Development of Organic Synthetic Methods Using Cobalt Carbonyl Reagents

A THESIS
SUBMITTED FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY

By

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Statement

I hereby declare that the matter embodied in this thesis is the result of investigations carried out by me in the School of Chemistry, University of Hyderabad, under the supervision of Professor M. Periasamy.

In keeping with the general practice of reporting scientific observations, due acknowledgement has been made wherever the work described is based on the findings of other investigators.

T. Rajesh

Certificate

Certified that the work embodied in this thesis entitled **'Development of Organic Synthetic Methods Using Cobalt Carbonyl reagents'** has been carried out by Mr. T. Rajesh, under my supervision and the same has not been submitted elsewhere for a Degree.

M. Periasamy
28/4/2000

PROF. M. PERIASAMY

(THESIS SUPERVISOR)

DEAN

SCHOOL OF CHEMISTRY

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Rajesh Thotapally

Abbreviations

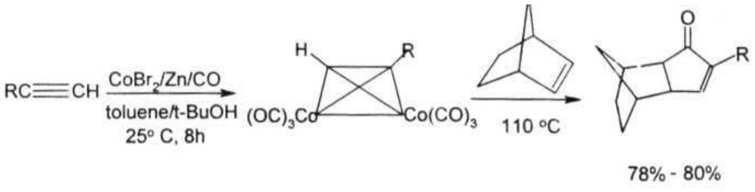
Bu	butyl
CAN	ceric ammonium nitrate
Cp	cyclopentadiene
CTAB	cetyltrimethyl ammonium bromide
DABCO	1,4-diazabicyclo [2.2.2] octane
DEPT	distortionless enhancement by polarisation transfer
DMF	N,N-dimethylformamide
DME	1,2-dimethoxyethane
DMSO	dimethylsulphoxide
DMS	dimethyl sulfide
EI	electron impact
eq.	equation
equiv.	equivalent
L or Ln	ligand
M	metal
Me	methyl
M.P	melting point
n	primary
NMO	N-methylmorpholine-N-oxide
Ph	phenyl
r.t	room temperature
t	tertiary
TFA	trifluoroacetic acid
THF	tetrahydrofuran
TMEDA	N,N,N',N'-tetramethylethylenediamine
TMS	trimethylsilane

Abstract

This thesis deals with the results of the investigations carried out on the "Development **of** Organic **Synthetic Methods Using Cobalt Carbonyl Reagents."** It comprises of three chapters. Each chapter is subdivided into three parts. "Introduction," "Results and Discussion" and "Experimental section" along with references. The work described in this thesis is exploratory in nature and the chapters are arranged in the order the investigations were executed.

Chapter 1 describes the preparation of alkyne-$Co_2(CO)_6$ complexes via reduction of $CoBr_2$ with Zn in the presence of CO in CH_2Cl_2/t-BuOH or toluene/t-BuOH for applications in Pauson-Khand cyclopentenone synthesis (Scheme 1). Recent developments in the Pauson-Khand reaction are briefly reviewed in the Introductory section. To facilitate the discussion, methods of preparation of (alkyne)$Co_2(CO)_6$ complexes are also briefly reviewed.

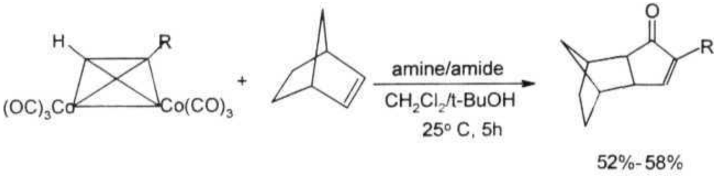
Scheme 1



It has been observed tha. the amines/amides promote the Pauson-Khand reaction (alkyne)$Co_2(CO)_6$ complexes prepared in this way in CH_2Cl_2/t-BuOH solvent

system at 25 °C (Scheme 2). Whereas **the** use of norbornylene gave **the** corresponding cyclopentenones in 52-58% yields, cyclopentene afforded the products in 30-32% yields.

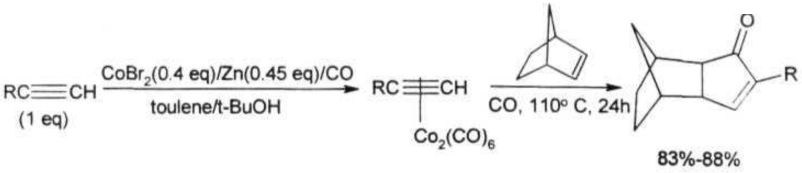
Scheme 2



The Pauson-Khand reactions were also carried out in CH_2Cl_2 in the presence of amines such as TMEDA, α-methylbenzylamine. The yields of cyclopentenones obtained were similar to the reactions that were carried out using CH_2Cl_2 and t-BuOH.

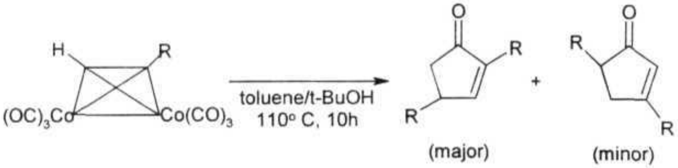
The Pauson-Khand reactions carried out using sub-stoichiometric amounts of $CoBr_2$ and Zn (Scheme 3) are also described in chapter 1. The cyclopentenones were obtained in good yields when norbornylene was used as olefin. In the case of cyclopentene, the products were obtained in 30-35% yields.

Scheme 3



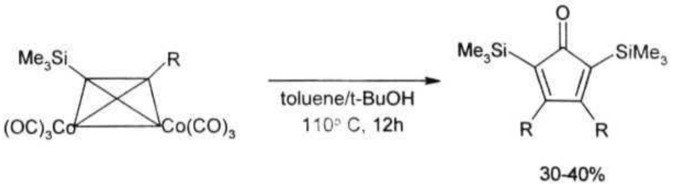
In chapter 2, results of the Investigations carried out on the reactions of (alkyne)$Co_2(CO)_6$ complexes without using an externally added olefin are described. The reactions of such complexes are briefly reviewed. The (alkyne)$Co_2(CO)_6$ complexes prepared *in situ* in toulene/t-BuOH solvent system by the reduction of $CoBr_2$ with Zn in the presence of CO and alkynes give cyclopentenones in 10-50% yields on heating at 110 °C (Scheme 4).

Scheme 4



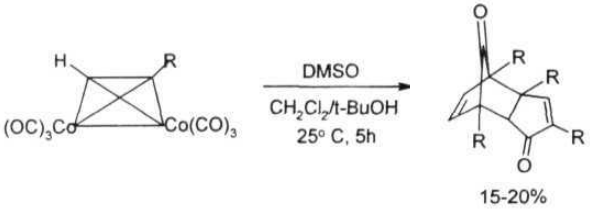
The reactions using ($RC \equiv CSiMe_3$)$Co_2(CO)_6$ complexes in toluene/t-BuOH gave the corresponding silyl substituted cyclopentadienones in 30-40% yields (Scheme 5). In all cases, symmetrically substituted cyclopentadienones were obtained except in phenyl substituted alkynyl silane, in which both symmetrically and unsymmetrically substituted cyclopentadienones were obtained.

Scheme 5



Interestingly, the reaction of (alkyne)$Co_2(CO)_6$ complexes with promoters such as DMSO, TMEDA in CH_2Cl_2/t-BuOH solvent system gave the corresponding dicyclopentadienones in 15-20% yields at 25 °C (Scheme 6). Possible mechanistic pathways and intermediates involved in these transformations are described.

Scheme 6



In chapter 3, the hydroformylation reactions of olefins using $CoBr_2/Zn/CO$ in toluene/t-BuOH solvent system are described. A brief account on the hydroformylation reaction using cobalt carbonyl reagents is presented in the introductory section.

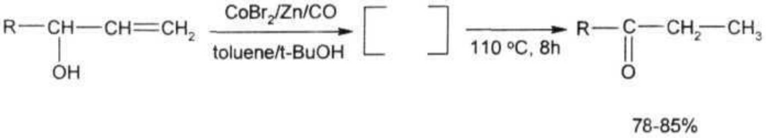
We have observed that the hydroformylation of alkenes can be carried out with the cobalt carbonyl reagent prepared using $CoBr_2$, Zn and CO in toluene/t-BuOH solvent mixture. Acyclic terminal olefins give both normal and branched isomers of aldehydes in 1:1 ratio in moderate yields under these conditions (Scheme 7). In these reactions, alkanes (25-30%) were also isolated. Results of efforts to optimize the reaction conditions are also described.

Scheme 7

$$RCH{=}CH_2 \xrightarrow[\text{toluene/t-BuOH}]{CoBr_2/Zn/CO} [\quad] \xrightarrow[110\ ^\circ C,\ 8h]{CO} RCH_2CH_2CHO + RCH(CH_3)CHO$$

The intermediacy of species such as $HCo(CO)_4$ is indicated in the hydroformylation reaction (Scheme 7). Accordingly, the use of such reagent system for other synthetic applications of the cobalt carbonyl species prepared in this way was also examined. It was observed that certain allylalcohols undergo isomerization reaction to form ketones in 78-85% yields (Scheme 8).

Scheme 8



The results are discussed in comparison with that reported in the literature.

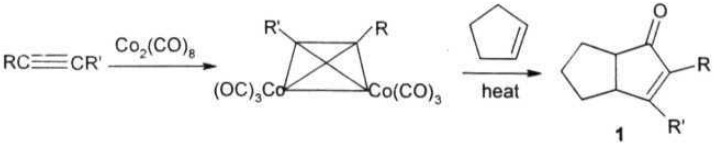
Chapter 1

Studies on the preparation of alkyne-$Co_2(CO)_6$ complexes for applications in Pauson-Khand cyclopentenone synthesis

1.1 Introduction

In recent years, there has been increasing interest in the application of transition metal mediated transformations in organic synthesis. The use of transition metal reagents in organic synthesis gives the strategic advantage primarily because of unusual selectivity and reactivity realized over classical organic reaction counterparts. However, if the transition metal mediated organic reactions are to find widespread general use, it is essential that they simplify complicated problems, and of course, be experimentally convenient. The Pauson-Khand reaction is one such reaction that has been intensively studied in recent years. A brief review of the reports on this reaction will be helpful for the discussion.

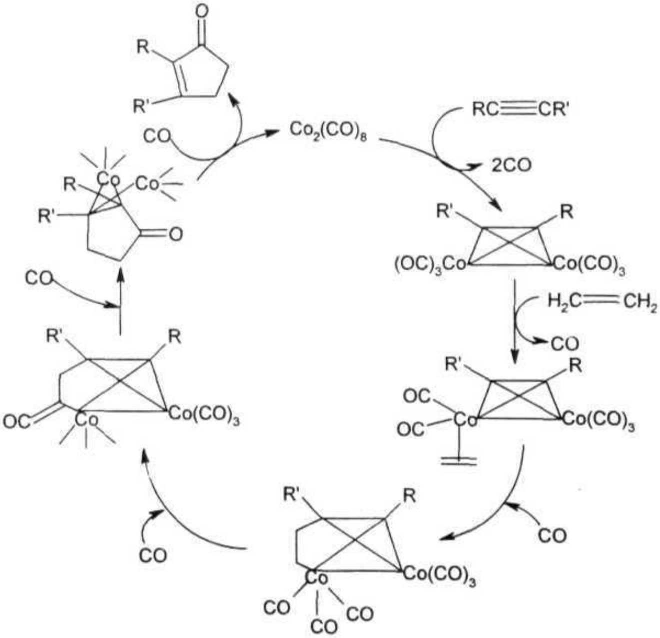
The Pauson-Khand reaction, first reported in 1973,[1] involves the dicobalt octacarbonyl mediated cocyclization of alkynes with alkenes and carbon monoxide to synthesize cyclopentenone derivatives (eq 1). Excellent reviews by Pauson,[2] de Meijere,[3] Schore[4] and more recently, by Schmalz[5] have been published on this reaction.



[1]

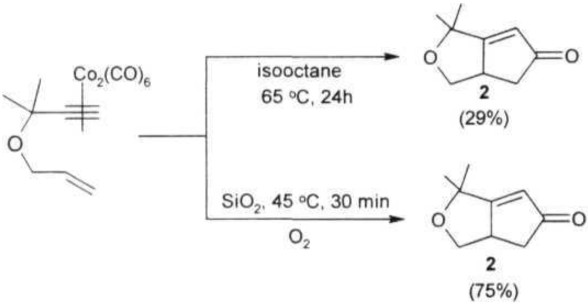
The Pauson-Khand reaction shows high degree of both regio- and stereoselectivity.[6] The mechanism of this reaction has not been established fully (Scheme 1).[2-4] Generally, it is assumed that the reaction proceeds through the insertion of alkene to one of the cobalt atoms *via* a dissociative mechanism involving the initial loss of CO. Subsequent insertion of the complexed face of the alkene π-bond into one of the formal cobalt-carbon bonds of the alkyne complex occurs, followed by the addition of the CO to the coordinatively unsaturated cobalt atom. The metallocycle thus formed leads to standard sequence of steps migratory insertion of a cobalt bound CO, addition of another CO molecule and finally reductive elimination of the cobalt carbonyl moiety to give the cyclopentenone derivative (Scheme 1).

Scheme 1



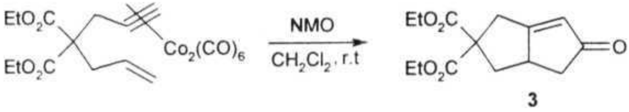
In recent years, considerable efforts were made by several groups to optimize the reaction conditions using various additives as promoters. First such modification has been made by Smit and Caple *et al*.[7] These authors reported that the use of adsorbents such as SiO_2, Al_2O_3 and $MgO.SiO_2$ facilitates the reaction (Scheme 2).

Scheme 2



Later, Pauson *et al*[8] studied the effect of ultrasound, phosphine and phosphine-oxides. Whereas the ultrasonic irradiation of the reaction mixture allows the reactions to proceed considerably faster at lower temperatures, it has little effect on the yields. Addition of phosphine oxides leads to significant yield enhancement in intramolecular Pauson-Khand reaction.

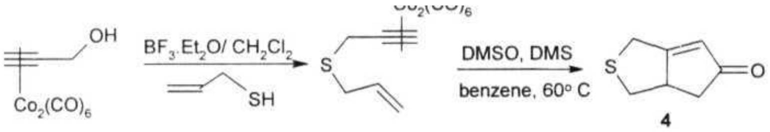
First significant modification has been reported by Shambayati[9] and Joeng[10] using N-oxides as promoter in both intra and inter molecular versions of the Pauson-Khand reaction at room temperature (eq 2).



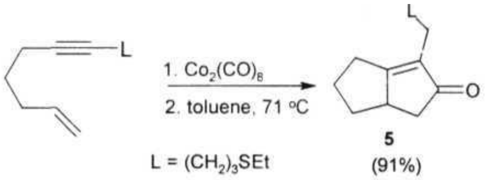
····· [2]

It has been also reported [11] that the dimethylsulphoxide (DMSO) promotes the Pauson-Khand reaction (Scheme 3).

Scheme 3

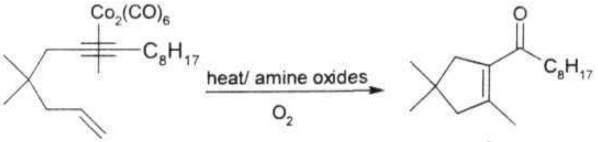


Kraft *et al* [12] observed that the presence of ligands such as sulfur, nitrogen in side chain leads to increase in both the reaction rates and yields (eq 3).



······· [3]

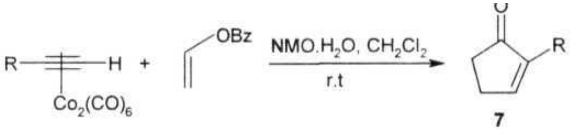
Also, these authors observed that the use of oxygenated atmosphere causes a change in the normal Pauson-Khand reaction pathway leading to monocyclic enones 6 instead of the anticipated bicyclic enones (eq **4**).[13]



6

...... [4]

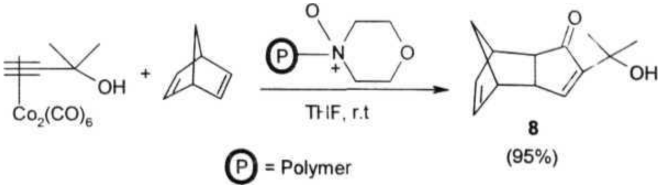
More recently, Kerr *et al*[14] developed a novel method in which vinyl esters are utilized as non-gaseous ethylene equivalents in Pauson-Khand annulation using NMO as a promoter at room temperature (eq 5).



7

.... [5]

Also, it was observed that the polymer supported N-oxide [15a] is useful as a promoter under mild conditions, affording good to excellent yields of cyclopentenones (eq 6). The advantage in this method is that the amine oxide supported on solid phase is found to be highly efficient and reusable, affording cyclopentenones in high purity without the need for purification by chromatography.

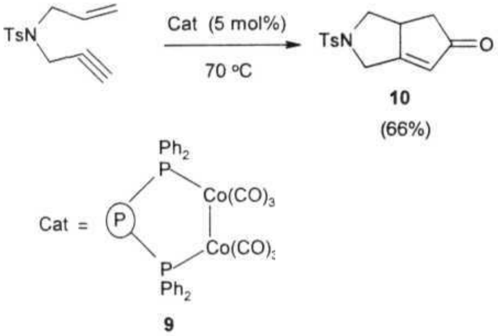


8

(95%)

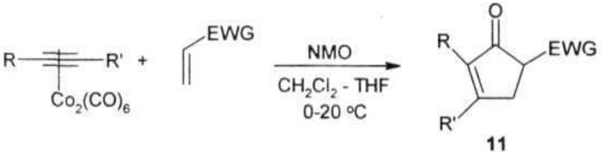
... [6]

Further, it has been reported that the cobalt carbonyl complexes immobilised onto a polymer bound triphenylphosphine solid support are effective, practical catalysts for Pauson-Khand reaction (eq 7).[15b]



...... [7]

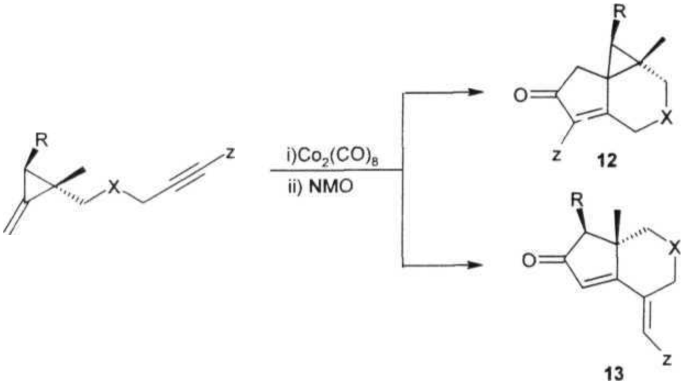
Also, it was observed that the NMO promotes the Pauson-Khand reaction of alkynes with electron deficient olefins at 0-20 °C (eq 8).[16]



...... [8]

The **methylenecyclopropenes** can function as a simple **olefin** component in the intra molecular Pauson-Khand reaction to give the product 12 or it can give rearranged hydroindenones 13 in which neither of the two carbon atoms of the alkyne component form part of the cyclopentenone moiety in the product (Scheme 4).[17]

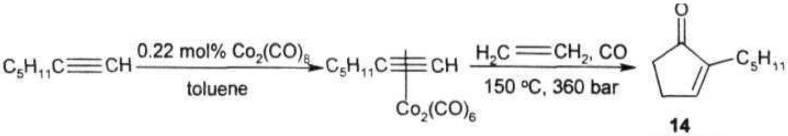
Scheme 4



The use of stoichiometric amounts of the transition metals is not acceptable commercially. Therefore, several groups focussed research efforts on **the** development of catalytic variants of the Pauson-Khand reaction.

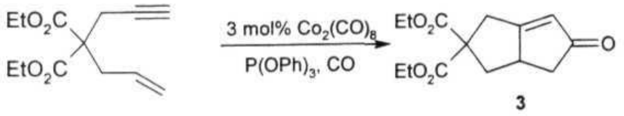
Pauson and Khand [1c] reported the catalytic version but the first success was achieved by Rautenstrauch [18] using 0.22 mol% of $Co_2(CO)_8$ (Scheme 5).

Scheme 5



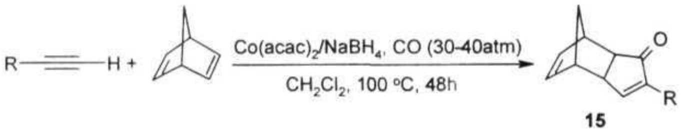
14
(47-49%)

Later, Joeng *et al*[19] observed the catalytic version of Pauson-Khand reaction using the phosphites as co-ligands (eq 9).



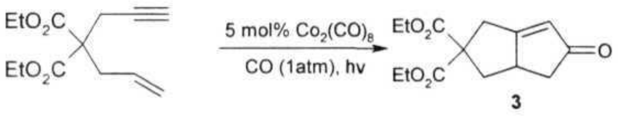
·····[9]

Further, not only $Co_2(CO)_8$ but also other cobalt complexes were employed successfully for the catalytic Pauson-Khand reaction (eq 10).[20]



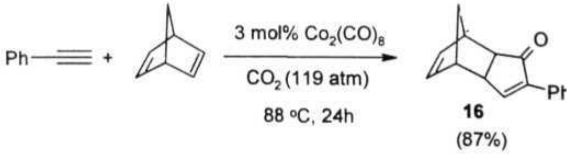
···[10]

Livinghouse [21] reported the photochemical method of promotion of the catalytic intramolecular Pauson-Khand reaction (eq 11).



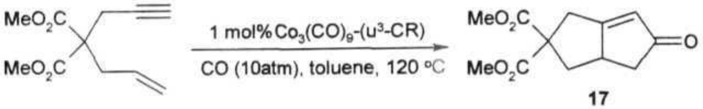
·····[11]

Supercritical CO_2 has been used for catalytic Pauson-Khand reaction (eq 12).[22]



·····[12]

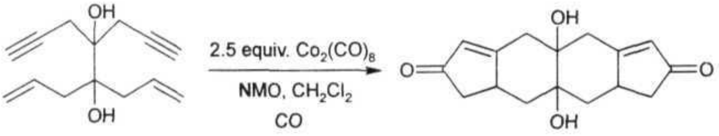
Sugihara and **Yamaguchi** [23] observed that the Pauson-Khand reaction could be catalyzed using catalytic amounts of alkylidynetricobalt nonacarbonyls (eq 13).



17

···[13]

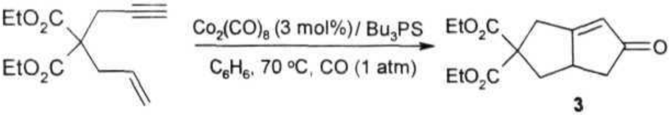
Also, it was observed that the catalytic Pauson-Khand reaction could be employed for the synthesis of cis-fused decalins (eq 14).[24]



18

···· [14]

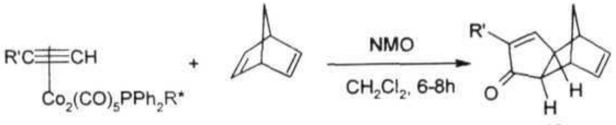
More recently, phosphane sulfide catalyzed Pauson-Khand reaction was observed under atmospheric pressure of CO.[25] In this way, both intra- and inter-molecular catalytic versions of Pauson-Khand reaction take place (eq 15).



3

[15]

Considerable efforts have been made to develop asymmetric variants of the classical Pauson-Khand reaction. Initially, it was observed that the chiral phosphane (glyphos) ligands give high enantioselectivity (eq 16).[26]

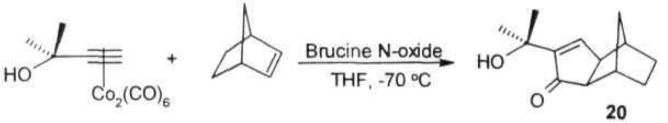


19

(>99% ee)

··· [16]

Kerr ef a/ [27] achieved significant enantioselectivities by employing the chiral amine-oxides as promoters (eq 17).

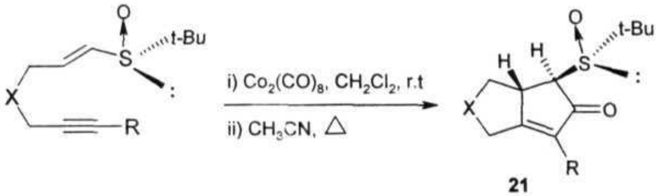


20

··· [17]

Pericas ef al [28] used chirally modified substrates to obtain asymmetric induction in Pauson-Khand reaction. The potential of this method was demonstrated in total syntheses of natural products.[29]

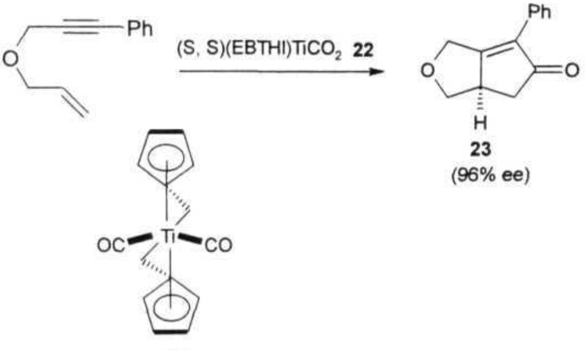
Also, the use of t-butylsulfinyl group as a highly efficient chiral auxiliary in asymmetric Pauson-Khand reaction has been reported (eq 18).[30]



21

···· [18]

Buchwald developed the first catalytic asymmetric Pauson-Khand type cyclization of enynes using a titanocene catalyst 22 [31] A variety of **1,6-enynes** were converted to corresponding cyclopentenones in high yield (70-94%) with excellent ees **(87-96%)** (eq 19).

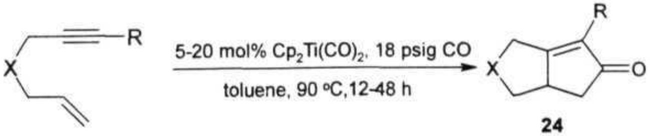


23
(96% ee)

22

···· [19]

These authors also devised an outstanding procedure for the direct, titanocene catalyzed cyclocarbonylation of **enynes**.[32] This catalytic method has a number of advantages, it occurs at low CO pressure, tolerates a variety of functional groups including disubstituted alkenes and gives the cyclopentenones in high yields (>85%) (eq 20).



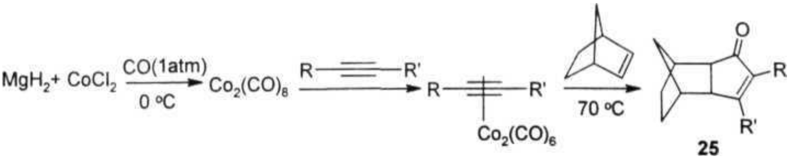
24

[20]

Apart from cobalt and titanium complexes, several other transition metals such as ruthenium,[33] rhodium [34]were employed in catalytic Pauson-Khand reaction. Also, carbonyls such as $Fe(CO)_5$,[35] $W(CO)_5$,[36] $Cp_2Mo_2(CO)_4$,[37] $Mo(CO)_6$ [38] are useful as catalysts in Pauson-Khand reaction. In addition, reagent systems such as Cp_2TiCl_2/CO,[39] Cp_2ZrCl_2/CO,[40] Cp_2TiCl_2-Mg-BTC,[41] $Cp_2Ti(PMe_3)/R_3SiCN$,[42] $Ni(COD)_2$ [43] and $Ni(CO)_4$ [44] have been shown to be effective for the conversion of enynes to bicyclic octenone derivatives.

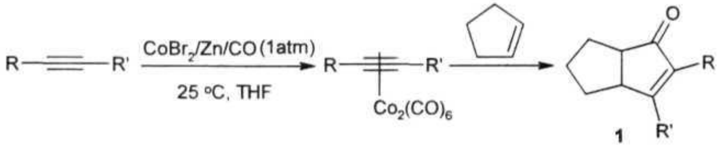
In recent years, several new convenient procedures have been developed in this laboratory for the preparation of cobalt carbonyls *in situ* through reduction of $CoCl_2$ or $CoBr_2$ using various reducing agents. For example, it was found that the reduction of $CoCl_2$ with MgH_2 at 0 °C under CO atmosphere gives $Co_2(CO)_8$. Reaction of an alkyne and norbornylene with the reagent prepared in this way gives the corresponding cyclopentenone at 70 °C (Scheme 6).[45a]

Scheme 6



25

It was also observed that the reduction of anhydrous $CoBr_2$ with Zn under CO atmosphere in THF at room temperature followed by reaction with alkynes, gives the corresponding (alkyne)$Co_2(CO)_6$ complexes. These complexes on reaction with olefins give the corresponding cylopentenones in moderate to good yields (eq 21).[45b]

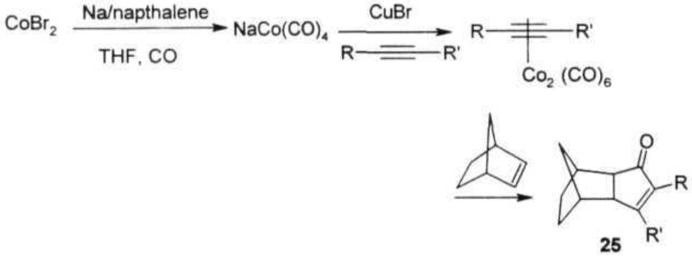


1

[21]

The (alkyne)$Co_2(CO)_6$ complexes can also be prepared *in situ* by the reduction of $CoBr_2$ with sodium/napthalene under CO atmosphere followed by CuBr treatment in the presence of alkynes. The complexes prepared in this way also give cyclopentenones on heating with norbornylene (Scheme 7).[45c]

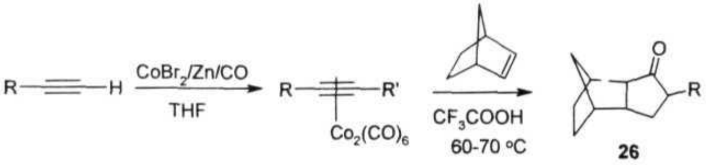
Scheme 7



25

It was observed that the (alkyne)$Co_2(CO)_6$ complexes prepared *in situ* using $CoBr_2$, Zn under CO atmosphere in THF, on reaction with norbornylene in presence of CF_3COOH (TFA) gives the reduced Pauson-Khand cyclopentanones (Scheme 8).[45d]

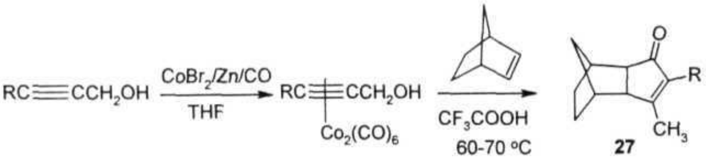
Scheme 8



26

Further, it was observed that the (RC≡CCH$_2$OH)Co$_2$(CO)$_6$ **complexes**, prepared *in situ* using CoBr$_2$, Zn under CO atmosphere, react with norbornylene in presence of TFA gives the methyl substituted **cyclopentenones** (Scheme 9).[45e]

Scheme 9



27

In continuation of these studies, we have undertaken further investigations on the preparation of these complexes *in situ* in solvents like CH$_2$Cl$_2$ and toluene. We have also examined the applications of the complexes prepared in this way in **Pauson-Khand** reaction. The results are described in this chapter.

1.2 Results and Discussion

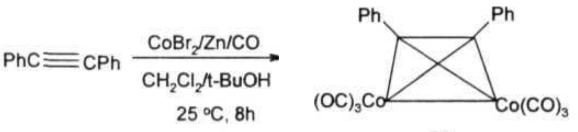
1.2.1 Studies on the preparation and utilization of (alkyne)$Co_2(CO)_6$ complexes

As outlined in the introductory section, methods have been developed in this laboratory for the preparation of (alkyne)$Co_2(CO)_6$ complexes *in situ* in THF through the reaction of $CoCl_2$ or $CoBr_2$ with different reducing agents under CO atmosphere. Since THF promotes the disproportionation of $Co_2(CO)_8$,[46] we have been looking for an alternative solvent system for the preparation of such complexes.

It has been reported that the reduction of CoI_2 in toluene/t-BuOH solvent mixture by Zn metal in presence of CO at atmospheric pressure, gives $Co_2(CO)_8$ in 38% yield after 24h (eq 22). [47]

$$CoI_2 + Zn \xrightarrow[\text{CO, r.t , 24 h}]{\text{t-BuOH, toluene}} Co_2(CO)_8 \qquad \cdots\cdots [22]$$

We have observed that the (alkyne)$Co_2(CO)_6$ complexes can be prepared *in situ* by the reduction of $CoBr_2$ by Zn dust in the CH_2Cl_2 and t-BuOH solvent mixture while bubbling CO at 25 °C for 6-8h. Since solubility of $CoBr_2$ in CH_2Cl_2 is less, to enhance the solubility 1-2 mL of t-BuOH was added. The formation of (alkyne)-$Co_2(CO)_6$ complex was confirmed by carrying out the reaction of diphenylacetylene with $CoBr_2$ and Zn in CH_2Cl_2/t-BuOH while bubbling CO for 8h at 25 °C. After workup, $(PhC{\equiv}CPh)Co_2(CO)_6$ 28 was isolated (eq 23).



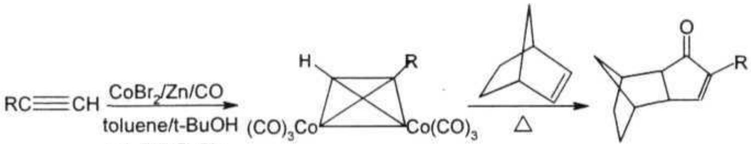
28

·····[23]

The IR spectra of the isolated complex 28 showed the absorptions at 2000, 2050, 2100 cm^{-1} (terminal CO), and the absence of absorption at 1910 cm^{-1} (bridging carbonyl).[48]

The (alkyne)$Co_2(CO)_6$ complexes prepared in this way, undergo Pauson-Khand reaction with norbornylene, upon heating to give the corresponding cyclopentenones in 75-80% yield in toluene/t-BuOH solvent system (Scheme 10).

Scheme 10



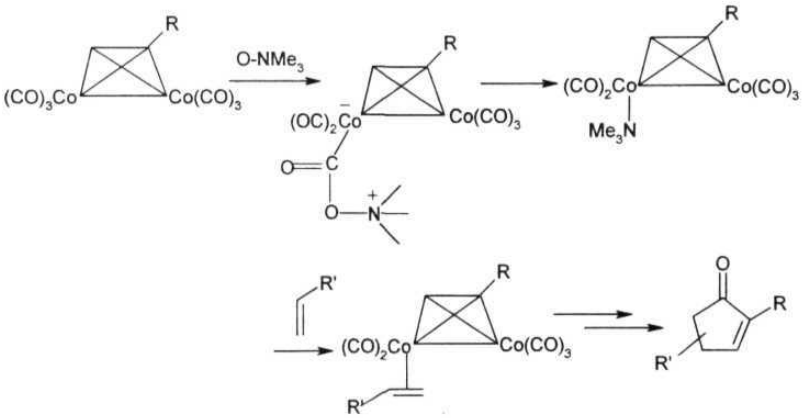
R		Yield
n-C_5H_{11}	**29**	80%
Ph	**30**	78%

1.2.2 Reactions of (alkyne)$Co_2(CO)_6$ complexes with olefins in presence of amine/amide in CH_2Cl_2/t-BuOH solvent system

As discussed earlier, in the presence of additives such as amine oxides and DMSO, the Pauson-Khand reaction can be carried out under ambient conditions.[9-11]

For example, amine oxides react with $(alkyne)Co_2(CO)_6$ complex to create a vacant coordination site in the $(alkyne)Co_2(CO)_6$ complex through the oxidation of CO to CO_2 (Scheme 11).[10] Hence, reactions that require initial dissociation of CO are facilitated in this way.

Scheme 11



Similar reaction of amine oxides with $Fe(CO)_5$ gives coordinatively unsaturated iron carbonyl species. [49]

The metal carbonyl complexes also react with amines to give carbomyl complexes (eq 24).[50] The reactions are rapid and essentially quantitative at room temperature. This reaction was observed with many transition metal carbonyls.

$$L_nM{=}C{=}O + 2HNRR' \rightleftharpoons L_n\overset{-}{M}C(=O)NRR' + H_2\overset{+}{N}RR'$$ ·······[24]

(M= Transition metal)
(L= Ligand)

(carbomyl complex)

It was also observed that the Lewis bases disproportionate $Co_2(CO)_8$ (eq 25).[51]

$$3\ Co_2(CO)_8 + 2n\ B \longrightarrow 2\ [Co(B)_n][Co(CO)_4]_2 + 8\ CO \qquad \text{.......} [25]$$
$$(B = \text{Lewis base})$$

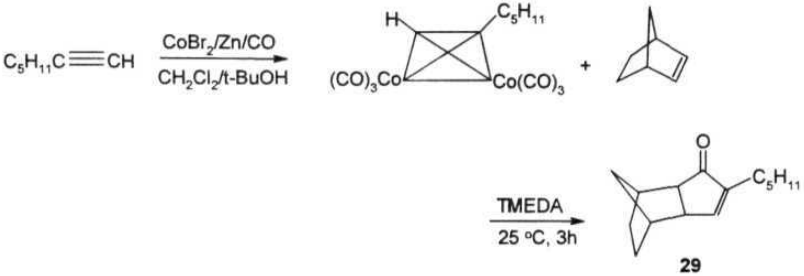
Reaction of aliphatic and alicyclic primary and secondary amines with $Co_2(CO)_8$ bring about carbonylation of the amine to the corresponding formamide (eq 26).[52]

$$3[Co(CO)_4] + 20(CH_3)_2NH \longrightarrow 2[Co\{NH(CH_3)_2\}_6]\ [Co(CO)_4]_2 + 8HCON(CH_3)_2 \quad [26]$$

As outlined in Scheme 11, the elimination of CO from $(alkyne)Co_2(CO)_6$ complex is the key step in the Pauson-Khand reaction. Hence, we have examined the effect of amines on the reaction of $(alkyne)Co_2(CO)_6$ complexes with olefins. We have carried out the reaction of $(C_5H_{11}C{\equiv}CH)Co_2(CO)_6$ complex generated *in situ* using 1-heptyne, $CoBr_2$, Zn and CO in CH_2Cl_2/t-BuOH solvent system with norbornylene and TMEDA at 25°C (Scheme 12). It has been observed that the corresponding cyclopentenone 29 is obtained in 53% yield besides some unreacted cobalt carbonyl complexes under these conditions.

This observation prompted us to further investigate the effect of different amines in the presence of olefins. The experiments were carried out using $(alkyne)Co_2(CO)_6$ complexes and norbornylene and cyclopentene employing amines and amides such as TMEDA, α-methylbenzylamine and DMF. The results are summarized in Table 1.[53] The cyclopentenones were obtained in somewhat lower yields than that obtained under refluxing conditions in THF or toluene (Scheme 10).

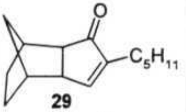
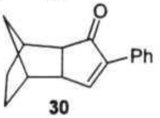
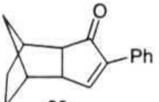
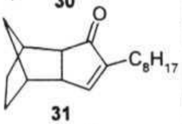
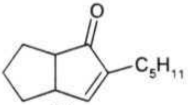
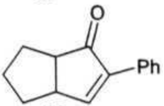
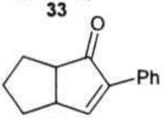
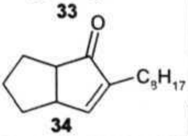
Scheme 12



29

It is evident from the Table 1, the yields of the cyclopentenones obtained are similar with different promoters. As expected, the yields are better with norbornylene and lower yields were realized in the case of the less reactive cylopentene. Also, a slight increase in yield of the cyclopentenones was observed when the reaction was carried out in open air after the complex formation (entries 3 and 7, Table 1).

Table 1 Reactions of (alkyne)$Co_2(CO)_6$ Complexes with olefin in presence of amine/amide in CH_2Cl_2/t-BuOH

No.	alkyne	alkene	amine/amide	Product[a]	Yield[b,c]
1	$C_5H_{11}C\equiv CH$		TMEDA	 **29**	53%
2	$PhC\equiv CH$		$C_6H_5CH(CH_3)NH_2$	 **30**	55%
3	$PhC\equiv CH$		$C_6H_5CH(CH_3)NH_2$	 **30**	58%^{d}
4	$C_8H_{17}C\equiv CH$		DMF	 **31**	52%
5	$C_5H_{11}C\equiv CH$		TMEDA	 **32**	30%
6	$PhC\equiv CH$		$C_6H_5CH(CH_3)NH_2$	 **33**	32%
7	$PhC\equiv CH$		$C_6H_5CH(CH_3)NH_2$	 **33**	35%^{d}
8	$C_8H_{17}C\equiv CH$		DMF	 **34**	32%

Foot notes to Table 1

a) All reactions were carried out using $CoBr_2$ (20 mmol), Zn (20 mmol), alkyne (10 mmol) in CH_2Cl_2 (50 mL)/t-BuOH (1.5 mL), olefin (15 mmol), amine (30 mmol) at 25 °C for 3h.

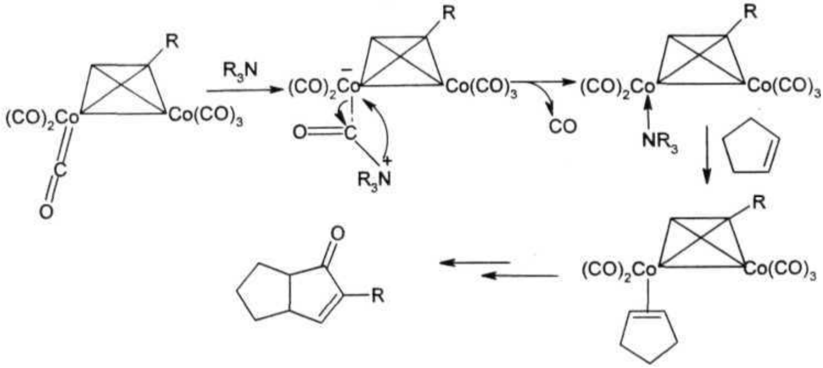
b) Products were identified by analysis of spectral data (IR, ^1H, ^{13}C NMR) and in comparison with the data available in the literature.

c) Yields reported are for products separated by column chromatography on silica gel using ethyl acetate in hexane as eluent and calculated on the basis of amount of alkyne used.

d) Reaction was carried out in open air atmosphere.

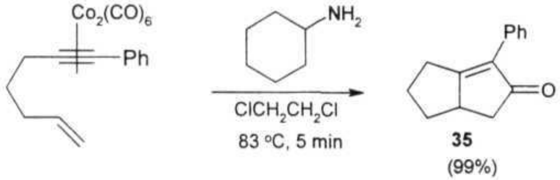
The mechanism of this transformation is not clear. Presumably, the amine may form weak complex with cobalt by eliminating CO, which could facilitate the Pauson-Khand reaction (Scheme 13). If this is so, the use of chiral amine is expected to induce asymmetric induction to some extent if it is present in the transition state of the reaction. To examine this, we have briefly investigated the reaction of $(PhC{\equiv}CH)$-$Co_2(CO)_6$ with norbornylene in the presence of the chiral a-methylbenzylamine at room temperature and 0 °C.

Scheme 13



We have not observed any asymmetric induction in the cyclopentenone formed. Presumably, the **amine** moiety is not present in the transition state after elimination of CO from (alkyne)$Co_2(CO)_6$ complex (Scheme **13**).

It may be of interest to note here that when these studies on the effect of amines on Pauson-Khand reaction were in progress in this laboratory, a report appeared describing the role of primary amines on the rate enhancement of Pauson-Khand reaction at 83 °C (eq 27) [54]



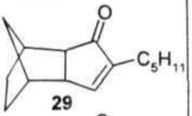
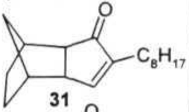
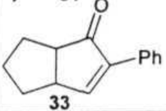
[27]

These authors observed that the cyclopentenone is obtained in only 46% yield at 25 °C after 25 days, besides unidentified polar by-products. At 83 °C, the conversion is complete within 5 minutes. The desired cyclopentenone was obtained in 99% yield.

1.2.3 Reactions of (alkyne)$Co_2(CO)_6$ complexes with olefins in CH_2Cl_2/ amine solvent system

We have observed that the (alkyne)$Co_2(CO)_6$ complexes can be also prepared using amines in CH_2Cl_2 without using t-BuOH. The Pauson-Khand reaction of the complex prepared in this way using 1-heptyne, $CoBr_2$, Zn and CO in CH_2Cl_2/TMEDA

Table 2 Reactions of (alkyne)$Co_2(CO)_6$ complexes with olefin in CH_2Cl_2/amine

No.	alkyne	alkene	amine	Product[a]	Yield[b,c]
1	$C_5H_{11}C\equiv CH$		TMEDA	 29	50%
2	$C_8H_{17}C\equiv CH$		$PhCH(CH_3)NH_2$	 31	52%
3	$PhC\equiv CH$		$PhCH(CH_3)NH_2$	 33	32%

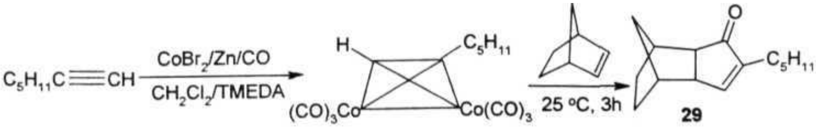
a) All reactions were carried out using $CoBr_2$ (20 mmol), Zn (20 mmol), alkyne (10 mmol) in CH_2Cl_2 (50 mL)/amine (1.5 mL), olefin (15 mmol), amine (30 mmol) at 25 °C for 3h.

b) Products were identified by analysis of spectral data (IR, ^1H, ^{13}C NMR) and comparison with the data available in the literature.

c) Yields reported are for products separated by column chromatography on silica gel using ethyl acetate in hexane as eluent and calculated on the basis of amount of alkyne used.

with norbornylene as an olefin was then carried out. The corresponding cyclopentenone 29 is obtained in 50% yield (Scheme 14). The yield of cyclopentenone is similar to that obtained in the reaction carried out using of t-BuOH. The results are summarized in Table 2.

Scheme 14



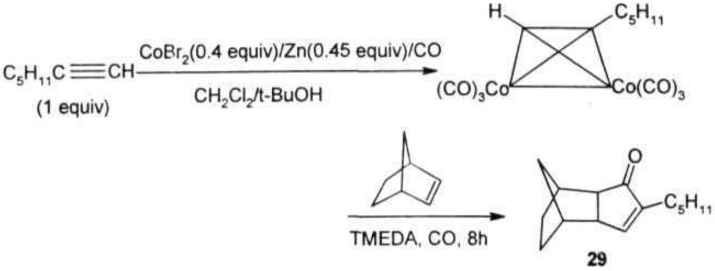
29

1.2.4 Reactions of (alkyne)$Co_2(CO)_6$ complexes prepared *in situ* using sub-stoichiometric amounts of $CoBr_2$, Zn and CO with olefins in toluene/t-BuOH solvent system

We then turned our attention towards the catalytic version of the Pauson-Khand reaction. A catalytic Pauson-Khand reaction that would allow the use of free alkyne and CO would be of great interest, especially for large scale synthetic operations. As discussed in the introductory section, there are several methods reported for the catalytic version of the Pauson-Khnad reaction. However, several of these reactions were carried out under high pressure of CO. We were interested in developing a simple method that can be carried out at atmospheric pressure of CO.

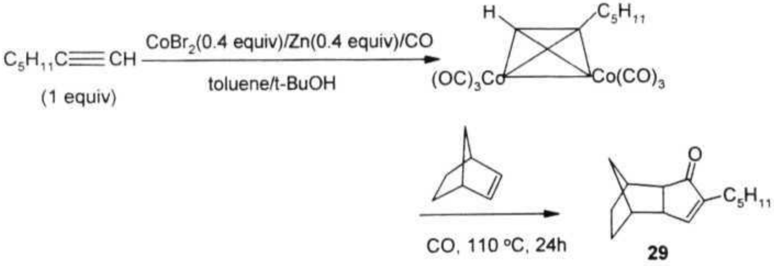
We have attempted the reaction of $(C_5H_{11}C{\equiv}CH)Co_2(CO)_6$ complex prepared *in situ* using sub-stoichiometric amounts of $CoBr_2$ and Zn under CO atmosphere with norbornylene in the presence of TMEDA in CH_2Cl_2/t-BuOH solvent system (Scheme 15). The desired cyclopentenone (29) was obtained in somewhat lower yield (30%).

Scheme 15



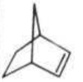
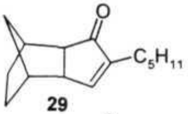
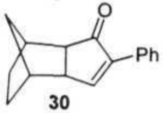
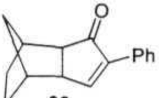
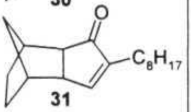
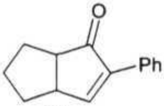
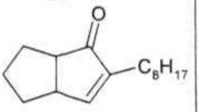
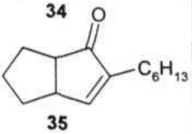
Since catalytic reactions are generally carried out at higher temperatures, we have examined the reaction under refluxing conditions in toluene. The $(C_5H_{11}C{\equiv}CH)$-$Co_2(CO)_6$ complex was prepared *in situ* using 0.4 equivalents each of $CoBr_2$ and Zn under CO atmosphere in toluene/t-BuOH solvent system. After the complex formation, the norbornylene was added and the contents were stirred at 110 °C while bubbling CO for 24h. After the workup, the cyclopentenone 29 was obtained in 88% yield (Scheme 16). Since the desired product is obtained in good yield at atmospheric pressure of CO, the reaction was carried out using different alkynes. The results are summarized in Table 3.[55]

Scheme 16



We have carried out experiments under different conditions so as to optimize the reaction conditions. For example, in a run using 0.2 equivalents each of $CoBr_2$ and Zn with phenylacetylene (1 equiv) and norbornylene (1.5 equiv), after refluxing the contents for 24h, the desired cyclopentenone 30 was obtained in 40% yield.

Table 3 Sub-Stoichiometric reactions of (alkyne)$Co_2(CO)_6$ complexes with olefins

No.	alkyne	alkene	time	Product[a]	Yield[b,c]
1	$C_5H_{11}C\equiv CH$		24h	 **29**	88%
2	$PhC\equiv CH$		24h	 **30**	83%
3	$PhC\equiv CH$		12h	 **30**	67%
4	$C_8H_{17}C\equiv CH$		24h	 **31**	85%
5	$PhC\equiv CH$		24h	 **33**	32%
6	$C_8H_{17}C\equiv CH$		24h	 **34**	35%
7	$C_6H_{13}C\equiv CH$		24h	 **35**	30%

a) All reactions were carried out using $CoBr_2$ (4 mmol), Zn (4.3 mmol), alkyne (10 mmol)), olefin (15-20 mmol), in toluene (50 mL)/t-BuOH (1.5 mL) at 110 °C.

b) Products were identified by analysis of spectral data (IR, ^1H, ^{13}C NMR) and in comparison with the data available in the literature.

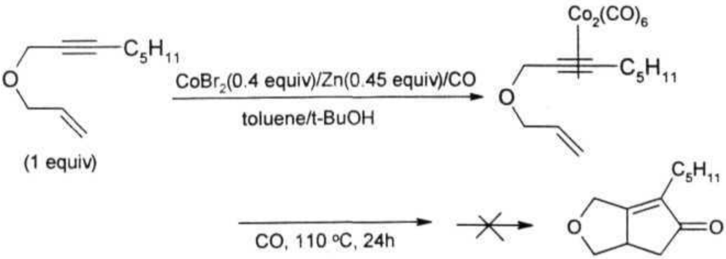
c) Yields reported are for products separated by column chromatography on silica gel using ethyl acetate in hexane as eluent and calculated on the basis of amount of alkyne used.

In a run, using 0.4 equivalents each of $CoBr_2$ and Zn with phenylacetylene (1 equiv) and **norbornylene** (1.5 equiv), under the above conditions for 12h, the cyclopentenone 30 was obtained in 67% yield. We have also carried out the reaction by replacing TMEDA in place of t-BuOH. In this case also, the cyclopentenone 30 was obtained in 67% yield.

Further, when the reaction of $(PhC{\equiv}CH)Co_2(CO)_6$ complex, prepared using sub-stoichiometric amounts of $CoBr_2$ and Zn, was performed with norbomylene in CH_2Cl_2/t-BuOH solvent system at 45 °C under atmospheric pressure of CO for 24h, the cyclopentenone 30 was obtained in lower in yields (48%) compared to that obtained at 110 °C in toluene (entry 2 in Table 3). This indicates that the catalytic Pauson-Khand reaction requires higher temperature to recycle the catalyst.

We have also carried out an intramolecular version of Pauson-Khand reaction using sub-stoichiometric amounts of $CoBr_2$ and Zn at atmospheric pressure of CO. Unfortunately, the corresponding cylopentenone was not formed even after heating the contents at 110 °C for 24h (Scheme 17).

Scheme 17



It appears that it is important to have a reactive olefin moiety for the Pauson-Khand reaction under the present conditions.

1.2.5 Conclusions

A simple and convenient method of preparation of (alkyne)$Co_2(CO)_6$ complexes has been developed through the reduction of $CoBr_2$ in CH_2Cl_2 and toluene with Zn and CO in the presence of alkynes The complexes prepared in this way undergo Pauson-Khand reaction in the presence of amines and amides at room temperature in CH_2Cl_2 to give the corresponding cyclopentenones in moderate to good yields. The Pauson-Khand reaction of (alkyne)$Co_2(CO)_6$ complexes was also carried out using sub stoichiometric amounts of $CoBr_2$ and Zn at atmospheric pressure of CO with olefins. Again, the corresponding cyclopentenones were obtained in moderate to good yields under these conditions.

1.3 Experimental Section

1.3.1 General Information

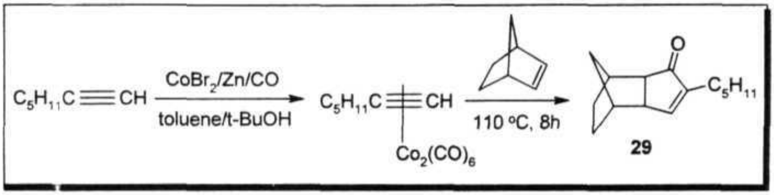
Melting points reported in this thesis are uncorrected and were determined using a Buchi-510 capillary point apparatus. Infrared spectra were recorded on Perkin-Elmer IR spectrometer Model JASCO FT 5300 with polystyrene as reference. ^1H (200 MHz) and ^{13}C NMR (50 MHz) spectra were taken in CDCI3 unless otherwise stated and TMS as reference (8 = 0 ppm). The ^{13}C chemical shifts are reported in ppm on the δ scale relative to CDCI3 (77.0 ppm) and coupling constants are reported in hertz. Elemental analyses were performed on a Perkin-Elmer elemental analyzer model-240 C. Column chromatography was carried out using Aceme's silica gel (100-200 mesh).

All glassware were predried at 140 "C in hot air oven for 4h, assembled in hot and cooled under a stream of dry nitrogen. Unless otherwise mentioned, all the operations and transformations of reagents were carried out using standard syringe, septum technique recommended for handling air sensitive organometallic compounds.[56] In all experiments, a round bottom flask of appropriate size with a side arm, a side septum, a magnetic stirring bar, a condenser and a connecting tube attached to a mercury bubbler were used. The outlet of the mercury bubbler was connected to a long tube to the atmosphere. All dry solvents and reagents (liquids) used were distilled from appropriate drying agents just before use. Toluene was distilled over bezophenone/sodium. CH_2Cl_2 was washed successively with H_2SO_4 and water then distilled over CaH_2. As a routine practice, all organic extracts were concentrated on Buchi-EL-rotary evaporator. All yields reported are isolated yields of material judged homogenous by TLC, IR and NMR spectroscopy. The phenyl-acetylene, 1-decyne and 1-octyne were prepared following the reported procudures.[57] 1-heptyne was supplied by Fluka, Switzerland. Norbornylene and cyclopentene used were supplied by Aldrich $CoBr_2$ was prepared from cobalt carbonate using 48% HBr solution. The $CoBr_2.H_2O$ was dehydrated initially on hot plate for 2h and then in hot air oven at 150 °C for 5-6h It was further dried at 150 °C for 4h under vaccum[58] and kept in a desiccator under nitrogen. Zinc dust was supplied by Ranbaxy, India. Activated Zn dust was prepared by treating the commercial Zn dust with 1% H_2SO_4, then washing with water, acetone and dried at 150°C for 4h under vaccum.[59] Carbon monoxide was generated by stow addition of formic acid (98%) to concentrated H_2SO_4 (96%) at 80-90 °C using an apparatus recommended for utilization in the carbonylation of organoboranes.[50] It was predried by passing through anhydrous KOH pellets before bubbling into reaction mixture.

1.3.2 Reaction of $(C_6H_{11}C\ CH)Co_2(CO)_6$ complex with Norbornylene in toluene/t-BuOH solvent system.

The $(C_5H_{11}C{\equiv}CH)Co_2(CO)_6$ complex was prepared by reducing $CoBr_2$ (2.36 g, 20 mmol) with Zn (1.35 g, 20 mmol) and $C_5H_{11}C{\equiv}CH$ (1.3 mL, 10 mmol) in toluene (50 mL)/ t-BuOH(1.5 mL) while bubbling CO at 25°C for 8h. The CO atmosphere was replaced by dry static nitrogen. The norbornylene (1.4 g, 15 mmol) was added. The contents were stirred at 110 °C for 8h and brought to room temperature. The reaction mixture was successively washed with water and brine solution. The organic layer was extracted with ether (2x25 mL) and dried over anhydrous MgSO< and concentrated.

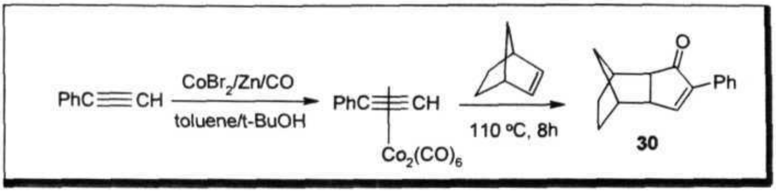
The crude product was subjected to column chromatography on a silica gel using **hexane/ethyl** acetate as eluent. The cyclopentenone 29 (80%, 1.74g) was isolated and identified by IR, ^{1}H and ^{13}C NMR spectral data. The spectral data obtained for product 29 are summarized below.



Yield	**80% (1.74** g)
IR(neat)	2957, 2872, 1699, 1456, **1186**, 1053 cm^{1}
^{1}H NMR	8 **ppm** 0.9 (t, 2.8 Hz,3H), **1.1-1.7** (m, 14H), 2.1 (**m**, 2H), 2.3(bs, 1H), 2.5 (bs, 1H), 7.1(bs,1H) **(Spectrum number 1)**
^{13}C NMR	8 ppm 13.9, 22.3, 24.6, 27.5.8, 28.4, 29.0, 30.9, 31.5, 38.0, 38.9, 48.1, 53.8, 149.5 (quaternary), 158.4, 210.9 (CO) **(Spectrum number 2)**

The spectral data are in 1:1 correspondence with the data reported in the literature.[45]

The above procedure was followed for the reaction of **(PhC≡CH)Co$_2$(CO)$_6$** with norbornylene.

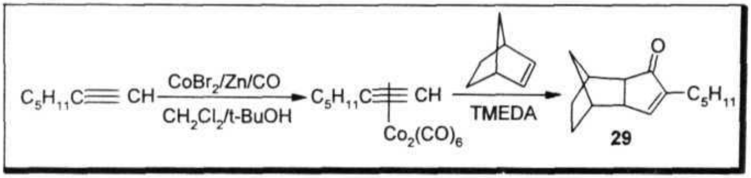


Yield	78% (1.74 g)
M.P.	**92-94 °C (Lit.**[1c] **m.p. 93-95** °C)
IR(KBr)	3025, 3040, 3025, 2950, 1695, 1610, 1600, 765, 700 cm^{1}
^{1}H NMR	6ppm 0.9-1.1 (m, 2H), 1.1-1.8 (m, 4H), 2.3 -2.5 (m, 3H), 2.6 (m, 1H), **7.2-7.8** (m,6H)
^{13}C NMR	**δppm** 28.4, 29.1, 31.2, 38.3, 39.4, 47.7, 54.9, 127.1, 128.4, 131.6, 146.1 (quaternary), 160.3, **209.1(CO)**

The spectral data show 1:1 correspondence with the data previously reported from this **laboratory**.[45]

1.3.3. Reaction of $(C_5H_{11}C\equiv CH)Co_2(CO)_6$ complex with Norbornylene in presence of TMEDA in CH_2Cl_2/ t-BuOH : A representative procedure

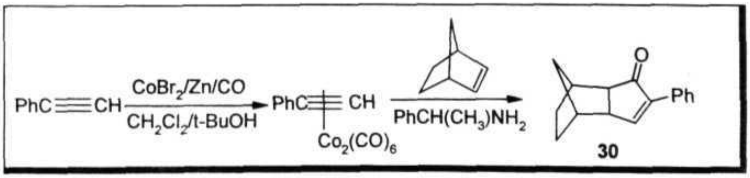
The $(C_5H_{11}C\equiv CH)Co_2(CO)_6$ complex was prepared by reducing $CoBr_2$ (2.36 g 20 mmol) with Zn (1.35 g, 20 mmol) and $C_5H_{11}C\equiv CH$ (1.3 mL, 10 mmol) in CH_2Cl_2 (50 mL)/t-BuOH (1.5 mL) while bubbling CO at 25 °C for 8h. The CO atmosphere was replaced by dry static nitrogen. The norbornylene (1.4 g, 15 mmol), TMEDA (4.5 mL, 30 mmol) were added. The contents were stirred at 25 °C for 3h. The mixture was successively washed with dil. HCl, water and brine solution. The organic layer was extracted with CH_2Cl_2 and dried over anhydrous $MgSO_4$ and concentrated. The crude product was subjected to column chromatography on silica gel using hexane/ethyl acetate as eluent The cyclopentenone 29 (53%, 1.15 g) was isolated and identified by IR, ^1H, ^{13}C NMR spectral data.



Yield 53% (1.15 g)

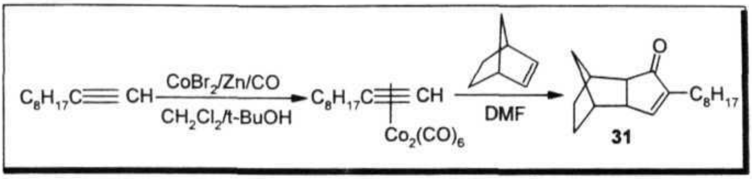
The spectral data were identical to the data of 29 obtained in the previous experiment.

The above procedure was followed for other (alkyne)$Co_2(CO)_6$ complexes with different olefins in the presence of different amines/amides. The results are summarized in Table 1.



Yield 55% (1.23 g)

The spectral data were identical to the data of 30 obtained in the previous experiment.



31

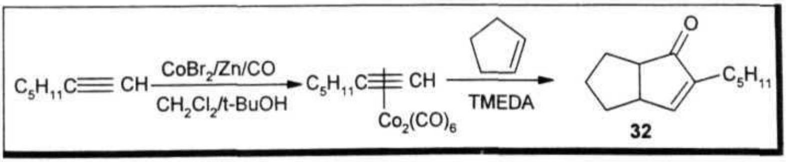
Yield 52% (1.35 g)

IR(neat) 2950 , 1705, 1630, 1440, 1040 cm^{-1}

^{1}H NMR 6ppm 0.8 (t, 2.5 Hz, 3H), 1.0-1.6 (m, 20H), 2.1 (m, 2H), 2.3 (bs, 1H), 2.5 (bs, 1H), 7.0 (bs, 1H)

^{13}C NMR 8ppm 13.6, 22.2, 24.3, 27.4, 28.0, 28.6, 28.8, 30.5, 31.4, 37.7, 38.5, 47.7, 53.4, 149.4 (quaternary), 158.1, 210.3 (CO)

The spectral data show 1:1 correspondence with the data previously reported from this laboratory.[45]



32

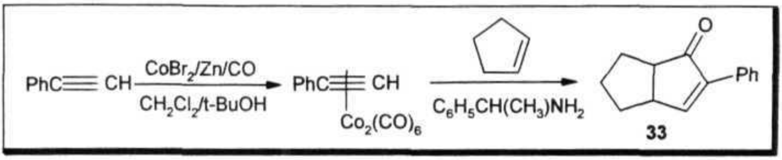
Yield 30% (0.57 g)

IR(neat) 2929, 2862, 1701, 1631 1458, 1259 cm'

^{1}H NMR 8ppm 0.8 (t, 3 Hz, 3H), 1.0-2.0 (m, 14 H), 2.0-2.7(m, 1H), 3.2 (bs, 1H), 7.1 (bs, 1H)

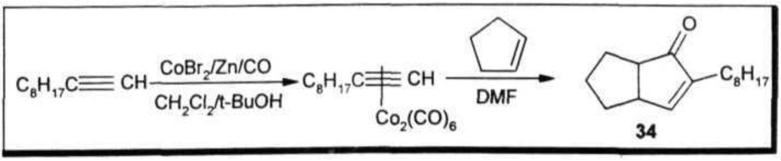
^{13}C NMR	6ppm **13.8**, 22.4, 23.3, 24.5, 27.6, 28.8, 30.0, 31.4, 43.7, 49.9, 146.6 (quaternary), 159.9, 212.4 (CO)

The spectral data show 1:1 correspondence with the data previously reported from this laboratory.[45]



Yield	32% (0.63 g)
M. P	**40-42 °C (Lit.[6e] m.p. 40-44** °C)
IR(KBr)	690, 755, 1290, 1600,1620, 1695, 2950, 3025, 3040 cm^{-1}
^{1}H NMR	5 ppm 1.1-2.0, (m, 6H), 2.9-3.4 (m, 2H), 7.2-7.8 (m, 6H)
^{13}C NMR	6 ppm 23.3, 29.4, 30.2, **42.2**, 50.9, 126.9, 127.7, 128.1, 129.6, 143.2 (quaternary), 161.8, 210.7 (CO)

The spectral data show 1:1 correspondence with the data previously reported from this laboratory.[45]



Yield	32% (0.74 g)
IR (neat)	1040, 1260, 1630, 1705, 2950 cm^{-1}

^{1}H NMR 8ppm 0.6-0.9 (t, 3 Hz, 3H), 0.9-2.1 (m, 20H), 2.5-2.8 (m, 1H), 3.2 (bs, 1H), 7.0 (bs, 1H)

^{13}C NMR δppm 13.9, 22.5, 23.4, 24.6, 27.8, 29.2, 29.6, 30.1, 31.5, 31.8, 43.8, 50.1, 147.0(quatenary), 160.2, 212.9 (CO)

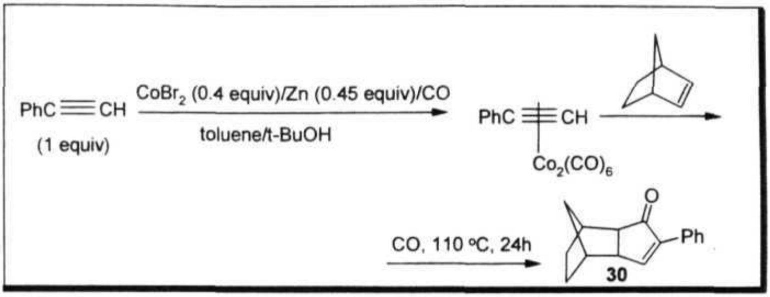
The spectral data show 1:1 correspondence with the data previously reported from this laboratory.[45]

1.3.4. Reaction of $(C_5H_{11}C\equiv CH)Co_2(CO)_6$ complex with Norbornylene in CH_2Cl_2/TMEDA solvent system

The $(C_5H_{11}C\equiv CH)Co_2(CO)_6$ complex was prepared by reducing $CoBr_2$ (2.36 g, 20 mmol) with Zn (1.35g, 20 mmol) and $C_5H_{11}C\equiv CH$ (1.3 mL, 10 mmol) in CH_2Cl_2 (50 mL)/TMEDA (1.5 mL) while bubbling CO at 25°C for 8h. The CO atmosphere was replaced by dry static nitrogen. The norbornylene (1.4 g, 15 mmol), TMEDA (4.5 mL, 30 mmol) were added. The contents were stirred at 25°C for 3h. The mixture was successively washed with dil. HCl, water and brine solution. The organic layer was extracted with CH_2Cl_2 dried over anhydrous $MgSO_4$ and concentrated. The crude product was subjected to column chromatography on silica gel using hexane/ethyl acetate as eluent. The cyclopentenone 29 (50%, 1.09 g) was isolated and identified by IR, ^{1}H, ^{13}C NMR spectral data. The results are summarized in Table 2.

1.3.5. Sub-stoichiometric reaction of $(PhC{\equiv}CH)Co_2(CO)_6$ complex with Norbornylene: A representative procedure

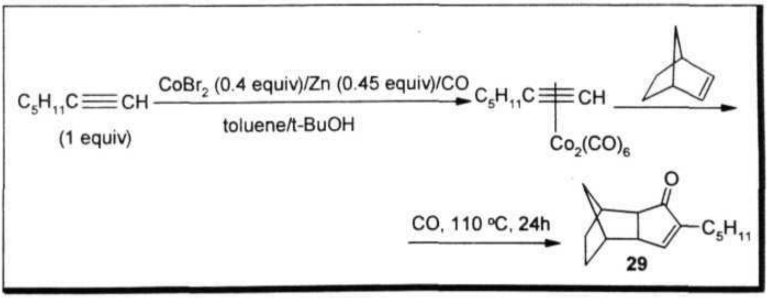
The $(PhC{\equiv}CH)Co_2(CO)_6$ complex was prepared by reducing $CoBr_2$ (0.88 g, 4 mmol) with Zn (0.28 g, 4.3 mmol) and $PhC{\equiv}CH$ (0.2 mL, 2mmol) in toluene (50 mL)/ t-BuOH(1.5 mL) while bubbling CO at 25 °C for 5h. After the complex formation, $PhC{\equiv}CH$ (0.8 mL, 8 mmol) and norbornylene (1.4 g, 15 mmol) were added. The contents were stirred at 110 °C for 24h while bubbling CO at atmospheric pressure and brought to room temperature, water (20 mL) was added and the organic layer was separated. The aqueous layer was extracted with ether (50 mL). The combined organic extract was washed successively with water (20 mL), brine solution (10 mL) and dried over anhydrous $MgSO_4$ and concentrated. The crude product was subjected to column chromatography on silica gel using hexane/ethyl acetate as eluent. The cyclopentenone 30 (83%, 1.85 g) was isolated and identified by IR, ^1H, ^{13}C NMR spectral data and comparison with reported data.



Yield 83% (1.85 g)

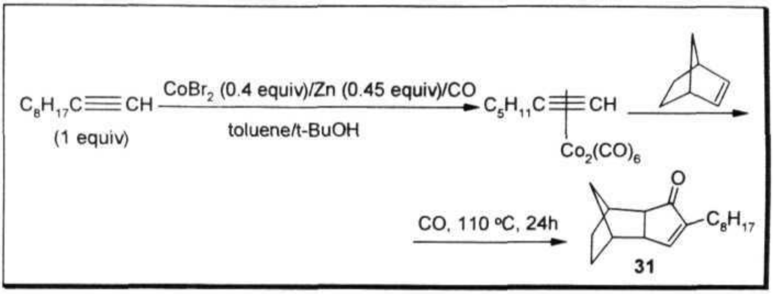
The spectral data were identical to the data of 30 obtained in the previous experiments.

The above procedure was followed for other **(alkyne)$Co_2(CO)_6$** complexes with different olefins and the results are summarized below (also in Table 3).



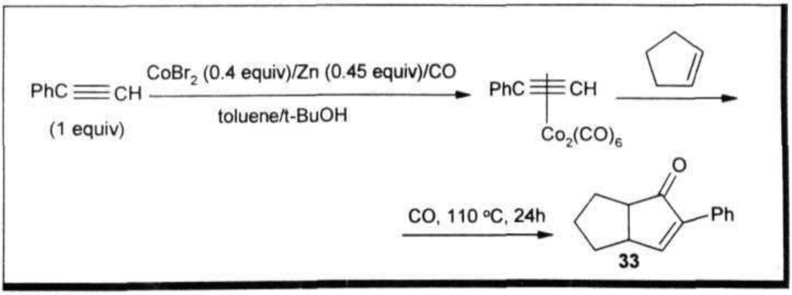
Yield 88% (1.91 g)

The spectral data were identical to the data of 29 obtained in the previous experiments.



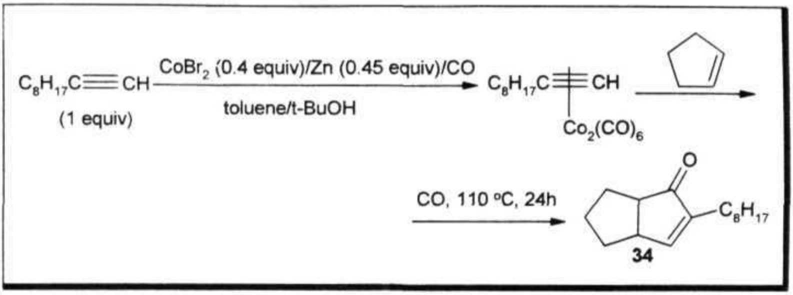
Yield 85% (2.21 g)

The spectral data were identical to the data of 31 obtained in the previous experiments.



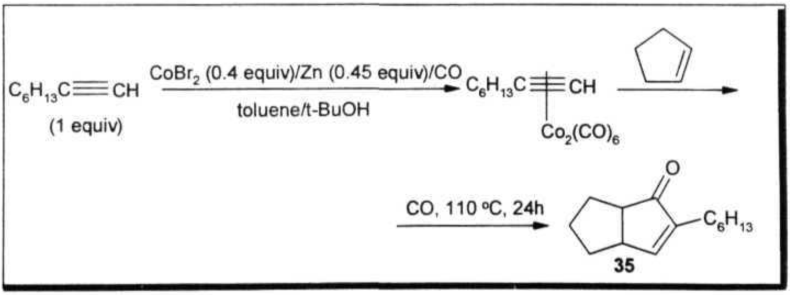
Yield 32% (0.63 g)

The spectral data were identical to the data of 33 obtained in the previous experiments.



Yield 35% (0.81 g)

The spectral data were identical to the data of 34 obtained in the previous experiments.



Yield 30% (0.61 g)

IR(neat) 2929, 2862, 1701, 1631, 1458, 1259 cm^{-1}

^{1}H NMR δppm 0.8 (t, 2.8 Hz, 3H), 1.0-2.0 (m, 16H), 2.7 (m, 1H), 3.2 (bs, 1H), 7.1 (bs, 1H). **(Spectrum number 3)**

^{3}C NMR δppm 13.8, 22.3, 23.3, 24.5, 27.6, 28.8, 29.5, 30.0, 31.4, 43.7, 49.9, 146.6 (quaternary), 159.9, 212.4 (CO) **(Spectrum number 4)**

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Chapter 2

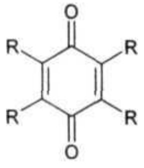
Studies on the carbonylation of alkynes with cobalt carbonyl complexes prepared using $CoBr_2$, Zn and CO

2.1 Introduction

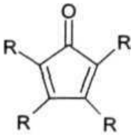
Early research work on addition of CO to acetylene in the presence of transition metals or metal carbonyls was carried out by two industrial research groups working under supervision of Reppe and Roelen. Reppe investigated the aspects of the reaction of carbon monoxide with acetylene and coined the term 'carbonylation'. Roelen investigated the hydroformylation reactions of olefins in the presence of cobalt catalysts, and as a logical extension tried to carry out the hydroformylation of acetylene. Our research efforts on the hydroformylation reaction are discussed in Chapter 3. The investigations on the carbonylation of alkynes are described in this chapter. A brief review of the reports on the carbonylation of alkynes will facilitate the discussion.

Due to the high reactivity of the acetylenic compounds and CO in the presence of transition metals, and to the great industrial importance of some of the products obtained, there has been a great deal of scientific and industrial activity in recent years in this area of research. As a consequence, the scope of the carbonylation of alkynes was extended. It is now possible to obtain derivatives of mono and dicarboxylic acids and keto acids, esters of aldehydic acids, cyclic ketones and hydroquinones in one step from relatively simple acetylenic compounds and CO.

Acetylenic substrates, unlike olefins, react with CO in the presence of metal carbonyls even in the absence of hydrogen or compounds containing hydrogen atoms. The metal carbonyls are able to organize two or more molecules of the acetylenic substrates forming organic structures, which may include CO and are bound to metal atom either through a a- or a rc-bond. The most common structures that can be synthesized by the reaction of metal carbonyls with acetylenic substrates are the doubly unsaturated keto structures 1 and 2 .[1]



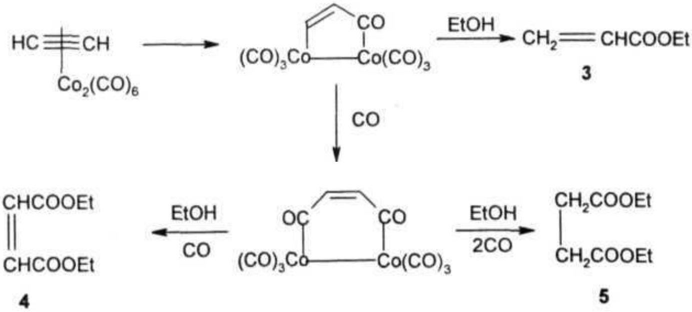
1



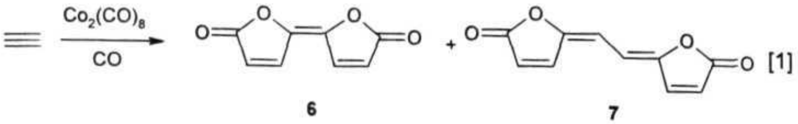
2

The carboxylation of acetylene catalyzed by cobalt carbonyl gives fumaric, acrylic and succinic esters ir. alcohol.[2] The mechanism and intermediates of this transformation are shown in Scheme 1.[3]

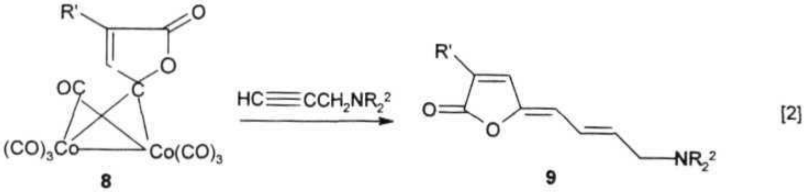
Scheme 1



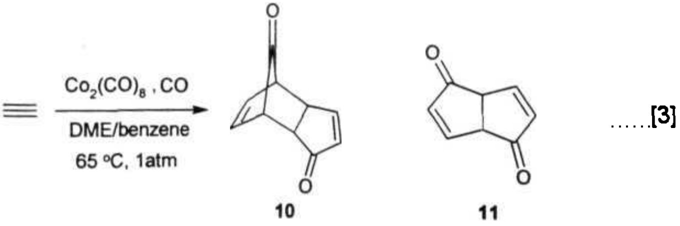
The reaction of acetylene and CO with $Co_2(CO)_8$ at high temperature under elevated pressures gives lactones 6 and 7 (eq 1).[4] In the absence of CO, the formation of 1,2,4-trisubstituted benzenes predominates.[5]



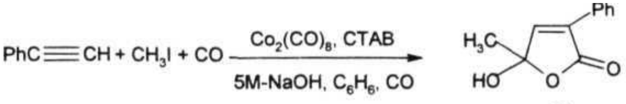
Later, it was observed that the reaction of (μ-butenolide)(μ-CO)$Co_2(CO)_6$ complexes 8 with prop-2-ynyl amines yields the new γ-substituted-α,β-unsaturated-γ-lactones 9 (eq 2).[6]



In the reaction of acetylene with CO in presence of $Co_2(CO)_8$ in DME and benzene, the major products are dicylopentadienone and cyclopentadienone derivatives along with traces of benzoquinone and indanone (eq 3).[7]



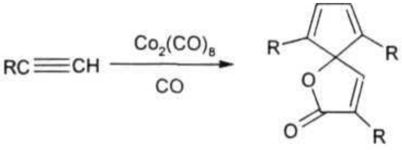
It was observed that 1-alkynes on reaction with $Co_2(CO)_8$ and methyl iodide in presence of phase transfer catalysts afford but-2-enolides (eq 4).[8]



12

.....[4]

The terminal alkynes substituted with bulky groups such as adamantyl react with CO to give 3,6,9-trisadamantyl-1-oxaspiro[4,4]nona-3,6,8-trien-2-one 13 as a major product under $Co_2(CO)_8$ catalysis (eq 5).[9] In addition, trisubstituted benzene, cyclopentadienone and cyclopentenone were also isolated.

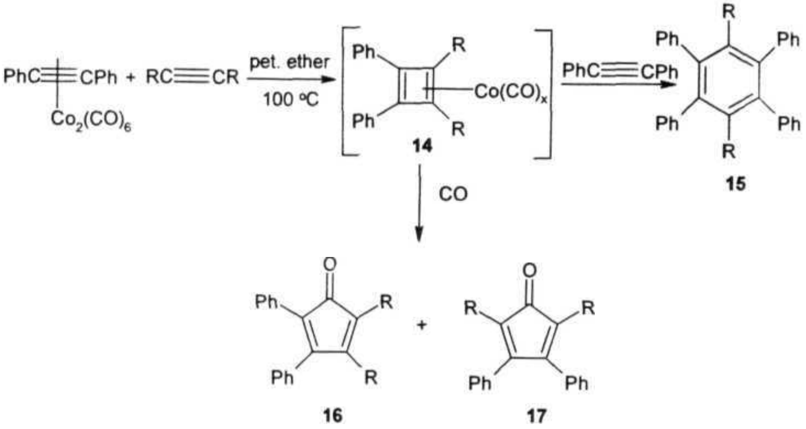


13

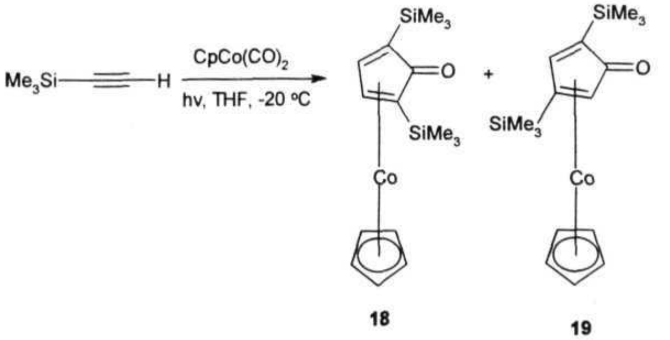
...... [5]

In the reaction of $(PhC{\equiv}CPh)Co_2(CO)_6$ with bistrimethylsilyl or phenyltrimethylsilylacetylene, cyclopentadiene and benzene derivatives were obtainbed.[9b] Some of these cyclic organic products can only be explained if the original acetylenic bond is broken in the course of this transformation. Since simple rupture of a triple bond under the conditions can be discounted, Whitesides[10] proposed a mechanism involving rather unstable cyclobutadiene complexes as intermediates that may undergo ring enlargement as shown in Scheme 2.

Scheme 2

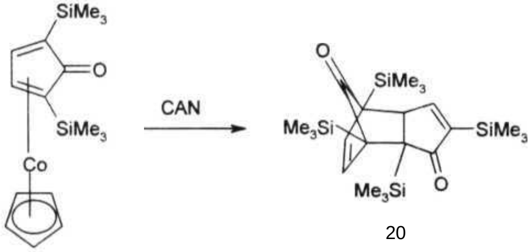


Cyclopentadienone cobalt carbonyl complexes are obtained in the reaction of $CpCo(CO)_2$ with acetylene.[11] It has been observed that irradiation of $CpCo(CO)_2$ in the presence of trimethylsilylacetylene in THF at -20 °C furnishes two isomeric complexes of cyclopentadienones 18 and 19 (eq 6).[12]



•••[6]

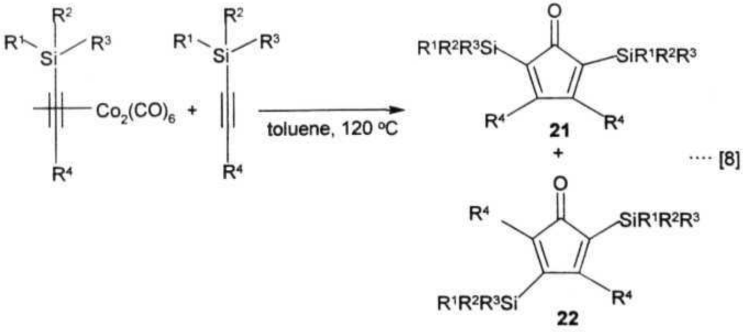
The cyclopentadienones constitute potentially valuable organic synthons, if decomplexation without dimerization is possible. However, the decomplexation of cyclopentadienone cobalt complex 18 with ceric ammonium nitrate (CAN) gives the corresponding cyclopentadienone only in 10% yield along with the dimer 20 (54% yield) (eq 7).



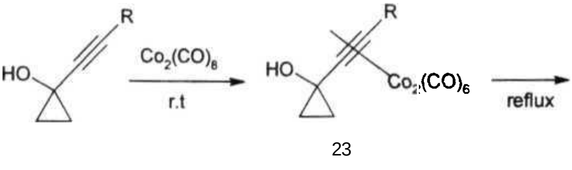
..... [7]

18

Recently, a direct synthesis of cydopentadienones mediated by cobalt carbonyl has been reported (eq 8).[13]

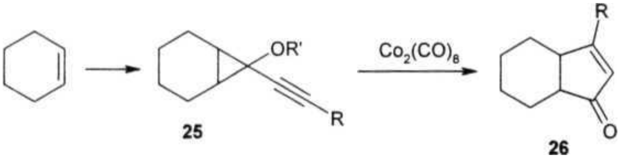


Also, a novel rearrangement of 1-(1-alkynyl) cyclopropanols to 2-cyclopenten-1-ones using $Co_2(CO)_8$ has been reported.[14] Substituted 2-cyclopenten-1-ones are selectively obtained (eq 9).



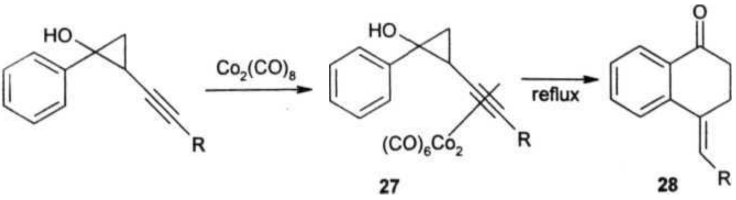
[9]

This rearrangement was successfully applied to the annulation of cyclopentenones on to cycloalkenes (eq 10). Furthermore, the rearrangement was found to proceed catalytically upon addition of triaryl phosphite as a ligand.[14]



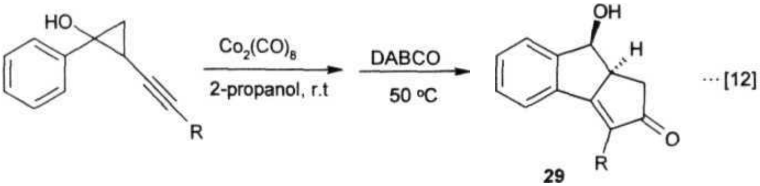
•-[10]

It was further observed that the phenyl substituted alkynyl cyclopropanols after complexation with $Co_2(CO)_8$ and heating gives the corresponding 2,3-dihydro-1-napthalenone derivatives 28 in moderate to good yields (49-86%) (eq 11).[14]



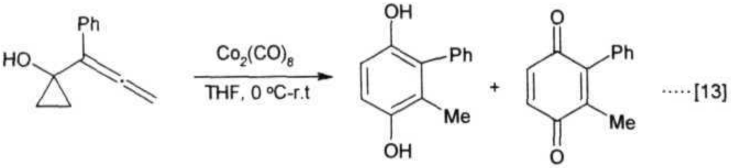
[11]

When this reaction was carried out in presence of bases such as DABCO, the corresponding **cyclopentainden-2-one** derivatives 29 were obtained in moderate to good yields (45-72%) (eq 12).[14]



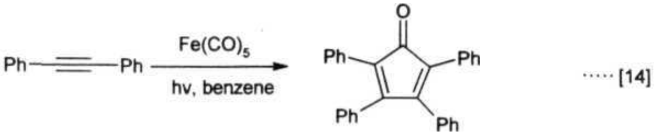
29

Further, it was observed that the reaction of 1-(1-phenyl-1,2-propadienyl) cyclopropanol with $Co_2(CO)_8$ under argon atmosphere gives the corresponding substituted hydroquinone (35%) and benzoquinone (20%) (eq 13).[14]



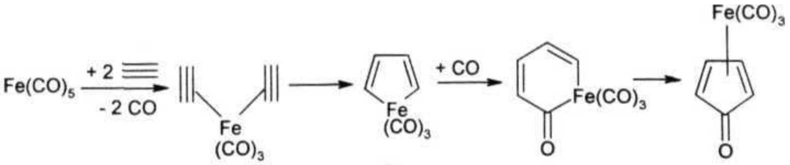
30 31

Apart from cobalt carbonyls, several other transition metal carbonyls were also exploited for the novel carbonylation reactions of alkynes. The $Fe(CO)_5$ is most commonly employed reagent for many transformations. For example, it has been observed that irradiation of diphenylacetylene in the presence of $Fe(CO)_5$ gives the corresponding cyclopentadienone along with other products (eq 14).[15] Since then, there have been several reports on this reaction.[16,17]



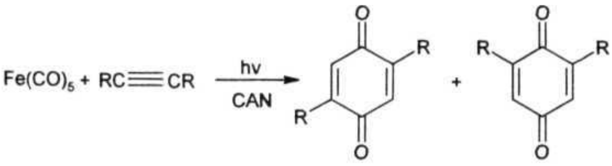
This iron mediated [2+2+1] **cycloaddition** is assumed to be initiated by sequential replacement of two CO ligands by two alkynes which generate the **tricarbonyl[bis-(η^2-alkyne)]iron** complex 33. Oxidative coupling of the two alkyne units at the transition metal center provides the intermediate ferracyclopentadiene 34. Insertion of CO into the metal carbon bond and subsequent rearrangement of ferracyclohexadieone afford the **tricarbonyliron-complexed** cyclopentadienone 36 (Scheme **3**).[17a]

Scheme 3



33 34 35 36

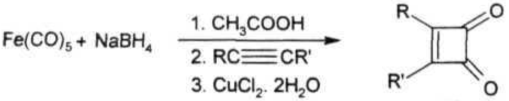
Photochemical irradiation[18] or thermolysis[19] of alkynes in the presence of **$Fe(CO)_5$** gives quinones (eq **15**).



37 **38**

…… [15]

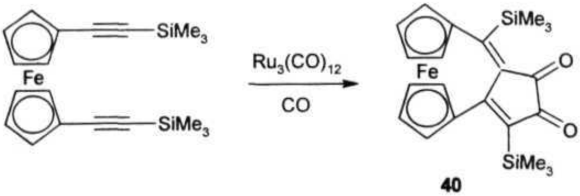
In this laboratory, an interesting double carbonylation of alkynes using $Fe(CO)_5$ has been developed (eq 16).[20]



39

…… [16]

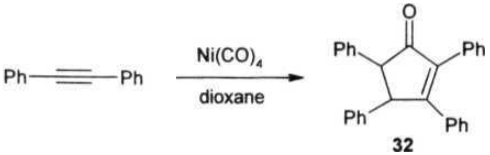
It has been reported that the reaction of 1,1'-bis(trimethylsilyl)ferrocene with catalytic amount (5 mol%) of $Ru_3(CO)_{12}$ under CO atmosphere at 150 °C results in a novel cyclocarbonylation involving 1,2-silyl migration to give the cyclopent-3-en-1,2-dione **40** (eq 17).[21]



40

….. [17]

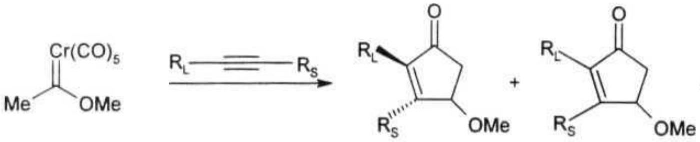
The $Ni(CO)_4$ reacts with the diphenylacetylene, HCl and ethanol in dioxane solution to give the corresponding cyclopentenone (eq 18).[22]



32

…… [18]

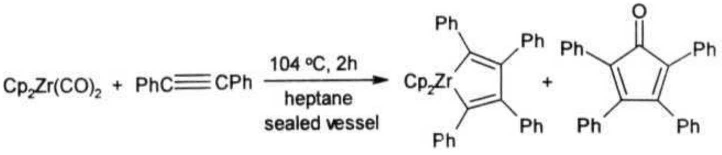
The methylmethoxy chromium carbene complexes on reaction with alkynes in hexane give the corresponding cyclopentenones (eq 19).[23] Cylopentenones are also obtained upon reaction of cyclopropyl substituted chromium complexes with alkynes.



41 **42**

···[19]

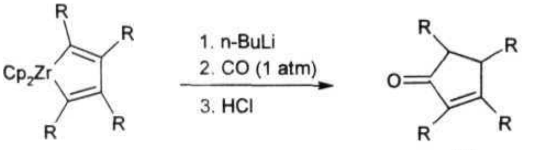
Photolysis or thermolysis of $Cp_2Zr(CO)_2$ and alkynes yields the zircona cylopentadiene complex. For example, thermolysis of diphenylacetylene and $Cp_2Zr(CO)_2$ in sealed vessel, give the zirconacyclopentadiene complex 43 and the corresponding cyclopentadienone (20%) (eq 20).[24]



43

.... [20]

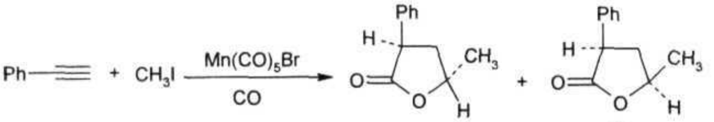
Recently, the zircona cyclopentadiene complex has been employed in the synthesis of **cyclopentenones** in the presence of **n-BuLi** and CO (eq **21**).[25]



44

·····[21]

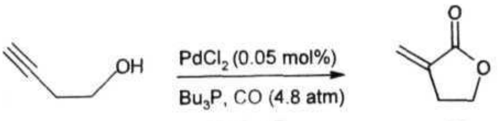
The alkynes react with methyl iodide in presence of **$Mn(CO)_5Br$** and CO under phase transfer catalysis to gve **γ-butyrolactones** (eq 22).[26]



45 (47%)

46 (31%)

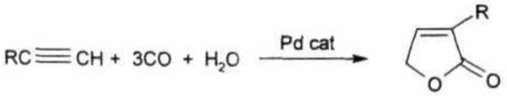
··· [22]



47

·····[23]

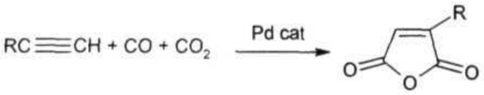
Reductive carbonylation of **1-alkynes** to **furan-2(5H)-ones** 48 takes place in dioxane-water, under **10** atm of CO in the presence of **PdI_2** (eq 24).[28]



48

……[24]

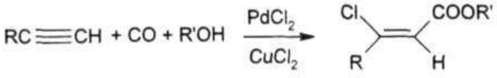
Also, in the presence of added CO_2 maleic anhydride derivatives were obtained (eq 25).[28]



49

……[25]

More recently, a simple method for the synthesis of (Z)-chloroacrylate esters in the reaction of 1-alkynes with catalytic amount of $PdCl_2$ and $CuCl_2$ under CO atmosphere has been reported (eq 26).[29]

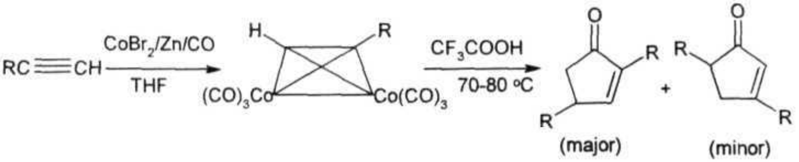


50

……[26]

Previously, it was observed in this laboratory that the reaction of (alkyne)$Co_2(CO)_6$ complexes in presence of CF_3COOH (TFA) gives the corresponding cyclopentenones in THF (Scheme 4).[30]

Scheme 4



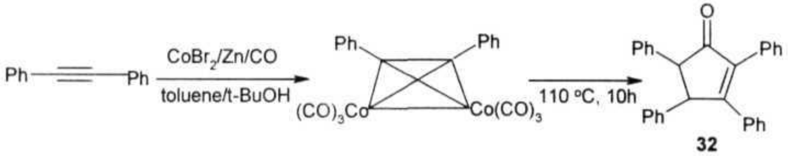
In continuation of these studies, we have explored the reactions of the **(alkyne)$Co_2(CO)_6$** complexes prepared using **$CoBr_2$**, Zn, under CO atmosphere in t-BuOH and **CH_2Cl_2** or toluene. The results are discussed in this chapter.

2.2 Results and Discussion

2.2.1 Reactions of (alkyne)$Co_2(CO)_6$ complexes in toluene/t-BuOH: Synthesis of cyclopentenones

Initially, we have examined the reaction of the $(PhC{\equiv}CPh)Co_2(CO)_6$ complex, prepared *in situ* in toluene/t-BuOH solvent system using $CoBr_2$, Zn in the presence of CO. The complex is fully decomposed upon heating at 110 °C for 10h. After workup, the product formed was identified as tetraphenylcyclopentenone 32 (Scheme 5).

Scheme 5



The cyclopentenone 32 was obtained earlier in this laboratory in the reaction of the $(PhC{\equiv}CPh)Co_2(CO)_6$ complex with triflouroaceticacid (TFA) in THF at 70 °C for 24h.[30] However, under the present conditions strong acid is not required and reaction takes shorter time. Hence, we have decided to investigate this transformation further.

We have carried out experiments using various (alkyne)$Co_2(CO)_6$ complexes in toluene/t-BuOH solvent system. It was found that this transformation is a general one and the corresponding cyclopentenones are obtained in moderate yields (Table 1).[31] In the case of terminal alkynes, two regio isomers are obtained. The regiochemistry of major isomer is in line with that of cyclopentenone derivative that is expected in the

Pauson-Khand reaction of the alkyne with olefin. However, whereas 3-substituted cyclopentenones are not formed in the Pauson-Khand reaction, they are obtained in minor amounts here. It should be noted that the 3-subsituted cyclopentenones are not formed in the Pauson-Khand reaction using the (alkyne)$Co_2(CO)_6$ complexes, prepared using $CoBr_2$/Zn/alkyne/CO system with olefins in toluene/t-BuOH system as discussed in Chapter 1.

Also, there is a possibility that the presence of Zn or $ZnBr_2$ in the reaction mixture may have effect on reaction course, since Lewis acids are known to mediate carbonylation reactions.[32]

In the case of phenylacetylene, 2,5-diphenyl substituted cyclopentenone was obtained as a major product, besides the corresponding trisubstituted benzene as minor product (5%) (eq 27). The formation of trisubstituted benzene is not unusual, as the alkynes are known to undergo trimerization reaction in presence of $Co_2(CO)_8$[33]

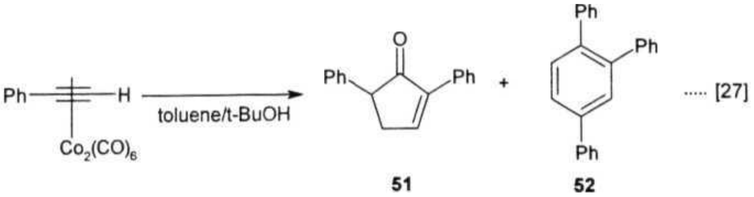
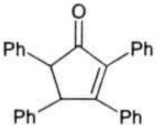
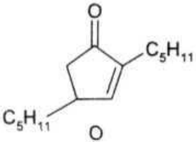
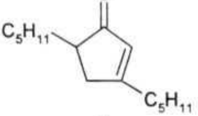
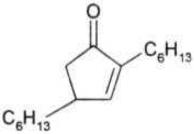
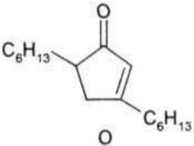
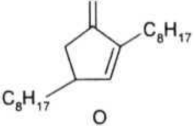
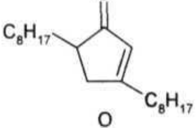
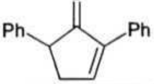


Table 1 Reactions of (alkyne)$Co_2(CO)_6$ complexes in toluene/t-BuOH

alkyne	Cyclopentenone[a]	Yield[b,c]
$Ph-\equiv-Ph$	 **32**	50%
$C_5H_{11}-\equiv-H$	 **53**	40%
	 **54**	10%
$C_6H_{13}-\equiv-H$	 **55**	38%
	 **56**	12%
$C_8H_{17}-\equiv-H$	 **57**	39%
	 **58**	10%
$Ph-\equiv-H$	 **51**	38%

Foot notes to Table 1

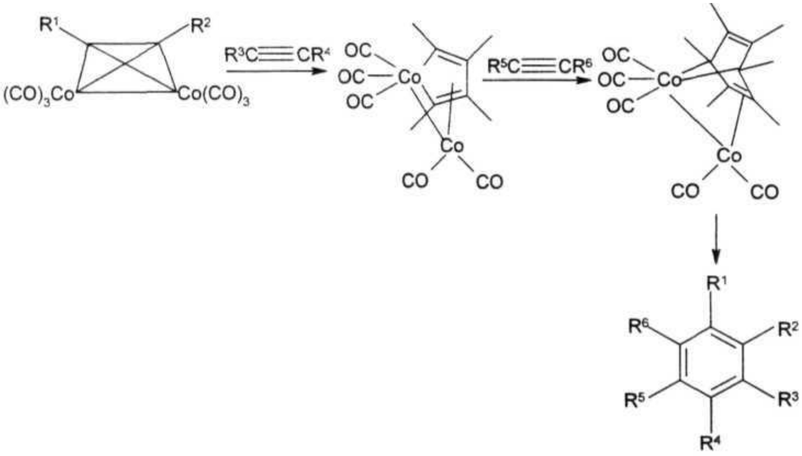
a) All reactions were carried out using $CoBr_2$ (20 mmol), Zn (20 mmol) and alkyne (10 mmol).

b) The products were identified by IR, ^1H NMR and ^{13}C NMR spectral data reported in the literature

c) Yields reported here are for products separated from chromatography on silica gel column using hexane and ethyl acetate as eluent and calculated based on the amount of alkyne used

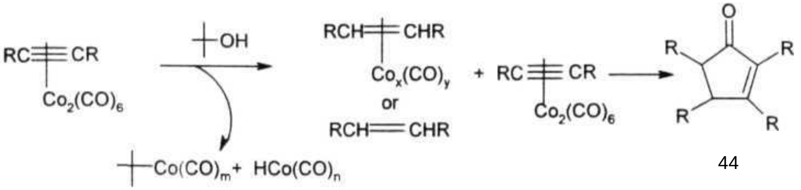
Recently, Pauson *et al* [34] isolated the intermediates involved in cyclotrimerization reaction of alkynes in the presence of $Co_2(CO)_8$ (Scheme 6).

Scheme 6



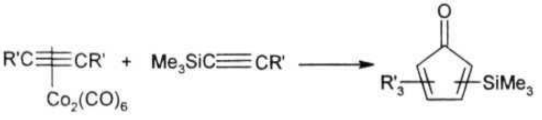
The formation of cyclopentenones may be rationalized by considering the reaction of (alkyne)$Co_2(CO)_6$ complexes with the complexed or decomplexed olefinic intermediate that might have formed through the cleavage of alkyne moiety by the $HCo(CO)_4$ species formed *in situ* in the medium (Scheme 7).

Scheme 7



44

Alternatively, the cyclopentenone may also result through the reduction of the initially formed cyclopentadienone intermediate by the hydrido cobalt carbonyl species such as $HCo(CO)_4$ formed *in situ* in the medium. It may of interest to note that formation of the cyclopentadienone derivatives was reported in the reaction of (alkyne)$Co_2(CO)_6$ complexes having bulky groups such as t-Bu, Ph, and Me_3Si substituents (eq **28**).[35]

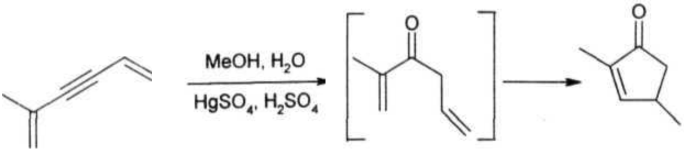


where R' = t-Bu, Ph

59

...... [28]

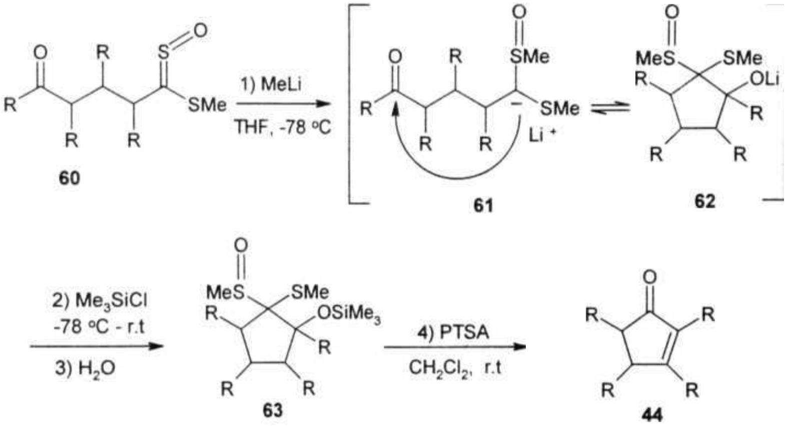
Several methods are available for the synthesis of cyclopentenone derivatives. For instance, Nazarov reaction[36] is the most commonly used for cyclopentenone synthesis (eq 29).



[29]

Recently, a novel synthesis of cyclopentenones based on the *Umpolung* chemistry strategy has been reported.[37] For example, sulfines of δ-oxodithioethers 60 undergo chemoselective addition of methyllithium to the electron poor sulfur atom of the thiocarbonyl moiety. Subsequent ring closure was effected by intramolecular addition of the carbanion, generated *in situ,* to the δ-carbonyl function leading to the cylopentenone 44 (Scheme 8).

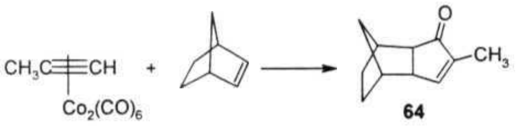
Scheme 8



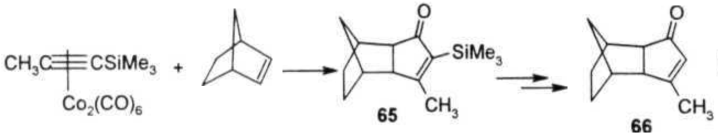
However, these methods require several steps. Accordingly, the present one pot method using simple bench top chemicals such as $CoBr_2$ and Zn is a simple alternative method for the synthesis of cyclopentenone derivatives.

2.2.2 Reactions of (RC CSiMe$_3$)Co$_2$(CO)$_6$ complexes in toluene/t-BuOH solvent system: Synthesis of cyclopentadienones

We have further studied the above transformation by examining the reaction of alkynes containing trimethylsilyl substituents. Previously, it has been observed that the trimethylsilyl-substituted alkynes have been used to change the regioselectivity in Pauson-Kahnd reaction. For example, whereas the (propyne)Co$_2$(CO)$_6$ complex reacts with norbornylene to give the corresponding 2-methyl substituted cyclopentenone (eq 30), the silyl substitution leads to the corresponding 3-methylderivative (eq 31).[38]

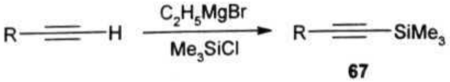


........[30]



[31]

It was anticipated that the effect of the silyl group would provide further information regarding the intermediates and mechanism involved in the present transformation. Various trimethyl substituted alkynes were prepared following a reported procedure (eq 32).[39]



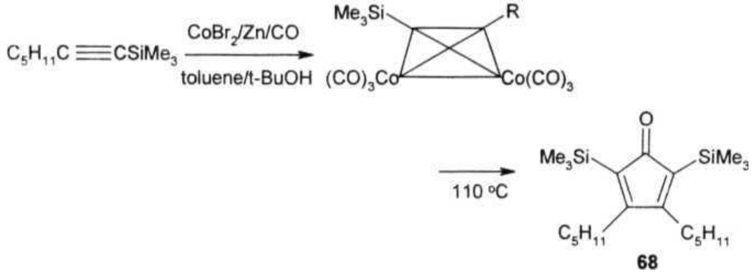
$$R-\!\!\equiv\!\!-H \xrightarrow[Me_3SiCl]{C_2H_5MgBr} R-\!\!\equiv\!\!-SiMe_3$$

67

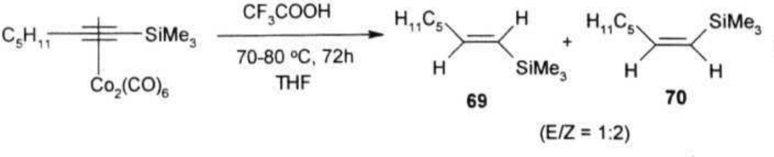
.... [32]

The reaction using $(C_5H_{11}C{\equiv}CSiMe_3)Co_2(CO)_6$ complex was examined in toluene/t-BuOH solvent system at 110 °C for 10h. It was found that the complex decomposed completely during this time. After workup, the product isolated was identified as the cyclopentadienone 68 (Scheme 9).

Scheme 9



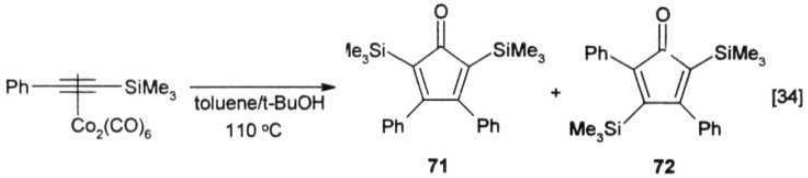
Previously, it was observed in this laboratory that a mixture of E/Z isomers of alkenylsilanes was obtained in the reaction of $(C_5H_{11}C{\equiv}CSiMe_3)Co_2(CO)_6$ complex with excess TFA in THF at 70-80 °C after 72h (eq 33).[30]



[33]

Presumably, the higher temperature and relatively less acidic medium employed under present reaction conditions may be responsible for the difference in the reactivity pattern. The cyclopentadienone formation is not unusual in reactions of alkynylsilanes with $Co_2(CO)_8$ as outlined in the introductory section (eq 8). However, the results obtained are interesting since the reactions are carried out through cobalt carbonyl prepared using simple bench top chemicals at atmospheric pressure of CO. Hence, we have further investigated the reactions using various $(RC{\equiv}CSiMe_3)Co_2(CO)_6$ complexes.

It was found that this transformation is a general one and the corresponding cyclopentadienones are obtained in moderate yields (Table 3).[31] In all cases, the symmetrically substituted cyclopentadienones were obtained except in the reaction using phenyl substituted alkynylsilane. In this case, both symmetrically and unsymmetrically substituted cyclopentadienones are obtained (eq 34).



The positions of phenyl and silyl moieties of the 3,5-diphenyl substituted cyclopentadieone 72 were also confirmed by X-ray crystal structure data analysis (Figure 1). The X-ray crystal structure data of 72 are summarized in Table 2 and Table 2A

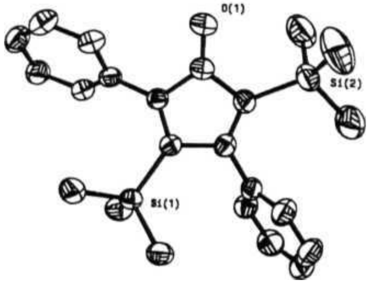


Figure 1. Ortep diagram of 72

Table 2 Crystal data and structure refinement for 72

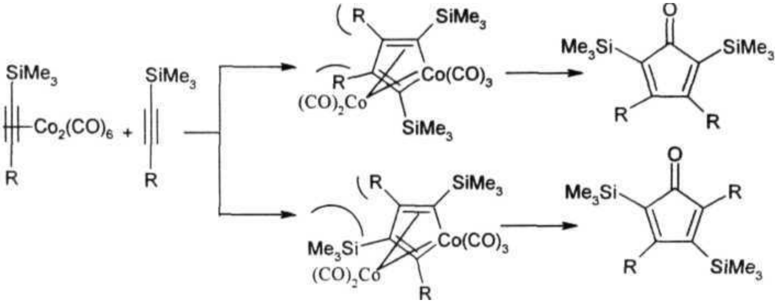
Identification code	72
Empirical formula	$C_{23} H_{28} O Si_2$
Formula weight	376.63
Temperature	293(2) K
Wavelength	0.71073 A
Crystal system	Monoclinic
Space group	P21/C
Unit cell dimensions	a = 11.7391(18) A a = 90.05 deg.
	b = 9.3290(13) A p= 94.042(13) deg.
	c = 20.689(3) A y = 89.99 deg.
Volume	2260.1(6) A^3
Z, Density (calculated)	4, 1.107 Mg/m^3
Absorption coefficient	0.165 mm^{-1}
F(000)	808
Crystal size	0.3 x 0.4 x 0.4 mm
Theta range for data collection	1.74 to 24.98 deg
Index ranges	0<=h<=13, 0<=k<=11, -24<=l<=24
Reflections collected	4151
Independent reflections	3956 [R(int) = 0.0134]
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3956/0/241
Goodness-of-fit on F^2	1.108
Final R indices [I>2sigma(I)]	R1 =0.0409, wR2 = 0.1097
R indices (all data)	R1 =0.0573, wR2 = 0.1303
Largest diff. peak and hole	0.266 and -0.299 e.A^3

Table 2A Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for 72. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor

	x	y	z	U(eq)
Si(1)	4589(1)	2317(1)	713(1)	47(1)
Si(2)	9304(1)	293(1)	1558(1)	66(1)
C(12)	4703(2)	-481(2)	1810(1)	46(1)
C(13)	3958(2)	411(2)	2112(1)	51(1)
C(4)	7078(2)	1510(2)	1067(1)	47(1)
C(3)	5803(2)	1279(2)	1145(1)	44(1)
C(17)	4468(2)	-1946(2)	1784(1)	56(1)
C(2)	5717(2)	126(2)	1532(1)	46(1)
C(14)	2978(2)	-123(3)	2356(1)	61(1)
0(1)	7123(2)	-1564(2)	1983(1)	86(1)
C(6)	7504(2)	2752(2)	709(1)	50(1)
C(5)	7727(2)	499(2)	1379(1)	54(1)
C(16)	3491(2)	-2476(3)	2033(1)	66(1)
C(1)	6898(2)	-479(2)	1678(1)	56(1)
C(8)	7820(2)	5293(3)	638(2)	76(1)
C(11)	8047(2)	2584(3)	142(1)	65(1)
C(7)	7381(2)	4127(2)	950(1)	61(1)
C(19)	4193(2)	3884(3)	1208(1)	68(1)
C(20)	5028(2)	2915(3)	-91(1)	66(1)
C(15)	2746(2)	-1568(3)	2312(1)	68(1)
C(9)	8358(2)	5106(3)	79(2)	83(1)
C(18)	3337(2)	1120(3)	534(1)	69(1)
C(10)	8459(2)	3766(3)	-173(2)	83(1)
C(22)	9552(3)	138(5)	2451(2)	112(1)
C(23)	10132(3)	1852(4)	1296(2)	112(1)
C(21)	9792(3)	-1335(4)	1158(2)	126(2)

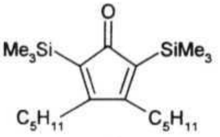
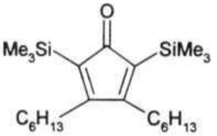
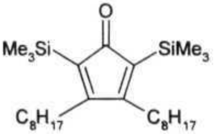
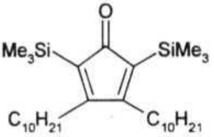
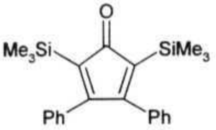
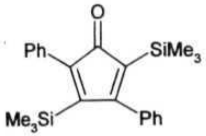
This difference in reactivity may be explained by considering the steric factors. As both phenyl and trimethylsilyl are bulky groups, the reaction is not as selective as with other alkynyl silanes. The transformation can be rationalized by the mechanism shown in Scheme 10.

Scheme 10



Earlier, we have observed that in presence of strong acids such as TFA, **(alkynylsilane)$Co_2(CO)_6$** complexes give alkenyl silanes (eq 31). Since the reactions are carried out in **toluene/t-BuOH**. without strong acids under the present conditions, the olefinic intermediate may not be formed. Presumably, the **(alkynylsilane)$Co_2(CO)_6$** complex may react with decomplexed alkynyl silane to form cyclopentadienone-cobalt carbonyl intermediate. At this **stage,** the steric factors may influence mode of coupling by which the regioselectivity of the product obtained is decided. Later, carbonyl insertion followed by demetallation results in the formation of corresponding cyclopentadienone (Scheme **11**).

Table 3 Reactions of (RC **$CSiMe_3)Co_2(CO)_6$ complexes in** toluene/t-BuOH

alkyne	Product [a,b]	Yield [c]
$C_5H_{11}-\equiv-SiMe_3$	 **68**	40%
$C_6H_{13}-\equiv-SiMe_3$	 **73**	38%
$C_8H_{17}-\equiv-SiMe_3$	 **74**	35%
$C_{10}H_{21}-\equiv-SiMe_3$	 **75**	35%
$Ph-\equiv-SiMe_3$	 **71** +  **72**	15% 30%

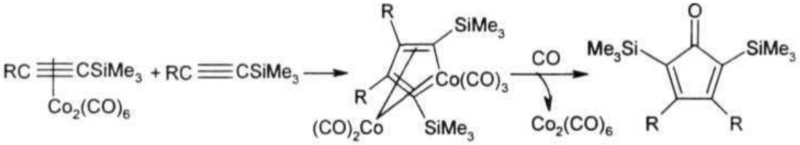
Foot **notes to Table 3**

a) All reactions were carried out using $CoBr_2$ (20 mmol), Zn (20 mmol) and alkyne (10 mmol).

b) The products were identified by IR, ^1H NMR, ^{13}C NMR spectral data and elemental analysis.

c) Yields reported here are for products separated from chromatography on silica gel column using hexane and ethyl acetate as eluent and calculated based on the amount of aikyne used.

Scheme 11



As discussed in the introductory section, the cyclopentadienones are generally isolated as cyclopentadienone metal complexes (eq 6). **Demetallation** of the complexes often lead to dimerisation of cyclopentadienone (eq 7).[12]

Hence, the simple one pot method described here is useful for the synthesis of silyl substituted cyclopentadienone derivatives from alkynes.

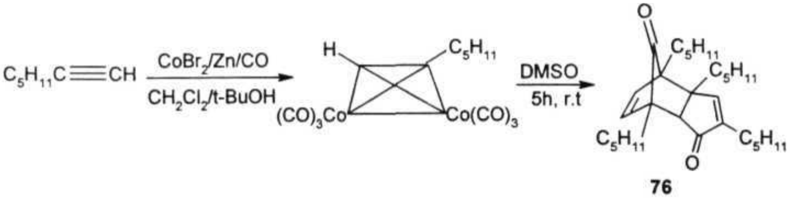
2.2.3 Reactions of $(RC\equiv CH)Co_2(CO)_6$ complexes in CH_2Cl_2/t-BuOH solvent system: Synthesis of dicyclopentadienones

In Chapter 1, the preparation of $(RC\equiv CH)Co_2(CO)_6$ complexes *in situ* in CH_2Cl_2/t-BuOH solvent system and the effect of amines and amides on the Pauson-

Khand reaction with olefins at 25 °C were described. Previously, Pauson ef a/ [40] reported the use of DMSO for a similar purpose. In continuation of the studies described in this chapter so far, we have examined the effect of these promoters on the $(RC\equiv CH)Co_2(CO)_6$ complexes without using an added **olefin**.

Accordingly, the reaction of $(C_5H_{11}C\equiv CH)Co_2(CO)_6$ complex with DMSO was studied at 25 °C for 5h. After workup, the major product formed was identified as the corresponding dicyclopentadienone, besides some amounts of unidentified cobalt complex (Scheme 12).

Scheme 12



76

The **regiochemistry** of dicylopentadienone 76 is assigned based on the proton NMR spectra of the product obtained. **It** shows two doublets at 5.9 and 6.1 **ppm** indicating the presence of two **olefinic** hydrogens present adjacent to each other. Singlet at 6.9 ppm indicating the presence of one olefinic hydrogen without any adjacent hydrogens.

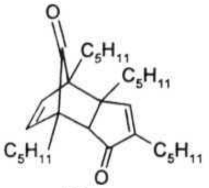
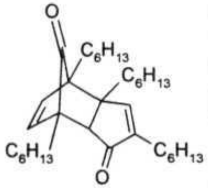
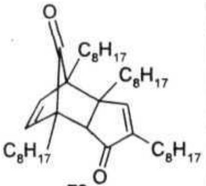
Previously, the formation of cyclopentadienone was reported in the reaction of acetylene with $Co_2(CO)_8$ in DME and **benzene**.[7] This reaction was carried out at 65 °C, for 5 days. Since the dicyclopentadienone is formed under ambient conditions employing the $(alkyne)Co_2(CO)_6$ complexes prepared using $CoBr_2/Zn/CO$, we have investigated this transformation further with different promoters.

Accordingly, we have carried out the reaction with various (alkyne)$Co_2(CO)_6$ complexes in the presence of DMSO, TMEDA and DMF. It was found that this transformation is a general one and the corresponding dicyclopentadienone derivatives are obtained, along with unidentified cobalt carbonyl complexes (Table 4).[31]

It is evident from the Table 4 that the products are obtained only in modest yields. We have made efforts to optimize the conditions to improve the yields of the dicyclopentadienoes by carrying out the reaction of $(C_5H_{11}C{\equiv}CH)Co_2(CO)_6$ with DMSO for longer duration. Even after 24h, the unreacted cobalt carbonyl species still remained Moreover, there was no improvement in the yield of the product obtained under these conditions.

Then, we have focussed attention on the effect of increasing the concentration of promoter. The reaction of $(C_5H_{11}C{\equiv}CH)Co_2(CO)_6$ was carried out using excess DMSO (6 equiv). Even after stirring the reaction mixture at 25 °C for 24h, there was no significance change in the yield of the product.

Table 4 Reactions of (alkyne)$Co_2(CO)_6$ complexes in the presence of promoters

Alkyne	Promoter	Product [a, b]	Yield [c]
$C_5H_{11}C{\equiv}CH$	DMSO	 **76**	20%
$C_6H_{13}C{\equiv}CH$	DMSO	 **77**	18%
$C_8H_{17}C{\equiv}CH$	DMSO	 **78**	16%
$C_5H_{11}C{\equiv}CH$	DMF	**76**	15%
$C_8H_{17}C{\equiv}CH$	TMEDA	**78**	15%

Foot notes to Table 4

a) All reactions were carried out using $CoBr_2$ (20 mmol), Zn (20 mmol), alkyne (10 mmol) and promoter (30 mmol).

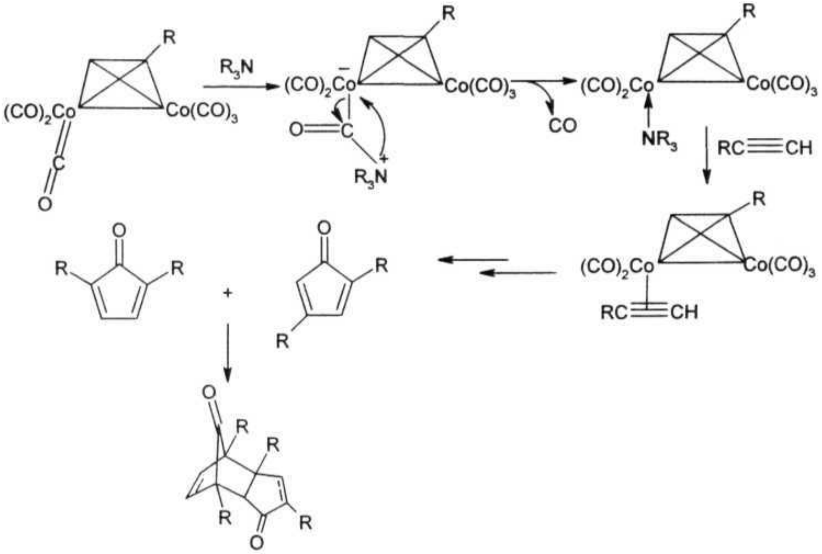
b) The products were identified by IR, ^1H NMR, ^{13}C NMR spectral data and elemental analysis

c) Yields reported here are for products separated by chromatography on a silica gel column using hexane and ethyl acetate as eluent and calculated based on the amount of alkyne used.

The mechanism of this transformation may involve similar steps as considered previously for the Pauson-Khand reaction in the presence of amines (Scheme 13 in Chapter 1).

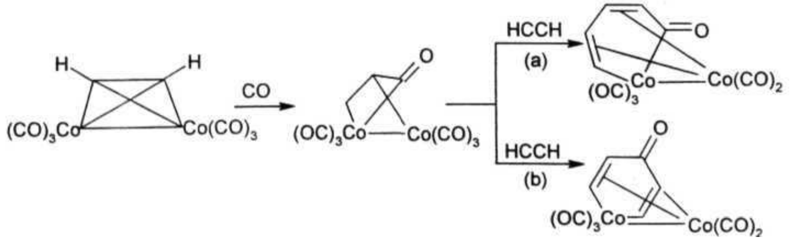
The promoter may create a vacant coordination site in the (alkyne)$Co_2(CO)_6$ complex. Presumably, the decomplexed alkyne may coordinate to the cobalt metal, which after demetallation gives the cyclopentadienone as shown in Scheme 13. Since the coordinating alkyne is unsymmetrical, two regio isomers are possible. Formation of two regio isomers is also observed in the Pauson-Khand reaction carried out using unsymmetrical olefins. Finally, the cyclopentadienones undergo [4+2] cycloaddition resulting in the formation of the corresponding dicyclopentadienone derivative.

Scheme 13

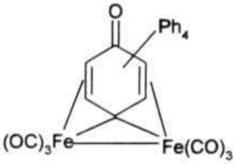


Schore *et al* [7] proposed another possible mechanism for a similar reaction (Scheme 14). Initial insertion of CO in to **(alkyne)$Co_2(CO)_6$** followed by reaction with free alkyne in either of two ways, (a) or (b) and subsequent demetallation would also give the cyclopentadienone.

Scheme 14



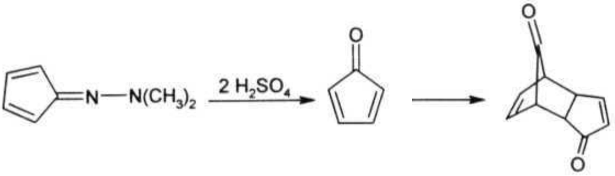
Similar intermediates such as diiron complexes 79 have been isolated in the reaction of $Fe_3(CO)_{12}$ with diphenylacetylene.



79

To trap the intermediate cyclopentadienone, we have carried out several experiments in the presence of dienophiles such as maliec anhydride, crotonaldehyde and dimethyl fumarate. However, these efforts were not successful. In all cases, only the dicyclopentadienones were isolated.

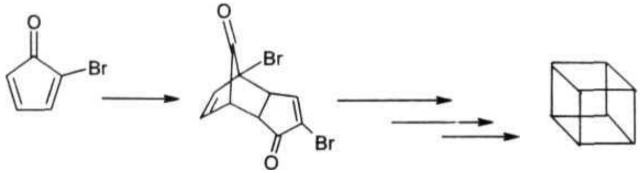
Besides, carbonylation of alkynes (eq 3),[7] such dicyclopentadienone derivatives were previously synthesized by the acid hydrolysis of N,N-dimethyl hydrazone of cyclopentadiene (eq 35).[41]



...... [35]

Some dicyclopentadienone derivatives were used as starting material in the synthesis of cubanes (Scheme 15).[42]

Scheme 15



Accordingly, the present method using alkynes under mild reaction conditions is potentially useful for such synthetic applications. Hence, it may be worthwhile to further examine this reaction to optimize the reaction conditions to obtain better yields.

2.2.4 Conclusions

A novel method for the conversion of alkynes to cyclopentenones in moderate yields has been developed using $CoBr_2$, Zn and CO in toluene/t-BuOH system. The trimethylsilyl substituted alkynes gave the cyclopentadienones under these conditions. In the presence of promoters, such as DMSO and amines, the dicyclopentadienones are obtained.

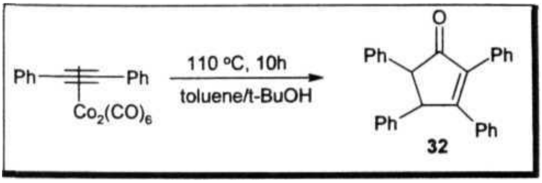
2.3 Experimental Section

2.3.1 General Information

Several informations given in the experimental section of Chapter 1 are also applicable for the experiments outlined here. **Trimethylsilyl** substituted alkynes were prepared following a reported **procedure**.[39] **TMEDA** ,**DMSO** and DMF were supplied by Sisco, India.

2.3.2 Reaction of (PhC- CPh)$Co_2(CO)_6$ complex in toluene/t-BuOH solvent system: A representative procedure

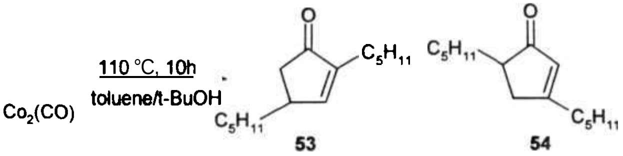
The (PhC≡CPh)$Co_2(CO)_6$ complex was prepared by reducing $CoBr_2$ (4.36 g, 20 mmol) with Zn (1.43 g, 20 mmol) and PhC≡CPh (1. 78 g, 10 mmol) in toluene(50 mL)/t-BuOH(1.5 mL) while bubbling CO with stirring for 5h at 25 °C. An additional amount of t-BuOH (2 mL) was added, and the contents were stirred at 110 °C for 10 h. The cobalt carbonyl species was completely decomposed during this time. The contents were brought to room temperature. Diethyl ether (25 mL) was added and the mixture was washed successively with water (20 mL) and brine solution (10 mL). The combined organic extract was dried over anhydrous $MgSO_4$. The solvent was removed, and the residue was subjected to chromatography on a silica gel column using hexane/ethyl acetate as eluent. The cyclopentenone 32 (50%, 0.95 g) was isolated and identified by IR, ^1H and ^{13}C NMR spectral data. The spectral data obtained for the product 32 (Table 1) are summarized below.



M.P	159-160 °C (Lit. [43] m. p. 161-162 °C)
IR (KBr)	3061,3024, 1952, 1876, 1693, 1628, 1601, 1493, 1149, 754, 694 cm^{-1}
^{1}H NMR	8ppm 3.8 (bs, 1H), 4.6(bs, 1H), 7.1-7.5 (m, 20H)
^{13}C NMR	δppm 57.7, 63.1, 127.0, 127.2, 127.6, 127.8, 128.1, 128.3, 128.4, 129.0, 129.4, 129.8, 131.8, 134.7, 139.3, 140.1, 141.5, 168.9, 205.8 (CO) **(Spectrum number 5)**

The spectral data show 1:1 correspondence with the previously reported data.[30]

The above procedure was followed for the other (alkyne)$Co_2(CO)_6$ complexes and the results are summarised in Table 1. The spectral data obtained for the products are given below.



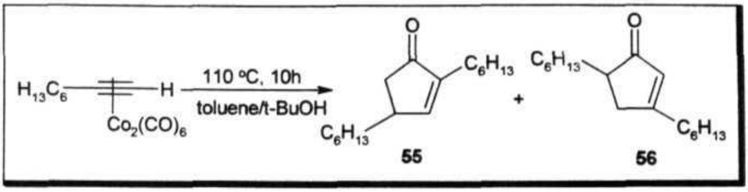
Cyclopentenone 53

Yield	40% (0.44 g)
IR(neat)	2928, 2858, 1707, 1631, 1464, 1379, **1107**, 729 cm^{-1}
^{1}H NMR	8 ppm 0.8-2.6 (m, 25H), 7.1 (bs, 1H)
^{13}C NMR	δppm 13.8, 22.4, 24.7, 26.8, 27.3, 31.5, 31.7, 33.4, 45.4,
	145.7(quatenary), **155.4** ,211.5 (CO) **(Spectrum number 6)**

Cyclopentenone 54

Yield	10% (0.11 g)
IR(neat)	2928, 2860, 1701, 1618, 1464, **1174,** 868, 727 cm^{1}
^{1}H NMR	δ ppm 0.8-2.8 (m, 25H), 5.9 (bs, 1H)
^{13}C NMR	8 ppm 13.9, 22.3, 22.4, 26.7, 26.8, 31.4, 31.7, 33.4, 38.3, **46.2,** 128.7,
	181.5 (quatenary), **212.1 (CO)** **(Spectrum number 7)**

The spectral data of 53 and 54 show 1:1 correspondence with the previously reported **data**.[30]



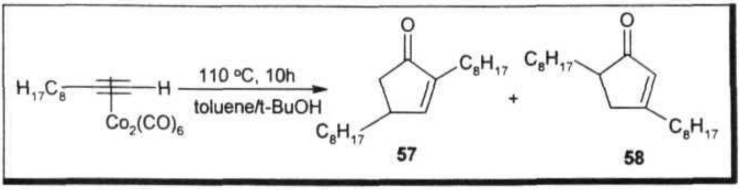
Cyclopentenone 55

Yield	38% (0.47 g)
IR(neat)	2928, 2858, 1707, 1631, 1464, 1379, 1107, 729 cm^1
^{1}H NMR	6ppm 0.8-2.6 (m, 29H), 7.1 (bs, 1H)
^{13}C NMR	6ppm 13.8, 22.3, 24.8, 26.9, 27.4, 29.0, 31.3, 31.4, 32.2, 33.1, 50.1, 145.5(quatenary), 154.8, 210.5 (CO)

Cyclopentenone 56

Yield	12% (0.15g)
IR (neat)	2928, 2860, 1701, 1618, 1464, 1174, 868, 727 cm^{-1}
^{1}H NMR	5 ppm 0.8-2.8 (m, 29H), 5.9 (bs, 1H)
^{13}C NMR	6 ppm 13.9, 22.5, 27.0, 27.1, 28.9, 29.2, 31.4, 31.6, 33.4, 38.2, 46.2, 128.7, 181.2 (quatenary), 211.8 (CO)

The spectral data of 55 and 56 show 1:1 correspondence with the previously reported data [3(]



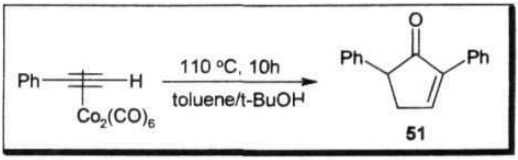
Cyclopentenone 57

Yield	39% (0.59 g)
IR (neat)	2926, 2854, 1709, 1464, 1377, 721 cm ^{1}
^{1}H NMR	5 ppm 0.8-2.5 (m, 37H), 7.1(bs, 1H)
^{13}C NMR	5 ppm 14.0, 22.6, 24.6, 27.6, 27.8, 29.2, 29.5, 29.6, 31.8, 35.2, 38.8, 41.7, 145.7 (quatenary), 161.0, 209.2 (CO)

Cyclopentenone 58

Yield	10%(0.15 g)
IR (neat)	2924, 2854, 1705, 1616, 1466, 1176, 1074, 798, 721 cm'
^{1}H NMR	8 ppm 0.8-2.6 (m, 37H), 5.9 (bs, 1H)
^{13}C NMR	δ ppm 14.0, 22.6, 23.0, 25.2,29.4, 29.6, 29.7, 31.4, 31.8, 32.5, 38.2, 46.2, 128.8, 181.8 (quaternary), 212.4 (CO)

The spectral data of 57 and 58 show 1:1 correspondence with the previously reported data.



Cyclopentenone 51

Yield	38% (0.44 g)
M.P.	75 °C (Lit.[44] m. p. 75-76 °C)
IR (KBr)	3061, 3026, 1693, 1599, 1494, 1118, 758, 696 cm^{-1}
^1H NMR	6 ppm 2.8-2.9 (m, 1H), 3.2-3.4 (m, 1H), 3.8 (m, 1H), 7.2-8.0 (m, 11H)
^{13}C NMR	δ ppm 36.0, 52.5, 127.0, 127.1, 127.7, 128.5, 128.8, 131.6, 139.6, 142.4 (quaternary), 157.5, 206.3 (CO) **(Spectrum number 8)**

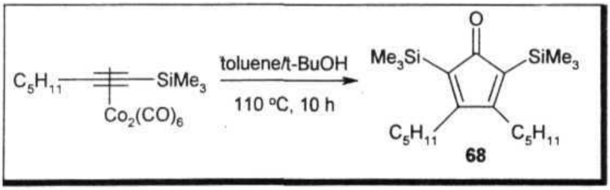
The spectral data of 51 show 1:1 correspondence with the previously reported data.[30]

2.3.3 The reactions of (RC CSiMe$_3$)Co$_2$(CO)$_6$ complexes in toluene/t-BuOH

The ($C_5H_{11}C{\equiv}CSiMe_3$)$Co_2(CO)_6$ complex was prepared by reducing $CoBr_2$ (4.36 g, 20 mmol) with Zn (1.43 g, 20 mmol) and $C_5H_{11}C{\equiv}CSiMe_3$ (1.68 g, 10 mmol) in toluene (50 mL)/t-BuOH (1.5 mL) while bubbling CO with stirring for 5h at 25 °C. An additional amount of t-BuOH (2 mL) was added, and the contents were stirred at 110

°C for 10 h. The cobalt carbonyl species was completely decomposed during this time. The contents were brought to room temperature. Diethyl ether (25 mL) was added and the mixture was washed successively with water (20 mL) and brine solution (10 mL). The combined organic extract was dried over anhydrous $MgSO_4$ The solvent was removed, and the residue was subjected to chromatography on a silica gel column using hexane/ethyl acetate as eluent.

The cyclopentadienone 68 (40%, 1.45g) was isolated and identified by IR, ^1H, and ^{13}C NMR spectral data. The spectral data obtained for the product 68 (Table 3) are summarized below. The above procedure was followed for other $(RC{\equiv}CSiMe_3)Co_2(CO)_6$ complexes and the results are summarized in Table 3. The cyclopentadienones were identified by IR, ^1H NMR, ^{13}C NMR, mass spectra and elemental analysis data. The spectral data obtained for the products are given below.

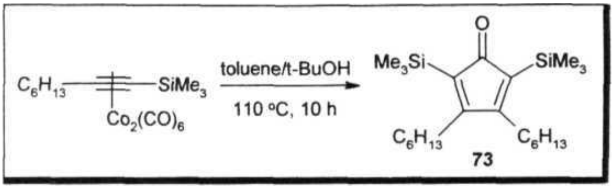


Yield	40% (1.45 g)
IR (neat)	2954, 2854, 1684, 1466, 1261, 798, 721 cm^{-1}
^1H NMR	8 ppm 0.2 (s, 9H), 1-2.5 (m, 11H)
^{13}C NMR	5ppm 0.060, 13.9, 22.4, 28.3, 30.4, 32.3, 128.2, 172.8, 210.8 (CO)
MS (m/z)	366

Anal. **Calcd.for $C_{21}H_{40}Si_2O$**

Calcd C, 69.23%, H, 10.98%

Found C, 69.28%, H, 11%



Yield 38% (1.48 g)

IR (neat) 2954, 2854, 1684, 1466, 1261, 798, 721 cm^{1}

^{1}H NMR δppm 0.2 (s, 9H), 1-2.5 (m, 13H)

^{13}C NMR δppm 0.015, 13.8, 22.5, 28.3, 29.7, 30.6, 31.5, 128.2, 172.6, 210.7 (CO)

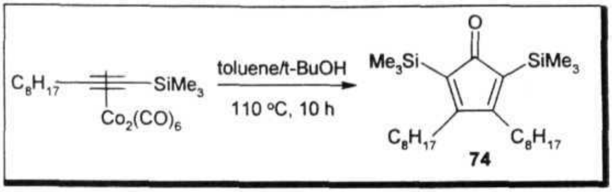
(Spectrum number 9)

MS (m/z) 392 **(Spectrum number 10)**

Anal. **Calc.** for $C_{23}H_{44}Si_2O$:

Calcd C, 70.40%, H, 11.20%

Found C, 70.45%, H, 11.26%



74

Yield 38% (1.70 g)

IR (neat) 2954, 2854, 1684, 1466, 1261, 798, 721 cm^{-1}

^{1}**H** NMR 6ppm 0.2 (s, 9H), 1-2.5 **(m, 17H)**

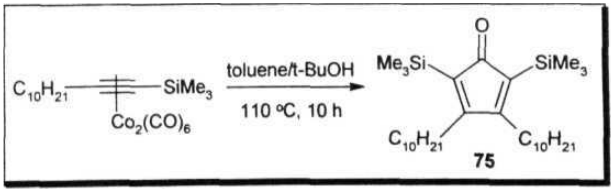
^{13}**C NMR** δ**ppm** 0.059, 14.0, 22.6, 28.4, 29.1, 29.3, 30.1, 30.7, 31.8, 125.3,172.3, **210** (CO)

MS (m/z) 449

Anal. **Calc**. for $C_{27}H_{52}Si_2O$

Calcd: C, 72.30%, H, **11.60%**

Found: C, 72.35%, H, **11.65%**



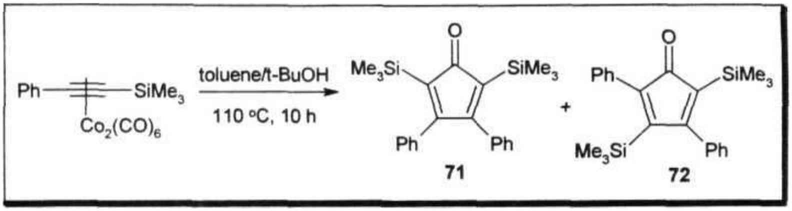
75

Yield 35%(1.76g)

IR (neat) 2954, 2854, 1684, 1466, 1261, 798, 721 cm^{-1}

^{1}**H NMR** Sppm 0.2 (s, 9H), 1-2.5 **(m,** 21H)

^{13}C NMR δppm 0.112, 14.0, 22.7, 28.4, 28.8, 29.1, 29.3, 29.5, 30.1, 30.8, 31.9, 125.3, 172.7, 210.9 (CO)



Cyclopentadienone 71

Yield 15% (0.56 g)

M. P **128 °C (Lit.[9] m. p. 128 °C)**

IR (KBr) **3061, 3024**, 1685,1628, 1440, 754, 694 cm^{-1}

^{1}H NMR δppm 0.3 (s, 9H), 7.2-7.4 (m, 5H) **(Spectrum number 11)**

^{13}C NMR δppm -0.11, 127.4, 128.0, 128.2, 130.1, 135.7, 171.1, 209.9 (CO) **(Spectrum number 12)**

Cyclopentadienone 72

Yield 30% (1.12 g)

M.P **144 °C (Lit.[9] m. p. 145** °C)

IR (KBr) **3061**, 3024, 1687, 1628,1440, 754,694 cm^{-1}

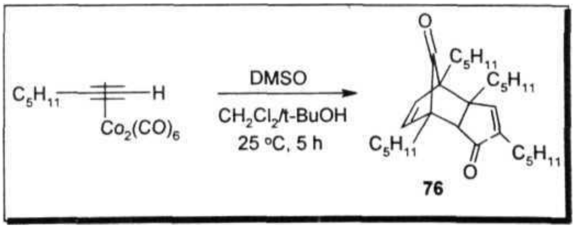
^{1}H NMR δ ppm -0.3 (s, 9H), 0.0 (s, 9H), 7.2-7.4 (m, 10H)

^{13}C NMR δppm -0.20, 0.39, 125.2, 127.2, 127.7, 128.0, 128.1, 128.3, 129.9, 133.7, **139.6, 145.1, 155.0, 176.6, 206.6 (CO)**

The structural assignment of 72 was further confirmed by X-ray crystallographic data (Figure 1).

2.3.4 Reaction of $(C_5H_{11}C\equiv CH)Co_2(CO)_6$ complex in the presence of DMSO in CH_2Cl_2/t-BuOH:

The $(C_5H_{11}C\equiv CH)Co_2(CO)_6$ complex was prepared by reducing $CoBr_2$ (4.36 g, 20 mmol) with Zn (1.43 g, 20 mmol), and 1-heptyne (1.3 mL, 10 mmol) in CH_2Cl_2 (50 mL) and t-BuOH (1.5 mL) while bubbling CO with stirring for 5h at 25 °C. The DMSO (30mmol, 2.1 mL) was added and the contents were stirred for 5h at 25 °C. The mixture was washed successively with dil. HCl (20 mL), water (2x20 mL) and brine solution (10 mL). The organic extract was dried over anhydrous $MgSO_4$. The solvent was removed and the residue was subjected to chromatography on a silica gel column using hexane/ethyl acetate as eluent. The dicyclopentadienone 76 (20%, 0.88 g) was isolated and identified by IR, ^{1}H NMR, ^{13}C NMRand DEPT experiments, mass spectral data and elemental analysis. The spectral data obtained for the dicyclopentadienone 76 (Table 4) are summarized below.

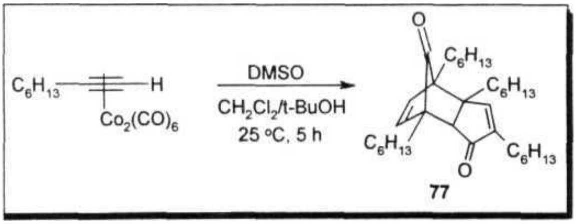


Yield	20% (0.88 g)
IR (neat)	2954, 2870, 1774,1701,1464, 1174,868, 727 cm"^{1}
^{1}H NMR	8ppm 0.5-2.5 **(m, 44H),** 3.1 (s, 1H), 5.9 (d, J=20Hz, 1H), 6.1 (d, J=20Hz, 1H), 6 9 (s, 1H) **(Spectrum number 13)**

^{13}C NMR 8ppm 13.9, 22.4, 23.0, 24.9, 25.2, 25.4, 25.5, 27.1, 27.5, 30.2, 31.4, 32.3, 32.5, 51.0, 55.6, 58.2, 61.8, 132.1, 133.0, 153.2, 154.6, 204.8, 208.6. **(Spectrum number 14)**

MS (m/z) 412 (-CO)

The above procedure was followed for other **(alkyne)Co$_2$(CO)$_6$** complexes and the results are summarized in Table 4. The spectral data obtained for the products are given below.



77

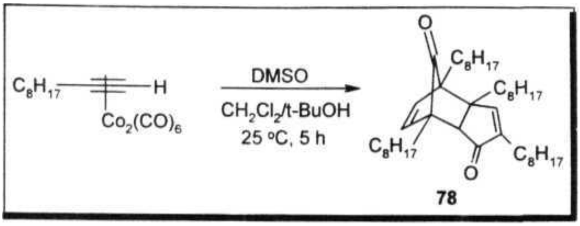
Yield 18% (0.89 g)

IR (neat) 2954, 2870, 1772, 1701, 1464, 1174, 868, 727 cm^{1}

^{1}H NMR 6ppm 0.5-2.5 (m, 52H), 3.1 (s, 1H), 5.9 (d, J=20Hz 1H), 6.1 (d, J=20Hz, 1H), 6.9 (s, 1H)

^{13}C NMR 5ppm 14.03 (-CH$_3$), 22.5, 23.1, 24.9, 25.5, 25.7, 25.8, 27.2, 27.8, 28.9, 29.8, 30.0, 30.3, 31.6 (-CH$_2$), 51.0 (-CH), 55.6, 58.3, 61.9 (quaternary), 132.1,133.0, 153.2 (-CH), 154.6 (quaternary), 204.9, 208.7 (CO)

MS (m/z) 469 (-CO)



78

Yield 16% (0.97 g)

IR (neat) 2950, 2870, 1772, 1703, 1464, 1174,868, 727 cm^{-1}

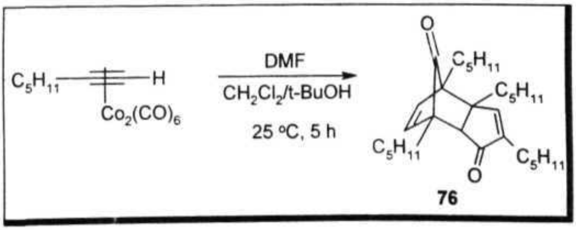
^{1}H NMR 5ppm 0.5-2.5 (m, 68H), 3.1 (s, 1H), 5.9 (d, J=20Hz, 1H), 6.1 (d, J=20Hz, 1H), 6.9 (s, 1H)

^{13}C NMR 6ppm 14.0, 22.6, 23.0, 24.9, 25.5, 25.7, 25.8, 27.2, 27.8, 29.2, 30.1, 30.3, 31.8, 51.0, 55.6, 58.2, 61.8, 132.1, 133.0, 153.1, 154.6, 204.8, 208.6

Anal. Cald for $C_{42}H_{72}O_2$:

Calcd: C, 82.8%, H, 11.8%

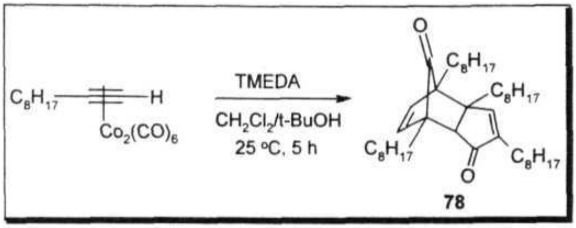
Found: C, 83.2%, H, 11.8%



76

Yield 15% (0.66 g)

The spectral data were identical to the data of 76 obtained in the previous experiment.



Yield 15% (0.90 g)

The spectral data were identical to the data of 78 obtained in the previous experiment.

2.4 References

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Chapter 3

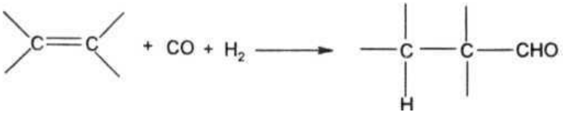
Synthetic applications of the cobalt carbonyl species prepared using $CoBr_2$/Zn/CO system for hydroformylation and related reactions

3.1 Introduction

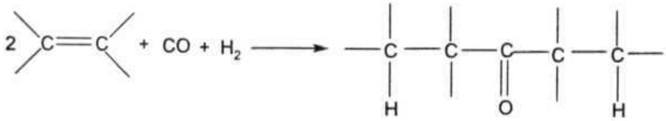
The investigations described in this chapter emerged from the results reported in Chapter 2. We have proposed that the reduced cobalt carbonyl species such as $HCo(CO)_4$ is responsible for the formation of cyclopentenones in the reaction of alkynes with $CoBr_2$, Zn and CO in toluene/t-BuOH mixture at 110 °C (Scheme 7, Chapter 2). Accordingly, we decided to explore the preparation of HCo(CO)< using $CoBr_2$/Zn/CO/t-BuOH for synthetic applications. It may be of interest to briefly review the reports on this topic.

The $HCo(CO)_4$ reagent secured its place in the history of chemistry because of its role in many commercially important chemical reactions. It is an intermediate in the important hydroformylation reaction of olefins with H_2 and CO catalyzed by $Co_2(CO)_8$ The hydrofromylation or oxo reaction is one of the oldest carbonylation reactions, discovered by Roelen in 1938 while investigating the origin of the oxygenated compounds present in the products of the Fischer-Tropsch (FT) synthesis.[1] Industrially, it is still the most important carbonylation reaction. Also, it is the reaction that has been most extensively investigated.

The oxo reaction involves the synthesis of carbonyl compounds from olefins, CO and H_2 (eq 1 and 2). However, the aldehyde synthesis is mucn more important than the ketone synthesis.



[1]

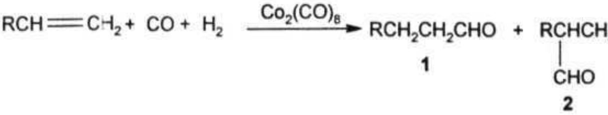


[2]

The only **hydroformylation** of industrial significance is restricted to olefinic hydrocarbons. Propene represents the most widely employed **olefin**.[2] The main product of the reaction, **n-butanal**, is subsequently hydrogenated to **n-butanol** or condensed to give **2-ethylhexanol**, the largest single product of hydroformylation **chemistry**.[3] Several excellent reviews have appeared on this **subject**.[4 5]

Although a number of transition metal complexes have been stated to catalyze the hydroformylation reaction, the cobalt derivatives are still the most widely used in industry. Although, initially heterogeneous catalysts were employed,[16] it was soon realized that the reaction could be catalyzed in the homogeneous phase by cobalt compounds soluble in the reaction medium. The cobalt carbonyls mainly $Co_2(CO)_8$ and cobalt hydrocarbonyl, $HCo(CO)_4$ play important roles in the catalysis.[7] Hydroformylation of olefins was also successfully achieved by using **stoichiometric** amounts of $HCo(CO)_4$ (eq 3) [8] or $Co_2(CO)_8$ and H_2 (eq 4).[9]

$$Co_2(CO)_8 + H_2 \rightleftharpoons HCo(CO)_4 \quad \cdots\cdots\cdots [3]$$

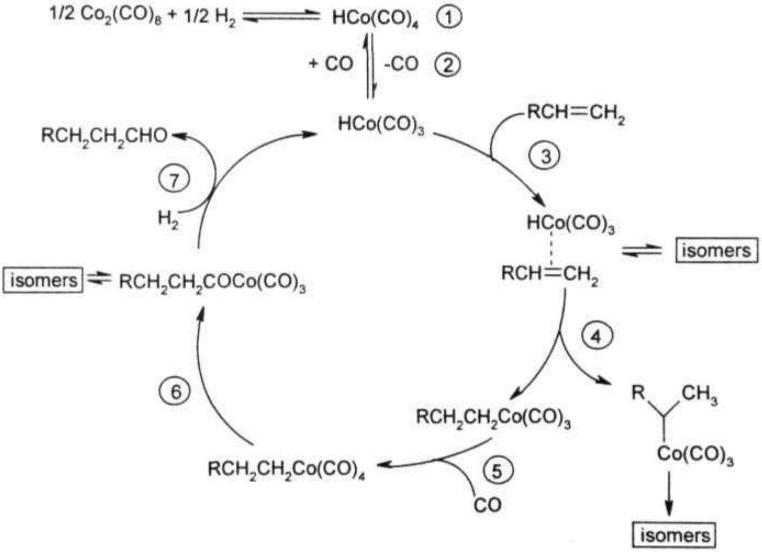


$$RCH{=}CH_2 + CO + H_2 \xrightarrow{Co_2(CO)_8} \underset{\mathbf{1}}{RCH_2CH_2CHO} + \underset{\mathbf{2}}{\underset{\displaystyle CHO}{RCHCH_3}} \quad [4]$$

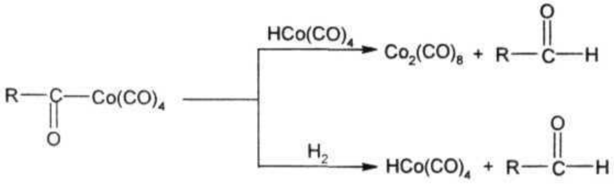
The handling of $HCo(CO)_4$ is difficult because of its instability at room temperature. The stoichiometric use of $Co_2(CO)_8$ requires high H_2 pressures. However, the latter method contributed much to present knowledge of the reaction mechanism.

In the early 1960s, Heck and Breslow formulated the generally accepted hydroformylation cycle depicted in Scheme 1.[10]

Scheme 1



Two possibilities are generally considered for the formation of aldehydes from the acylcobalt carbonyl species (eq 5).[11]

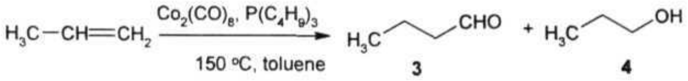


……[5]

It was observed that the reaction of the acylcobalt complex with $HCo(CO)_4$ is a minor pathway and the reaction with H_2 dominates the catalytic cycle in the hydroformylation of 1-octene and cyclohexene. On the other hand, another group reported that the hydridocobalt complex reacts 12 times faster with the acylcobalt complex than does hydrogen.[5e]

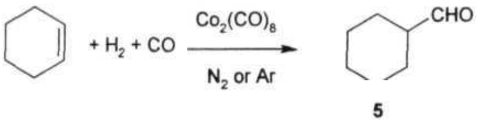
One of the main drawbacks of the hydroformylation reaction in synthetic organic chemistry is the simultaneous production of two or more isomeric aldehydes. The importance of controlling the isomeric composition of products, therefore, can hardly be overemphasized. Moreover, it is difficult to separate the isomers. Since the n-isomer has more industrial applications over other isomers, there have been several modifications to achieve selective formation of n-alkanals. It was observed that the Co catalyst containing phosphine ligands have more n-selectivity (70-90%).[12]

The influence of the reaction variables on the isomeric distribution of the aldehydes and alcohols obtained in the hydroformylation of propene using $Co_2(CO)_6[P(C_4H_9)_3]_2$ was studied.[13] It was observed that the pressure of CO has a greater influence than the other variables on the reaction product composition (eq 6).



[6]

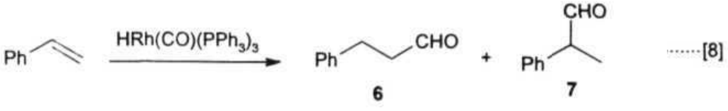
Also, the rate of hydroformylation of cydohexene using $Co_2(CO)_8$ was strongly reduced by the presence of inert gases such as nitrogen or argon, under high pressure, other conditions being kept constant (eq 7).[14]



..... [7]

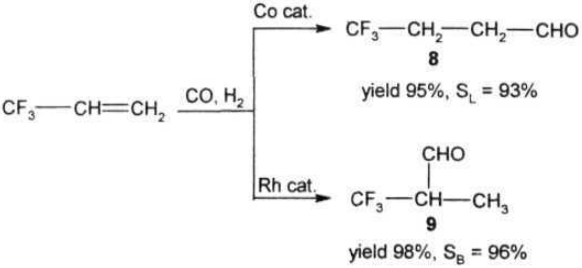
Apart from cobalt, rhodium is also employed in hydroformylation reaction. These catalysts are of particular interest because of their activities are 10^2 to 10^4 times greater than that of cobalt hydridocarbonyls.[4] The Rh catalyzed hydroformylation of olefins occurs under mild conditions compared to the corresponding reaction with cobalt catalysts.[15]

Aryl substituted olefins when hydroformylated in presence of Rh catalysts, give the expected aldehydes in very good yields. For example, styrene forms 2-phenylpropanal and 3-phenylpropanal in almost equal amounts when operating at high temperature and pressure (eq 8).[16] However, 2-phenylpropanal predominates (90%) when operating at room temperature and atmospheric pressure.[17]

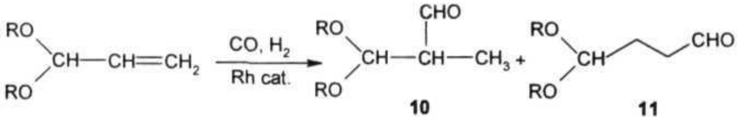


Many olefinic compounds containing functional groups such as esters, alcohols, nitriles and acetals have been successfully hydroformylated.[18] However, no commercial processes employing these substrates are operative The olefins containing halogen atoms have been hydroformylated using Co, Rh catalysts.[4a] The aldehydes produced in this case are unstable and hence, more difficult to obtain in pure form. Hydroformylation of 3,3,3-trifloropropene gives the corresponding aldehydes 8 and 9 (Scheme 2).[19]

Scheme 2



The hydroformylation of unsaturated acetais, catalyzed mainly by Rh catalysts, has received much attention. It has been observed that the acrolein acetais are smoothly converted to both methylmalonaldehyde and succinaldehyde monoacetals by the reaction with CO and H_2 under various conditions (eq 9).[20]

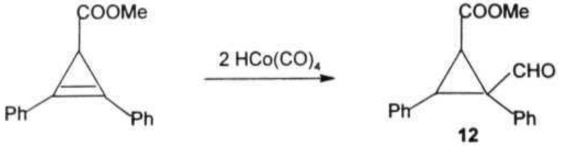


[9]

Hydroformylation reaction of olefins containing alcohol, ether, cyano, amide and imide moities were also reported.[18]

Other synthetic applications of $HCo(CO)_4$

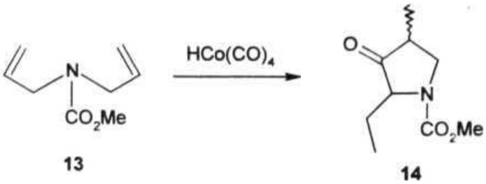
It has been observed that the reaction of $HCo(CO)_4$ with cyclopropene carboxylate gives formyl cyclopropane carboxylates in 18-22% yield besides hydrogenated products (eq 10).[21]



12

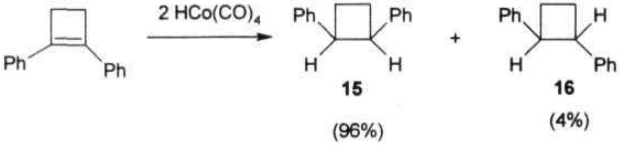
..... [10]

The hydroformylation of the olefinic amine derivatives are catalyzed by both Co and Rh complexes.[22] For example, N-acetyl carbomate 13 on reaction with $HCo(CO)_4$ give the corresponding pyrrolidine 14 in 45% yield (eq 11).



...... [11]

Apart from **hydroformylation**, $HCo(CO)_4$ is also used for several other organic transformations. For example, Orchin *et al* [23] observed that the reaction of 1,2-**diphenyl-1-cyclobutene** with stoichiometric amounts of $HCo(CO)_4$ gives about 30% of conversion to **1,2-diphenylcyclobutanes** consisting of 96% cis and 4% trans isomers (eq 12).

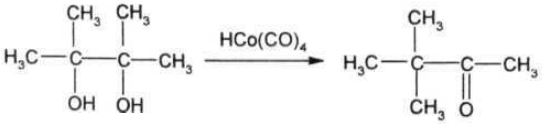


.....[12]

Also, the $HCo(CO)_4$ is used for **homologation** of alcohols. For example, benzyl alcohols under oxo conditions gave β-**phenyl** ethyl alcohol (eq 13).[24] This homologation reaction is an acid, $HCo(CO)_4$ catalyzed reaction that proceeds via **carbonium** ion formation.

$$PhCH_2OH \xrightarrow{HCo(CO)_4} \underset{\mathbf{17}}{PhCH_2CH_2OH} \qquad \cdots\cdots [13]$$

Also, the pinacol under catalytic oxo conditions gives pinacolone besides side products (eq 14).[25] In this reaction, $HCo(CO)_4$ behaves as a strong acid.



$$(CH_3)_2C(OH){-}C(OH)(CH_3)_2 \xrightarrow{HCo(CO)_4} H_3C{-}C(CH_3)_2{-}C(=O){-}CH_3 \quad ......[14]$$

18

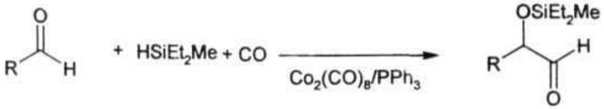
The property of $HCo(CO)_4$ as an acid is also revealed in several other reactions. For example, the triphenyl carbinol on treatment with $HCo(CO)_4$ in acetone solution at room temperature gives **triphenylmethane** (eq 15).[26]

$$\underset{}{Ph_3C{-}OH} \xrightarrow{HCo(CO)_4} \underset{\textbf{19}}{Ph_3C{-}Co(CO)_4} \xrightarrow{HCo(CO)_4} \underset{\textbf{20}}{Ph_3CH} + Co_2(CO)_8 \quad \cdots\cdots[15]$$

The $HCo(CO)_4$ is also used for hydrogenation of aldehydes. It has been observed that the reaction of **monomeric** formaldehyde with $HCo(CO)_4$ at 0 °C in the presence of CO (1 atm) leads to the formation of glycoaldehyde in high yield (eq 16).[27]

$$HCHO + HCo(CO)_4 \xrightarrow[0\ ^{\circ}C,\ CH_2Cl_2]{CO\ (1\ atm)} \underset{\textbf{21}}{HOCH_2CHO} \quad \cdots\cdots[16]$$

Later, it has also been reported that the aldehydes are converted to higher a-siloxy aldehydes by hydrosilane and CO in presence of $Co_2(CO)_8$ and Ph_3P (eq 17).[28]



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....[17]

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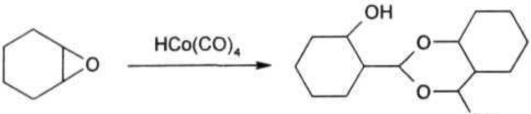
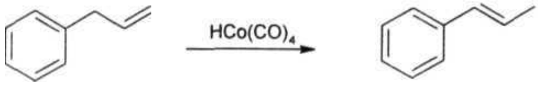


24

.....[19]

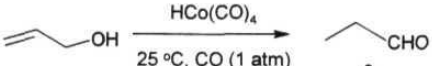
Another application of $HCo(CO)_4$ is for isomerization of olefins. It was reported that the $HCo(CO)_4$ catalyzes the isomerization of allylbenzene to trans-propenylbenzene (eq 20).[31]



25

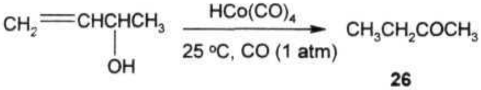
······[20]

The $HCo(CO)_4$ was also employed for **isomerization** of allylalcohols to carbonyl compounds. The simple allylalcohol is isomerized to propanaldehyde and secondary alcohol to the corresponding ketone in moderate yields (eq 21 and **22**).[32]



3

······· [21]



$$CH_2{=}\underset{\displaystyle OH}{\underset{|}{C}H}CH_3 \xrightarrow[25\ ^\circ C,\ CO\ (1\ atm)]{HCo(CO)_4} CH_3CH_2COCH_3$$

26

······ [22]

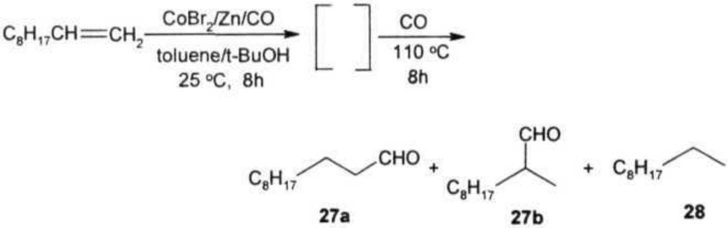
We have proposed that the hydrido cobalt carbonyl species is produced *in situ* in the carbonylation of alkynes in Chapter 2. Since $HCo(CO)_4$ is a well known catalyst for the hydroformylation reactions of olefins, we have examined the reactivities of the species prepared in this way with **olefins** The results are described in this chapter.

3.2 Results and Discussion

3.2.1 Reactions of olefins with the cobalt carbonyl species prepared using $CoBr_2$, Zn and CO

We have observed that 1-decene reacts with the cobalt carbonyl species, prepared using $CoBr_2$ Zn and CO in toluene/t-BuOH solvent system at atmospheric pressure, when heated at 110 °C for 8h under CO atmosphere. After workup, a mixture of aldehydes 27a and 27b was isolated in 40% yield along with the hydrogenated product decane in 30% yield (Scheme 3).

Scheme 3



The formation of aldehydes is though not unusual, is important because usual cobalt carbonyl catalyzed hydroformylation reactions are generally carried out using CO and H_2 at high pressure. Here, we have obtained the products without using hydrogen at atmospheric pressure of CO. So, we have decided to investigate this transformation further with various acylic and cyclic olefins. In the case of acyclic terminal olefins, a mixture of isomeric aldehydes (n- and iso-) was obtained. In the reactions with cyclic olefins only one isomer was obtained. In all acyclic olefins, 25-30% of corresponding alkanes are also formed. However, the aldehydes can be readily separated from this side product by column chromatography. The results are summarized in Table 1.

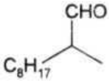
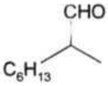
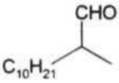
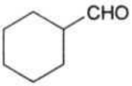
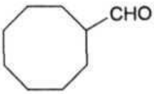
We have also examined the reactions using olefins substituted with aromatic group. Initially, we have carried out experiments using styrene. Only traces of aldehyde was obtained besides ethylbenzene as a major product (75%). In the case of α-methylstyrene, isopropylbenzene (cumene) was obtained in high yield (70%). The formation of hydrogenated product in high yields is not unusual since the cobalt carbonyl catalyzed hydroformylation reactions also give these side products.[4b]

As discussed in the introductory section, the mechanism of hydroformylation reaction is still unclear. The present transformation takes place in the absence of hydrogen. Orchin[33] reported a catalytic cycle in the oxo reaction, which involves the formation and regeneration of $HCo(CO)_4$. The olefin receives both the hydrogen and CO for aldehyde formation from the $HCo(CO)_4$ (eq 23).

$$2HCo(CO)_4 + RCH{=}CH_2 + CO \longrightarrow \underset{\mathbf{1}}{RCH_2CH_2CHO} + \text{isomers} + Co_2(CO)_8 \ \ldots\ldots \ [23]$$

The formation of $HCo(CO)_4$ under the present conditions may be tentatively rationalized as shown in Scheme 4.

Table 1 Hydroformylation reactions of olefins in toluene/t-BuOH

No.	olefin	product[a,b]	n : i[c]	yield[d]
1	$C_8H_{17}CH{=}CH_2$	 **27a** +  **27b**	1:1	40%[e]
2	$C_6H_{13}CH{=}CH_2$	 **29a** +  **29b**	1:1	35%[f]
3	$C_{10}H_{21}CH{=}CH_2$	 **30a** +  **30b**	1:1	38%[g]
4		 **5**		28%
5		 **31**		30%

a) All reactions were carried out using $CoBr_2$ (20 mmol), Zn (20 mmol) and olefin (10 mmol).

b) The products were identified by IR, ^1H NMR and ^{13}C NMR spectral data and comparison with the reported data.

c) The ratio of isomers was determined by ^1H NMR spectral data.

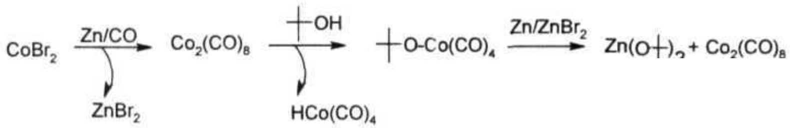
d) Yields reported here are for products separated from chromatography on silica gel column using hexane and ethyl acetate as eluent and calculated based on the amount of olefin used.

e) Decane was also obtained in 30% yield.

f) Octane was also obtained in 25% yield.

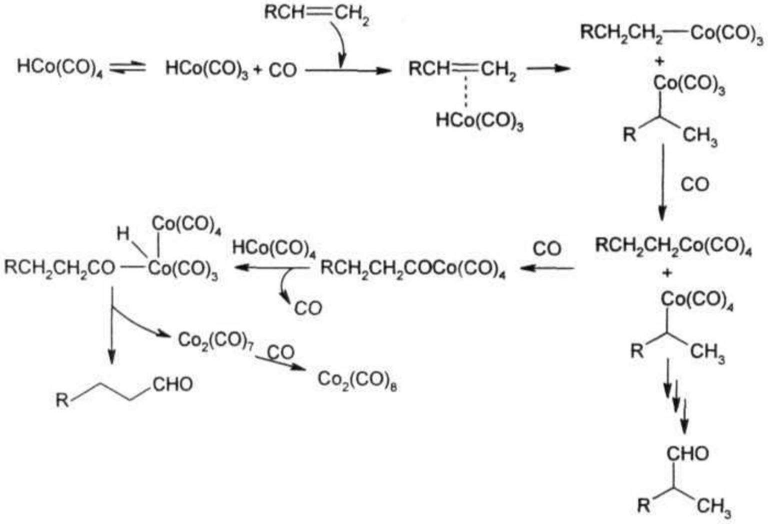
g) Dodecane was also obtained in 30% yield.

Scheme 4



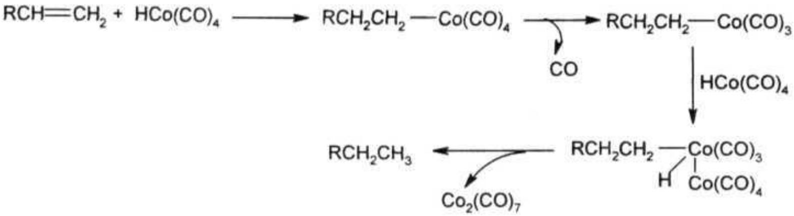
The reaction can be tentatively explained considering the mechanism shown in Scheme 5.

Scheme 5



Generally, the $HCo(CO)_3$ is postulated [10b] to exist in equilibrium with the $HCo(CO)_4$. Since the tricarbonyl species is coordinatively unsaturated, it can form a it-**complex** with olefin (Scheme 5).

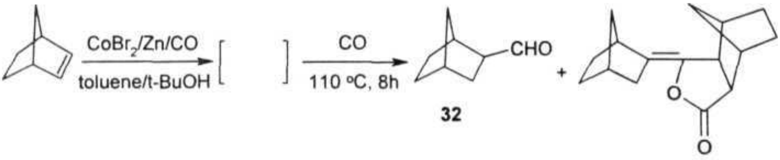
The hydrogenation of the olefin results in the saturated hydrocarbon through the reaction of alkylcobalt species with $HCo(CO)_4$. This is a parallel reaction which results in an irreversible decrease in **yield**.[34,35] Under the present reaction conditions, $HCo(CO)_4$ may be the source for the hydrogen. Formation of this side product can be explained by the mechanism shown in Scheme 6.



3.2.2 Reaction of norbornylene with $CoBr_2$/Zn/CO in toluene/t-BuOH solvent system

In the reaction of norbornylene with $CoBr_2$, Zn and CO, the formation of enol lactone 33 was observed as a side product along with the aldehyde 32 (Scheme 7)

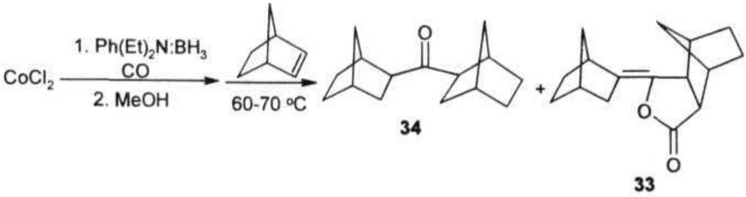
Scheme 7



32

33

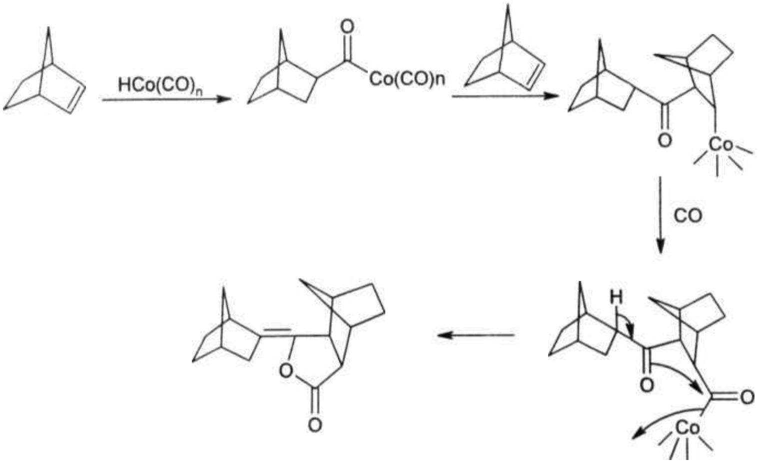
Earlier, it was observed in this laboratory that the cobalt carbonyl species prepared using $CoCl_2$, $NaBH_4/Ph(Et)_2N{:}BH_3$ in the presence of CO and methanol, gives the dialkyi ketone 34 and enol lactone 33 (eq 24).[36]



...[24]

Presumably, in this case the $HCo(CO)_4$ formed *in situ,* reacts with norbornylene by migratory insertion of CO followed by carbometallation to give the enol lactone as shown in Scheme 8

Scheme 8



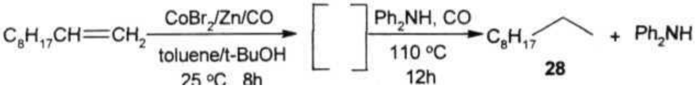
3.2.3 Studies on the effects of additives on the hydroformylation reaction

As mentioned in the introductory section, certain ligands containing phosphorus or arsenic have been employed to increase the selectivity of n-isomer of aldehydes. The ligand structure appears to have a striking effect on the composition of the reaction products.[12] The highest selectivity towards formation of straight chain aldehydes or alcohols is observed when trialkylphosphines are used as ligands.[13]

We have examined the effect of additives such as isopropyl amine, diphenyl amine and triphenylphosphine under various conditions in the reaction of 1-decene with $CoBr_2$, Zn and CO in toluene/t-BuOH solvent system (Scheme 9).

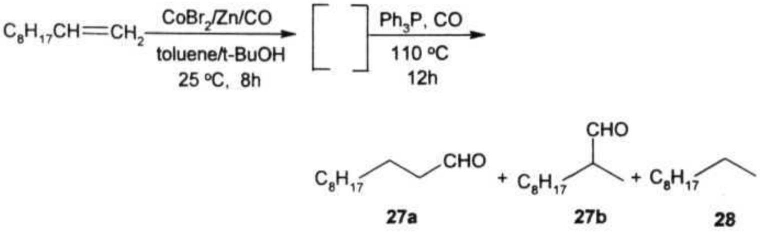
In the runs using amines, only decane was isolated in small amounts (15-20%).

Scheme 9



In the run using triphenylphosphine, there was no significant change in either isomer ratios or yields of aldehydes obtained. The yields of aldehydes were somewhat lower (25%). Moreover, there was slight increase in the yield of the hydrogenated product decane (50%) in this case (Scheme 10).

Scheme 10



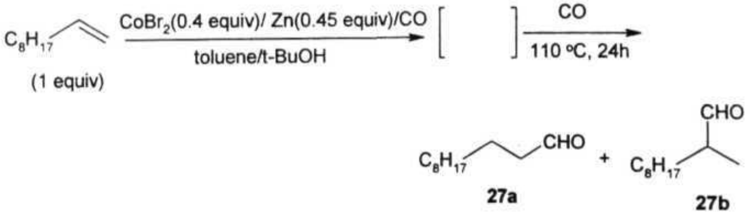
The hydrido metal carbonyls modified with electron donor ligands such as phosphines are more stable. This is due to the superior σ donor and weaker *n* acceptor properties of phosphines compared to CO. The result is an increase in electron density at the central atom and thus the stability of $HCo(CO)_mL_n$ via stronger electron back donation.[37] Since the stability of catalyst is increased, the reactivity drops compared to unmodified oxo catalysts. Another possible consequence of higher electron density at metal atom is that H atom of hydrido metal carbonyl complex gets a stronger hydride character. The phosphine ligand modified oxo catalysts are more active in hydrogenation than their unmodified counterparts.[38] Hence, more of hydrogenated product is obtained in the presence of phosphine ligand.

It has been reported that the temperature also affects the isomer ratio of the aldehydes in the hydroformylation reaction. A pattern of decrease in the normal/iso-ratio has been observed with raising temperature.[4a] To study the effect of temperature under the present conditions, the reaction of 1-decene was carried out with $CoBr_2$, Zn and CO at 90 °C. There was no significant change in the ratios of isomeric aldehydes. Instead, the aldehydes were obtained in lower yields (30%) compared to that realized at 110 °C. When the same reaction was carried out in the absence of CO at 110 °C, again the yield was low (28%). **In** this case, the ratio of n:i increased slightly (1.5 :1) compared to the reaction under CO atmosphere. Since the reactions are carried out at normal atmospheric pressure, the yields of the products may be low.

3.2.4 Reaction of **1-decene** using catalytic amounts of $CoBr_2$ and Zn

Previously, we have observed that the Pauson-Khand reaction can be carried out using catalytic amounts of $CoBr_2$ and Zn at atmospheric pressure of CO (Chapter 1). Since, the catalytic version has more commercial importance compared to **stoichiometric** reactions, we have decided to investigate the catalytic version of **hydroformylation** reaction at atmospheric pressure of CO. Accordingly, we have carried out a reaction using **1-decene** (1 **equiv**), $CoBr_2$ (**0.4** equiv) and Zn (0.45 equiv) **for 24h** (Scheme 11).

Scheme **11**

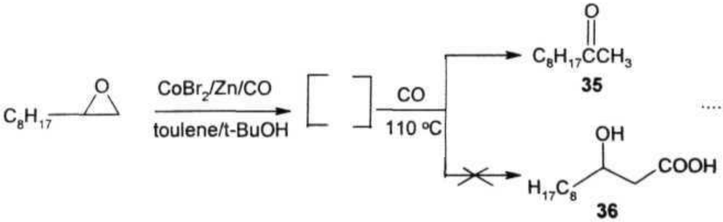


The mixture of aldehydes were obtained in lower yields **(10%)** in almost 1:1 ratio besides usual hydrogenated product, decane in 30% yield. Since the conversion of decene to aldehydes is poor, we have not pursued experiments on the catalytic hydroformylation further.

3.2.5 Reaction of epoxide with the $CoBr_2/Zn/CO$ reagent system in toluene/t-BuOH

Apart from hydroformylation of olefins, the $HCo(CO)_4$ has been used for many other organic transformations. As mentioned in the introductory section, $HCo(CO)_4$ on reaction with epoxides gives hydroxy acids, their derivatives or rearranged carbonyl products.[29]

We have examined the reaction of the deceneoxide using the cobalt carbonyl species, prepared using the $CoBr_2/Zn/CO$ reagent system in toluene/t-BuOH. It was observed that the epoxide rearranges to carbonyl compound and the corresponding hydroxy acid is not formed (eq 25).



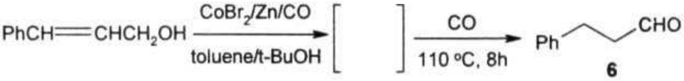
……[25]

The Lewis acidr such as BF_3 and its etherate [39] and $ZnBr_2$ [40] are known to rearrange epoxides to carbonyl compounds. Presumably, the $HCo(CO)_4$ or the Lewis acid $ZnBr_2$ that would be formed along *with the cobalt carbonyl species, may be* responsible for this rearrangement.

3.2.6 Reactions of allylalcohols with the $CoBr_2/Zn/CO$ reagent system in toluene/t-BuOH

We have carried out the reaction of $PhCH{=}CHCH_2OH$ in the presence of the cobalt carbonyl species, prepared using $CoBr_2$, Zn and CO in toluene/t-BuOH, under the hydroformylation reaction conditions. It was observed that the aldehyde 6 is formed in trace amount (< 5%) (Scheme 12).

Scheme 12

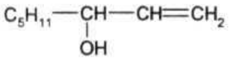
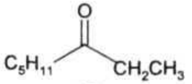
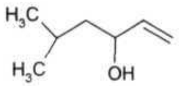
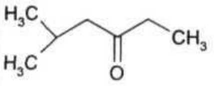
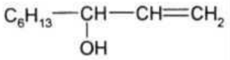
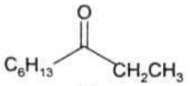


The reaction using secondary allylalcohol, 1-octene-3-ol gave the ketone 37 in good yield (85%) (Scheme 13).

Scheme 13

To generalize this observation, we have carried out experiments with other substituted allylalcohols. The substituted allylalcohols were prepared following a reported procedure.[41] In these cases, the isomerized ketones were obtained in good yields. The results are summarized in Table 2.

Table 2 Reactions of allylalcohols with $CoBr_2$ /Zn/CO in toluene/t-BuOH

No.	allylalcohol	product [a,b]	yield [c]
1	 $C_5H_{11}-CH(OH)-CH=CH_2$	 **37**	85%
2		 **38**	78%
3	 $C_6H_{13}-CH(OH)-CH=CH_2$	 **39**	80%

a) All reactions were carried out using $CoBr_2$ (20 mmol), Zn (20 mmol) and allylalcohol (10 mmol).

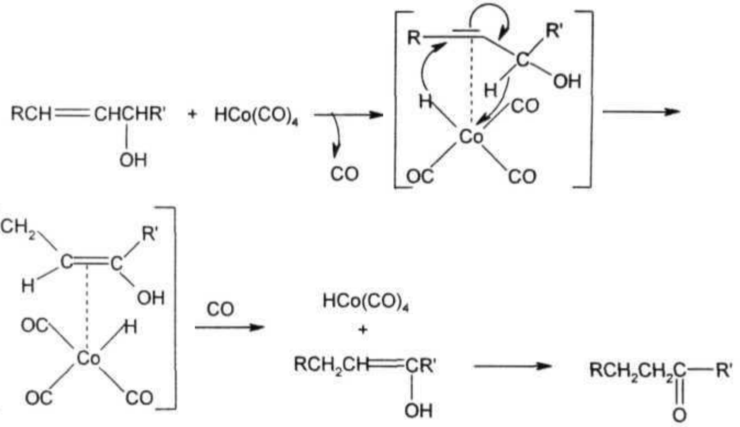
b) The products were identified by IR, ^1H NMR and ^{13}C NMR spectral data reported in the literature.

c) Yields reported here are for products separated from chromatography on silica gel column using hexane and ethyl acetate as eluent and calculated based on the amount of allylalcohol used.

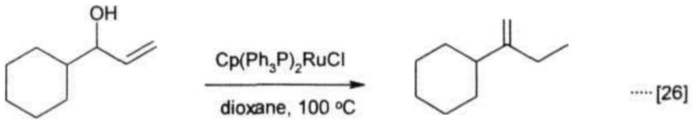
We have also carried out a control reaction using $C_6H_{13}CH(OH)CH=CH_2$ with $CoBr_2$ and Zn in toluene/t-BuOH solvent system, without passing CO at 110 °C for 5h. We have not observed any isomerization of allylalcohol to ketone. This indicates that the $HCo(CO)_4$ does play a role in this transformation. It has been observed by Orchin *et al* [32] that the allylalcohols undergoe isomerization to carbonyl compounds in the presence of $HCo(CO)_4$. They have noted that the primary allylalcohols give the corresponding aldehydes and secondary allylalcohols give the corresponding ketones at 25 °C in CO atmosphere.

The mechanism of this transformation may be visualized as shown in Scheme 14.

Scheme 14



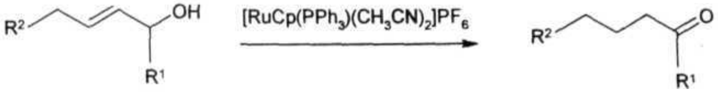
Such isomerization of allylalcohols was observed earlier with many transition metal **reagents**.[42] For example, it has been reported that the **$Cp(Ph_3P)_2RuCl$** reagent effectively isomerizes allylalcohols to saturated aldehydes or ketones (eq 26).[43]



······[26]

40

More recently, isomerization of allylalcohols was reported using catalytic amounts of the **$[RuCp(PR_3)(CH_3CN)_2]PF_6$** complex (eq 27).[44]



41

····· [27]

Accordingly, the readily accessible cobalt carbonyl species, prepared using $CoBr_2/Zn/CO$ reagent system, would serve as an alternative reagent for this transformation.

3.2.8 Conclusions

A simple method for hydroformylation of olefins with cobalt carbonyl species prepared using $CoBr_2$ and Zn, in toluene at atmospheric pressure of CO, was developed. The allylalcohols isomerize to the corresponding aldehydes or ketones under these conditions.

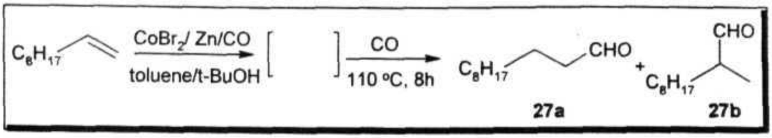
3.3 Experimental Section

3.3.1 General Information

Several informations given in the experimental section of Chapter 1 are also applicable for the experiments outlined here. Substituted allylalocohols were prepared following a reported procedure.[41] Olefins supplied by Aldrich, USA were used.

3.3.2 Reaction of 1-decene with $CoBr_2$, Zn and CO in toluene/t-BuOH: A representative procedure

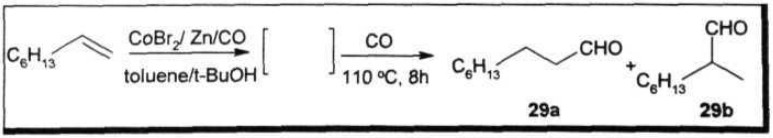
$CoBr_2$ (4.36 g, 20 mmol) was reduced with Zn (1.43 g, 22 mmol) and 1-decene (1.89 mL, 10 mmol) in toluene (50 mL) and t-BuOH (3 mL) while bubbling CO at 25 °C for 8h. The contents were further stirred for 8h at 110 °C, while bubbling CO. The contents were brought to 25 °C. Diethyl ether (30 mL) was added and the mixture was washed with water (2x10 mL). The organic layer thus obtained was dried over anhydrous $MgSO_4$ and concentrated. The crude product was subjected to column chromatography on silica gel using hexane/ethyl acetate as eluent. The decane 28 (30% , 0.46 g) was eluted with hexane. The mixture of aldehydes **27a** and **27b** (40%, 0.68 g) were isolated using 4-5% ethyl acetate in hexane as eluent. The mixture of aldehydes was identified by IR, ^1H, ^{13}C NMR spectral data. The spectral data obtained for the products **27a** and **27b** are summarized below.



Yield	40% (0.68 g)
IR (neat)	2956, 2926, 2706, 1728, 1464, 1238, 723 cm^{-1}
^{1}H NMR	5 ppm 0.8-2.1 (m, 39 H), 2-2.5 (m, 3H), 9.5 (t, J =3 Hz,1H), 9.6 (d, J =2 Hz, 1H)
^{13}C NMR	5 ppm 13.9, 22.6, 26.9, 28.8, 28.5, 28.8, 29.3, **29.4,** 30.4, 31.7, 43.8, 46.2, 204.9 (CO), 205.2 (CO)

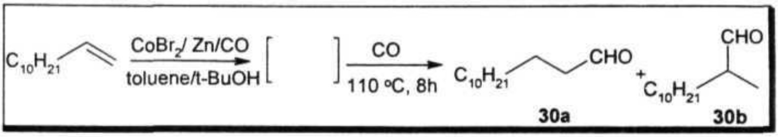
The spectral data show 1:1 correspondence with the data reported in the literature. [46]

The above procedure was followed for other olefins and the results are summarized in Table 1. The spectral data obtained for the products are given below.

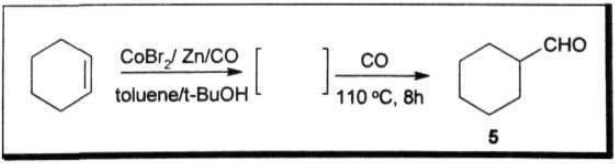


Yield	35% (0.49 g)
IR (neat)	2956, 2925, 2709, 1728, 1463, 1259, 703 cm^{-1}
^{1}H NMR	8 ppm 0.8-2.1 (m, 31H), 2-2.5 (m, 3H), 9.5 (t, J =2 Hz,1H), 9.6 (d, J =2 Hz,1H) **(Spectrum number 15)**
^{13}C NMR	δ ppm **14.0,** 22.6, 26.8, 29.2, 29.5, 30.5, 31.6, 31.8, **43.8, 46.3,** 205.2 (CO), 205.5 (CO) **(Spectrum number 16)**

The spectral data show 1:1 correspondence with the data reported in the literature. [45]

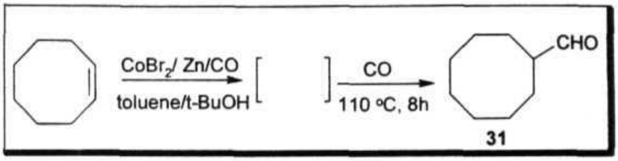


Yield	**38% (0.75 g)**
IR (neat)	**2956, 2926, 2706, 1728, 1464, 1238, 723 cm^{-1}**
^{1}H NMR	**8 ppm 0.8-2.1 (m, 47H), 2-2.5 (m, 3H), 9.5 (t, J =2.2Hz, 1H), 9.6 (d, J=2Hz,1H)**
^{13}C NMR	**8 ppm 13.9, 22.6, 28.4, 28.5, 28.8, 29.3, 29.4, 29.8, 30.4, 31.7, 43.8, 46.2, 204.9 (CO), 205.2 (CO)**

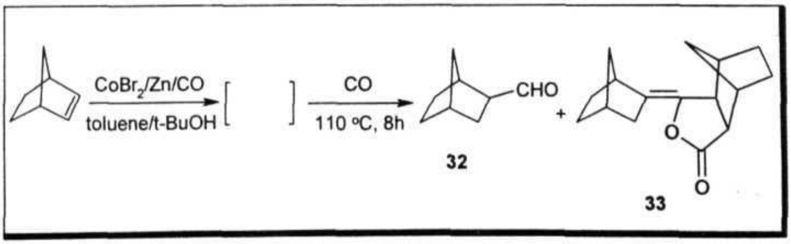


Yield	28% (0.31 g)
IR (neat)	2924, 2854, 2706, 1726, 1448, 1261, 804 cm^{-1}
^{1}H NMR	8 ppm 0.8-2.0 (m, 10H), 2-2.25 (m, 1H), 9.5 (s, 1H)
^{13}C NMR	8 ppm 25.3, 25.4, 25.9, 26.5, 49.9, 204.9 (CO)

The spectral data show 1:1 correspondence with the data reported in the literature. [45]



Yield	30% (0.42 g)
IR (neat)	2924, 2854, 2706, 1726, 1448, 1261, 804 cm^{-1}
^{1}H NMR	δ ppm 0.8-2.0 **(m, 14H),** 2.2-2.5 (m, 1H), 9.5 (s, **1H) (Spectrum number 17)**
^{13}C NMR	δ ppm 25.2, 25.5, 26.1, 26.7, 26.8, 50.7, **204.4 (CO). (Spectrum number 18)**



Aldehyde 32

Yield	**15%** (0.20g)
IR (neat)	2952, 2862, 2705, 1724, 1454, 1259, 1095, 667 **cm^{-1}**
^{1}H NMR	δ ppm 0.8-2.5 **(m, 11H)**, 9.6 (s, **1H)**

^{3}C NMR	8 ppm 28.5, 29.4, 34.0, 36.0, 36.5, 40.9, 46.3, 213.7 (CO)

Enol lactone 33

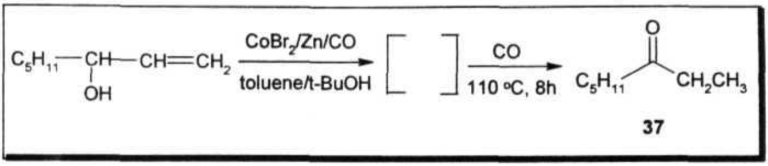
Yield	60% (0.724 g)
IR (neat)	2959, 2872, 1790, 1722, 1452, 1172, 1140, 827, 734 cm^{-1}
^{1}H NMR	δ ppm 0.9-1.6 (m), 1.9-2.7(m)
^{13}C NMR	δ ppm 26.8, 27.0, 27.2, 27.6, 27.9, 28.1, 28.3, 28.8, 29.0, 29.1, 33.9, 34.2, 34.9, 35.2, 36.0, 36.2, 36.5, 38.9, 39.2, 39.5, 39.8, 40.0, 40.4 42.8, 44.7, 44.9, 48.5, 48.7, 120.0, 120.1, 141.8, 142.2, 176.9

The spectral data of 33 show 1:1 correspondence to the data previously obtained in this laboratory. [36]

3.3.3 Reaction of allylalcohol with $CoBr_2$, Zn and CO in toluene/t-BuOH:

$CoBr_2$ (4.36 g, 20 mmol) is reduced with Zn (1.43 g, 22 mmol) and 1-octene-3-ol (1.54 mL, 10 mmol) in toluene (50 mL) and t-BuOH (3 mL) while bubbling CO at 25 °C for 8h. The contents were further stirred for 8h at 110 °C, while bubbling CO. The contents were brought to 25 °C. Diethyl ether (30 mL) was added. The combined organic extract washed successively with water (2x10 mL) and brine solution (10 mL). The organic layer thus obtained was dried over anhydrous $MgSO_4$ and concentrated. The crude product was subjected column chromatography on silica gel using hexane/ethyl acetate as eluent. The ketone 37 (85%, 1.08 g) was isolated using 3%

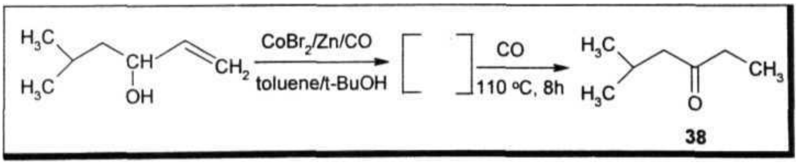
ethyl acetate in hexane as eluent. It was identified by IR, ^{1}H, ^{13}C NMR spectral data. The spectral data obtained for the ketone 37 are summarized below



37

Yield	85% (1.08 g)
IR (neat)	2954, 2932, 1716, 1460, 1261, 727, 704 cm^{-1}
^{1}H NMR	6 ppm 0.8-1.0 (m, 8H), 1.1-1.4 (m, 6H) 2.3 (q, 2H)
^{13}C NMR	8 ppm 7.2, 13.7, 22.3, 23.5, 31.4, 35.7, 42.2, 211.6 (CO)

The spectral data show 1:1 correspondence with the data reported in the literature. [45]



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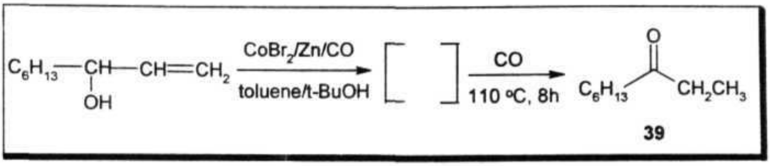
Yield	78% (0.88 g)
IR (neat)	2958, 2875, 1712, 1461, 1409, 1371, 1026, 705 cm^{-1}
'H NMR	8 ppm 0.8-0.9 (m, 9H), 1.8-2.3 (m, 5H)
^{13}C NMR	8 ppm 7.5, 22.4, 24.5, 36.2, 51.2, 210.9 (CO)

The spectral data show 1:1 correspondence with the data reported in the literature. [45]



Yield	80% (1.13 g)
IR (neat)	2954, 2929, 2862, 1714, 1460, 1413, 1261, 1026, 806 cm^{-1}
^{1}H NMR	6 **ppm** 0.8-1.0 **(m,** 8H), **1.1-1.4 (m,** 8H) 2.3 (q, 2H) **(Spectrum number 19)**
^{13}C NMR	6 ppm 7.7, 13.8, 22.4, 23.8, 28.8, 31.5, 35.7, 42.3, 211.5 (CO) **(Spectrum number 20)**

The spectral data show 1:1 correspondence with the data reported in the literature. [46]

3. 4. References

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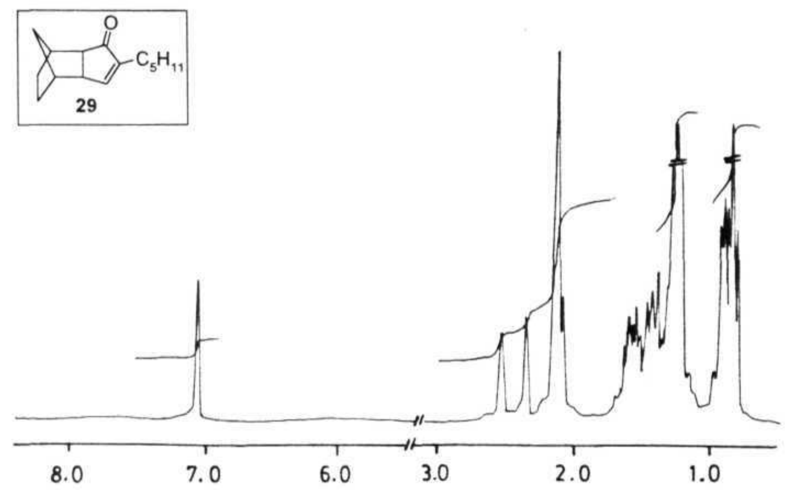
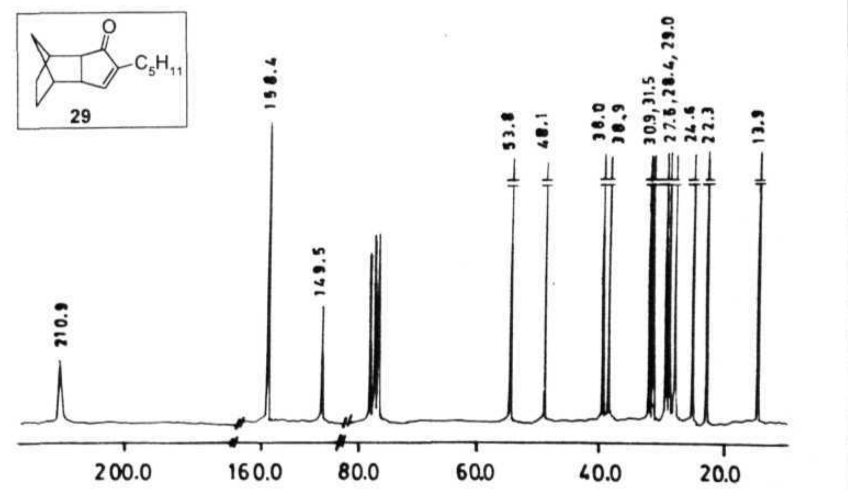
Representative Spectra

Spectrum No 1 (Chapter 1), ^{1}H NMR Spectrum (200 MHz, CDCl$_3$)



Spectrum No 2 (Chapter 1), ^{13}C NMR Spectrum (50 MHz, CDCl$_3$)



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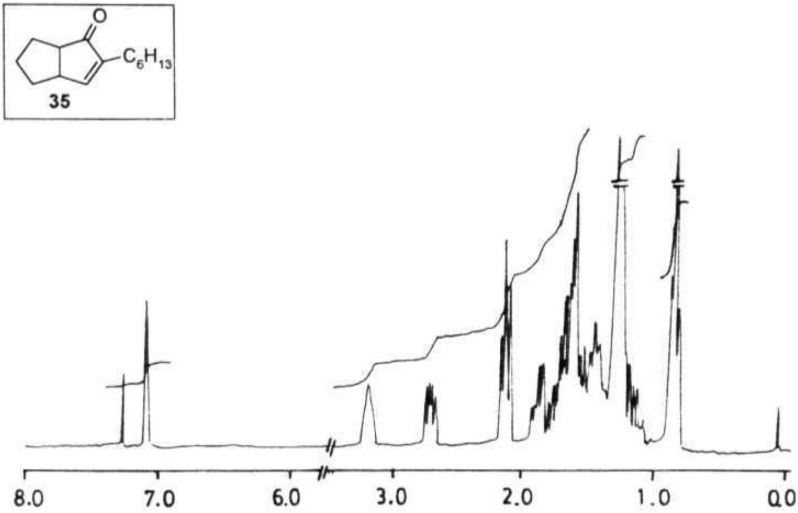

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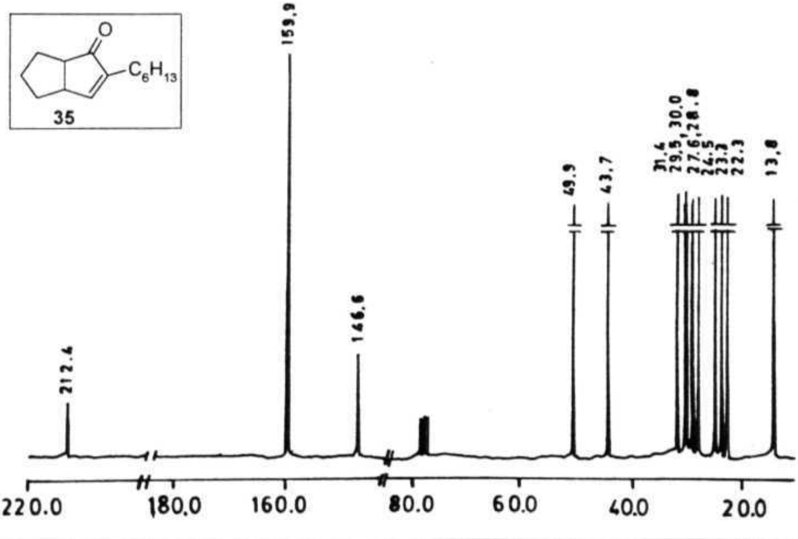

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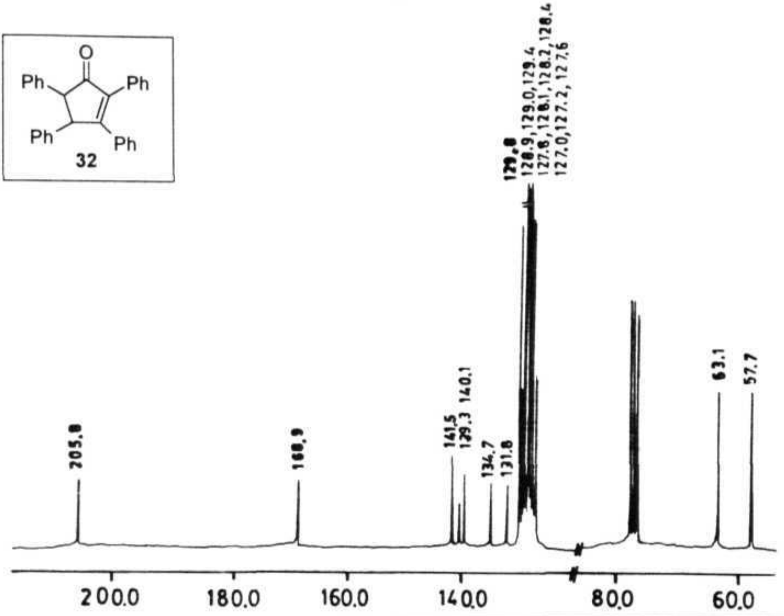
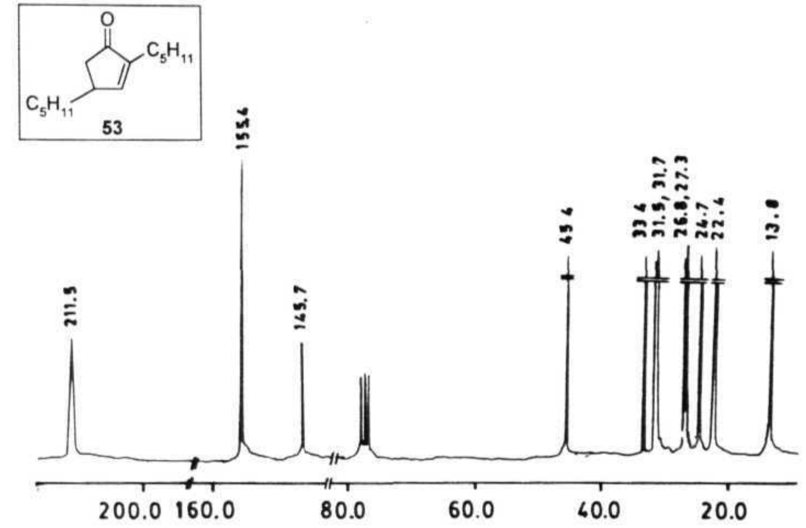


Spectrum No 6 (Chapter 2), ^{13}C NMR Spectrum (50 MHz, $CDCl_3$)



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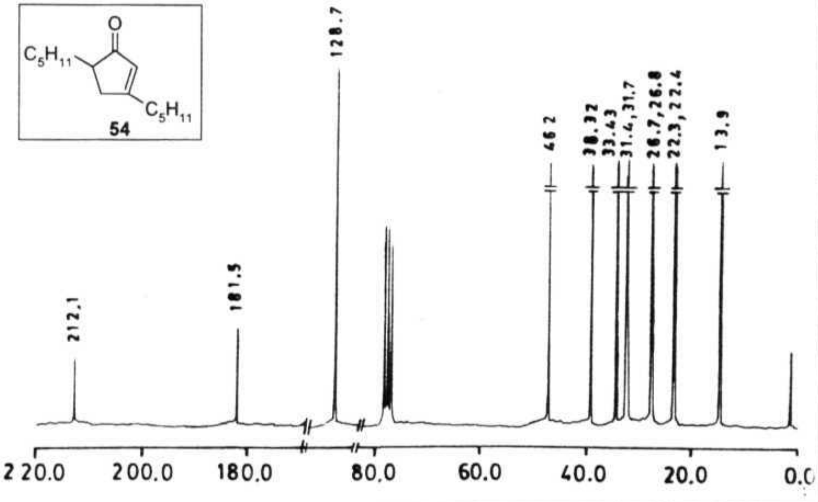
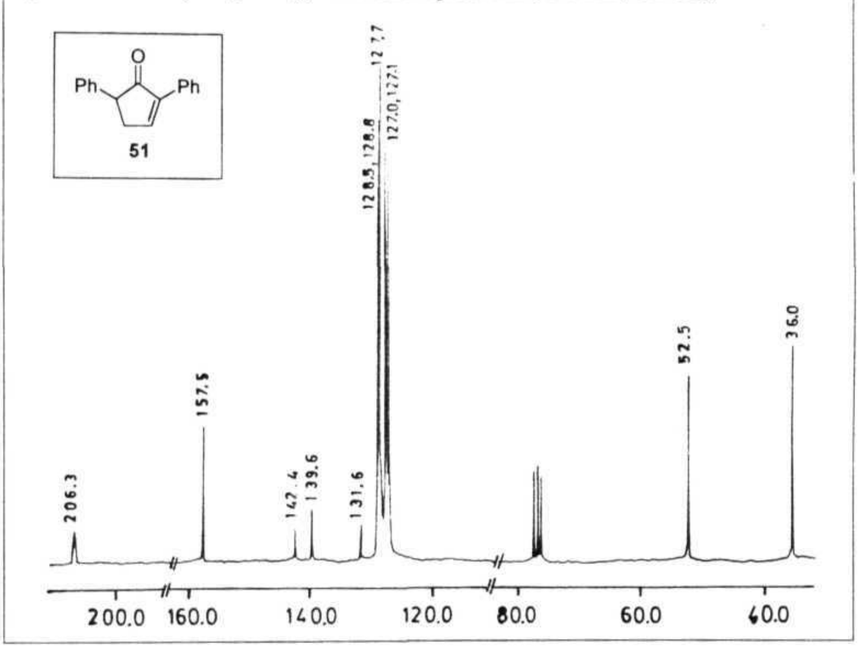
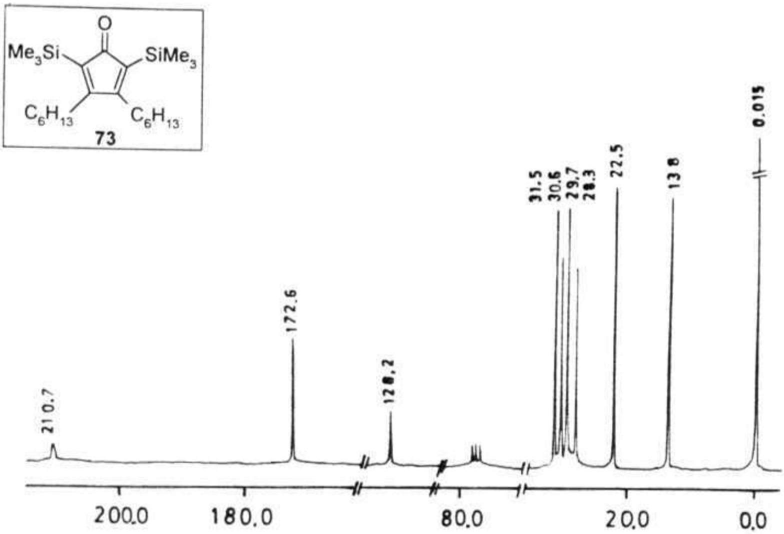


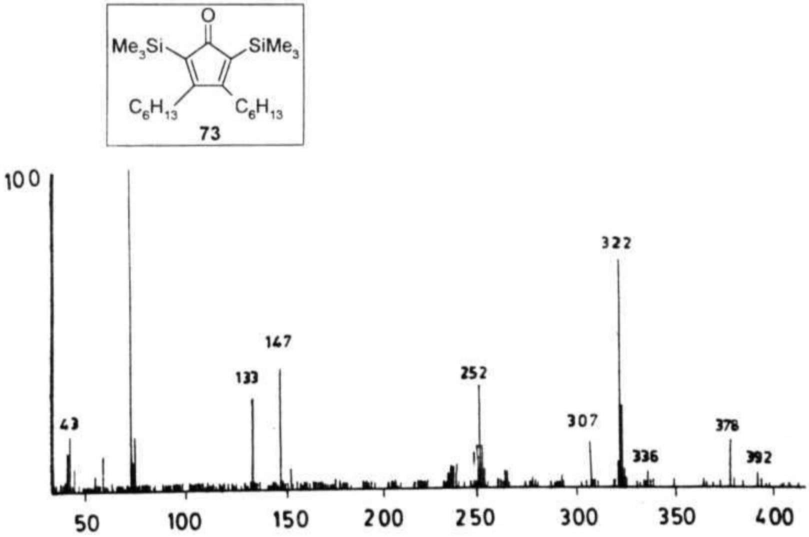
Spectrum No 8 (Chapter 2), ^{13}C NMR Spectrum (50 MHz, CDCl$_3$)



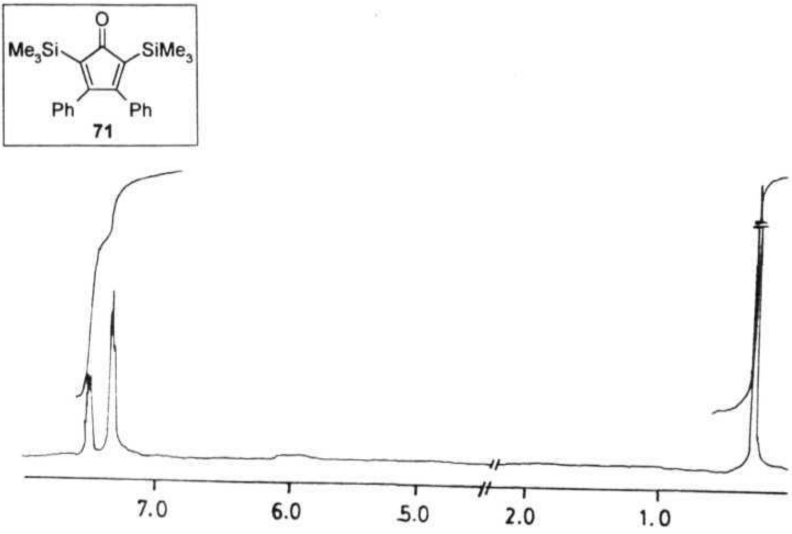
Spectrum No 9 (Chapter 2), ^{13}C NMR Spectrum (50 MHz, $CDCl_3$)



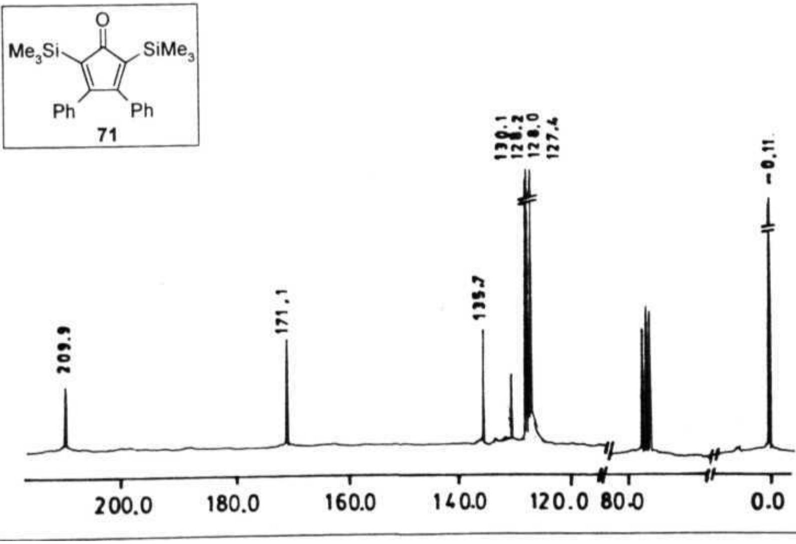
Spectrum No 10 (Chapter 2), Mass Spectrum (EI)



Spectrum No 11 (Chapter 2), ^{1}H NMR Spectrum (200 MHz, $CDCl_3$)



Spectrum No 12 (Chapter 2), ^{13}C NMR Spectrum (50 MHz, $CDCl_3$)



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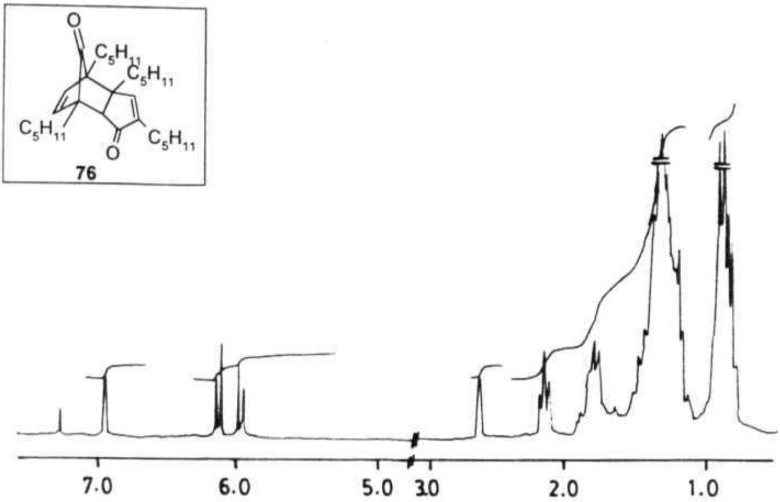

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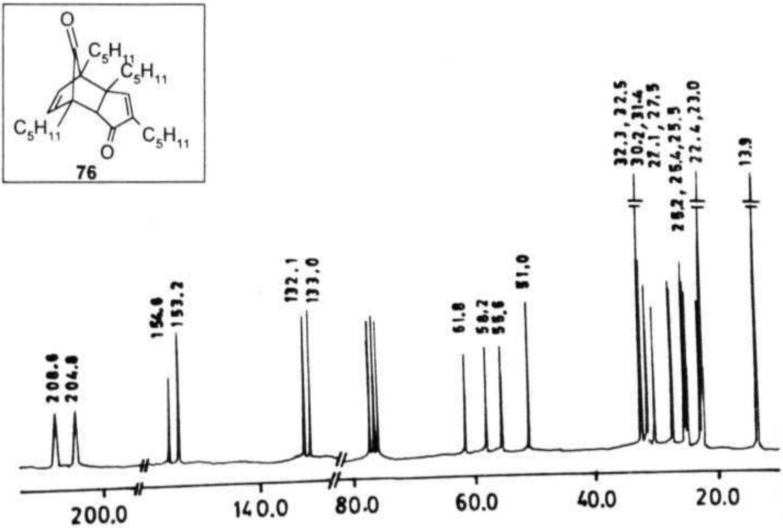
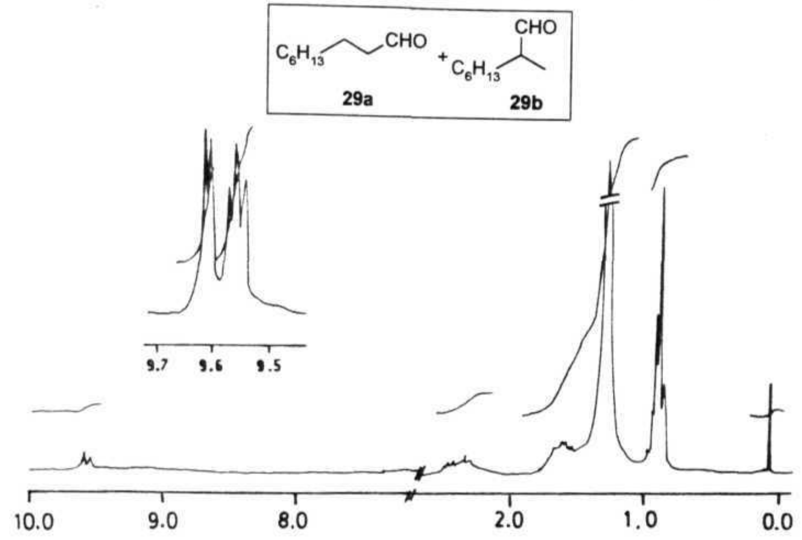
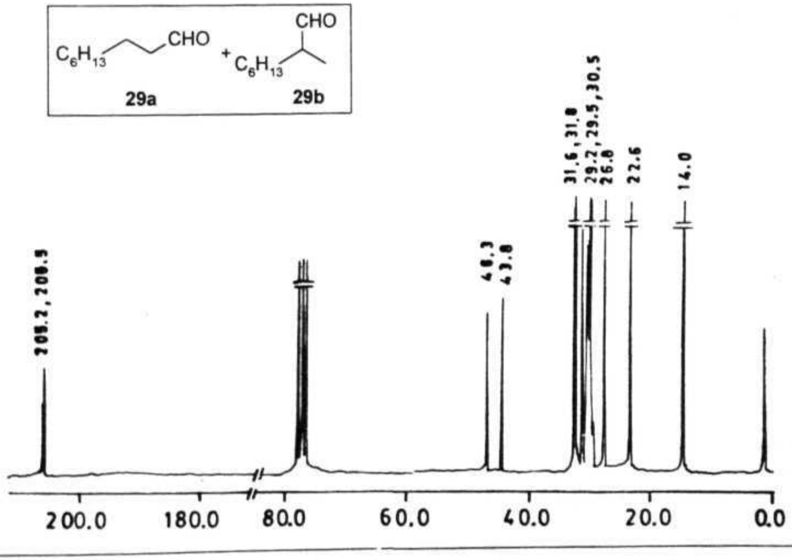


Spectrum No 15 (Chapter 3), ^{1}H NMR Spectrum (200 MHz, CDCl$_3$)



Spectrum No 16 (Chapter 3), ^{13}C NMR Spectrum (50 MHz, CDCl$_3$)



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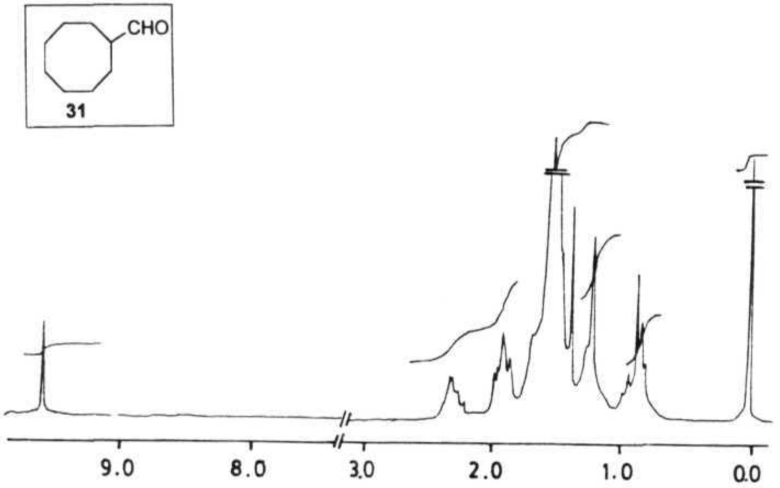
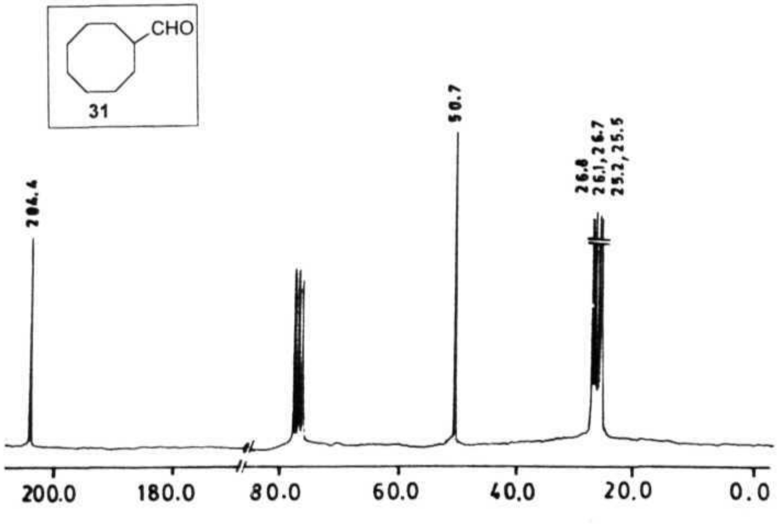
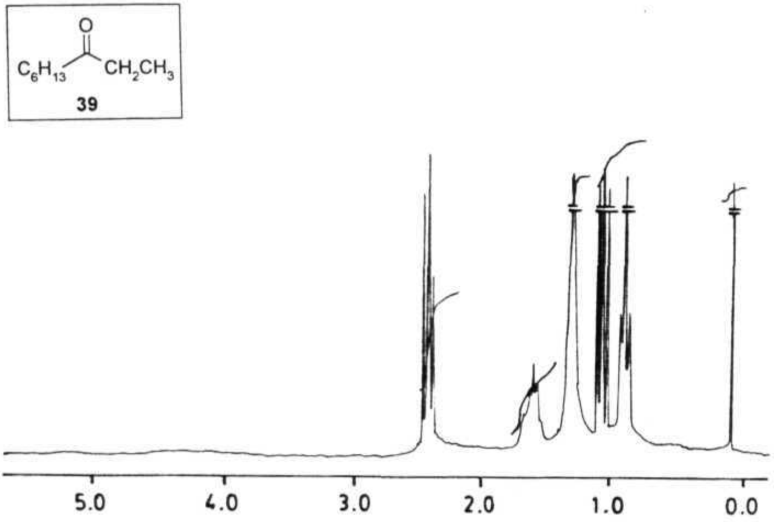


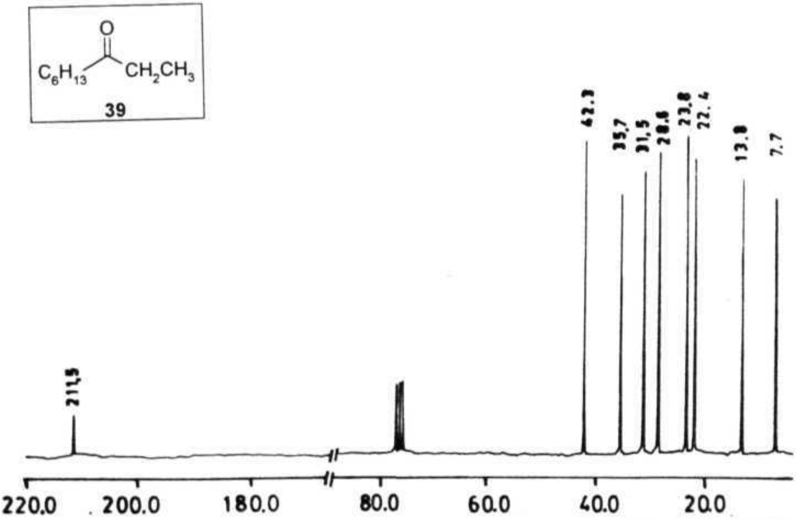
Spectrum No 18 (Chapter 3), ^{13}C NMR Spectrum (50 MHz, $CDCl_3$)



Spectrum No 19 (Chapter 3), ^{1}H NMR Spectrum (200 MHz, $CDCl_3$)



Spectrum No 20 (Chapter 3), ^{13}C NMR Spectrum (50 MHz, $CDCl_3$)



LIST OF PUBLICATIONS

1. New Reactivity of $(RC{\equiv}CCH_2OH)Co_2(CO)_6$ complexes in the Pauson-Khand reaction in the presence of CF_3COOH : synthesis of methyl substituted cyclopentenones

   M. Periasamy, M. Lakshmi Narayan Rao and T. Rajesh, *J. Organomet. Chem.*, **1998,** *571,* 183.

2. Amine induced Pauson-Khnad reaction

   T. Rajesh and M. Periasamy, *Tetrahedron Lett.,* **1998,** *39,* 117.

3. A sub-stoichiometric version of the Pauson-Khand reaction

   T. Rajesh and M. Periasamy, *Tetrahedron Lett.,* **1999,** *40,* 817.

4. Carbonylative cyclizations of alkynes using cobalt carbonyl species generated *in situ* via reduction of $CoBr_2$ with Zn under carbon monoxide atmosphere

   T. Rajesh and M. Periasamy, *Organometallics*, **1999,** *18,* 5709.

5. Hydroformylation reactions of olefins using cobalt carbonyl species generated *in situ* via reduction of $CoBr_2$ with Zn under carbon monoxide atmosphere
   M. Periasamy and T. Rajesh, *Manuscript under preparation*