. alkynes bearing a pyridyl or an ester group. However, an electron-deficient alkyne was a poor substrate as anticipated. The reaction mechanism is not yet clear. They propose the ruthenacyclopentene, which is generated by oxidative cyclization of enynes to ruthenium, as a key intermediate. The subsequent insertion of CO and reductive elimination produce the cyclopentenone.

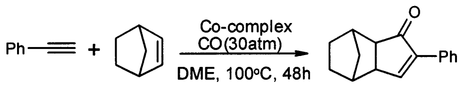
Chung et al. [25] have screened the following cobalt complexes as variants: $CoCl_2$, $CpCo(CO)_2$, $Co(PPh_3)_3Cl$, Cp*Co(acac), and $Co(acac)_2$. To explore the reactivity of each cobalt complex, they have set the following standard conditions: 5 mmol of phenylacetylene, 20 mmol of norbornene, 10 ml of DME, 30–40 atm of CO, 48 h, and 80–100°C. Interestingly, $CoCl_2$, $CpCo(CO)_2$, $Co(PPh_3)_3Cl$, Cp*Co(acac), $Co(acac)_2$, all showed the catalytic activities in the cocyclization and gave bicyclopentenone (Table 5). Among them, $Co(acac)_2$ gave the best result.

When $Co(PPh_3)_3Cl$ was used as a catalyst, cyclopentenone was obtained in a moderate yield (56%, turnover number: 28), but the separation of product from triphenylphosphine liberated from $Co(PPh_3)_3Cl$ was laborious. Compounds $CoCl_2$, $CpCo(CO)_2$, and Cp*Co(acac) provided lower catalytic turnovers (4–8.4).

The scope of the catalytic reaction employing using $Co(acac)_2$ as a catalyst was somewhat narrow and the yield obtained was not satisfactory. Phenylacetylene was the most satisfactory substrate. $Co(acac)_2$ was inactive to other alkynes. However, introduction of $NaBH_4$ as a reducing agent dramatically improved both the yield and range of a substrate (Table 6). These results show that a system of $Co(acac)_2$ with $NaBH_4$ is a new and practical catalytic system in the cyclopentenone synthesis. All attempts to identify or isolate an intermediate have so far not been successful. The liberation of free acetylacetone from $Co(acac)_2$ was confirmed by experiment. Thus, the role of $NaBH_4$ seemed to be generation of low valent cobalt species. For the reaction of 1-(ethynyl)cyclohexene with $Co(acac)_2$ and $NaBH_4$ under CO, cobalt carbonyl complex having terminal carbonyl groups was characterized. The formation of $Co_2(CO)_8$ from $Co(acac)_2$ is justified by the earlier reported methods [40]. Based on these observations, $Co(acac)_2$ and $NaBH_4$ under CO pressure should form $Co_2(CO)_8$.

The compounds (indenyl)Co(cod) and $(indenyl)Co(CO)_2$ have been used as a catalyst precursor [37]. Due to the instability of $(indenyl)Co(CO)_2$, the use of (indenyl)Co(cod) was preferred. Compound (indenyl)Co(cod) is moderately stable and can be stored for a long time under nitrogen in a freezer. The standard reaction condition for the intermolecular cycloaddition reaction is as follows: 5 mmol of alkyne, 25 mmol of norbornadiene, 10 ml of DME, 1 mol% of catalyst, 15 atm of CO, 40–48 h, and 100–100°C. The maximum turnover number for the intermolecular cycloaddition reaction between propargyl alcohol and norbornadiene was ca. 480. Results obtained from several representative substrates under standard conditions are summarized in Table 7. Terminal alkynes except entries 7 and 8 gave cyclopentenones in excellent yields. Conjugated alkynes with carbonyl or alkene-group (entries 7 and 8) did not yield the corresponding products. Free hydroxyl

Table 5

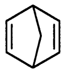
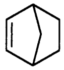
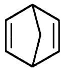
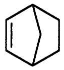
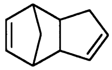
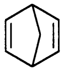
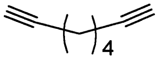
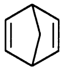
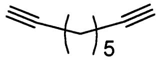
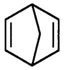
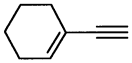
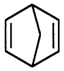


	Co-complex	Yield (%)	Turnovers
0.02 eq.	$CoCl_2$	8	4
0.50 eq.	$CpCo(CO)_2$	40	8
0.05 eq.	$Cp^*Co(acac)/MePPh_2$	42	8.4
0.02 eq.	$Co(PPh_3)_3Cl$	56	28
0.02 eq.	$Co(acac)_2$	quant.[a]	50

[a] Reaction time : 96 hr.

Table 6

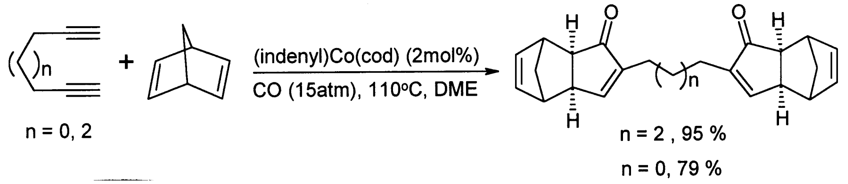
$$\text{Alkyne} + \text{Alkene} \xrightarrow[\text{CH}_2\text{Cl}_2\text{, 100}^\circ\text{C, 48 h}]{\text{0.05 eq. Co(acac)}_2/\text{NaBH}_4\text{, CO(30}\sim\text{40 atm.)}} \text{Cyclopentenone}$$

Entry	Alkyne	Alkene	Yield(%)
1	Ph—≡		quant.[a]
2	Ph—≡		quant.[b]
3	n-Bu—≡		quant.
4	n-Bu—≡		quant.[b]
5	n-Bu—≡		60 [b]
6	n-Hex—≡		95 [c]
7			80
8			85
9			80

[a] 0.01 mol% of catalyst was used. [b] The reaction was performed for 4 days. [c] The reaction was performed for 3 days.

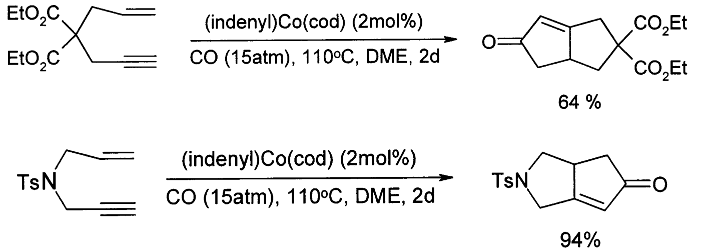
group (entries 3–6) was compatible with the reaction condition. In the case of acetylene, a turnover number of 22 was observed under 1.8 atm of acetylene and 20 atm of CO. Disubstituted alkynes (entries 9 and 10) were not as good substrates as terminal alkynes. Similarly, 1,7-octadiyne and 1,5-hexadiyne also reacted with norbornadiene to give the corresponding cyclopentenones (Eq. (57)) which can be precursors for the synthesis of *ansa*-metallocenes [58].

(57)



An intramolecular reaction has also been tested employing 2 mol% of catalyst (Eqs. (58 and 59)).

(58, 59)



Enynes were not effective as the terminal alkynes. Under similar condition as the intermolecular reaction, turnover numbers of 30–50 were obtained. Attempts with less reactive alkenes such as ethylene, cyclopentene, allyl alcohols, and methyl acrylate were not successful.

When the reaction was done with $CpCo(CO)_2$ or CpCo(cod) under the same conditions, the reaction was negligible. Thus, the indenyl ligand is essential for this cocylization reaction. However, which step in the catalytic cycle would be assisted by the indenyl group was not clear.

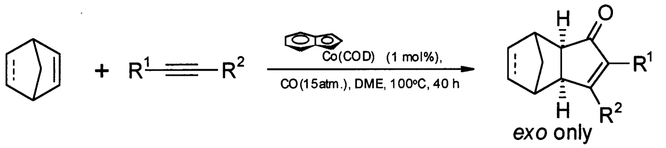
Recently, Periasamy et al. [9a,45,59] reported several simple, convenient methods for the preparation of $(alkyne)Co_2(CO)_6$ by the reaction of $NaCo(CO)_4$ with CuBr in the presence of alkynes, the reduction of $CoBr_2$ with sodium naphthalenide under CO atmosphere followed by CuBr treatment in the presence of alkynes, and the reduction of $CoBr_2$ with zinc under bubbling of CO in the presence of alkynes. They did not use $Co_2(CO)_8$ in order to prepare $(alkyne)Co_2(CO)_6$, but used the in situ generated $(alkyne)Co_2(CO)_6$. Thus, this reaction can be considered as the PKR in some points and a variant of the PKR in other points. They understood that the in situ generation of $Co_2(CO)_8$ from the cobalt salt by the reduction in the presence of CO was crucial to the formation of $(alkyne)Co_2(CO)_6$. However, they did not realize that, at high pressure of CO, $Co_2(CO)_8$ can be continuously generated and the reaction can be catalytic.

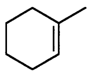
Each variation has its own advantages and/or disadvantages in terms of the scope of substrate compatibility, yield, and practicability. Most of the known variants of the PKR are quite active toward the intramolecular reactions. However, most of the recent reports described so far, especially the cases of the transition metals other than cobalt, have a critical limitation of their reactivities toward the intermolecular PKR. In contrast with this limitation, cobalt complex systems such as (indenyl)Co(cod) and $Co(acac)_2$ with $NaBH_4$ are quite effective for the intermolecular and intramolecular cycloaddition reactions. One notable observation is that the titanium complex in Eq. (40) functions as a highly enantioselective catalyst for the conversion of enynes to cyclopentenones.

8. Application to the synthesis of cyclopentadienyl complexes

The Pauson–Khand reaction has been used as a key step in numerous organic

Table 7.



	R^1	R^2	Alkene	Yield (%)
1	Ph	H	Norbornadiene	93
2	$(CH_2)_5CH_3$	H	Norbornadiene	95
3	$CH(CH_3)OH$	H	Norbornadiene	85[a]
4	$C(CH_3)_2OH$	H	Norbornadiene	95
5	CH_2CH_2OH	H	Norbornadiene	96
6	$(CH_2)_4OH$	H	Norbornadiene	97
7	CO_2Et	H	Norbornadiene	0
8		H	Norbornadiene	0
9	Ph	Ph	Norbornadiene	59[b]
10	Ph	Me	Norbornadiene	53[b]
11	Ph	H	Norbornene	82
12	$(CH_2)_5CH_3$	H	Norbornene	95
13	$(CH_2)_4CH_3$	H	Norbornadiene	86[c]

[a] Both diastereomers were obtained(1 : 1 by ^{13}C NMR). [b] 5 mol% of catalyst, 30 atm.of CO and 110°C~120°C. [c] 30 atm.of CO and 3 eq.of norbornadiene.

syntheses. Excellent shorter reviews on the application of the PKR to organic syntheses have been published [4]. However, the utilization of the PKR product in the synthesis of other organometallic compounds has not attracted much attention. In this chapter we present the use of the PKR products in synthesis of cyclopentadienyl and fulvalene complexes.

Cyclopentadienyl ligands are one of the most popular ligands in organometallic chemistry and have been synthesized by various methods [60]. One of the strategies for synthesizing cyclopentadienylmetal compounds is to use cyclopentenone as a starting material [61].

Substituted cyclopentadienyl complexes differ greatly from their unsubstituted counterparts in reactivity, structural features and physical properties [62]. To synthesize the appropriate cyclopentadienyl ligand, the high yield synthesis of cyclopentenones by the intermolecular PKR between phenylacetylene and alkenes such as ethylene, styrene, and cyclopentene has been utilized [8,21a,c] (Eqs. (60–62)).

(60, 61, 62)

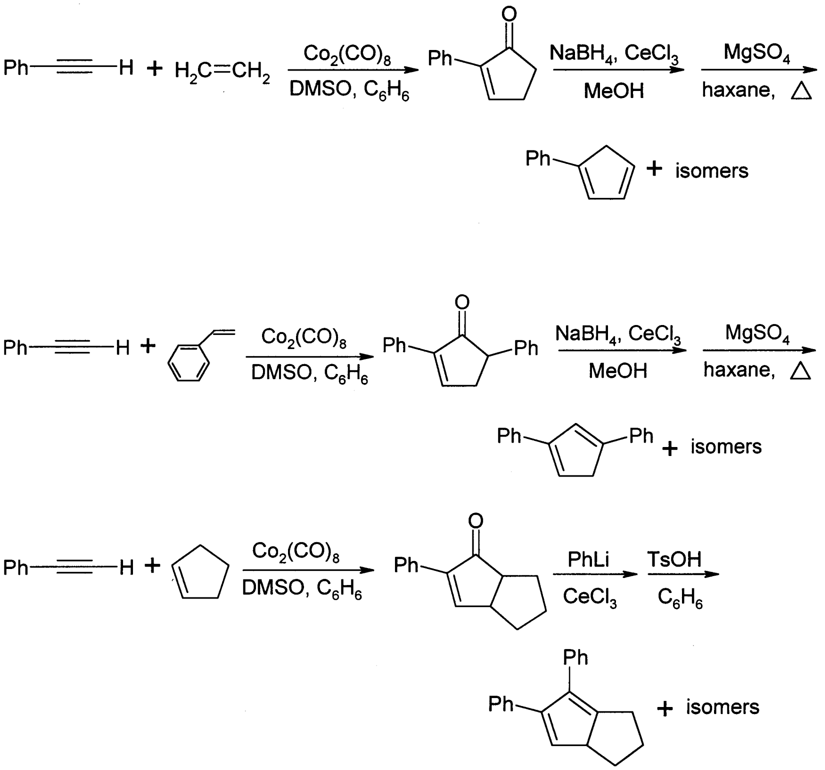
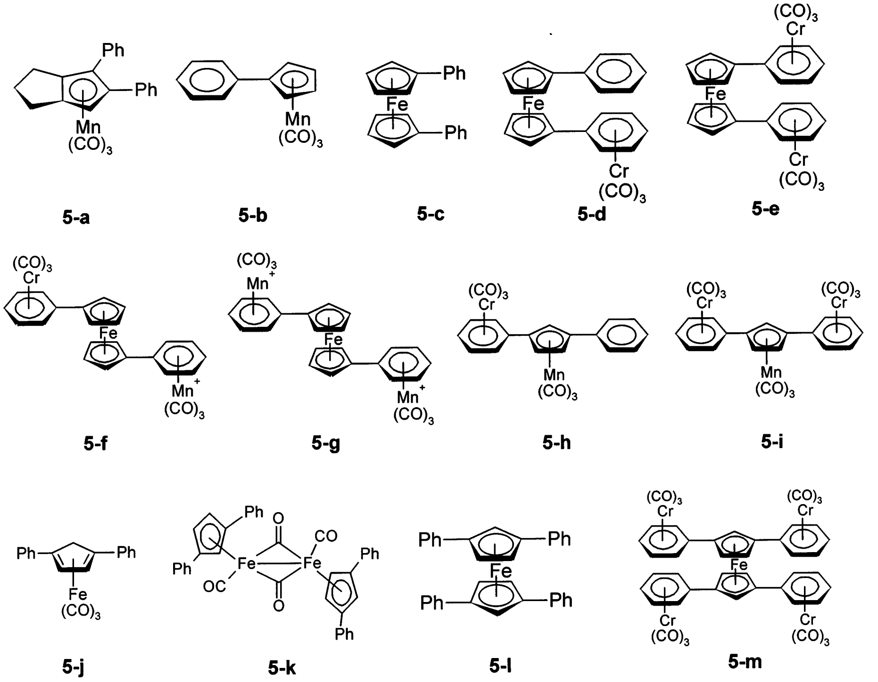


Chart 5 shows organometallic compounds which have been synthesized from cyclopentenones produced by Eqs. (60–62). Chart 6 has also demonstrated di-arene-bridged hetero bi- and polymetallic complexes by which chromium, manganese, and iron metals can be rationally introduced. Recently, bimetallic compounds linked by pairs of cyclopentadienyl moieties, as in fulvalene, fluorene, and indenyl have been reported [63]. Ligands of these types will be able to hold several metals in close proximity, thereby allowing researchers to investigate whether cooperative effects can enhance or modify the chemical reactivity of metal complexes with regard to the mono-Cp analogs. In this respect, **5-d**–**5-i** and **5-k**–**5-m** in Chart 5 are bi- and polymetallic compounds bridged by phenylcyclopentadienyl and 1,3-diphenylcyclopentadienyl ligands and are quite competent for testing cooperative effects. Especially, **5-m** in Chart 5 contains five metals in a single molecule. X-ray crystal structures of **5-e**, **5-g**, and **5-h** in Chart 5 are shown in Figs. 1–3. Compounds **5-b**, **5-c**, **5-e** and **5-l** in Chart 5 have already been synthesized by other methods [64].



5-a **5-b** **5-c** **5-d** **5-e**

5-f **5-g** **5-h** **5-i**

5-j **5-k** **5-l** **5-m**

Chart 5

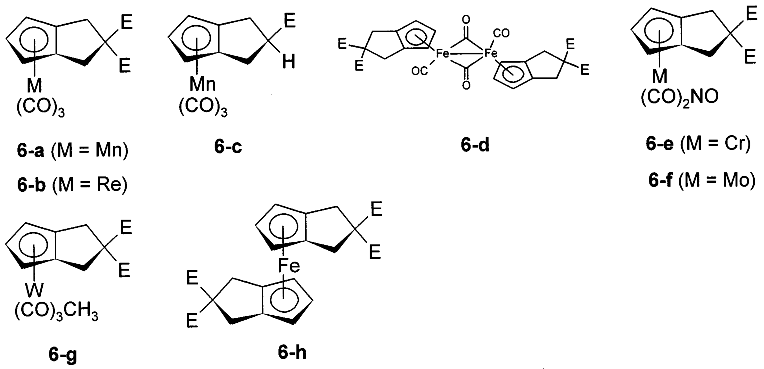


Chart 6

Eq. (63) shows the use of the intramolecular PKR of α,ω-enyne to synthesize bicyclic cyclopentadiene [21a].

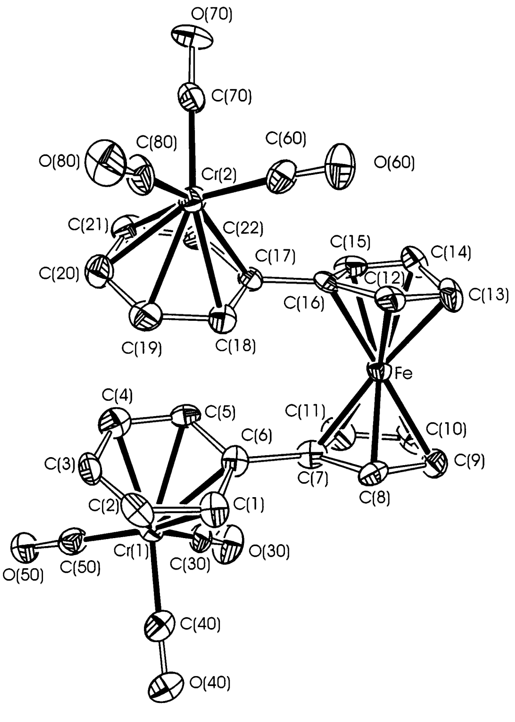
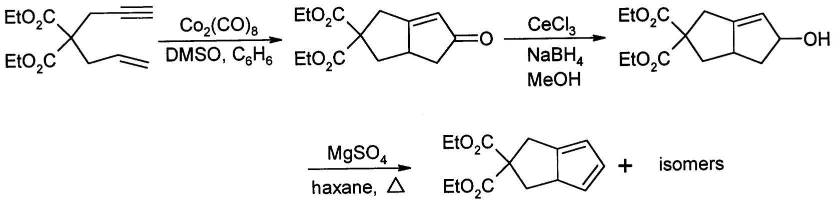


Fig. 1. ORTEP drawing of **5-e** in Chart 5.



(63)

Chart 6 shows compounds **6-a**–**6-h** which have been synthesized from cyclopenare shown in Figs. 4 and 5.

Eq. (64) shows a powerful method for the preparation of 1,2-disubstituted or 1,2,3-trisubstituted cyclopentadienyl ligands via the retro-Diels–Alder reaction of the intermolecular Pauson–Khand reaction products [21b].

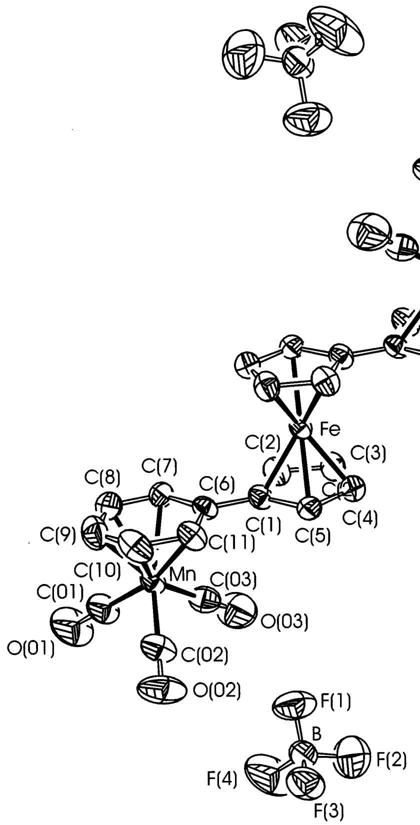
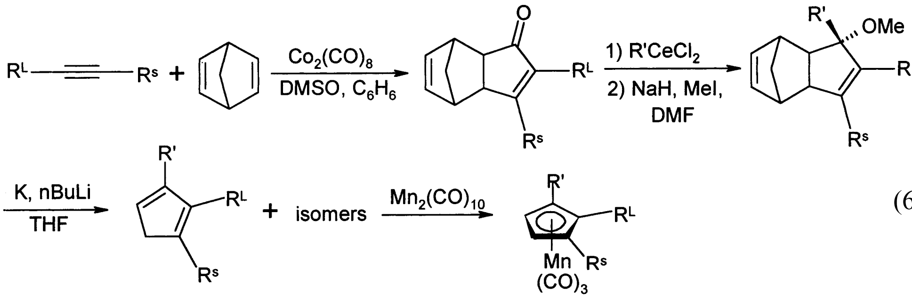


Fig. 2. ORTEP drawing of **5-g** in Chart 5.



(64)

As shown in Table 7, various alkynes gave good yields. In the cases of disubstituted alkynes, longer reaction time was required. A free hydroxyl group and a double bond did not hamper the reaction.

The retro-Diels–Alder reaction of the Pauson–Khand reaction product with potassium and *n*-BuLi was straightforward at room temperature within 2–3 h. Workup furnished an isomeric mixture of cyclopentadienes in 61–95%. The presence of one phenyl group is required to do the retro-Diels–Alder reaction. Metalation of cyclopentadiene was carried out by treatment with $Mn_2(CO)_{10}$.

By the same methodology as above, the novel ligand for the ansa-metallocene complexes could be prepared [58]. Treatment of 1,7-octadiyne or 1,5-hexadiyne with norbornadiene in the presence of (indenyl)Co(COD) gave the corresponding cy-

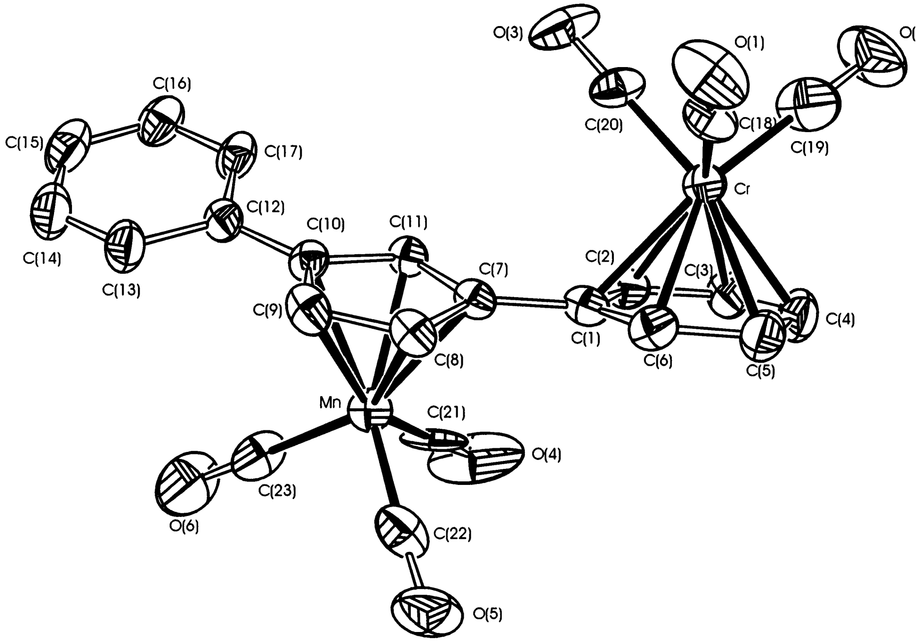
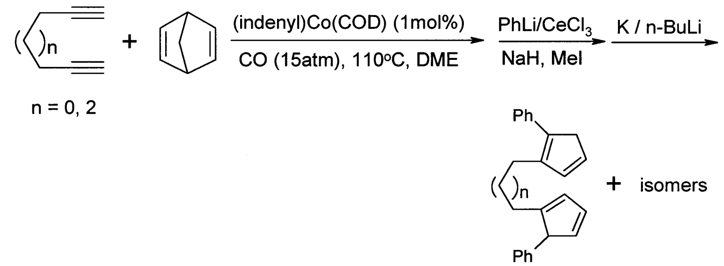


Fig. 3. ORTEP drawing of **5-h** in Chart 5.

clopentenones, respectively, which were transformed into an ansa-cyclopentadienyl ligand (Eq. (65)).

(65)



Many research groups have been interested in redox switches that can be turned on or off by electron transfer [65]. To modulate the chemical reactivity of a molecular system, a redox active switch is attached. A well-known example is by attaching a ferrocenyl group. Thus, preparation of ferrocenyl attached organometallic compounds have attracted much attention [66].

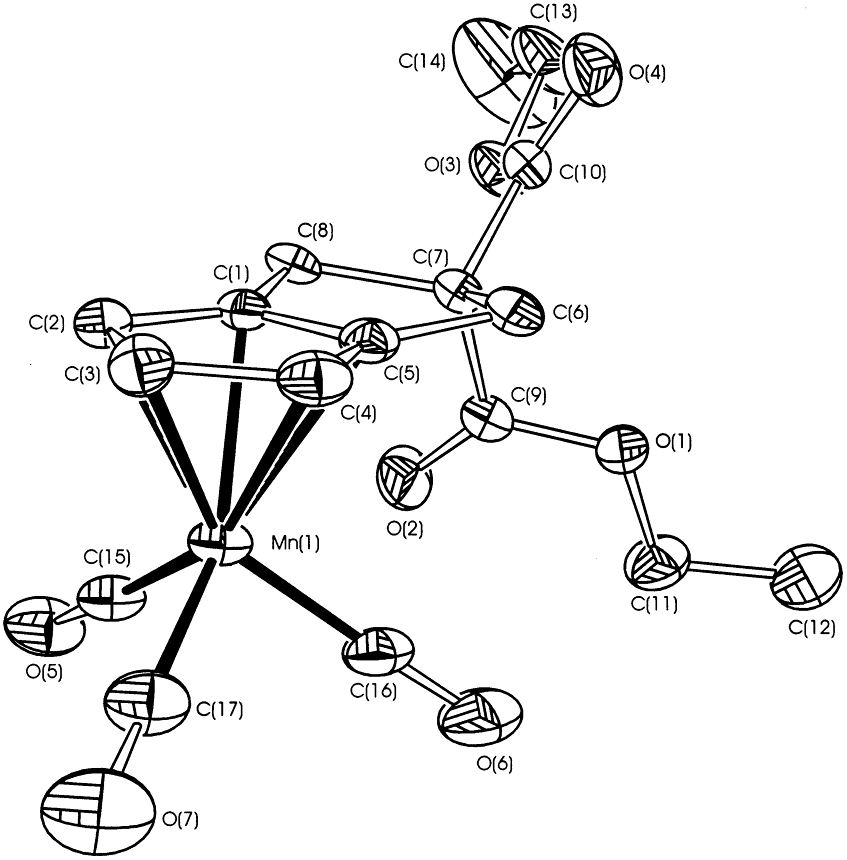


Fig. 4. ORTEP drawing of **6-a** in Chart 6.

Eq. (66) [21d] shows the synthesis of a ferrocenyl-substituted cyclopentadienyl employing the high yield synthesis of intermolecular PKR between ethynylferrocene and ethylene or propylene in the presence of DMSO as a promoter.

(66)

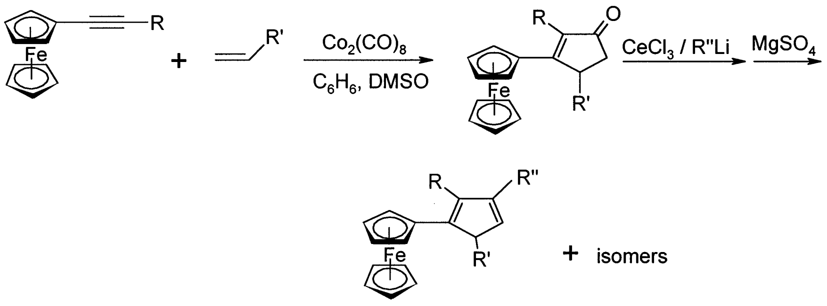


Chart 7 shows compounds which have been synthesized from the ferrocenyl-substituted cyclopentenone produced by Eq. (66). Using the PKR products as starting materials, ferrocenyl-attached organometallic compounds including various fulvalenyl bimetallic compounds were obtained in reasonable yields. X-ray crystal structures of **7-d** and **7-e** in Chart 7 are shown in Figs. 6 and 7.

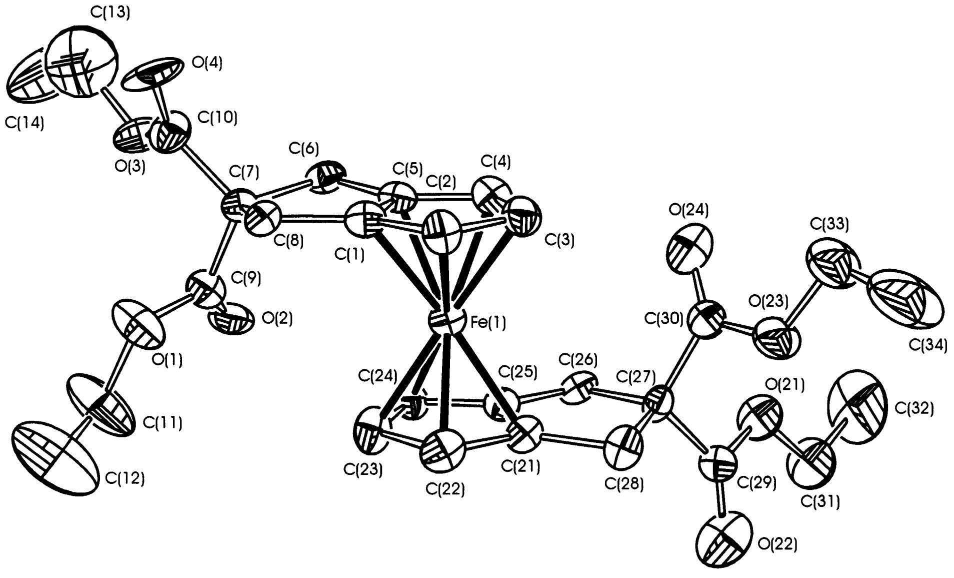


Fig. 5. ORTEP drawing of **6-h** in Chart 6.

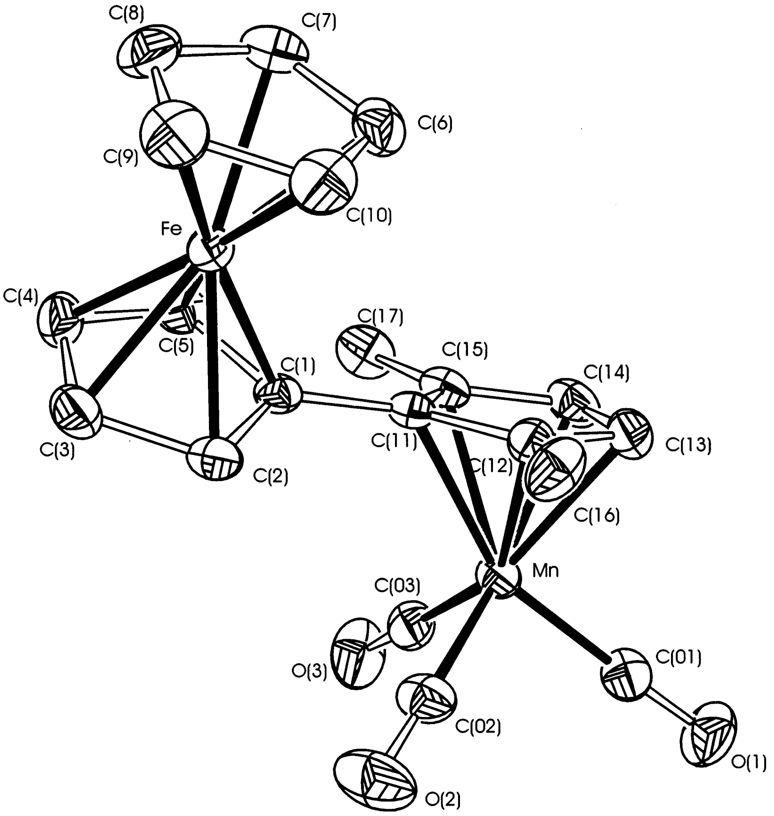
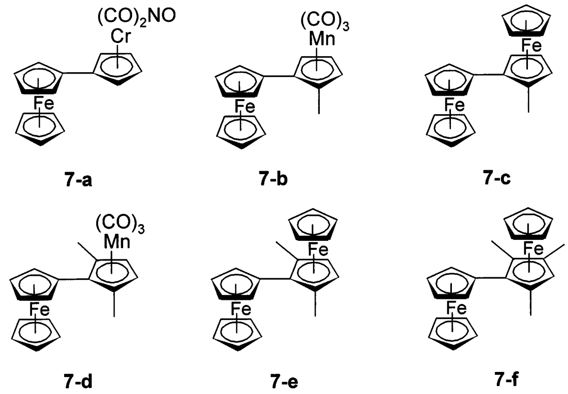


Fig. 6. ORTEP drawing of **7-d** in Chart 7.



7-a **7-b** **7-c**

7-d **7-e** **7-f**

Chart 7

Application to the synthesis of cyclopentadienyl and related other organometallic compounds is still in an early stage of exploration and has a great deal of promise

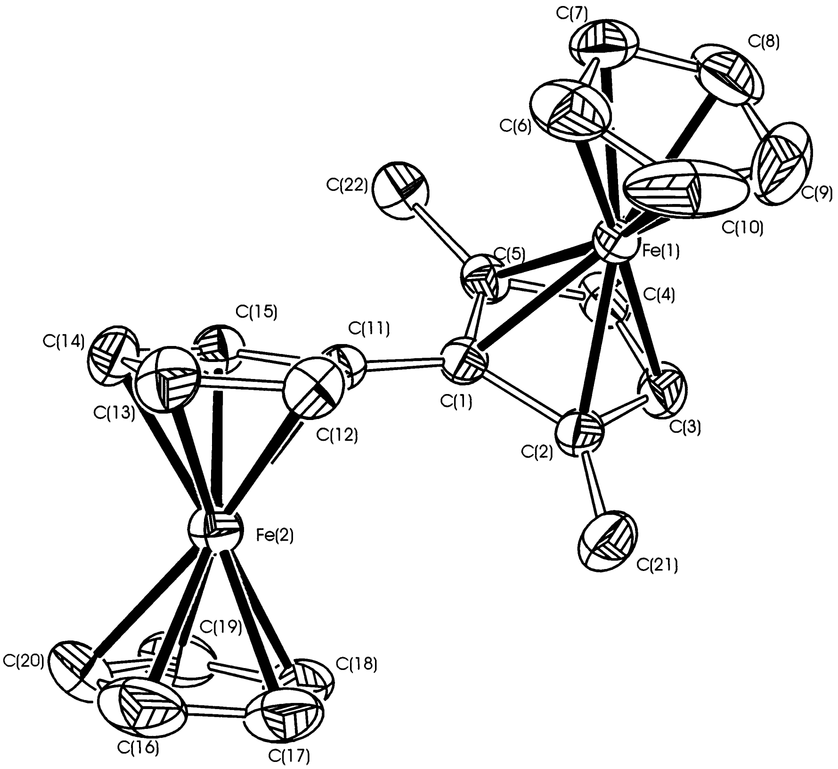


Fig. 7. ORTEP drawing of **7-e** in Chart 7.

as demonstrated in the generation of high yields of cyclopentadienyl precursors which are difficult to access via other routes.

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