Chapter 3

Studies on the Preparation of Reactive
Iron Carbonyl Species via Reduction of FeCl₃
Using NaBH₄ and CO for Synthetic Applications
3.1 Introduction

Studies undertaken towards the preparation of iron carbonyl species in situ via reduction of FeCl$_3$ using NaBH$_4$ in the presence of CO for synthetic applications are described in this chapter. It may be of interest to briefly review the methods reported for the preparation of metal carbonyls through reductions in the presence of carbon monoxide.

In recent years, there has been sustained interest in the preparation of unusual early transition metal carbonyls. For example, it has been reported that the matrix cocondensation reaction of Ti atoms with CO, either pure or diluted with the inert gases, at 10-15 K gives the unusual 16-electron Ti(CO)$_6$ complex 1 (eq. 1).

![Reaction diagram]

The synthesis of hexacarbonyltitanate, zirconate, and hafnate, was achieved by reductive carbonylation of [M(CO)$_4$L]$_2$ with potassium naphthalenide as reducing agent in the presence of cryptands and CO (eq. 2).
The 'exhaustively' reduced carbonylmetalates $\textbf{M(CO)}_4^6$ ($\text{M} = \text{Ti, Zr, Hf}$) have not yet been prepared. However, Ellis et al isolated the corresponding triphenylstannyl derivatives.\(^1\)

Recently, it has been reported that the reaction of the $\textbf{K ([15]crown-5)}_2\text{Ti(CO)}_6$ complex 4 with $\text{BH}_3:\text{THF}$ in THF at -60 °C gives the air sensitive compound 5 (eq. 3).\(^2\)

Also, the $\textbf{[Ti(CO)}_4(\eta^3-\text{BH}_4)]^+$ undergoes nucleophilic reactions with $\text{L}$ ($\text{L} = \text{C}_5\text{H}_5^-, \text{C}_5\text{Me}_5^-, \text{Ph}_3\text{C}^-$) to give the titanium carbonyl complex 7 (eq. 4).
First examples of eight-coordinate metal carbonyls of Zr and Hf have been synthesized recently (eq. 5).²

\[
\text{MCl}_4 \cdot 2\text{THF} + 2\text{NaC}_{10}\text{H}_8 + 4\text{PMe}_3 + 4\text{Ph}_2\text{SnNa}, \text{CO} \rightarrow \text{Na}_4[(\text{Ph}_3\text{Sn})_2\text{M(CO)}_4]_8 + 2\text{C}_{10}\text{H}_8
\]

(M = Zr, Hf)

The carbonyls of vanadium, niobium and tantalum were first prepared by reductive carbonylation of the corresponding metal halides under CO. For example, the preparation of \([\text{V(CO)}_6]^-\) involves the reaction of VCl₃ with CO (200 atm) and Na in diglyme at 160 °C. The Fe(CO)₅ has been used as a catalyst in this reaction. After filtration and precipitation, \([\text{Na(diglyme)}_2][\text{V(CO)}_6]\) complex 9 was obtained (eq. 6).³

\[
\text{VCl}_3 \xrightarrow{\text{CO (200 atm)}} \xrightarrow{\text{Na/diglyme}} \xrightarrow{160 \, ^\circ\text{C}} \text{[V(CO)}_6]\text{[Na(diglyme)}_2]\]

³

The \text{Cr(CO)}_6 can be synthesized by the reaction of anhydrous \text{CrCl}_3 at atmospheric pressure of CO and a large excess of phenylmagnesium bromide at 4 °C, followed by acid hydrolysis (eq. 7).⁴ It is a commercially available reagent.

\[
\text{CrCl}_3 + \text{PhMgBr} + 6\text{CO} \xrightarrow{4 \, ^\circ\text{C}} \xrightarrow{\text{H}_2\text{O}^+} \text{Cr(CO)}_6
\]
A preferred method for the synthesis of \( \text{Cr(CO)}_6 \) involves the reaction of a chromium(III) salt with a suitable reducing agent in the presence of CO. These reductive carbonylation reactions give higher yields and reproducible results (eq. 8).\(^4\)

\[
\begin{align*}
\text{CrCl}_3 + \text{CO} & \xrightarrow{\text{Na/diglyme}} \text{Cr(CO)}_6 + \text{NaCl} \quad (8)
\end{align*}
\]

In 1958, Closson et al described the synthesis of \( \text{Mn}_2(\text{CO})_{10} \)\(^{11}\) using sodium ketyl of benzophenone as a reducing agent with \( \text{MnCl}_2 \) at 200 to 700 \( \text{atm} \) of CO pressure (eq. 9).\(^5\)

\[
\begin{align*}
\text{MnCl}_2 + \text{CO} & \xrightarrow{\text{Na/PhCOPh}} \text{Mn}_2(\text{CO})_{10} \quad (9)
\end{align*}
\]

The best method of preparation of \( \text{Mn}_2(\text{CO})_{10} \) requires the use of aluminium alkyl as reducing agent.\(^6\)\(^a\) The \( \text{Mn}_2(\text{CO})_{10} \) is also commercially available.

The \( \text{Ni(CO)}_4 \) is one of the earliest metal carbonyls prepared. It is a volatile compound (b.p.\(^{6b} 43 \, ^\circ\text{C} \) and highly toxic. The objective in this laboratory is to prepare useful cobalt and iron carbonyls via reduction of the readily accessible cobalt and iron complexes. Hence, a brief review on the
preparation and synthetic applications of these carbonyls will be helpful for the discussion.

3. 1.1 Preparation and synthetic applications of cobalt carbonyls

There are several reports on the preparation of the useful \( \text{Co}_2(\text{CO})_8 \) reagent (12). A low pressure preparation of \( \text{Co}_2(\text{CO})_8 \) was reported using cobalt(II) iodide and Zn powder under CO (eq. 10).\(^7\)

\[
\text{Co}_2 + \text{Zn} \xrightarrow{\text{t-ButOH, Toluene}} \text{Co}_2(\text{CO})_8 \quad \text{(10)}
\]

Reduction of cobalt oxalate with \( \text{H}_2 \) (5 atm) and CO (40 atm) at high temperature and pressure gives the \( \text{Co}_2(\text{CO})_8 \) (eq. 11).\(^8\)

\[
\text{CO (40 atm.)} / \text{H}_2 (5 \text{ atm.)} \xrightarrow{300^\circ \text{C}} \text{Co}_2(\text{CO})_8 \quad \text{(11)}
\]

Also, it has been reported that the cobalt acetate, suspended in acetic anhydride, on reaction with 1:4 mixture of \( \text{H}_2 \) and CO at 160-180 °C under 200 atm pressure gives the \( \text{Co}_2(\text{CO})_8 \) (eq. 12).
A convenient laboratory synthesis of $\text{Co}_2(\text{CO})_8$ requires the initial preparation of $\text{KCo(CO)}_4$ (13) by passing CO through an alkaline suspension of cobalt cyanide. On acidification, the initially formed $\text{HCo(CO)}_4$ decomposes thermally to give $\text{Co}_2(\text{CO})_8$ (Scheme 1).\textsuperscript{9,10}

Scheme 1

Several simple, practical methods have been developed in this laboratory for the preparation of cobalt carbonyls in situ from its halides using different reducing agents under CO. These cobalt carbonyl species have been used for several interesting organic transformations. For example, it was found that the reduction of $\text{CoCl}_2$ with $\text{MgH}_2$ at 0 °C under CO gives cobalt carbonyl 12, which undergoes the Pauson-Khand reaction with alkyne and norbornene to give the corresponding cyclopentenones 14 upon heating at 70 °C (Scheme 2).
Scheme 2

The reductive carbonylation of CoBr$_2$ using Zn at CO atmosphere in THF gives cobalt carbonyl, which reacts with diphenylacetylene to give alkyne-Co$_2$(CO)$_6$ complex 15. Formation of this complex in the reaction mixture was spectroscopically confirmed (eq. 13)$^{11}$

Interestingly, the alkyne-cobalt complex prepared following the above procedure using phenylacetylene on further heating with two more equivalents of phenylacetylene gives the corresponding tri-substituted benzene 16a and 16b (eq. 14)$^{12}$
The alkyne-cobalt complex, prepared using diphenylacetylene, CoBr₂/Zn under CO atmosphere at 70-80 °C in THF, gives tetraphenylcyclopentenone 17 after decomplexation with CF₃COOH (Scheme 3).\textsuperscript{13}

Scheme 3

Also, the cobalt carbonyl complex of 1-heptyne reacts with norbornene in the presence of TFA, to give the reduced Pauson-Khand product 18 (Scheme 4).\textsuperscript{14}
However, the Pauson-Khand reaction, carried out using the cobalt complex derived from propargyl alcohol with norbornene at 65-70 °C for 12h, in the presence of TFA, gives the corresponding methyl substituted cyclopentenone 19 (Scheme 5).\textsuperscript{15}

Recently, a new protocol for the Pauson-Khand reaction of alkyne-Co\textsubscript{2}(CO)\textsubscript{6} complexes, prepared using sub-stoichiometric amounts of CoBr\textsubscript{2}, and Zn at atmospheric pressure of CO, has been reported.\textsuperscript{15} These complexes on heating with olefins give the corresponding Pauson-Khand products 20 and 21 (Scheme 6).\textsuperscript{15}
Also, the alkyne-Co$_2$(CO)$_6$ complexes prepared in situ in the absence of added olefins, give the corresponding cyclopentenones 22 & 23 on heating in toluene (eq. 15, 16).
Further, the Pauson-Khand reaction can be carried out under ambient conditions in the presence of DMSO or amines.\textsuperscript{16} Moreover, the alkyne-$\text{Co}_2(CO)_6$ complexes, prepared as above, give substituted dicyclopentadienones 24 under ambient conditions in the presence of amines or DMSO (Scheme 7).\textsuperscript{17}

Scheme 7

A practically simple method for the generation of Na[Co(CO)$_4$] 25 has been developed by reducing cobalt halides ($\text{CoCl}_2$ or $\text{CoBr}_2$) using sodium naphthalenide. The cobalt carbonyl 25 prepared in this way was used for the carbonylative cyclization of certain benzyl halides (eq. 17).
Also, it was found that the iodoalkylboranes prepared by the hydroboration of alkenes with BH$_2$I-complex can be carbonylated in the presence of NaCo(CO)$_4$ to obtain the corresponding dialkyl ketones 26 after H$_2$O$_2$/NaOH oxidation (eq. 18).$^{18}$

The cobalt carbonyl reagent, prepared in the reaction of Ph(Et)$_2$N: BH$_3$ 27 complex (1 equiv.) in benzene and anhydrous CoCl$_2$ (1 equiv.) in THF under CO, is useful for the carbonylation of alkene (2 equiv.) to obtain the corresponding dialkyl ketone 28 after oxidation with H$_2$O$_2$/NaOH. The alcohol resulting from hydroboration-oxidation was also obtained as a side product (eq. 19).$^{19}$
Presumably, the Ph(Et)$_2$N:BH$_3$ on reaction with CoCl$_2$ would give the H$_2$BHCl and cobalt hydride species. The latter could yield the cobalt carbonyl Co$_2$(CO)$_8$, in the presence of CO (eq. 20)$^{20}$

$$\text{Ph(Et)$_2$N:BH$_3$} + \text{CoCl}_2 \xrightarrow{\text{CO}} \text{H}_2\text{BHCl} + \text{HCoCl} \xrightarrow{\text{CO}} \text{Co$_2$(CO)$_8$} \quad \text{(20)}$$

Also, the cobalt carbonyl species, prepared using the Ph(Et)$_2$N:BH$_3$ complex (1 equiv.) in methanol and anhydrous CoCl$_2$ (1 equiv.) in THF under CO, is useful for the carbonylation of norbornene to give the ketone 29 and the lactone 30 (Scheme 8)$^{21}$

Scheme 8
The reduction of \textbf{CoCl}_2 with \textbf{NaBH}_4 under CO also produces cobalt carbonyl species. For example, the cobalt carbonyl species prepared \textit{in situ} in THF under CO atmosphere using \textbf{CoCl}_2 and \textbf{NaBH}_4 reagent system on treatment with aq.NaOH gives Co(CO)$_4$ \textsuperscript{31}. The species prepared in this way was utilized for the carbonylation of benzyl halide to phenyl acetic acid (32) and 2,2'-bis(bromomethyl)biphenyl to the corresponding cyclic ketone 33 (Scheme 9). \textsuperscript{22}

Scheme 9

Several other synthetic applications have been carried out using the cobalt carbonyl species prepared \textit{in situ} by the reduction of \textbf{CoCl}_2 with \textbf{NaBH}_4 and CO. They are summarized in equations \textbf{21-23}.\textsuperscript{21,22}
3. 1. 2 Preparation and applications of iron carbonyl Is

The butadiene iron carbonyl complex 34 has been prepared via carbonylation of an ether solution of FeCl₃, butadiene and isopropylmagnesium chloride while bubbling CO (5 atm) (eq. 24). The butadiene complex prepared following this procedure has been used as a catalyst for the oligomerization of 1,3-butadiene in toluene to a mixture of cyclic and linear dimers²³⁻²⁶.
Interesting reactive species (termed FeCRACO) (35) were prepared in situ by the reduction of FeCl$_3$ by NaH-sodium tert-amyloxide combination under CO (eq. 25). The reagent prepared in this way has been used for the carbonylation of primary, secondary and tertiary alkyl halides.$^{27,28}$

It has been reported that the RuCl$_3$ in CH$_3$OH in the presence of Zn under CO (5-10 atm) at 65 °C, gives the Ru$_3$(CO)$_{12}$ (36) in good yield (eq. 26).$^{29}$

Early studies in this laboratory indicated that the reduction of FeCl$_3$ with Zn at 1 atm. of CO does not produce iron carbonyls.$^{11}$ However, the super nucleophile Na$_2$Fe(CO)$_4$ (Collman's reagent) (37)$^{30}$ was prepared in THF, by reducing the anhydrous FeCl$_3$ using sodium naphthalenide under CO (1 atm) at 25 °C. The Na$_2$Fe(CO)$_4$ prepared by this method was used in several reactions characteristic of Na$_2$Fe(CO)$_4$ (Scheme 10).$^{31}$ This reagent has also been used for the preparation of NaHFe(CO)$_4$ for applications in the reaction with alkyl halides.
and alkynes to obtain cyclobutenediones after CuCl$_2$·2H$_2$O oxidation (introductory section, Chapter 1).

Scheme 10

Also, a brief earlier investigation indicated that the NaBH$_4$ and MgH$_2$ reagents reduce FeCl$_3$ under CO atmosphere to unidentified iron carbonyl species (eq. 27). The presence of iron carbonyl species in the reaction mixture was confirmed by analyzing the IR spectrum.$^{11}$

As discussed in the chapter 1, reduction of Fe(CO)$_5$ with NaBH$_4$ followed by CH$_3$COOH treatment leads to reactive iron carbonyl species. It would be advantageous to prepare such reactive iron carbonyl derivatives using readily accessible reagents such as FeCl$_3$ and NaBH$_4$ under CO. Hence, we have undertaken the investigations described in this chapter.
3.2 Results and Discussion

3.2.1 Preparation of iron carbonyl species via reduction of FeCl$_3$ using NaBH$_4$ in the presence of CO

It has been reported that the reduction of FeCl$_3$ with excess LiBH$_4$ in diethyl ether gives iron(II) borohydride that decomposes slowly at -10 °C and rapidly at 0 °C to produce the diborane, hydrogen and pyrophoric residue containing boron and iron (eq. 28).$^{32}$

$$3 \text{LiBH}_4 + \text{FeCl}_3 \xrightarrow{\text{Et}_2\text{O}} 3 \text{LiCl} + \frac{1}{2} \text{H}_2 + \frac{1}{2} \text{B}_2\text{H}_6 + \text{Fe(BH}_4)_2 \quad (28)$$

Preliminary studies in this laboratory indicated that the reaction of NaBH$_4$ (3 equiv.) with FeCl$_3$ in THF results in the formation of species that hydroborates olefins (eq. 29).$^{33}$

$$\text{RCH}==\text{CH}_2 \xrightarrow{1. \text{FeCl}_3 / \text{NaBH}_4 / \text{THF}} \xrightarrow{2. \text{H}_2\text{O}_2 / \text{OH}} \text{RCH}_2\text{CH}_2\text{OH} \quad (29)$$

We have observed that the reduction of anhydrous FeCl$_3$ (10 mmol) with NaBH$_4$ (40 mmol) in THF at 25 °C followed by addition of CH$_3$COOH (68 mmol) while bubbling CO at atmospheric pressure for 9h gives iron carbonyl species (eq. 30).$^{34}$ The presence of iron carbonyl species in the reaction mixture
was confirmed by the I.R spectral data of the solution (strong bands at 2044 cm\(^{-1}\) and 1986 cm\(^{-1}\)).\(^{35a}\) The U.V spectrum of the solution (\(\lambda_{max}: 490\) nm) (Figure 1) indicated the presence of metal carbonyl species of the type \([\text{HFe(CO)}_4]\) (eq. 30).\(^{35b}\)

**Figure 1. U.V spectrum for iron carbonyl prepared**
The formation of $\text{HFe(CO)}_4^-$ in situ using the $\text{FeCl}_3$, $\text{NaBH}_4$, CO and CH$_3$COOH reagent system can be tentatively visualized as shown in Scheme 11. However, presence of other iron carbonyl species along with the $\text{HFe(CO)}_4^-$ species cannot be ruled out.

Scheme 11

We have also undertaken efforts towards isolation of the iron carbonyl species as $\text{PPh}_3$, pyrazine or pyridine derivatives. However, these efforts were not successful. Accordingly, we proceeded with the synthetic applications of the $\text{HFe(CO)}_4^-$ species prepared in this way.

3.2.2. Reaction of iron carbonyl species prepared using $\text{FeCl}_3$, $\text{NaBH}_4$, CH$_3$COOH and CO with 1-alkynes

It was observed that the reagent prepared as above, reacts with 1-alkynes in THF, at refluxing temperature for 12h to give disubstituted benzoquinones 38
(a) and 38(b) in moderate to good yields (51-80%) after CuCl₂.2H₂O oxidation (Scheme 12).³⁴ Several 1-alkynes were converted to the corresponding benzoquinones. The results are summarized in Table 1. Percentage composition of isomer (a) and (b) were calculated from the ¹H NMR signal intensities.³⁷

Scheme 12

Also, it was found that the reaction at 25 °C gave the corresponding benzoquinones in poor yields (10-20%). Further, internal alkynes such as diphenylacetylene, 1-heptynyl-(trimethyl)-silane and propargyl alcohol derivatives did not react even under refluxing conditions.³⁴

Here, it may be of interest to note that the Fe(CO)₅ on reaction with 1-alkynes under photolysis gives a mixture of benzoquinones 39(a) and 39(b) in moderate yields (27-50%) after oxidation (eq. 31).³⁷ The internal alkynes failed to give the expected benzoquinones under these conditions.
Also, it was reported that the iron carbonyl reagent prepared using Fe(CO)$_5$ in alkaline solution, on reaction with acetylene at high temperature gives the hydroquinone 40 (eq. 32).\(^{38a}\)

\[
\begin{align*}
\text{Fe(CO)}_5 + \text{R} \equiv \text{H} & \xrightarrow{\text{hv}} \xrightarrow{\text{Ce (IV)}} \xrightarrow{\text{C}_6\text{H}_6 \text{aq.} \text{EtOH}} \text{R} \equiv \text{O} \\
\text{39(a) + 39(b)} & \xrightarrow{\text{31}}
\end{align*}
\]

It is well-known that Fe(CO)$_5$ reacts with NaOH to give HFe(CO)$_4{^{38c}}$. Accordingly, the formation of hydroquinone may be rationalized by considering the intermediacy of similar reactive species (Scheme 12). Presumably, at high temperature the hydrido iron carbonyl [HFe(CO)$_4$] species reacts with acetic acid (or H$_2$O, eq. 32) to give coordinatively unsaturated species that on further reaction with 1-alkynes gives the intermediate complex of the type 41 or the corresponding hydroquinone.\(^{38a,39,40}\) Oxidation of 41 or the
corresponding hydroquinone using $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ would give the benzoquinones 38(a) and 38(b) (Scheme 13).

Scheme 13

Similarly, the photochemical reaction of alkyne with Fe(CO)$_5$ in THF, would also give the intermediate complex 41 through coordinatively unsaturated iron carbonyl species (eq. 33, see also eq. 31).$^{40}$
Table 1: Reaction of iron carbonyl species prepared using FeCl$_3$, NaBH$_4$, and CH$_3$COOH under CO with ROCH at 70 °C

<table>
<thead>
<tr>
<th>S.No</th>
<th>1-Alkyne</th>
<th>Product $^a$</th>
<th>Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>R = C$<em>6$H$</em>{13}$</td>
<td>42a (65%) + 42b (35%)</td>
<td>72 %</td>
</tr>
<tr>
<td>1.</td>
<td>R = Ph</td>
<td>43a (52%) + 43b (48%)</td>
<td>51 %</td>
</tr>
<tr>
<td>2.</td>
<td>R = C$<em>6$H$</em>{11}$</td>
<td>44a (60%) + 44b (40%)</td>
<td>80 %</td>
</tr>
<tr>
<td>3.</td>
<td>R = C$<em>6$H$</em>{17}$</td>
<td>45a (71%) + 45b (29%)</td>
<td>51 %</td>
</tr>
</tbody>
</table>

$a$) Products were identified from the spectral data IR, $^1$H NMR and $^{13}$C NMR and comparison with the reported data. The spectral data for the compounds 42a, 42b and 43a, 43b show 1:1 correspondence with the reported data. The spectral data for the compounds 44a, 44b and 45a, 45b are comparable with the data for the compounds 42a, 42b. The percentage compositions of isomers (a) and (b) were calculated from the $^1$H NMR signal intensities and compared with the reported data.

$b$) Yields are of products isolated by column chromatography using hexane as eluent and based on the 1-alkynes used.
Previously, we have prepared reactive iron carbonyl species from $\text{HFe(CO)}_4^+$ through reaction with $\text{CH}_3\text{I}$ (see introductory Section, Chapter 1). Accordingly, we have examined the reaction of the $\text{HFe(CO)}_4^+$ species prepared using $\text{FeCl}_3$, $\text{NaBH}_4$ and CO (Scheme 11) with $\text{CH}_3\text{I}$. The results obtained are presented in the next section.

3.2.3 Reaction of iron carbonyl species prepared using $\text{FeCl}_3$, $\text{NaBH}_4$, $\text{CH}_3\text{COOH}$ and CO with $\text{CH}_3\text{I}$ and 1-alkynes

The method of generating coordinatively unsaturated iron carbonyl species “$\text{Fe(CO)}_4$” using the $\text{HFe(CO)}_4^+$/CH$_3$I reagent system (eq. 34) is practically simple and convenient for further synthetic applications.\textsuperscript{41}
As discussed in the Chapter 1, the coordinatively unsaturated species prepared using the NaHFe(CO)$_4$ (prepared in situ from Na$_2$Fe(CO)$_4$ and CH$_3$COOH) and CH$_3$I has been used for the double carbonylation of alkynes to the corresponding cyclobutenediones 46 and $\alpha,\beta$-unsaturated carboxylic acids 47 after CuCl$_2$.2H$_2$O oxidation (eq. 35).$^{42}$

![Diagram](image)

We examined the preparation of such coordinatively unsaturated species by adding CH$_3$I to the NaHFe(CO)$_4$, prepared using FeCl$_3$, NaBH$_4$, acetic acid and CO to study its reactivity with alkynes. Interestingly, addition of CH$_3$I at 0 °C to the iron carbonyl species, prepared in situ using the FeCl$_3$/NaBH$_4$-CO/CH$_3$COOH reagent system, followed by reaction with 1-alkynes at 25 °C for 12h in THF, gives the corresponding cyclobutenediones 46 after CuCl$_2$.2H$_2$O oxidation. However, the yields are only moderate (30-37%) (eq. 36). Several 1-alkynes were converted to the corresponding cyclobutene-diones. The results are summarized in Table 2. The benzoquinones 38 are not formed under these conditions.
We have also examined the effect of temperature on this reaction. It was observed that the addition of CH$_3$I at 0 °C followed by reaction with 1-alkynes at 70 °C gives a mixture of benzoquinones 38 and cyclobutenediones 46.$^{34}$

Internal alkynes such as diphenylacetylene, trimethylsilyl substituted alkynes and propargyl alcohol derivatives did not give the expected cyclobutenediones under these conditions.

A tentative mechanistic pathway for the formation of cyclobutenediones can be visualized as shown in Scheme 14. Presumably, the coordinatively unsaturated iron carbonyl species generated after the addition of CH3I,$^{41}$ reacts with the 1-alkyne moiety followed by CO insertion to give the intermediate alkyne-iron complex 47. Oxidation of 47 with CuCl$_2$.2H$_2$O would lead to the formation of the corresponding cyclobutenediones 46 (Scheme 14).$^{47}$ However, due to the presence of reducing agents in the reaction mixture, the possibility of formation of the hydroxy ferrole iron complex 48 cannot be ruled out (see Scheme 12, Chapter 1).
Table 2: Reaction of iron carbonyl species prepared using FeCl₃, NaBH₄, CH₃COOH and CO with CH₃I and RC=CH

<table>
<thead>
<tr>
<th>S.No</th>
<th>1-Alkyne</th>
<th>Product</th>
<th>Yield</th>
</tr>
</thead>
</table>
| 1.   | H₁₁C₆⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻˓
Though, the yields of cyclobutenediones obtained are only moderate, the one-pot synthetic operation described here, through preparation of the reactive iron carbonyl species starting from simple bench-top chemicals, should be useful for further synthetic exploitation.
3.3 Conclusions

A new method for the preparation of iron carbonyl species in situ in THF using simple bench-top chemicals $\text{FeCl}_3$, $\text{NaBH}_4$ and $\text{CH}_3\text{COOH}$ in the presence of CO under mild conditions has been developed. The spectral data recorded show that species prepared in this way may be $\text{HFe(CO)}_4^-$.

The iron carbonyl species prepared in this way is useful for the conversion of 1-alkynes to the corresponding benzoquinones and cyclobutenediones under different conditions. The cyclobutenediones and benzoquinones are versatile starting materials for the synthesis of biologically active compounds. Accordingly, this one-pot method of conversion of 1-alkynes to the corresponding benzoquinones and cyclobutenediones using the simple bench-top chemicals should be useful for further synthetic applications.
3.4 Experimental Section

3.4.1 General information:

Several informations given in the experimental section of Chapter 1 are also applicable for the experiments outlined here. The commercially available anhydrous FeCl$_3$, CH$_3$COOH and CH$_3$I were used in the experiments. The alkynes used in the reactions (except 1-heptyne) were prepared by following reported procedure. All reactions and manipulation were conducted under a dry nitrogen atmosphere. Carbon monoxide was generated by dropwise addition of formic acid (98%) to conc. H$_2$SO$_4$ (96%) at 90 °C using an apparatus recommended for use in the carbonylation of organoboranes. The CO was pre-dried by passing through a jar filled with anhydrous KOH pellets before passing into the reaction mixture.

3.4.2 Preparation of HFe(CO)$_4$ in situ in THF using FeCl$_3$, NaBH$_4$, and CH$_3$COOH under CO atmosphere

Anhydrous FeCl$_3$ (1.26 g, 10 mmol) in THF (50 mL) was added slowly for 1h to NaBH$_4$ (1.54 g, 40 mmol) in THF (100 mL) while bubbling CO at 25 °C. The reaction mixture was further stirred for 9h at 25 °C under CO. Acetic acid (4 g, 68 mmol) was added slowly and the mixture was stirred further for 30
min. The CO bubbling was replaced by N₂ atmosphere. The IR and UV spectra were recorded.³⁵

![](image)

IR (neat) : 2044, 1986 cm⁻¹
UV (λ_max) : 490 nm (see Figure 1)

3.4.3 Reaction of iron carbonyl species prepared using FeCl₃, NaBH₄, CH₃COOH and CO with RC≡CH

Anhydrous FeCl₃ (1.26 g, 10 mmol) in THF (50 mL) was added slowly for 1h to NaBH₄ (1.54 g, 40 mmol) in THF (100 mL) while bubbling CO at 25 °C. The reaction mixture was further stirred for 9h at 25 °C under CO. Acetic acid (4 g, 68 mmol) was added slowly and the mixture was stirred further for 30 min. The CO bubbling was replaced by N₂ atmosphere and 1-octyne (0.090 g, 1.25 mmol) was added and the contents were refluxed at 70 °C for 12h. The metal carbonyls in the reaction mixture were decomposed by adding CuCl₂·2H₂O (6.8 g, 40 mmol) in acetone (20 mL) at 25 °C. Saturated aq. NaCl (40 mL) was added and the contents were extracted with ether (100 mL). The combined
organic extract was washed with brine (20 mL), dried over anhydrous MgSO$_4$ and concentrated. The residue was subjected to column chromatography (silica gel, hexane). Hexane eluted the benzoquinones 42a(65%) and 42b(35%) (72%, 0.113 g).³⁷

The spectral data for the compounds 42-45 were identical to the data reported for the same compounds obtained in the experiments described earlier (Experimental Section 2.4.2, Chapter 2).

The above procedure was followed for the conversion of other 1-alkynes to the corresponding benzoquinones. The data are summarized in Table 1. The spectral data are comparable with the reported data.³⁷ Also, these data show 1:1 correspondence with the data reported for the same compounds (see Experimental Section 2.4.2, Chapter 2). The percentage compositions of isomers (a) and (b) were calculated from the $^1$H NMR signal intensities. Similar $^1$H NMR analysis of benzoquinone mixtures has been previously reported.³⁷
3. 4. 4 Reaction of iron carbonyl species prepared using FeC₁₃, NaBH₄, CH₃COOH and CH₃I under CO with RC≡CH

Anhydrous FeCl₃ (1.26 g, 10 mmol) in THF (50 mL) was added slowly for 1h to NaBH₄ (1.54 g, 40 mmol) in THF (100 mL) while bubbling CO at 25 °C. The reaction mixture was further stirred for 9h at 25 °C under CO. Acetic acid (4 g, 68 mmol) was added slowly and stirred further for 30 min. The CO bubbling was replaced by N₂ atmosphere and CH₃I (2.84 g, 20 mmol) was added at 0 °C. Stirring was continued for 30 min. Subsequently, 1-heptyne (0.12 g, 1.25 mmol) was added and the contents were stirred for 12h at 25 °C. The metal carbonyls in the reaction mixture were decomposed by adding CuCl₂·2H₂O (6.8 g, 40 mmol) in acetone (20 mL) at 25 °C. Saturated aq. NaCl solution (40 mL) was added and the contents were extracted with ether (100 mL). The organic extract was washed with brine (20 mL), saturated aq. Na₂S₂O₃ solution, dried over anhydrous MgSO₄ and concentrated. The residue was subjected to column chromatography (silica gel, hexane/ethyl acetate). Ethyl acetate (2:98) in hexane eluted the cyclobutenedione 49 (37%, 0.070 g).⁴⁴a
The above procedure was followed for the conversion of other 1-alkynes to the corresponding cyclobutenediones. The data are given in Table 2. The spectral data for the compounds 49-53 were identical to the data reported for the same compounds obtained in the experiments described earlier (see Experimental Section 1.4.2 Chapter 1).^{44,45}

### 3.5 References:


34. C. Rameshkumar and M. Periasamy, *Organometallics* (in press)


REPRESENTATIVE SPECTRA
Spectrum No 3 (Chapter 1), $^1$H NMR Spectrum (200 MHz, CDCl$_3$)

Spectrum No 4 (Chapter 1), $^{13}$C NMR Spectrum (50 MHz, CDCl$_3$)
Spectrum No 5 (Chapter 1), $^1$H NMR Spectrum (200 MHz, CDCl$_3$)

Spectrum No 6 (Chapter 1), $^{13}$C NMR Spectrum (50 MHz, CDCl$_3$)
Spectrum No 7 (Chapter 1), Mass Spectrum (m/z)

Ph

Ph

36

100

50 100 150 200 250 300

225
Spectrum No 8 (Chapter 1), $^1$H NMR Spectrum (200 MHz, CDCl$_3$)

Spectrum No 9 (Chapter 1), $^{13}$C NMR Spectrum (50 MHz, CDCl$_3$)
Spectrum No 12 (Chapter 2), $^{13}$C NMR Spectrum (50 MHz, CDCl$_3$)

Spectrum No 13 (Chapter 2), $^{13}$C NMR Spectrum (50 MHz, CDCl$_3$)
Spectrum No 16 (Chapter 2), Mass Spectrum (m/z)
Spectrum No 19 (Chapter 2) Mass Spectrum (m/z-H₂O)

H₃C₆H₁₁ OH

O

CH₂(CH₂)₂CH₃

54