Chapter 2

Studies on the carbonylation of alkynes with cobalt carbonyl complexes prepared using CoBr₂, 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 α- 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

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 Co₂(CO)₆ 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 \((\mu\text{-butenolide})(\mu\text{-CO})\text{Co}_2(\text{CO})_6\) complexes 8 with prop-2-ynyl amines yields the new \(\gamma\)-substituted-\(\alpha,\beta\)-unsaturated-\(\gamma\)-lactones 9 (eq 2).⁶

In the reaction of acetylene with CO in presence of \(\text{Co}_2(\text{CO})_8\) 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 \(\text{Co}_2(\text{CO})_8\) and methyl iodide in presence of phase transfer catalysts afford but-2-enolides (eq 4).⁸
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)$_6$ catalysis (eq 5). In addition, trisubstituted benzene, cyclopentadienone and cyclopentenone were also isolated.

In the reaction of (PhC≡CPh)Co$_2$(CO)$_6$ with bistrimethylsilyl or phenyltrimethylsilylacetylene, cyclopentadiene and benzene derivatives were obtained.

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 proposed a mechanism involving rather unstable cyclobutadiene complexes as intermediates that may undergo ring enlargement as shown in Scheme 2.
Cyclopentadienone cobalt carbonyl complexes are obtained in the reaction of \( \text{CpCo(CO)}_2 \) with acetylene.\(^{11}\) It has been observed that irradiation of \( \text{CpCo(CO)}_2 \) in the presence of trimethylsilylacetylene in THF at -20 °C furnishes two isomeric complexes of cyclopentadienones 18 and 19 (eq 6).\(^{12}\)
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).

Recently, a direct synthesis of cyclopentadienones mediated by cobalt carbonyl has been reported (eq 8).\(^\text{13}\)
Also, a novel rearrangement of 1-(1-alkynyl) cyclopropanols to 2-cyclopenten-1-ones using $\text{Co}_2(\text{CO})_8$ has been reported.\textsuperscript{14} Substituted 2-cyclopenten-1-ones are selectively obtained (eq 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.\textsuperscript{14}

It was further observed that the phenyl substituted alkynyl cyclopropanols after complexation with $\text{Co}_2(\text{CO})_8$ and heating gives the corresponding 2,3-dihydro-1-naphthalenone derivatives 28 in moderate to good yields (49-86%) (eq 11).\textsuperscript{14}
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).\textsuperscript{14}

Further, it was observed that the reaction of 1-(1-phenyl-1,2-propadienyl) cyclopropanol with $\text{Co}_2(\text{CO})_8$ under argon atmosphere gives the corresponding substituted hydroquinone (35%) and benzoquinone (20%) (eq 13).\textsuperscript{14}

Apart from cobalt carbonyls, several other transition metal carbonyls were also exploited for the novel carbonylation reactions of alkynes. The $\text{Fe}(\text{CO})_5$ is most commonly employed reagent for many transformations. For example, it has been observed that irradiation of diphenylacetylene in the presence of $\text{Fe}(\text{CO})_5$ gives the corresponding cyclopentadienone along with other products (eq 14).\textsuperscript{15} Since then, there have been several reports on this reaction.\textsuperscript{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-(η²-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 ferracyclohexadiene afford the tricarbonyliron-complexed cyclopentadienone 36 (Scheme 3).^17a

Scheme 3

Photochemical irradiation^18 or thermolysis^19 of alkynes in the presence of Fe(CO)₅ gives quinones (eq 15).
In this laboratory, an interesting double carbonylation of alkynes using Fe(CO)\(_5\) has been developed (eq 16).\(^{20}\)

\[
\text{Fe(CO)}_5 + \text{RC} = \text{CR} \xrightarrow{\text{hv}} \text{CAN} \quad 37 + 38
\]

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).\(^{21}\)

\[
\text{Ni(CO)}_4 \text{ reacts with the diphenylacetylene, HCl and ethanol in dioxane solution to give the corresponding cyclopentenone (eq 18).}^{22}\]
The methylmethoxy chromium carbene complexes on reaction with alkynes in hexane give the corresponding cyclopentenones (eq 19). Cylopentenones are also obtained upon reaction of cyclopropyl substituted chromium complexes with alkynes.

Photolysis or thermolysis of \( \text{Cp}_2\text{Zr(CO)}_2 \) and alkynes yields the zirconacyclopentadiene complex. For example, thermolysis of diphenylacetylene and \( \text{Cp}_2\text{Zr(CO)}_2 \) in sealed vessel, give the zirconacyclopentadiene complex 43 and the corresponding cyclopentadienone (20%) (eq 20).
Recently, the zirconia cyclopentadiene complex has been employed in the synthesis of cyclopentenones in the presence of n-BuLi and CO (eq 21).\textsuperscript{25}

The alkynes react with methyl iodide in presence of Mn(CO)\textsubscript{5}Br and CO under phase transfer catalysis to give $\gamma$-butyrolactones (eq 22).\textsuperscript{26}

Reductive carbonylation of 1-alkynes to furan-2(5H)-ones \textsuperscript{48} takes place in dioxane-water, under 10 atm of CO in the presence of PdI\textsubscript{2} (eq 24).\textsuperscript{28}
Also, in the presence of added CO$_2$ maleic anhydride derivatives were obtained (eq 25).$^{28}$

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).$^{29}$

Previously, it was observed in this laboratory that the reaction of (alkyne)Co$_2$(CO)$_6$ complexes in presence of CF$_3$COOH (TFA) gives the corresponding cyclopentenones in THF (Scheme 4).$^{30}$
In continuation of these studies, we have explored the reactions of the (alkyne)Co₂(CO)₆ complexes prepared using CoBr₂, Zn, under CO atmosphere in t-BuOH and CH₂Cl₂ 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=CPH)Co_2(CO)_6 complex, prepared \textit{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=CPh)Co_2(CO)_6 complex with trifluoroaceticacid (TFA) in THF at 70 °C for 24h.\textsuperscript{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).\textsuperscript{31} In the case of terminal alkynes, two regio isomers are obtained. The \textit{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 \((\text{alkyne})\text{Co}_2(\text{CO})_6\) complexes, prepared using \(\text{CoBr}_2/\text{Zn/alkyne/CO}\) system with olefins in toluene/t-BuOH system as discussed in Chapter 1.

Also, there is a possibility that the presence of Zn or \(\text{ZnBr}_2\) 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 \(\text{Co}_2(\text{CO})_8\)\(^{33}\)
Table 1 Reactions of \((\text{alkyne})\text{Co}_2(\text{CO})_6\) complexes in toluene/t-BuOH

<table>
<thead>
<tr>
<th>alkyne</th>
<th>Cyclopentenone (^a)</th>
<th>Yield (^b,c)</th>
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</thead>
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<td>(\text{Ph} \equiv \text{Ph})</td>
<td>![Image](85x53 to 337x463)</td>
<td>50%</td>
</tr>
<tr>
<td>(\text{C}<em>6\text{H}</em>{11} \equiv \text{H})</td>
<td>![Image](159x485 to 222x492)</td>
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</tr>
<tr>
<td>(\text{C}<em>6\text{H}</em>{17} \equiv \text{H})</td>
<td><img src="79x486" alt="Image" /></td>
<td>39%</td>
</tr>
<tr>
<td>(\text{Ph} \equiv \text{H})</td>
<td><img src="79x486" alt="Image" /></td>
<td>38%</td>
</tr>
</tbody>
</table>
Footnotes to Table 1

a) All reactions were carried out using CoBr₂ (20 mmol), Zn (20 mmol) and alkyne (10 mmol).

b) The products were identified by IR, ¹H NMR and ¹³C 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 Co₂(CO)₈ (Scheme 6).

Scheme 6

The formation of cyclopentenones may be rationalized by considering the reaction of (alkyne)Co₂(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).
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$_3$Si substituents (eq 28).$^{35}$

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).
Recently, a novel synthesis of cyclopentenones based on the *Umpolung* chemistry strategy has been reported.\(^{37}\) For example, sulfines of \(\delta\)-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 \(\delta\)-carbonyl function leading to the cyclopentenone 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 $(RC\text{ CSI}Me_3)Co_2(CO)_6$ 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-Khand 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-methyl derivative (eq 31). \(^3\)

![Chemical structure](image)

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). \(^3\)

![Chemical structure](image)
The reaction using \((\text{C}_5\text{H}_{11}\text{C}≡\text{CSiMe}_3)\text{Co}_2(\text{CO})_6\) 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 \((\text{C}_5\text{H}_{11}\text{C}≡\text{CSiMe}_3)\text{Co}_2(\text{CO})_6\) complex with excess TFA in THF at 70-80 °C after 72h (eq 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 \(\text{Co}_2(\text{CO})_8\) 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 \textit{atmospheric} pressure of CO. Hence, we have further investigated the reactions using various \((RC=CSiMe_3)\text{Co}_2(CO)_8\) complexes.

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

![Equation 34]

\[
\begin{align*}
\text{Ph} & \quad \text{SiMe}_3 \\
\text{Co}_2(CO)_8 & \quad \text{toluene/t-BuOH} \\
\quad & \quad 110 \degree C \\
\rightarrow & \\
71 & + 72
\end{align*}
\]

The positions of phenyl and \textit{silyl} moieties of the \textit{3,5-diphenyl} substituted cyclopentadiene 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

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<th>Identification code</th>
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<td>Wavelength</td>
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<td></td>
<td>α = 90.05 deg., β = 94.042(13) deg., γ = 89.99 deg.</td>
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<td>R indices (all data)</td>
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<td>Largest diff. peak and hole</td>
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Table 2A  Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^2 x 10^3) for 72. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

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</table>

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.
Earlier, we have observed that in presence of strong acids such as TFA, (alkynylsilane)Co₂(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)Co₂(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 \((RC\text{SiMe}_3)\text{Co}_2(\text{CO})_6\) complexes in toluene/t-BuOH

<table>
<thead>
<tr>
<th>alkyne</th>
<th>Product a,b</th>
<th>Yield c</th>
</tr>
</thead>
<tbody>
<tr>
<td>(C_6H_{11}\equiv\text{SiMe}_3)</td>
<td><img src="image1" alt="Image" /></td>
<td>40%</td>
</tr>
<tr>
<td>(C_6H_{13}\equiv\text{SiMe}_3)</td>
<td><img src="image2" alt="Image" /></td>
<td>38%</td>
</tr>
<tr>
<td>(C_8H_{17}\equiv\text{SiMe}_3)</td>
<td><img src="image3" alt="Image" /></td>
<td>35%</td>
</tr>
<tr>
<td>(C_{10}H_{21}\equiv\text{SiMe}_3)</td>
<td><img src="image4" alt="Image" /></td>
<td>35%</td>
</tr>
<tr>
<td>(\text{Ph}\equiv\text{SiMe}_3)</td>
<td><img src="image5" alt="Image" /></td>
<td>15%</td>
</tr>
<tr>
<td></td>
<td><img src="image6" alt="Image" /></td>
<td>30%</td>
</tr>
</tbody>
</table>
Footnotes 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, $^1$H NMR, $^{13}$CNMR 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 alkyne 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=CH)Co$_2$(CO)$_6$ complexes in CH$_2$Cl$_2$/t-BuOH solvent system: Synthesis of dicyclopentadienones

In Chapter 1, the preparation of (RC=CH)Co$_2$(CO)$_6$ complexes in situ in CH$_2$Cl$_2$/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 et al. 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=CH)Co₂(CO)₆ complexes without using an added olefin.

Accordingly, the reaction of (C₅H₁₀C=CH)Co₂(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](image)

The regiochemistry of dicyclopentadienone 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 Co₂(CO)₆ 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)Co₂(CO)₆ complexes prepared using CoBr₂/Zn/CO, we have investigated this transformation further with different promoters.
Accordingly, we have carried out the reaction with various \((\text{alkyne})\text{Co}_2(\text{CO})_6\) 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 dicyclopentadienones by carrying out the reaction of \((\text{C}_5\text{H}_1\text{C=CH})\text{Co}_2(\text{CO})_6\) 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 focused attention on the effect of increasing the concentration of promoter. The reaction of \((\text{C}_5\text{H}_1\text{C=CH})\text{Co}_2(\text{CO})_6\) 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

<table>
<thead>
<tr>
<th>Alkyne</th>
<th>Promoter</th>
<th>Product</th>
<th>Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>C$<em>5$H$</em>{11}$C≡CH</td>
<td>DMSO</td>
<td><img src="image" alt="Product 76" /></td>
<td>20%</td>
</tr>
<tr>
<td>C$<em>6$H$</em>{12}$C≡CH</td>
<td>DMSO</td>
<td><img src="image" alt="Product 77" /></td>
<td>18%</td>
</tr>
<tr>
<td>C$<em>8$H$</em>{17}$C≡CH</td>
<td>DMSO</td>
<td><img src="image" alt="Product 78" /></td>
<td>16%</td>
</tr>
<tr>
<td>C$<em>5$H$</em>{11}$C≡CH</td>
<td>DMF</td>
<td><img src="image" alt="Product 76" /></td>
<td>15%</td>
</tr>
<tr>
<td>C$<em>8$H$</em>{17}$C≡CH</td>
<td>TMEDA</td>
<td><img src="image" alt="Product 78" /></td>
<td>15%</td>
</tr>
</tbody>
</table>
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, $^1$H 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.
Schore et al.\textsuperscript{7} proposed another possible mechanism for a similar reaction (Scheme 14). Initial insertion of CO in to \(\text{(alkyne)Co}_2\text{(CO)}_6\) followed by reaction with free alkyne in either of two ways, (a) or (b) and subsequent demetallation would also give the cyclopentadienone.
Similar intermediates such as diiron complexes 79 have been isolated in the reaction of \( \text{Fe}_3(\text{CO})_{12} \) with diphenylacetylene.

![Diagram of complex 79](image)

To trap the intermediate cyclopentadienone, we have carried out several experiments in the presence of dienophiles such as malieic 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).\(^{41}\)

![Diagram of reaction sequence](image)

Some dicyclopentadienone derivatives were used as starting material in the synthesis of cubanes (Scheme 15).\(^{42}\)
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 \( \text{CoBr}_2 \), 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.\textsuperscript{36} 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 5 h 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, \(^1\)H 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. m. p. 161-162 °C)

IR (KBr) 3061, 3024, 1952, 1876, 1693, 1628, 1601, 1493, 1149, 754, 694 cm⁻¹

¹H NMR 8ppm 3.8 (bs, 1H), 4.6 (bs, 1H), 7.1-7.5 (m, 20H)

¹³C 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)Co₂(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

¹H NMR δ ppm 0.8-2.6 (m, 25H), 7.1 (bs, 1H)

¹³C 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

¹H NMR δ ppm 0.8-2.6 (m, 25H), 5.9 (bs, 1H)

¹³C NMR δ 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 6 ppm 0.8-2.6 (m, 29H), 7.1 (bs, 1H)

$^{13}$C NMR 6 ppm 13.8, 22.3, 24.8, 26.9, 27.4, 29.0, 31.3, 31.4, 32.2, 33.1, 50.1, 145.5 (quaternary), 154.8, 210.5 (C=O)

Cyclopentenone 56

Yield 12% (0.15 g)

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 (quaternary), 211.8 (C=O)

The spectral data of 55 and 56 show 1:1 correspondence with the previously reported data.
Cyclopentenone 57

Yield 39% (0.59 g)

IR (neat) 2926, 2854, 1709, 1464, 1377, 721 cm⁻¹

¹H NMR 5 ppm 0.8-2.5 (m, 37H), 7.1 (bs, 1H)

¹³C 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 (quaternary), 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

¹H NMR 8 ppm 0.8-2.6 (m, 37H), 5.9 (bs, 1H)

¹³C NMR 8 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. m. p. 75-76 °C)

IR (KBr) 3061, 3026, 1693, 1599, 1494, 1118, 758, 696 cm⁻¹

¹H NMR δ ppm 2.8-2.9 (m, 1H), 3.2-3.4 (m, 1H), 3.8 (m, 1H), 7.2-8.0 (m, 11H)

¹³C 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 (RC₂SiMe₃)Co₂(CO)₆ complexes in toluene/t-BuOH

The (C₅H₁₁C≡CSiMe₃)Co₂(CO)₆ complex was prepared by reducing CoBr₂ (4.36 g, 20 mmol) with Zn (1.43 g, 20 mmol) and C₅H₁₁C≡CSiMe₃ (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\textsubscript{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, \textsuperscript{1}H, and \textsuperscript{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=CSI\textsubscript{Me}_{3}) Co\textsubscript{2}(CO)\textsubscript{6} complexes and the results are summarized in Table 3. The cyclopentadienones were identified by IR, \textsuperscript{1}H NMR, \textsuperscript{13}C NMR, mass spectra and elemental analysis data. The spectral data obtained for the products are given below.

\begin{center}
\includegraphics[width=0.5\textwidth]{cyclopentadienone.png}
\end{center}

Yield 40% (1.45 g)

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

\textbf{\textsuperscript{1}H NMR} 8 ppm 0.2 (s, 9H), 1-2.5 (m, 11H)

\textbf{\textsuperscript{13}C NMR} 5ppm 0.060, 13.9, 22.4, 28.3, 30.4, 32.3, 128.2, 172.8, 210.8 (CO)

\textbf{MS (m/z)} 366
Yield 38% (1.48 g)

IR (neat)  2954, 2854, 1684, 1466, 1261, 798, 721 cm⁻¹

¹H NMR  δ ppm 0.2 (s, 9H), 1-2.5 (m, 13H)

¹³C NMR  5 ppm 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 C₂₁H₄₂Si₂O:

Calcd  C, 69.23%, H, 10.98%

Found  C, 69.28%, H, 11%

Anal. Calc. for C₂₃H₄₄Si₂O:

Calcd  C, 70.40%, H, 11.20%

Found  C, 70.45%, H, 11.26%
Yield 38% (1.70 g)

IR (neat) 2954, 2854, 1684, 1466, 1261, 798, 721 cm⁻¹

¹H NMR δppm 0.2 (s, 9H), 1-2.5 (m, 17H)

¹³C NMR δppm 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 C₂₇H₅₂Si₂O
Calcd: C, 72.30%, H, 11.60%
Found: C, 72.35%, H, 11.65%

Yield 35% (1.76 g)

IR (neat) 2954, 2854, 1684, 1466, 1261, 798, 721 cm⁻¹

¹H NMR δppm 0.2 (s, 9H), 1-2.5 (m, 21H)
\(^{13}\)C NMR
5 ppm 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 6 ppm 0.3 (s, 9H), 7.2-7.4 (m, 5H) (Spectrum number 11)
\(^{13}\)C NMR 6 ppm -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 8 ppm -0.3 (s, 9H), 0.0 (s, 9H), 7.2-7.4 (m, 10H)
\(^{13}\)C NMR 8 ppm -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 (C₅H₅=C=CH)Co₂(CO)₆ complex in the presence of DMSO in CH₂Cl₂/t-BuOH:

The (C₅H₅=C=CH)Co₂(CO)₆ complex was prepared by reducing CoBr₂ (4.36 g, 20 mmol) with Zn (1.43 g, 20 mmol), and 1-heptyne (1.3 mL, 10 mmol) in CH₂Cl₂ (50 mL) and t-BuOH (1.5 mL) while bubbling CO with stirring for 5 h at 25 °C. The DMSO (30 mmol, 2.1 mL) was added and the contents were stirred for 5 h at 25 °C. The mixture was washed successively with dil. HCl (20 mL), water (2×20 mL) and brine solution (10 mL). The organic extract was dried over anhydrous MgSO₄. 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, ¹H NMR, ¹³C NMR and 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

¹H NMR 8 ppm 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)
\(^{13}\text{C}\) NMR 8 ppm 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.

![Diagram](image)

<table>
<thead>
<tr>
<th>Yield</th>
<th>18% (0.89 g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>IR (neat)</td>
<td>2954, 2870, 1772, 1701, 1464, 1174, 868, 727 cm(^{-1})</td>
</tr>
<tr>
<td>(^1\text{H}) NMR</td>
<td>6 ppm 0.5-2.5 (m, 52H), 3.1 (s, 1H), 5.9 (d, J=20Hz 1H), 6.1 (d, J=20Hz, 1H), <strong>6.9</strong> (s, 1H)</td>
</tr>
<tr>
<td>(^{13}\text{C}) NMR</td>
<td>5 ppm 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), <strong>154.6</strong> (quaternary), 204.9, 208.7 (CO)</td>
</tr>
<tr>
<td>MS (m/z)</td>
<td>469 (-CO)</td>
</tr>
</tbody>
</table>
Yield 16% (0.97 g)

IR (neat) 2950, 2870, 1772, 1703, 1174, 868, 727 cm⁻¹

¹H 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)

¹³C 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. Calcd for C₄₂H₇₂O₂:

Calcd: C, 82.8%, H, 11.8%

Found: C, 83.2%, H, 11.8%

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


