INVESTIGATIONS ON THE REACTIVITIES OF ORGANOCOBALT REAGENTS GENERATED UTILIZING THE $CoCl_2$ / $NaBH_4$ SYSTEM

A THESIS
SUBMITTED FOR THE DEGREE OF

DOCTOR OF PHILOSOPHY

BY

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MARCH, 1988

To

Amma Nanna

CONTENTS

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, Hyderabad, under the supervision of Dr. M. Periasamy.

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

N. Satyanarayana

N. SATYANARAYANA

C E R T I F I C A T E

Certified that the work contained in this thesis entitled **"INVESTIGATIONS ON THE REACTIVITIES OF ORGANOCOBALT REAGENTS GENERATED UTILIZING $CoCl_2/NaBH_4$"** has been carried out by Mr. N. Satyanarayana, under my supervision and the same has not been submitted elsewhere for a degree

M. Periasamy 16/3/88

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N. SATYANARAYANA

ABBREVIATIONS

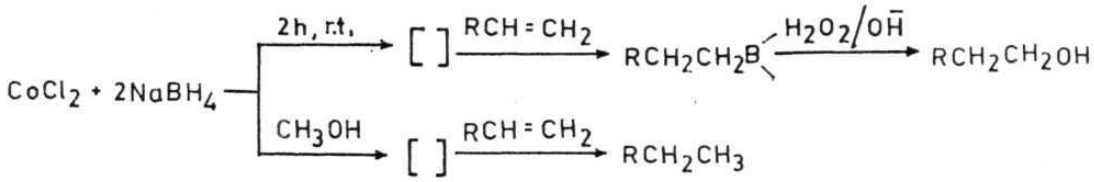
Ac	:	acetyl
acac	:	acetylacetonate anion
Ar	:	aryl such as phenyl
^{n}Bu	:	n-butyl
^{t}Bu	:	t-butyl
Cp	:	π - cyclopentadienyl, η^5-C_5H_5
diphos	:	1,2-bis-(diphenylphosphino)ethane
DME	:	1,2-dimethoxyethane
DMF	:	N,N-dimethylformamide
DMSO	:	dimethylsulphoxide
Et	:	ethyl
HMPA	:	hexamethylphosphoric triamide
L	:	any unidentate ligand
M	:	the central metal in a complex
Me	:	methyl
OAc	:	acetate anion
Ph	:	phenyl
$P^{n}Bu_3$	:	tri-n-butylphosphine
PCy_3	:	tricyclohexylphosphine
$P(OMe)_3$	:	trimethylphosphite
$P(OEt)_3$	:	triethylphosphite
PPh_3	:	triphenylphosphine
^{i}Pr	:	isopropyl
THF	:	tetrahydrofuran
X	:	a halogen

ABSTRACT

This thesis deals with investigations on the reactivities of organocobalt reagents generated utilizing $CoCl_2/NaBH_4$ system under various conditions. It comprises of three chapters. Each chapter is subdivided into three parts; Introduction, Results and Discussion, and Experimental section along with references.

The first chapter describes the reactivities of the $CoCl_2/NaBH_4$ system towards organic substrates. In order to facilitate the discussion, synthesis and reactions of transition metal borohydride complexes generated utilizing $NaBH_4$ and transition metal halides have been briefly reviewed in the introductory section. It was observed that the $CoCl_2/NaBH_4$ reagent system in THF hydrogenates or hydroborates alkenes at appropriate conditions (Scheme 1).

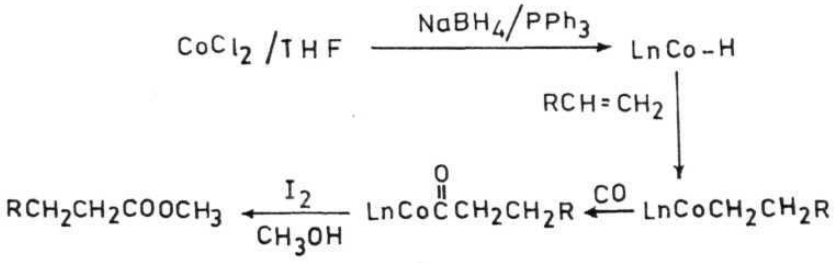
Scheme 1



This reagent system has been also utilized for reduction of imines and enamines. The nature of the reactive species generated under the present reaction conditions is discussed. It appeared that either cobalt boride "Co_2B" species or LnCo-H species is responsible for the reduction of organic substrates. In an effort to utilize cobalt hydride

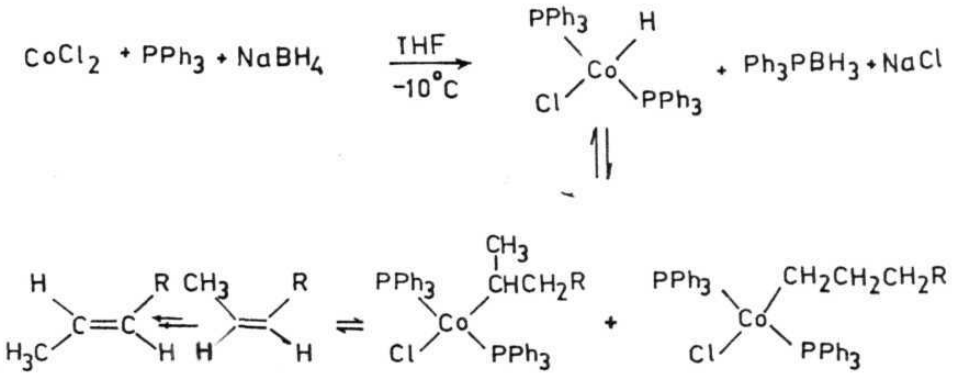
species generated in this way for hydrocobaltation - carbonylation of alkenes, several experiments were carried out. It was found that addition of $NaBH_4/PPh_3$ mixture into $CoCl_2$/alkene in THF while bubbling carbon monoxide followed by I_2/CH_3OH treatment gives the corresponding one carbon homologated ester in 20-25% yields (Scheme 2).

Scheme 2



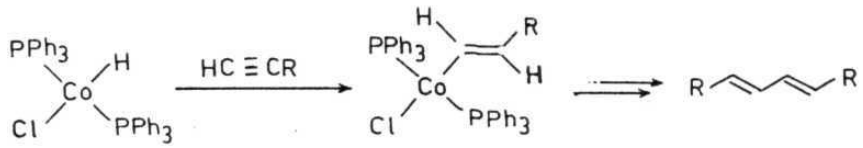
The 2nd chapter describes the studies on the reactivities of the $CoCl_2/NaBH_4$ system in the presence of Ph_3P towards alkenes and alkynes. The synthesis of transitionmetal phosphine hydrides and their reactivities towards organic substrates were reviewed in the introductory section. A novel hydridocobalt(II) reagent, $(Ph_3P)_2CoHCl$, was generated <u>in situ</u> utilizing $CoCl_2/Ph_3P/NaBH_4$ in 1:3:1 ratio in THF at -10^oC. This system isomerizes 1-alkenes into predominantly cis-2-alkenes or trans-2-alkenes (Scheme 3).

Scheme 3



The $(Ph_3P)_2CoHCl$ reagent also hydrodimerizes 1-alkynes into the corresponding (E,E)-1,3-dienes, which constitutes a simple method for this useful transformation (Scheme 4).

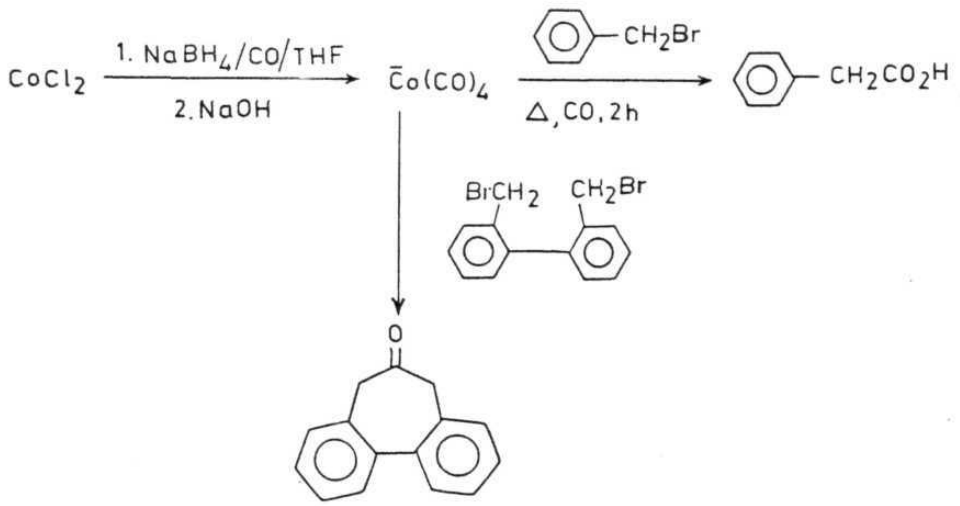
Scheme 4



The mechanism of this transformation has been discussed considering relevant literature reports.

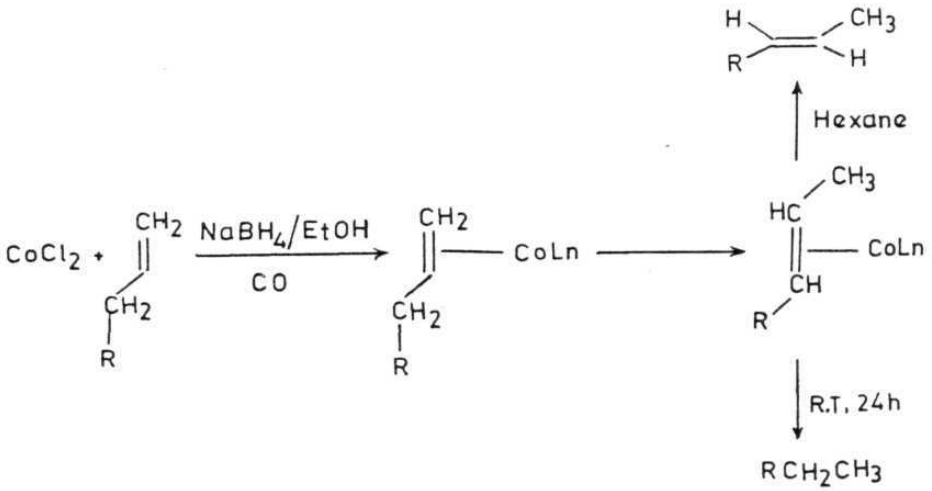
In chapter 3, the reactivities of the cobalt reagents, generated utilizing $CoCl_2$ and $NaBH_4$ in the presence of carbon monoxide, towards organic substrates are described. The introductory section reviews the synthesis and reactivities of transitionmetal carbonyl derivatives, particularly the reactions of cobalt carbonyl reagents. The reagent prepared <u>in situ</u> in THF under carbon monoxide atmosphere using $CoCl_2$ and $NaBH_4$ reagent system, on treatment with NaOH gives $\bar{C}o(CO)_4$ or its equivalent. The $\bar{C}o(CO)_4$ reagent prepared in this way has been utilized for carbonylation of benzyl halides into phenylacetic acids and 2,2'-bis(bromomethyl)-biphenyl into the corresponding cyclic ketone (Scheme 5).

Scheme 5



During the present studies we have observed that the low valent cobalt reagent, generated from $CoCl_2/NaBH_4/EtOH/CO/THF$ system in the presence of 1-alkenes isomerizes or reduces 1-alkenes under appropiate conditions (Scheme 6).

Scheme 6

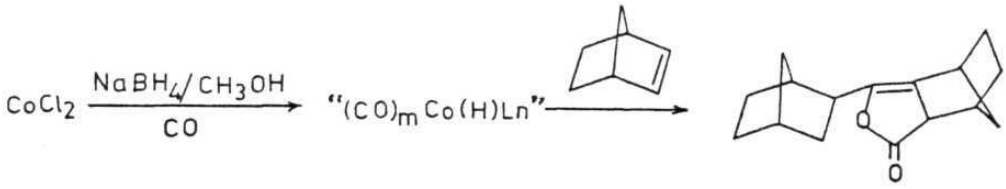


In the absence of EtOH, this system hydroborates alkenes. This system (Scheme 6) also gives $\bar{C}o(CO)_4$ or its equivalent on treatment

with aqueous NaOH as revealed by its ability to carbonylate benzyl halides.

The versatility of the cobalt reagent is further illustrated by the observation that the reagent, prepared by the addition of $NaBH_4$ into a mixture of $CoCl_2$ and CH_3OH in THF at 0^oC under carbon monoxide atmosphere, cooligomerises norbornene and carbon monoxide into the lactone (1) (Scheme 7)

Scheme 7



1

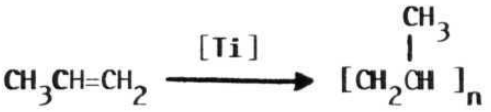
This transformation is found to be novel. It involves <u>three</u> C-C bond formations leading to the construction of a butenolide ring from <u>four</u> fragments in a single pot reaction. The reactivity of the above reagent towards other olefins and alkynes was investigated. In the case of diphenylacetylene, a metal carbonyl-alkyne complex was isolated. The mechanisms involved in these transformations are discussed.

IR and ESR spectral studies of the intermediates produced have been also carried out.

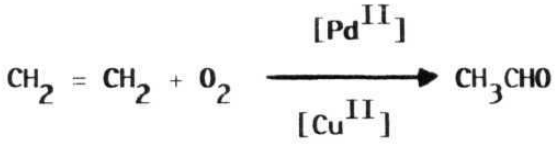
GENERAL INTRODUCTION

Number of useful, important organic reactions take place only in the presence of transition metal complexes[1].

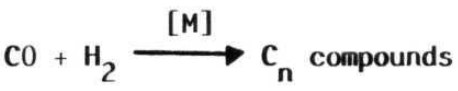
Ziegler - Natta polymerisation[2-4] :



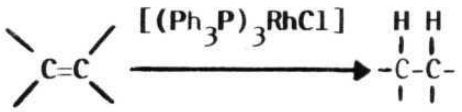
Wacker process[5-7] :



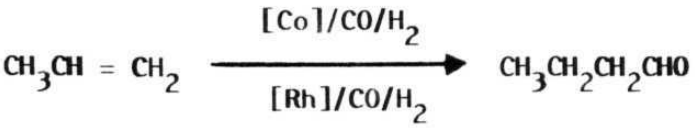
Fischer - Tropsch synthesis[8,9] :



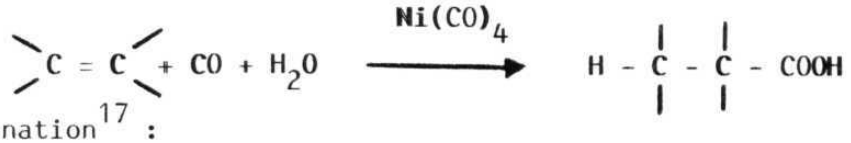
Homogeneous hydrogenations using Wilkinson's catalyst[10-12]:



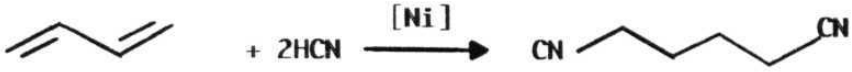
Hydroformylation : Oxo process[13,14]



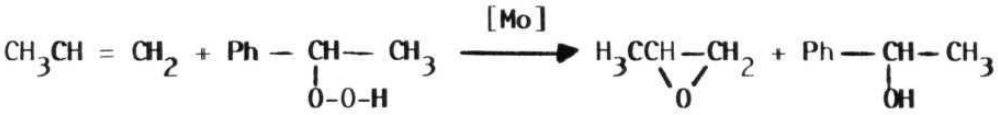
Hydrocarboxylation : Reppe Reaction[15,16]



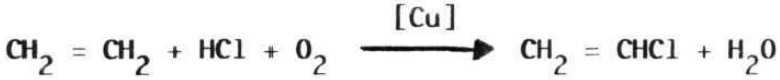
Hydrocyanation[17] :



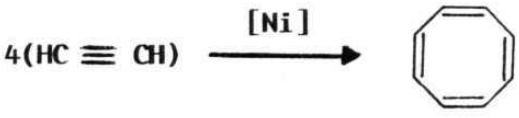
Epoxidation[18] :

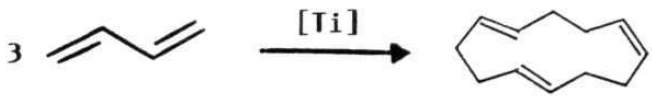


Oxychlorination[19] :

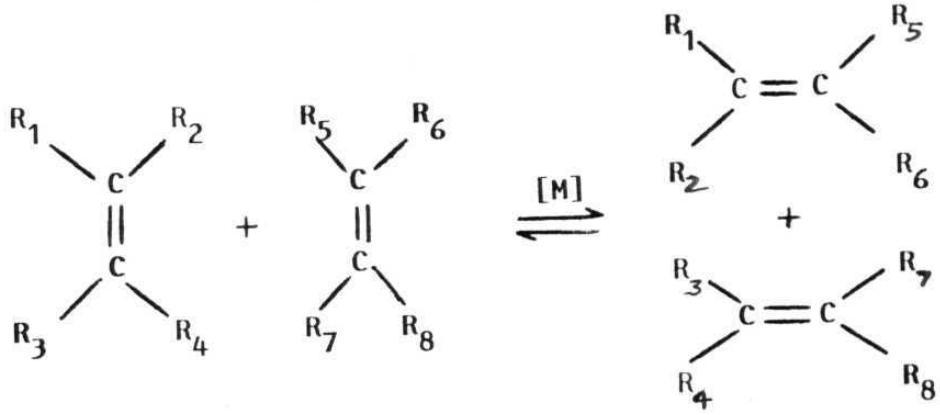


Oligomerization[20,21] :





Metathesis Reaction[22-24] :

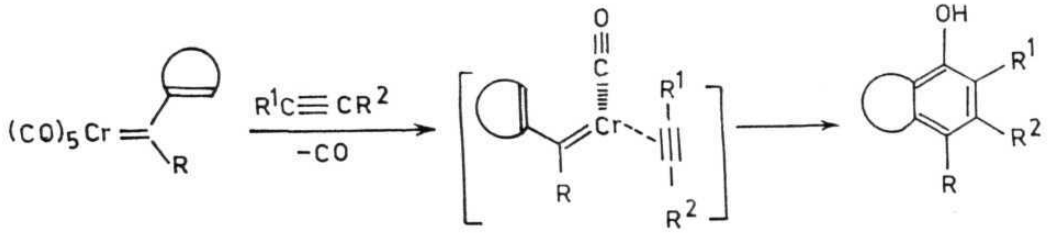


These transformations and many other catalytic processes involving transition metal complexes have been put into industrial applications. Research and development of these industrial reactions required understanding of the mechanisms and intermediates involved in these processes. It was realized that these processes involve the intermediacy of an organometallic intermediate at least in one of the steps and hence there is immense interest in studying the structure and reactions of organometallic compounds.

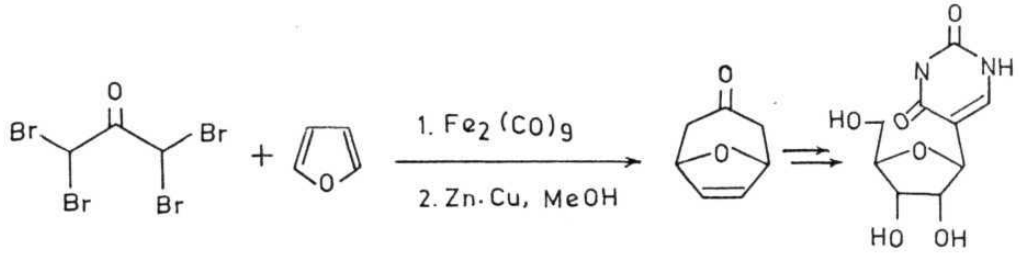
Studies on the structure and reactivities of the transiton metal organometallic compounds constitute the major part of the organometallic chemistry which has been developing rapidly over the past 30 years. In recent years, there is immense interest among organic chemists to exploit this type of chemistry in synthesis. Many useful reactions and applications of organocopper[25-27] and organopalladium[28] reagents have been uncovered. Several other transition metal complexes

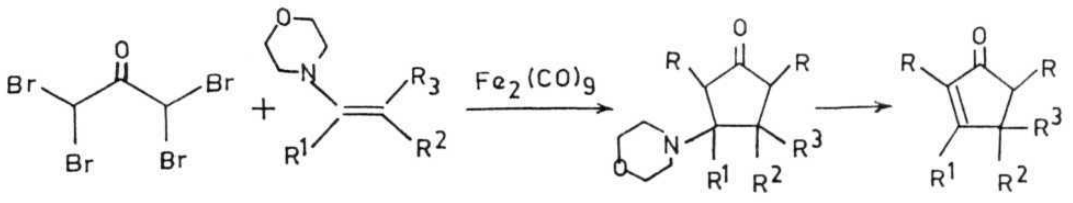
have been found to give transformations hitherto unknown to organic chemists. Many reagent systems involving organometallic compounds of titanium and zirconium compounds have been developed.[29-31]

Interesting cyclization reactions utilizing chromium carbene complexes have been observed.[32]



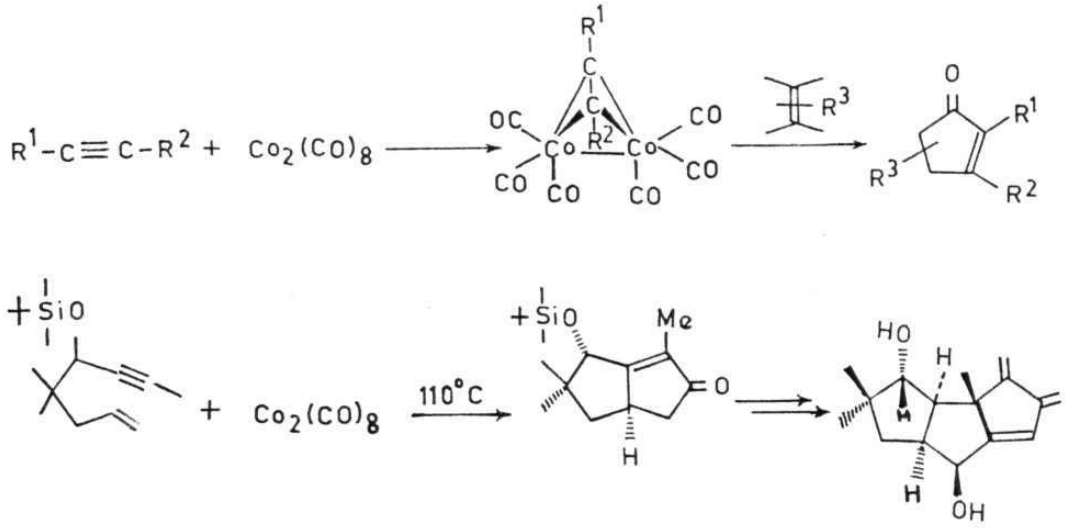
Organoiron reagents have been found to give many interesting applications.[33] Several interesting transformations have been realised with $Fe_2(CO)_9$.[33-35]



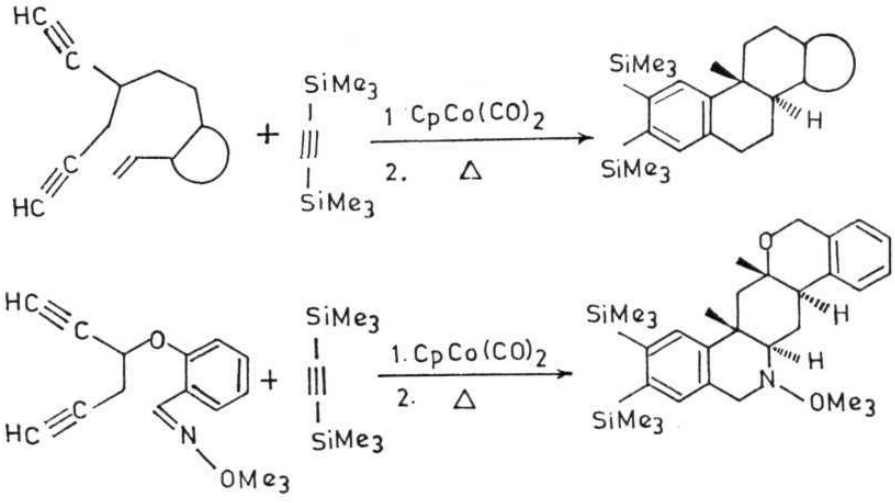


A new method of constructing five membered rings via cooligomerization of an alkyne and alkene with carbon monoxide utilizing $Co_2(CO)_8$

has been discovered by Pauson and Khand.[36] This reaction has been already extensively utilized for the synthesis of many cyclopentanoid natural products.[36]



Several cobalt catalysed (2+2+2) cycloadditions and cyclizations utilizing $CpCo(CO)_2$ and their applications in the synthesis of natural products have been reported by Vollhardt and his coworkers.[37]



Organonickel complexes have been found to give many interesting reactions and an excellent compilation has appeared.[38]

Despite the availability of several excellent review articles on the interesting synthetic methods utilizing transition metal complexes, still there is hesitation among synthetic chemists in utilizing these methods. This may be due to complexities involved in the synthesis of the transition metal organometallic reagents required for these transformations. Our objective is to investigate the reactions of transition metal hydrides and low-valent transition metal complexes, generated by reduction of transition metal halides utilizing simple reducing agents such as $NaBH_4$ with organic substrates. We have selected the cobalt(II) chloride for the present investigation. The relevant literature reports are discussed in the introductory, and results and discussion sections of chapters 1-3.

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CHAPTER 1

Studies on the reactivities of $CoCl_2/NaBH_4$ system with olefins

INTRODUCTION

The metal hydrides, particularly $NaBH_4$ and $LiAlH_4$, have become reagents of choice for the reduction of functional groups in modern organic chemistry.[1-3] The reducing ability of these hydrides can be modified in several ways.[3] In recent years, there is great deal of interest in utilizing transition metal salts in conjunction with $NaBH_4$ and $LiAlH_4$ in order to modify or enhance the reactivities of these reagents.[4,5] Several detailed reviews have appeared concerning the reactions of $NaBH_4$ with transition metal salts and their applications in the development of new synthetic methods.[5,6,7] However, it will be helpful to briefly survey the literature in these topics.

Reactions of MBH_4 (M = Na or Li) with MX_n

The alkalimetal borohydrides react with transition metal salts in several ways.[7,8] In many cases, one metal salt can give several types of reactions depending on the reaction conditions.

(i) Simple metathesis[9]

$$(Ph_3P)_3CuCl + NaBH_4 \longrightarrow (Ph_3P)_2Cu(BH_4)$$

(ii) Reduction of metal salt[10]

$$CuCl + LiBH_4 \longrightarrow CuBH_4$$

$$2CuBH_4 \longrightarrow 2Cu + H_2 + B_2H_6$$

(iii) Formation of metal borides[11]

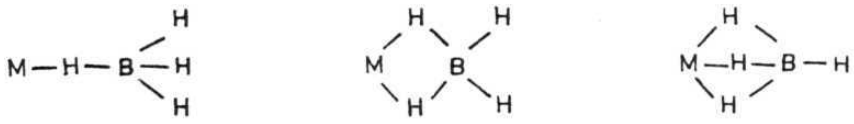
$$2NiCl_2.6H_2O + 4NaBH_4 + 2H_2O \longrightarrow Ni_2B + 3H_3BO_3 + 4NaCl + 12.5H_2$$

(iv) Formation of metal hydrides[12]

$$RuCl_2(PPh_3)_3 + NaBH_4 \xrightarrow{PPh_3} RuH_2(PPh_3)_4$$

In most cases, the borohydride complexes are initially formed which then decompose to the metal or low-valent species, borides or hydrides. However, many borohydride complexes have been isolated and characterised although not all of them are stable at ambient temperature.[7,8]

Three types of bondings by the BH_4^- moiety have been identified in the transition metal complexes containing BH_4^- ligands.[7,8] Depending on the metal and other ligands bonded to the metal, the tetrahydroborate unit can function as a monodentate, bidentate or tridentate ligand .



Borohydride complexes of Group IIIA metals (Sc, Y, La)

The tetrahydroborate complex of scandium, $Sc(BH_4)_3.2THF$ has been prepared by treating anhydrous $ScCl_3$ with $LiBH_4$ in THF.[13] Anhydrous

YCl_3 reacts in a similar fashion with $LiBH_4$, but gives the complex with two BH_4 ligands $Y(BH_4)_2Cl.2THF$.[14]

$$YCl_3 + 2LiBH_4 \xrightarrow{THF} YCl(BH_4)_2.2THF + 2LiCl$$

However, by heating this complex, $YCl(BH_4)_2.2THF$, at 150°C under vacuum, $Y(BH_4)_3$ and $Y(BH_4)Cl_2$ are obtained.[15] Treatment of $Y(BH_4)_2Cl.2THF$ with two equivalents of $NaOCH_3$ gives a new complex $Y(BH_4)(OMe)_2$.[16] The tetrahydroborate complex of lanthanum, $La(BH_4)_3.3THF$, has been reported. The synthesis of this complex has been achieved by the reaction of lanthanum(III)alkoxide with diborane in the presence of THF.[17]

Group IV A metals (Ti, Zr, Hf)

The tetrahydroborate complex of titanium, $Ti(BH_4)_3$, has been prepared by the reaction of $TiCl_4$ vapour with solid $LiBH_4$.[18] In diethyl ether, the solvated complex $Ti(BH_4)_3.Et_2O$ is formed.[19] The zirconium and hafnium tetrahydroborate complexes have also been prepared in a similar manner.[18] The use of $Al(BH_4)_3$ as BH_4^- transfer agent in the reaction of $TiCl_4$ at -30°C results in the formation of $Ti(BH_4)_2Cl$, which may exists as dimer, $[Ti(BH_4)Cl]_2$.[18] Treatment of this complex with THF yields $Ti(BH_4)_3.THF$.[20]

A 1:2 molar ratio of Cp_2TiCl_2 and $LiBH_4$ in diethyl ether at 0°C presumably gives $Cp_2Ti(BH_4)_2$.[21] But the complex decomposes at room temperature to give $Cp_2Ti(BH_4)$.[21] The corresponding zirconium

and hafnium derivatives form complexes with two BH_4 ligands with excess $LiBH_4$.[21,22] Trimethylamine reacts with $Cp_2Zr(BH_4)_2$ to give $(CH_3)_3NBH_3$ and the hydridotetrahydroborato zirconium complex, $Cp_2Zr(H)(BH_4)$.[23] Use of large amount of trimethylamine results in the formation of $[Cp_2ZrH_2]_n$ and $(CH_3)_3NBH_3$.[23]

$$Cp_2Zr(BH_4)_2 + (CH_3)_3N \longrightarrow Cp_2Zr(H)(BH)_4 + (CH_3)_3NBH_3$$

$$Cp_2Zr(BH_4)_2 + \text{excess } (CH_3)_3N \longrightarrow [Cp_2ZrH_2]_n + (CH_3)_3NBH_3$$

Group VA metals (V, Nb, Ta)

In this group, very few tetrahydroborate complexes have been reported. The reaction of $CpVCl_2$ with $NaBH_4$ in 1,2-dimethoxyethane yields $CpV(BH_4)$.[24] The niobium and tantalum tetrahydroborate complexes have been prepared in a similar manner. The niobium analogue was also prepared by treating $NbCl_5$ with sodium cyclopentadienide, $LiBH_4$ and H_2.[25] The tantalum complex, $Me_3Ta(BH_4)_2$ has been reported to be formed by the reaction of Me_3TaCl_2 and BH_4^-.[26]

Group VIA metals (Cr, Mo, W)

The chromium tetrahydroborate complex, $Cr(BH_4)_2.2THF$, has been prepared by the reaction of diborane with $Cr(OBu^t)_4$ in THF.[27] Reaction of excess $NaBH_4$ with $Cp_2MoCl_2(O)$ in THF produces $Cp_2Mo(BH_4)(O)$.[28] The tungston complex $Cp_2W(BH_4)(O)$ has been prepared in the same manner.[28]

Group VIIA metals (Mn, Tc, Re)

Reactions of $LiBH_4$ with $MnCl_2$ or MnI_2 in diethyl ether result in the formation of tetrahydroborate complexes, $Mn(BH_4)_2$ or $Li_2MnX_2(BH_4)_2$ depending on the reactants ratio.[29]

Group VIII metals

(i) **Iron sub-group (Fe, Ru, Os)**

The unstable iron(II) complex $Fe(BH_4)_2$ has been prepared by the reaction of $LiBH_4$ with $FeCl_3$ in diethyl ether at low temperatures.[30] The use of $FeCl_2$ in the above reaction results in the formation of lithium salts, $Li[Fe(BH_4)_3]$ and $Li_2[Fe(BH_4)_3]$.[29] The ruthenium complex, $Ru(H)(BH_4)(PPh_3)_3$ is formed in the reaction of $RuCl_3$ with a mixture of $NaBH_4$ and PPh_3 in ethanol.[31,32] Synthesis of several other complexes of type $Ru(H)(BH_4)(CO)_n(L)_m$, L = PPh_3, PCy_3 has also been reported.[32]

(ii) Cobalt sub-group (Co, Rh, Ir)

The unstable Co(II) complex, $Co(BH_4)_2$, is reported to have been formed in the reaction of $LiBH_4$ with $CoBr_2$ in diethyl ether and $Li_2[CoBr_4]$ in diethyl ether at -80°C.[33] The product decomposes upon warming to give cobalt boride, diborane and H_2.

$$CoBr_2 \xrightarrow[-80^oC]{LiBH_4} [Co(BH_4)_2]$$

$$Li_2[CoBr_4] \xrightarrow[-80^oC]{LiBH_4} [Co(BH_4)_2]$$

$$[Co(BH_4)_2] \longrightarrow "Co_2B" + H_2 + B_2H_6$$

The tetrahydroborate complex $Co(BH_4)(PPh_3)_3$ has been prepared from the reaction of $CoCl(PPh_3)_3$ with $NaBH_4$ in EtOH in presence of PPh_3.[34] $CoCl_2$ reacts with a $NaBH_4/PPh_3$ mixture in toluene-ethanol (2:1) to give $Co(BH_4)(PPh_3)_2$.[35] The complex $Co(H)(BH_4)(PCy_3)_2$ has been prepared in a similar fashion.[36] This complex catalyses the hydrogenation and isomerization reactions. Reaction of $NaBH_4$ with $RhCl(PPh_3)_3$ in ethanol produces trans-$Rh(BH_4)(PPh_3)_2$ or $Rh(H)(PPh_3)_2$ depending on the reaction time.[37]

(iii) **Nickel sub-group (Ni, Pd, Pt)**

Complexes of the type $MH(BH_4)L_2$, M=Ni, L=PCy_3 or P^iPr_3; M=Pd, L=PCy_3 or P^iPr_3 have been prepared by the reaction of MCl_2L_2 with $NaBH_4$ in acetone/ethanol.[38,39] These complexes have been used as catalysts in the rearrangement of 1,4-dienes and oligomerization of butadiene.[38,39] The nickel(II) tetrahydroborates $Ni(BH_4)L(ClO_4)$, $Ni(BH_4)L(BH_4)$ and $Ni(BH_4)_2L$, where L=a cyclic tetramine or an acyclic tetradentate Schiff base, have been prepared from the reaction of nickel complex of L with $NaBH_4$.[40] The reaction of $NaBH_4$ with $NiCl_2.6H_2O$

in the presence of 1,10-phenanthroline in EtOH produces [Ni(BH_4)(phen)-(H_2O)].[41]

Group IB metals (Cu, Ag, Au)

The simple tetrahydroborate complexes Cu(BH_4) and Ag(BH_4) decompose to the metal, B_2H_6 and H_2 below room temperature.[42] Only the decomposed products were isolated from the reaction of $AuCl_3$ with $LiBH_4$ at -120°C in diethyl ether, instead of the expected Au(BH_4)$_3$.[43] Reaction of a $CHCl_3$ solution of CuCl(PPh_3)$_2$ with $NaBH_4$ in ethanol produces Cu(BH_4)(PPh_3)$_2$.[44] Another procedure involves the addition of $NaBH_4$ to copper(II) sulfate and PPh_3 in ethanol.[45] Similar procedures were followed for preparing the corresponding silver and gold analogues.

Organic transformations involving $MX_n/NaBH_4$ or $LiBH_4$ systems

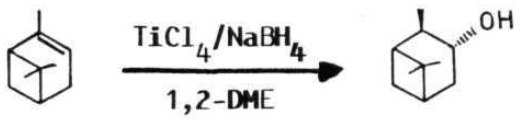
The combination of alkalimetal borohydrides with transition metal halides has immense potential in organic synthesis.[4,5] Almost all conceivable combination of transition metal salt and $NaBH_4$ (or $LiBH_4$) has been investigated to develop new organic synthetic methods.[4,5] Recently, an excellent review article describing the utilization of the $MX_n/NaBH_4$ or $LiBH_4$ has appeared.[5] However, the transformations are briefly reviewed here in order to facilitate discussion.

Group IIIA metals (Sc, Y, La)

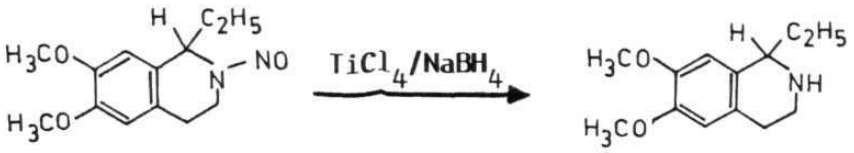
Though the tetrahydroborate complexes of Sc,Y and La are known, they have not been utilized in organic synthesis.

Group IVA metals (Ti, Zr, Hf)

In this triad, titanium has found extensive applications in organic synthesis. $TiCl_4|NaBH_4$ system reduces carboxylic acids and esters into alcohols and nitriles into amines.[46,47] It was noted that nitrocompounds and amides give unsatisfactory results. However, later it was observed that the $TiCl_4/NaBH_4$ can also be utilized satisfactorily for the reduction of amides, nitrocompounds, acidchlorides, oximes and sulfoxides.[48] It was also demonstrated that the reaction of alkenes with $TiCl_4|NaBH_4$ in 1,2-dimethoxyethane gives anti-Markovnikov alcohols.[49] The possibility of hydrotitanation followed by hydrolysis/oxidation of the resulting organotitanium intermediate via radical mechanism was suggested.[49]



Reductive denitrosation of nitrosamines to secondary amines was also observed with this system.[50]



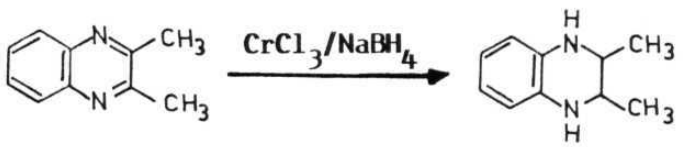
Deoxygenation of pyridine, quinoline and isoquinoline-N-oxides utilizing the $TiCl_4/NaBH_4$ system has been reported.[51]

Group VA metals (V, Nb, Ta)

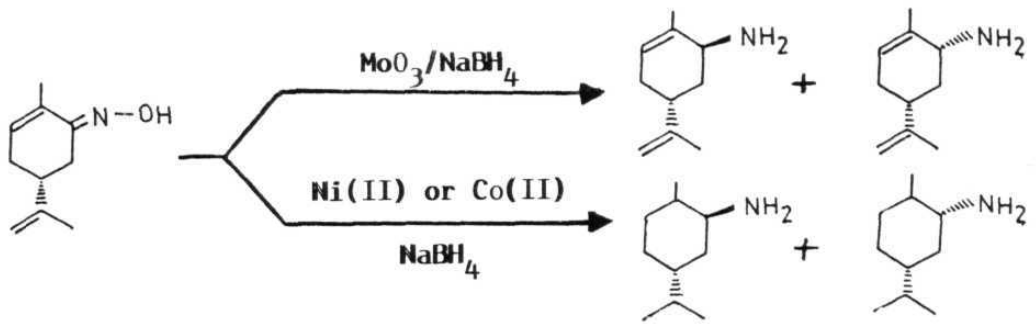
The borohydride complexes of this triad have not been utilized for organic synthesis.

Group VIA metals (Cr, Mo, W)

The $CrCl_3/NaBH_4$ system, has been utilized for the reduction of heterocyclic compounds. For example, conversion of several quinolines, isoquinolines and quinoxalines to their tetrahydroderivatives were carried out utilizing this reagent system.[52]



The $MoO_3/NaBH_4$ system reduces allylic oximes selectively to allylic amines while corresponding combinations of Ni(II) and Co(II) salts with $NaBH_4$ give saturated amines.[53]



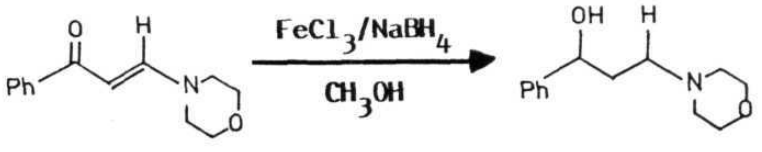
Group VIIA metals (Mn, Tc, Re)

In this group, only manganese forms tetrahydroborate complexes, but their synthetic utility has not been explored.

Group VIII metals

(i) **Iron sub-group (Fe, Ru, Os)**

The $FeCl_3/NaBH_4/CH_3OH$ system reduces nitroarenes to amines in good yields.[54] The β- dialkyl amino- α - β -unsaturated ketones which are normally resistant to $NaBH_4$, afford the corresponding saturated γ-amino alcohols in high yields with this system.[55]

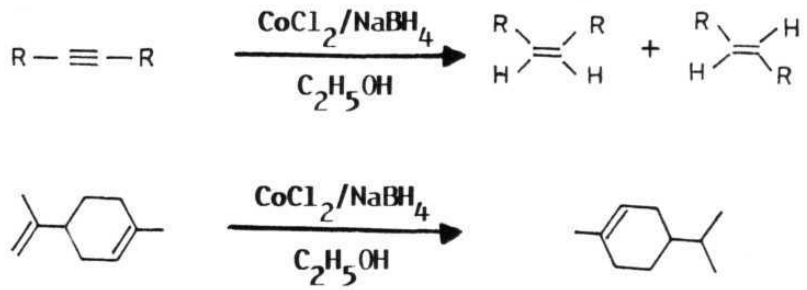


Reduction of nitrobenzenes to anilines was achieved utilizing catalytic amount of ruthenium and osmium salts in combination with

$NaBH_4$.[56] The ruthenium(III)/$NaBH_4$ system has been utilized for the reduction of arenes to the corresponding saturated hydrocarbons.[57]

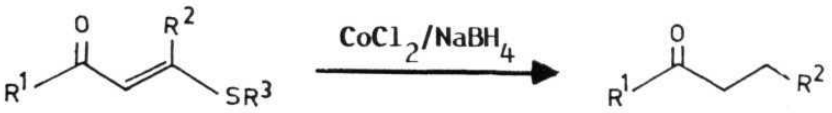
(ii) **Cobalt sub-group (Co, Rh, Ir)**

The cobalt(II) salts in combination with $NaBH_4$ reduce a vide spectrum of organic substrates. It has been reported that alcoholic $NaBH_4/CoCl_2.6H_2O$ system selectively reduces alkynes as well as mono-substituted, di-substituted alkenes in the presence of more highly substituted olefins.[58] Selective hydrogenation of limonene was reported.[58]



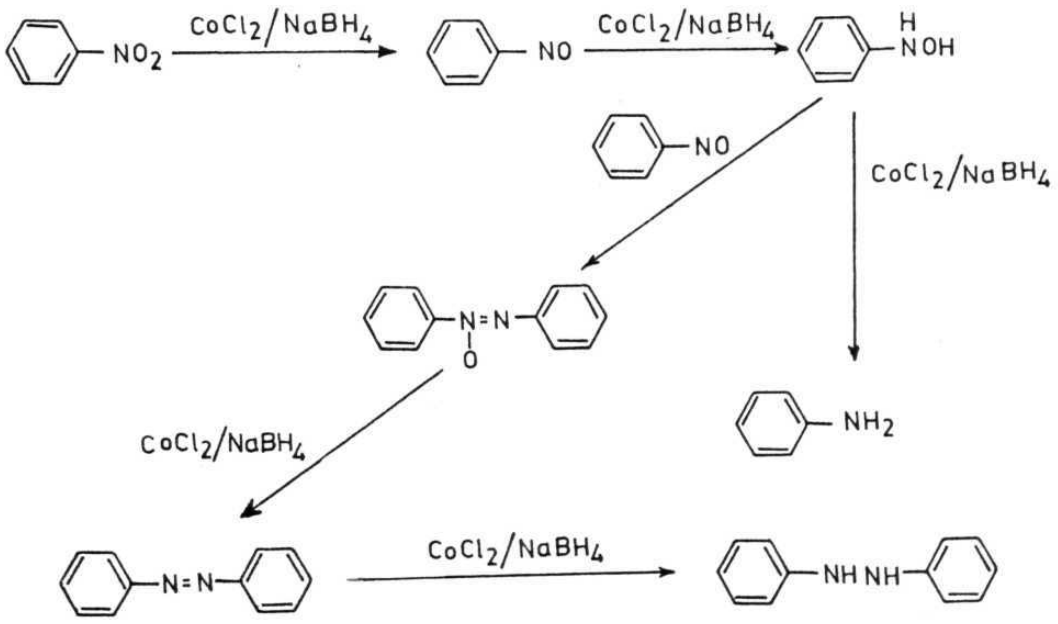
The possibility of the intermediacy of cobalt hydride as active species was suggested.[58] However, more recently, it has been demonstrated that the selective hydrogenation of limonene can also be performed utilizing Co_2B and H_2 gas.[6] It was suggested that the cobalt hydride species can be at most present as a fleeting intermediate in the reductions with the $CoCl_2/NaBH_4$ system and it was proposed that the reduction takes place by delivery of hydride from $NaBH_4$ to the alkyne or alkene adsorbed on the cobalt boride.[6] Catalytic quantities

of $CoCl_2$ and $NiBH_4$ reduce methylcinnamate to methyl dihydrocinnamate.[59] Selective reduction of alkenes in the presence of ketone can be achieved utilizing the $CoCl_2/NaBH_4/CH_3OH$ system. For example, β -sulfenylated, α , β -unsaturated ketones were reduced to the corresponding saturated desulfurised ketones in good yields.[60]

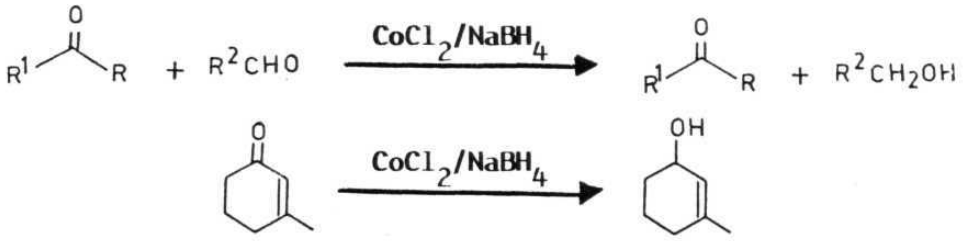


The $CoCl_2/NaBH_4$ system has also been utilized for the reduction of quinoline and isoquinoline derivatives.[52] This system also reduces nitriles, nitroarenes, amides, nitrobenzenes and sulfoxides.[61-72] However, nitroalkanes are inert toward this system. At lower temperatures (-60°C), $CoCl_2/NaBH_4/CH_3OH$ system reduces azoxybenzenes, azobenzenes and nitrobenzenes to hydrazobenzenes (Scheme 1).[73]

Scheme 1



It is interesting to note that the $CoCl_2/NaBH_4$ system in DMSO solvent selectively reduces aldehydes in the presence of ketones and converts α, β -unsaturated ketones to the corresponding unsaturated alcohols.[74]

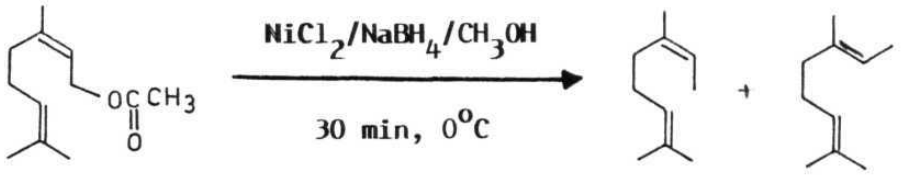


The $RhCl_3/NaBH_4$ in ethanol reduces aromatic compounds into the corresponding saturated derivatives.[75,76] The $IrCl_3/NaBH_4$ system also exhibits similar reactivity but it is less effective.[57]

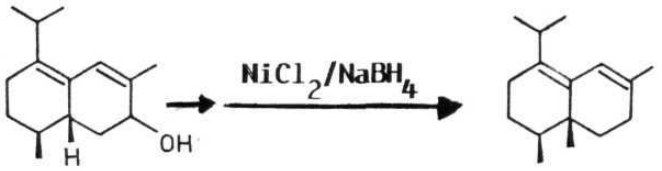
(ii) **Nickel sub-group (Ni, Pd, Pt)**

In 1952, it was reported that the material prepared from the $NiCl_2/NaBH_4$ reagent system serves as a heterogeneous hydrogenation catalyst.[77] This was followed by several studies utilizing other transition metals. The $NiCl_2/NaBH_4$ system was shown to work equally well as the $CoCl_2/NaBH_4$ system in several reductions. For example, the $NiX_2/NaBH_4$ system reduces methyl cinnamates,[59] nitroarenes and heterocyclic compounds,[52] nitrobenzenes, nitrosobenzenes, azoxybenzenes and azobenzenes.[73,78] In addition, several other substrates were also reduced. For example, nitroalkanes which are unreactive towards $CoCl_2/NaBH_4$ system, can be readily reduced using the $NiCl_2/NaBH_4$ system.[79] Allylic and benzylic oximes were completely reduced to

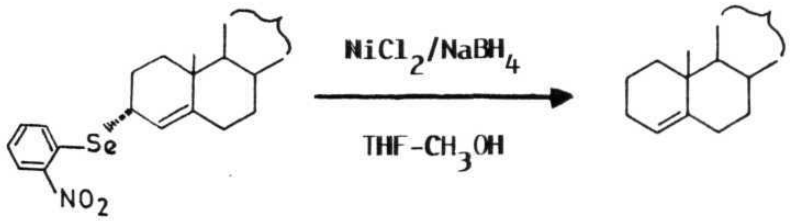
saturated amines in contrast to $MoO_3/NaBH_4$ system which gives allylic amines.[53] Another interesting transformation achieved utilizing the $NiCl_2/NaBH_4/CH_3OH$ reagent is the reductive removal of allylic, propargylic and benzylic acetate esters.[80]



The material prepared from $NiCl_2/NaBH_4$ reagent has been utilized for reductive clevage of allylic alcohols to alkenes in a one pot process via the corresponding trimethylsilyl ethers.[81]

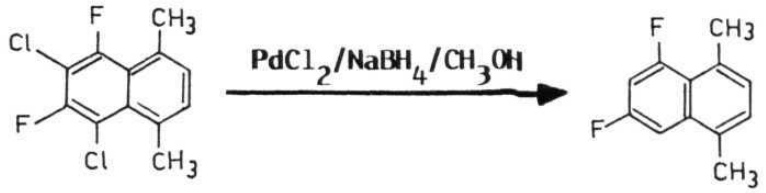


This reagent system has also been utilized for desulfurization reactions.[82,83] The $NiCl_2/NaBH_4$ system has also been utilized for the reductive deselenization of alkyl, allyl and alkenyl selenides in THF-CH_3OH at 0°C.[84]



The $PdCl_2/NaBH_4$ system reduces diphenylacetylene and methyl-hex-3-ynoate into the corresponding cis-alkenes.[85,86] Recently, the $PdCl_2/NaBH_4/CH_3OH$ system was reported to reduce arylketones to

arenes.[87] This reagent system also selectively dechlorinates 5,7-dichloro-6,8-difluoro-1,4-dimethylnapthalene into 5,7-diflouro-1,4-dimethylnapthalene.[88]



Group IB metals (Cu, Ag, Au)

In this group, the $CuCl_2/NaBH_4$ system has been reported to reduce nitroarenes and heterocyclic compounds.[52] This system has also been utilized for reduction-desulfurization of β -sulfenylated α, β -unsaturated ketones into the corresponding saturated desulfurized ketones in good yields.[60] The complex $(Ph_3P)_2CuBH_4$ has been extensively utilised in organic synthesis.[89] For example, 2-adamantyl tosylhydrazone has been reduced to the corresponding hydrocarbon by this system in good yield.[89a]

As outlined above, the transition metal salts in combination with $NaBH_4$ give promising reactivities which have good potentials in organic synthesis. The mechanisms of many of these transformations have not been studied in detail. In several cases, involvement of transition metal hydrides and related species have been suggested. It was demonstrated that in some cases the reactive species may not be the transition metal hydrides.[5,6] However, we were attracted by the possibility of generating transition metal hydride species in

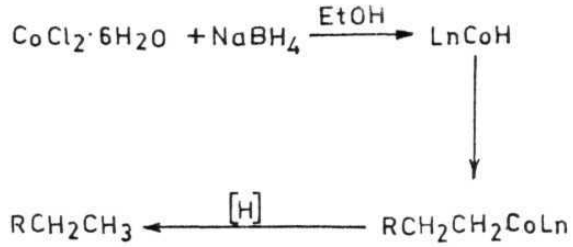
this way since hydrometallation of unsaturated substrates utilizing these hydrides would constitute non-carbanionic routes to transition metal organometallic reagents (i.e., synthesis of transition metal organometallic reagents without utilizing RMgX or RLi). We have selected the $CoCl_2/NaBH_4$ system for the present studies.

RESULTS AND DISCUSSION

Hydroboration of Alkenes with the $CoCl_2/NaBH_4$ system in THF

As outlined previously, it has been reported that the $CoCl_2.6H_2O/NaBH_4/C_2H_5OH$ system reduces alkenes to alkanes.[58] It was suggested that the reaction proceeds through hydrocobaltation of the olefin and gives organocobalt species as intermediates (Scheme 2) since alcoholic $NaBH_4$ was previously reported to react with Co(II) to produce Co metal, $Co(BH_4)_2$, complexed cobalt hydrides.[58] Results of the experiments utilizing $NaBD_4$ and EtOD have been presented in support of the intermediacy of cobalt hydride intermediate.[58]

Scheme 2



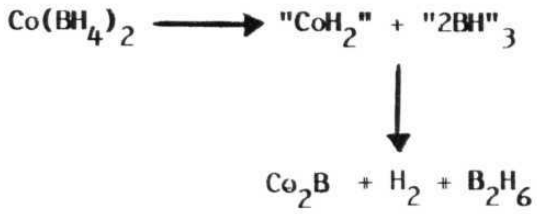
We have decided to examine the possibility of utilizing the organocobalt species produced in this way (Scheme 2). Since the organocobalt species readily undergoes carbonylation reactions (e.g., oxoprocess), we have attempted to carbonylate the organocobalt species formed in the reaction outlined in Scheme 2. However, addition of $NaBH_4$ (20 mmol) into a mixture of 1-decene (10 mmol) and $CoCl_2.6H_2O$ (10 mmol) in ethanol under nitrogen atmosphere at 0^oC followed by carbonylation of the reaction mixture with carbon monoxide (atmospheric

pressure) for 3h at room temperature, gave only the reduction product decane and no carbonylated product was formed.

It was thought that the difficulty may be due to the instability of the organocobalt species formed under alcoholic reaction conditions utilizing hydrated $CoCl_2$. Accordingly, we have carried out the reaction as outlined above, replacing $CoCl_2.6H_2O$ with anhydrous $CoCl_2$ and using THF as the solvent instead of ethanol. It was observed that addition of $NaBH_4$ (20 mmol) into a mixture of 1-decene (20 mmol) and anhydrous $CoCl_2$ (10 mmol) in THF (60 ml) under nitrogen atomosphere at 0^oC followed by carbonylation by bubbling carbon monoxide for 5h did not give any carbonylated product. The crude product on distillation gave decane (40-50%) and lot of less volatile residue was left behind in the distillation flask. Our experience with organoboranes indicated that the product could be organoboron compound.[90,92] Oxidation of this residue with H_2O_2/OH^- gave 1-decanol.[91] Similar results were obtained when the experiment was carried out in the absence of carbon monoxide. Clearly, the anhydrous $CoCl_2/NaBH_4$ system in THF is able to hydrogenate and hydroborate 1-decene.

As mentioned previously, the $CoBr_2/LiBH_4$ system in diethyl ether at -80^oC gives the corresponding $Co(BH_4)_2$ which decomposes into cobalt boride "Co_2B" (non-stoichiometric), H_2 and B_2H_6.[33] Although the mechanism of cobalt boride formation is not known, it may be most probably formed by the reaction of Co-H and $\rangle$B-H moieties formed by the decomposition of $Co(BH_4)_2$ (Scheme 2).

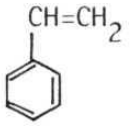
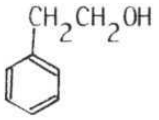
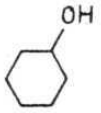
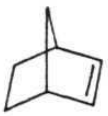
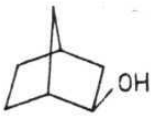
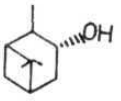
Scheme 3



The residual diborane comes out of the ether solution (Scheme 3). It is possible that the $NaBH_4$ (2 eq.) and $CoCl_2$(1 eq) reagents in THF at 0^oC would most probably give the $Co(BH_4)_2$ which then undergoes decomposition to cobalt boride, BH_3THF and H_2. It is well-known that diborane is soluble in THF and remains as BH_3THF.[91] If the decomposition of $Co(BH_4)_2$ takes place as outlined in Scheme 3 by the reaction of CoH_2 and BH_3, then residual BH_3THF will be left out in the solution after decomposition is complete. Accordingly, if the "Co_2B"/BH_3THF combination does not reduce 1-decene, hydroboration will be the only reaction if the olefin is added after the decomposition of the cobalt borohydride into "Co_2B", H_2 and BH_3THF.

In order to examine this possibility, we carried out the following experiment: $NaBH_4$ (20 mmol) was added during 15 minutes to $CoCl_2$ (10 mmol) in THF (60 ml) at 0^oC under nitrogen atmosphere and the mixture was stirred for 1h at 0^oC and further stirred at room temperature for 2h. 1-Decene (40 mmol) was added and the reaction mixture was stirred for 3h at room temperature. Workup and oxidation of the crude product in THF (20 ml) with H_2O_2/NaOH gave 1-decanol in 70% yield besides small amount of 1-decane (5%) (Table 1).

Table 1: Hydroboration of alkenes with $CoCl_2/NaBH_4$[a]

Alkene	Product[b]	Yield [%][c]
$CH_3(CH_2)_7\ CH{=}CH_2$	$CH_3(CH_2)_7CH_2CH_2OH$	70
		68[d]
		85
		90
		70

[a] The reactions were carried out using 40 mmol of alkenes, 20 mmol of $NaBH_4$ and 10 mmol of $CoCl_2$ in THF (40 mmol) under nitrogen atmosphere. THF used was distilled over benzophenone-sodium. Cobalt(II) chloride supplied by Alfa-USA and the sample prepared by the dehydration of $CoCl_2.6H_2O$ using 2,2-dimethoxypropane work equally well. Sodium borohydride supplied by Fluka-Switzerland and the sample supplied by Loba-Cheme-India give identical results.

[b] Products obtained after oxidation with $H_2O_2/NaOH$. The products were identified by spectral data (IR, ^{1}H-NMR and ^{13}C-NMR) and comparison with the data reported in the literature.

[c] Yields are of the isolated and distilled products.

[d] The isomeric 1-phenylethanol is present to the extent of 18%. Products in other cases contain only small amount of the isomeric alcohols (< 5%).

The reaction was found to be a general one and many other olefins can be hydroborated with this system. The regio- and stereoselectivities observed with this system are similar to those obtained utilizing the BH_3THF reagent.[91]

We have also observed that addition of triethylamine (20 mmol) instead of olefins under the hydroboration reaction conditions (Table 1, also see experimental section) gives triethylamine-borane complex in 82% yield. Also, the reaction of $CoCl_2/Ph_3P/NaBH_4$ system gives Ph_3PBH_3 (Chapter 2). Clearly, the $CoCl_2/NaBH_4$ system is able to supply the BH_3 moiety. Recently, Ganem and Osby attempted to give evidence for the BH_3THF formed in the $CoCl_2/NaBH_4$ system by performing the hydroboration with 1,5-cyclooctadiene in order to examine whether 9-BBN is formed but concluded that their evidence is inconclusive.[6] However, the reported formation of B_2H_6 in the decomposition of $Co(BH_4)_2$ in diethyl ether[33] and our experiments with Et_3N and Ph_3P clearly indicate that the $CoCl_2/NaBH_4$ system does produce BH_3 moeity.

Reduction of Alkenes, anils, imine and enamine with $CoCl_2/NaBH_4/CH_3OH$ system in THF

As outlined in the introductory section, it has been reported that the $CoCl_2.6H_2O/NaBH_4/C_2H_5OH$ system reduces alkenes to alkanes.[58] As discussed previously, we have found that the anhydrous $CoCl_2$ and $NaBH_4$ system in THF gives both hydroboration and hydrogenation products with 1-decene. It appeared that the $CoCl_2.6H_2O/NaBH_4/C_2H_5OH$ system does not give hydroboration product as the intermediate borane species will be

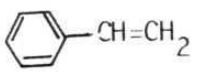
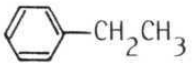
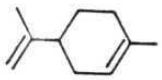
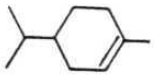
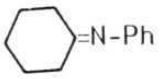
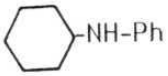
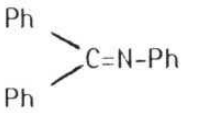
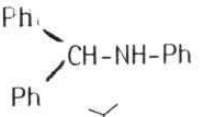
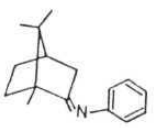
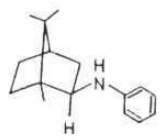
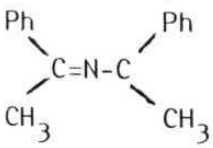
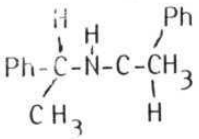
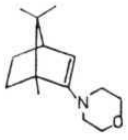
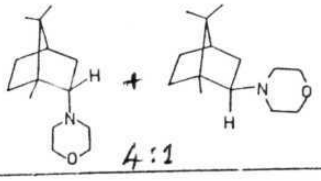
destroyed by the water (from the water of hydration in $CoCl_2.6H_2O$) and C_2H_5OH present. Accordingly, it should be possible to prevent hydroboration by performing the anhydrous $CoCl_2$ and $NaBH_4$ reaction in presence of calculated quantities of CH_3OH (i.e., at least 6 equivalents of CH_3OH, Scheme 3).

In order to examine the reactivity of the cobalt reagent generated in this way, we carried out the following experiment: $CoCl_2$ (10 mmol) and CH_3OH (60 mmol) were taken in THF (60 ml) under nitrogen atmosphere and $NaBH_4$ (20 mmol) was added at 0^oC during 1h with stirring.1-Decene was added and the mixture was stirred further for 2h at 0^o. After work up decane was isolated in 80% yield and no hydroboration product was formed. Clearly, the methanol present in the medium reacts with the borane (if any) generated and the resulting mixture is able to reduce 1-decene to decane (Table 2). The reagent system also reduces styrene to ethylbenzene and 4-octene to octane in good yields (Table 2).

The reagent system does not affect the trisubstituted alkenes as indicated by the inertness of α-pinene and cholesterol under the present reaction conditions. The difference in reactivities can be taken into advantage for selective reductions as revealed by the partial reduction of limonene by this reagent system (Table 2). Similar reactivities towards various olefins were also observed with the $CoCl_2.6H_2O/NaBH_4/C_2H_5OH$ system.[58] However, in this system excess $CoCl_2.6H_2O$ and $NaBH_4$ reagents were utilized compared to the present system.

In connection with studies on the mechanism of the hydroboration reaction in our laboratory, we required some chiral tertiary amines.[92]

Table 2: Reduction of organic substrates with $CoCl_2/NaBH_4/CH_3OH$ in THF[a]

Substrates	Product[b]	Yield (%)
$CH_3(CH_2)_7CH{=}CH_2$	$CH_3(CH_2)_7CH_2CH_3$	80
		65
trans-4-octene	$CH_3(CH_2)_6CH_3$	70
	No reaction	
Cholesterol	No reaction	
		75
PhCH=N-Ph	$PhCH_2NH$-Ph	78[d]
		74
		63[d]
		74[e]
		64[d,f]
	 4:1	82[g]

[a] For all substrates, the reactions were carried out in the same scale, under the same conditions as given in the representative procedures (see experimental section).

[b] Products were identified by spectral data (IR, ^{1}H-NMR and ^{13}C-NMR) and comparison with physical constant data reported in the literature.

[c] Yields are of isolated and distilled products.

[d] These experiments carried out by Mr. A. Devasagayaraj of our laboratory.[96]

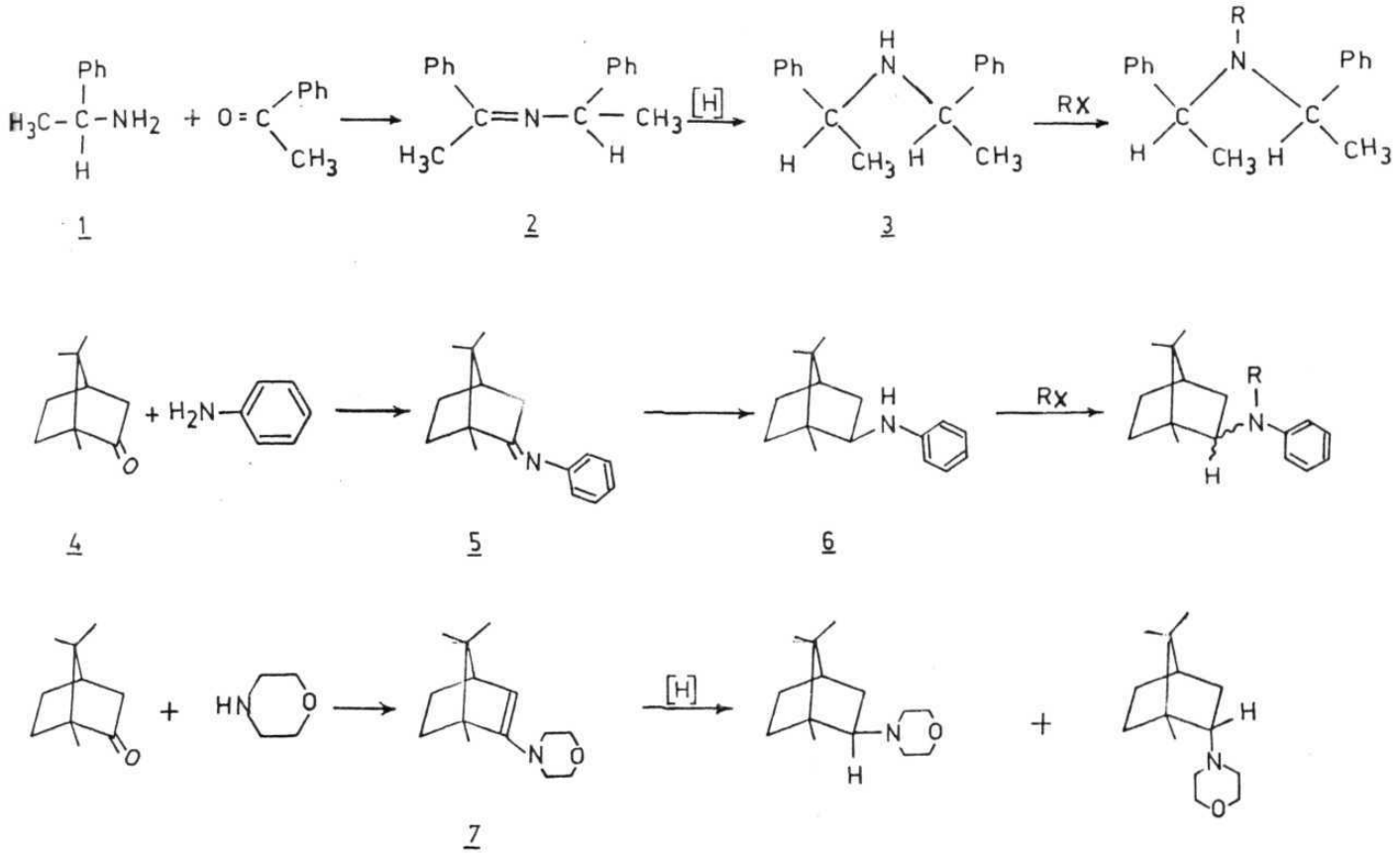
[e] $[\alpha]_D^{20} = -71.5^{o}$ (C=11.6, EtOH), Lit.[97] $[\alpha]_D^{20} = -89.1^{o}$ (unverified).

[f] $[\alpha]_D^{20} = 121.7^{o}$ (C=4.4, $CHCl_3$), Lit.[98] $[\alpha]_D^{20} = -196.3^{o}$ (C=5, EtOH).

[g] The ratio of isomers is only a crude estimate as it was calculated by the comparison of the signal intensities.

We envisaged the synthesis starting from the commercially available (+)- α -methylbenzylamine and (+) camphor as outlined in Scheme 4 which require the reduction of anils, imine or enamine.

Scheme 4



Initially, we utilized the simple, readily available reducing agents such as HCOOH,[93] $NaBH_4$[94] and BH_3THF[94] for the reduction of camphor-a-nil. Whereas the HCOOH and $NaBH_4$ did not effect the desired reduction, the BH_3THF reagent[95] gave a 2:3 mixture of bornyl and isobornyl aniline.[92] In order to examine whether the $CoCl_2/NaBH_4/CH_3OH$ system can be utilized for this purpose, we carried out the reduction of cyclohexanone-anil,

benzophenone-anil and Schiff base prepared from benzaldehyde.[96] In all these cases, the reduced secondary amine was isolated in good yields (Table 2).

Reduction of camphor-anil (Scheme 4) with the $CoCl_2/NaBH_4/CH_3OH$ system at -10°C for 3h gave the isomerically pure **6** in 74% yield. The ^{13}C-NMR spectrum of the product does not show signals corresponding to the isomeric bornyl aniline.

The reduction of imine **2** (Scheme 4) prepared from R(+)- α-methylbenzylamine, $[\alpha]_D^{20} = +30^o \pm 2$, gave the secondary amine **3** in 64% yield with $[\alpha]_D^{20} = +121.7^o$ (C=4.4, $CHCl_3$) (Table 2). This $[\alpha]_D$ value compares with the value of -196.3° (C=5, ethanol) obtained for the product prepared by $Pd/C/H_2$ reduction of imine **2** prepared from α-methylbenzylamine with $[\alpha]_D = -37.5^o$.[98]

Reduction of morpholine-enamine **7** prepared from camphor (Scheme 4) gave a 4:1 mixture of bornyl and isobornyl morpholine (Table 2). It may be of interest to note that the reduction of enamine **7** with HCOOH at 100°C gave pure bornyl morpholine in 90% yield.[93]

The results indicate that the $CoCl_2/NaBH_4/CH_3OH$ system serves as a simple system for the reduction of alkenes, anils, imine and enamine under mild conditions.

Hydrocobaltation - Carbonylation of Alkenes with the $CoCl_2/NaBH_4$ system

As discussed in the introductory section, it was suggested that the reduction of alkenes with the $CoCl_2.6H_2O/NaBH_4/C_2H_5OH$ system proceeds through the intermediacy of complexed cobalt hydride species.[58] It was also suggested that the reaction goes through hydrocobaltation of olefin followed by reductive cleavage of the resulting organocobalt species.[58] However, as discussed earlier, we have observed that the organocobalt species (if any) produced utilizing this reagent system does not undergo carbonylation when carbon monoxide was bubbled through the reaction mixture. A possibility is that the organocobalt reagent produced by this system may undergo protonation by the water and C_2H_5OH present in the medium.

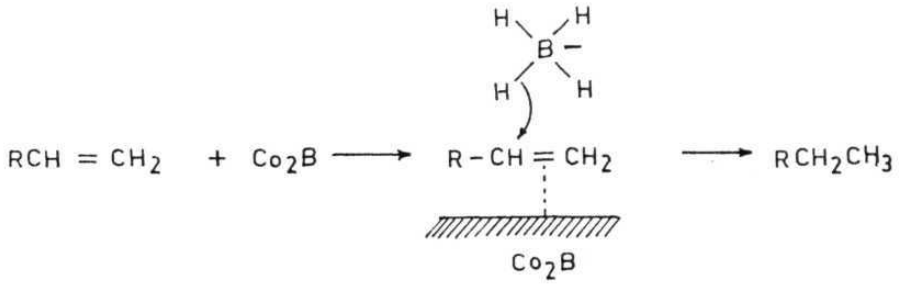
In the present anhyrous $CoCl_2/NaBH_4/CH_3OH$ system, since the methanol was utilized only in calculated amounts to destroy the borane, it appeared that this system may be more suitable to intercept the organocobalt species generated. In order to examine this, we carried out the following experiment. To a suspension of $CoCl_2$ (10 mmol) and CH_3OH (60 mmol) in THF (60 ml) under nitrogen atmosphere, $NaBH_4$ (20 mmol) was added in portions during 15 minutes at 0^oC. 1-Decene (20 mmol) was added and carbon monoxide was bubbled through the reaction mixture for 3h at room temperature. After workup, only decane (70%) was isolated.

Also, in the reduction experiments utilizing the $CoCl_2/NaBH_4/CH_3OH$ system and 1-decene, when D_2O was added into the reaction mixture before workup and the contents were stirred for 1h at room temperature, no incor-

poration of deuterium was observed in the decane product. Clearly, hydrogenolysis of the organocobalt intermediate should have taken place before carbonylation or treatment with D_2O by the residual $\rangle$B-H/LnM-H/CH_3OH present in the medium. Also, it is possible that the reagent system may not give any cobalt hydride or organocobalt species at all.

Recently, it has been suggested that even if the $CoCl_2$ or $CoCl_2.6H_2O$/$NaBH_4$/ROH system gives cobalt hydride species, it may not be stable under the reaction conditions and it can be present only as a fleeting intermediate.[6] It was suggested that the reduction of organic substrates with this system takes place by delivery of hydride from $NaBH_4$ to the alkene adsorbed on cobalt boride surface (Scheme 5)

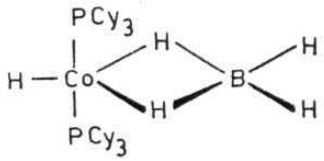
Scheme 5



It has been observed that the $CoCl_2.6H_2O/NaBH_4/C_2H_5OH$ system reacts with diphenylacetylene to give both cis-stilbene (30%) and trans-stilbene (10%) besides 1,2-diphenylethane (10%).[58] It is difficult to account for the formation of trans-stilbene without invoking the possibility of cobalt hydride and organocobalt intermediates.

By now it occured to us that it may be possible to achieve hydrocobaltation-carbonylation only by performing the reaction of the $CoCl_2/NaBH_4$ system with alkenes under conditions in which prevention of hydroboration and stabilization of the intermediate cobalt hydride and organocobalt intermediates can be achieved. Triphenylphosphine appeared to be a suitable reagent for this purpose. It forms the less reactive PPh_3BH_3 complex with BH_3THF and it is well-known that the phosphines stabilize transtion metal hydrides and alkyls.[8]

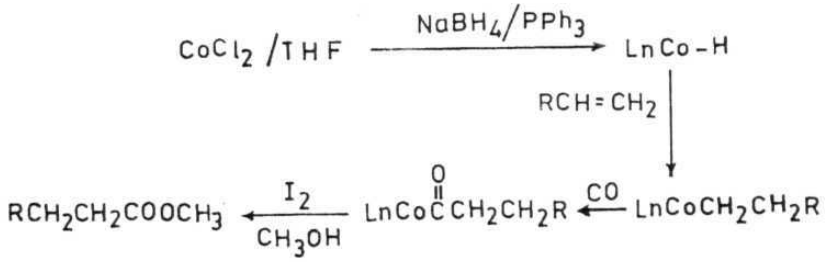
A rich inorganic and structural chemistry of the transition metal borohydride complexes containing phosphine ligands have been uncovered.[8] The stable cobalt complex $(PCy_3)_2CoH(BH_4)$ can be prepared by the reaction of $NaBH_4$ with $CoCl_2$ in the presence of tricyclohexylphosphine (PCy_3) in toluene-CH_3OH mixture.[36]

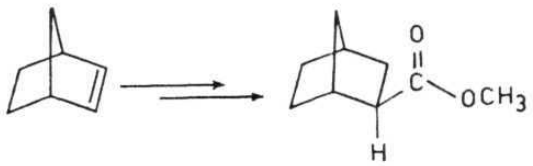


We carried out the carbonylation experiments utilizing $CoCl_2/NaBH_4$ system with 1-decene in the presence of PPh_3 under various conditions. We have found that the reaction gives good results when a mixture of $NaBH_4$ (20 mmol) and PPh_3 (20 mmol) is added to the THF containing anhydrous $CoCl_2$ (10 mmol) and 1-decene (10 mmol) at 0^oC while bubbling corbon monoxide and further stirring the reaction mixture for 4h at room temperature. Iodination-methanolysis followed by workup (see experimental section) and distillation of the crude product gave a mixture of 2-decenes (cis/trans mixture, 30%, for further exploration of this transformation see chapter

2) and undecanoic acid methyl ester (25%, Spectrum no. 1) (Scheme 6). However, considerable amount of less volatile residue was left behind in the distillation flask. Oxidation of this residue with H_2O_2/OH^- gave 1-decanol (35%). Clearly, hydroboration is not completely prevented utilizing Ph_3P in this way. Following this procedure, norbornene was converted into the corresponding exo-ester in 28% yield (Spectrum no. 1).

Scheme 6





Although much to be desired regarding yields of the hydrocobaltation-carbonylation process utilizing the $CoCl_2/Ph_3P/NaBH_4/CO$ system (Scheme 6), the results clearly indicate that the $CoCl_2/Ph_3P/NaBH_4$ system does give cobalt hydride species capable of giving hydrocobaltation-carbonylation of olefins under the present reaction conditions. Even the yields are not so poor, considering that the $HCo(CO)_4$ reagent converts norbornene to exo-norbornyl aldehyde only in 20% yield under stoichiometric reaction conditions under atmospheric pressure of carbon monoxide.[99] It is worth-

while to find means to improve the yields utilizing the simple $CoCl_2/NaBH_4/Ph_3P/CO$ system. Since the present method utilizes simple chemicals for hydrocarboxylation of olefins, it will be attractive for utilization in bench-top organic synthesis. It was decided to explore the reactivities of the cobalt reagent generated utilizing $CoCl_2/NaBH_4$ system in the presence of Ph_3P and carbon monoxide systematically so that the hydrocarboxylation utilizing the $CoCl_2/NaBH_4/Ph_3P/CO$ system can be achieved in reasonable yields at a later stage.

SUMMARY

The anhydrous $CoCl_2/NaBH_4$ reagent in THF hydrogenates or hydroborates alkenes under appropriate conditions. The system in the presence of calculated amount of CH_3OH has been utilized for reduction of alkenes, imines and enamines. Carboxylation of the supposed intermediate organocobalt species was carried out under several conditions. It was observed that addition of $NaBH_4/Ph_3P$ mixture into a mixture of $CoCl_2$/alkene in THF while bubbling carbon monoxide followed by I_2/CH_3OH treatment gives the corresponding one carbon homologated ester in $\sim$25% yield. It was decided to explore the reactivity of the cobalt reagents generated utilizing the $CoCl_2/NaBH_4$ system in the presence of Ph_3P and carbon monoxide (chapters 2 and 3).

EXPERIMENTAL

Melting points reported are uncorrected and were determined using a Buchi-510 capillary point apparatus. Infrared spectra were recorded on Perkin Elmer I.R. spectrometer Model-257 with polystyrene as reference. ^{1}H-NMR and ^{13}C-NMR spectra were recorded on a JEOL-MH-100 spectrometer with chloroform-d as a solvent and TMS as reference (δ = 0 ppm). Elemental analyses were performed on a Perkin Elmer Elemental analyzer model-240C. Gas chromatography analyses were carried out on a Packard model -42 instrument equipped with a flame ionization detector on a SE-30 or carbowax column using nitrogen as carrier gas. Analytical thin layer chromatographic tests were carried out on glass plates (3x10 cm) coated with (250 mμ) Acme's silica gel G or GF_{254} containing 13% calcium sulfate as binder. The spots were visualized by short exposure to iodine vapour or uv light. Column chromatography was carried out using Acme silica gel (100-200 mesh).

All the glasswares were predried in an air oven, assembled hot and cooled under a stream of dry nitrogen. Unless otherwise mentioned all the operations/ transformations of reagents/reactions were carried out using standard syringe, septum techniques recommended for handling air sensitive organometallic compounds.[91]

In all experiments, round bottom flask of appropriate size with a side arm, a side septum, a magnetic stirring bar, a condensor and a connecting tube attached to a mercury bubbler were used. The outlet of

the mercury bubbler was connected by a long tube to the atmosphere.

All the dry solvents were distilled from appropriate drying agents just before use. As a routine all organic extracts were washed with saturated sodium chloride solution, dried over anhydrous $MgSO_4$ and concentrated on a Buchi-EL rotary evaporator. All yields reported are isolated yields of materials judged homogeneous by TLC, IR and NMR spectroscopy.

Tetrahydrofuran (THF) was distilled over benzophenone-sodium. Sodium borohydride (97%, 100 gm) supplied by LOBA - Cheme, India and Fluka, Switzerland were utilized and were kept under nitrogen in a dessicator after opening the bottle. The olefins utilized were commercial samples supplied by Fluka, Switzerland. Triphenylphosphine supplied by LOBA - Cheme, India was utilized.

Anhydrous $CoCl_2$ was prepared by dehydrating $CoCl_2.6H_2O$ in air oven at 140^oC for 12h and further drying at 100^oC for 3h under vacuum. The sample prepared by dehydration of $CoCl_2.6H_2O$ by refluxing with 2,2-dimethoxypropane (50 ml for 10 g of $CoCl_2.6H_2O$) followed by evaporation of the solution also work equally well. The imines, anils and enamine utilized were prepared following standard procedures.[93,100,101] Carbon monoxide was generated by dropwise addition of formic acid (98%) to concentrated sulfuriç acid (96%) at 90^oC using apparatus recommended for utilization in the carbonylation of organoboranes.[91] R(+)- α-Methylbenzylamine $[\alpha]_D^{20} = +30\pm2^o$ and R(+) camphor $[\alpha]_D^{20} = +43.5\pm1^o$, supplied by Fluka, Switzerland were utilized.

Reduction of 1-decene using $CoCl_2.6H_2O/NaBH_4/EtOH$

To a solution of $CoCl_2.6H_2O$ (10 mmol, 2.38 g) and 1-decene (10 mmol, 1.4 g) in ethanol (60 ml) under nitrogen atmosphere, $NaBH_4$ (20 mmol, 0.8 g) was added in portions during 15 minutes at 0^oC. The reaction mixture immediately becomes dark with evolution of hydrogen. The mixture was stirred under nitrogen atmosphere at room temperature for 3h. The reaction mixture was poured into 3N HCl (50 ml) and ether (60 ml) was added. The mixture was saturated with solid sodium chloride and the organic layer was separated. The aqueous layer was extracted with ether (3x30 ml) and the combined organic extract was dried over anhydrous $MgSO_4$. The solvent was evaporated and the residue was distilled to isolate decane, 1.2 g, 84%, b.p. $55^oC/10$ mm, Lit.[102] b.p. $58^o/10$ mm. IR spectrum of the product showed 1:1 correspondence with the spectrum reported in the literature.[103]

Attempted carbonylation of 1-decene using $CoCl_2.6H_2O/NaBH_4$ in ethanol

To a solution of $CoCl_2.6H_2O$ (10 mmol, 2.38 g) and 1-decene (10 mmol, 1.4 g) in ethanol (60 ml) under nitrogen atmosphere, $NaBH_4$ (20 mmol, 0.8 g) was added in portions during 15 minutes at 0^oC using a solid addition flask. Carbon monoxide was bubbled through the reaction mixture for 3h. The reaction mixture was poured into 3N HCl and ether (60 ml) was added. The contents were saturated with solid sodium chloride. The organic layer was separated. The aqueous layer was extracted with ether (3x30 ml). The combined organic extract was washed with brine and dried

over anhydrous $MgSO_4$. The solvent was evaporated and the residue was distilled to isolate decane 1.0 g, 70%. IR spectrum of the crude product indicated that no carbonylated product was formed.

Attempted carbonylation of 1-decene using anhydrous $CoCl_2/NaBH_4$ in THF

To a solution of $CoCl_2$ (10 mmol, 1.30 g) and 1-decene (10 mmol, 1.4 g) in THF (60 ml) under nitrogen atmosphere, $NaBH_4$ (20 mmol, 0.8 g) was added in portions during 15 minutes at 0^oC by a solid addition flask while bubbling carbon monoxide through the reaction mixture for 5h at room temperature. The reaction mixture was poured into 3N HCl (50 ml) and saturated with sodium chloride. The organic layer was separated and the aqueous layer was extracted with ether (3x30 ml). The combined organic layer was washed with water (10 ml), saturated sodium chloride solution (10 ml) and dried over anhydrous $MgSO_4$. The solvent was evaporated and the residue was distilled to isolate decane 0.7 g, 49%. A white crystalline residue was left out in the distillation flask (organoborane compounds?)

To a solution of the residue left in the distillation flask in the above experiment, THF (20 ml) and 3N NaOH (10 ml) were added. 20 ml of H_2O_2 (16%) was added dropwise at 0^oC.[91] The reaction mixture was stirred further for 1h. The reaction mixture was poured into 3N HCl (50 ml) and saturated with solid sodium chloride. The organic layer was separated and the aqueous layer was extracted with ether (3x30 ml). The combined organic layer was washed with water (10 ml), saturated sodium chloride solution (10 ml) and dried over anhydrous $MgSO_4$. The solvent was

evaporated and the residue was distilled to isolate 1-decanol, 0.64 g, 40%, b.p. 80°C/3 mm, Lit.[102] b.p.107°C/7 mm. The IR spectrum was identical with the spectrum reported for 1-decanol.[103]

Examination of the reaction of 1-decene using anhydrous $CoCl_2/NaBH_4$ in THF in the absence of carbon monoxide

To a solution of $CoCl_2$ (10 mmol, 1.30 g) and 1-decene (10 mmol, 1.4 g) in THF (60 ml) under nitrogen atmosphere, $NaBH_4$ (20 mmol, 0.8 g) was added in portions during 15 minutes at 0°C using a solid addition flask and the mixture was stirred for 3h at room temperature. The contents were poured into 3N HCl (50 ml) and saturated with solid sodium chloride. The organic layer was separated. The aqueous layer was extracted with ether (3x30 ml). The combined organic layer was washed with water (10 ml), saturated sodium chloride solution (10 ml) and dried over anhydrous $MgSO_4$. The solvent was evaporated and the residue was distilled to isolate decane 0.6 g, 42%. A white crystalline residue was left behind in the distillation flask. Oxidation of this product with $H_2O_2/NaOH$,[91] as outlined in the previous experiment, gave 1-decanol 0.64 g, 40%. The IR spectra of these products were identical with the spectra of products obtained in the previous experiments.

Hydroboration of 1-decene using $CoCl_2/NaBH_4$ in THF

To a solution of $CoCl_2$ (10 mmol, 1.30 g) in THF (60 ml) under nitrogen atmosphere, $NaBH_4$ (20 mmol, 0.8 g) was added in portions during 1h using a solid addition flask at 0°C. The reaction mixture was stirred

further for 1h at room temperature. 1-Decene (40 mmol, 5.6 g) was added and the reaction mixture was stirred further for 3h at room temperature 3N NaOH (10 ml) was added carefully to the reaction mixture at $0^{o}C$ and H_2O_2 (20 ml, 16%) was introduced dropwise. The contents were stirred further for 1h at room temperature and poured into 3N HCl (50 ml). The reaction mixture was saturated with solid sodium chloride and the organic layer was separated. The aqueous layer was extracted with ether (3x30 ml). The combined ether extract was washed with water (10 ml), saturated sodium chloride solution (10 ml) and dried over anhydrous $MgSO_4$. The solvent was evaporated and the residue was distilled to isolate 1-decanol 4.4 g, 70%.

IR (neat): ν_{max}	:	3350, 1140 cm^{-1}
^{1}H-NMR (100 MHz, $CDCl_3$): δ ppm	:	0.9 (t, CH_3), 1.2 (s, CH_2) 3.6 (t, CH_2), 5.3 (s, OH)
^{13}C-NMR (25.0 MHz, $CDCl_3$): δ ppm	:	62.4, 32.8, 31.8, 29.6, 29.4, 29.2, 25.7, 22.6, 13.9

Signals due to isomeric 2-decanol were not observed in the ^{13}C-NMR spectrum which indicates that the isomeric 2-decanol cannot be present more than 3%.

Several other olefins were hydroborated following the above procedure and the resulting organoboranes were oxidised with H_2O_2/OH^-. The results are summarized below.

Yield : 68% (2.7 g)

B.P. : 60°C/10mm, Lit.[102] 157°C/760 mm.

IR (neat): ν_{max} : 3330, 1140 cm^{-1}

^{13}C-NMR (25.0 MHz, $CDCl_3$) : δppm : 69.0, 34.6, 25.0, 23.7

Yield : 85% (4.0 g)

B.P. : 115°C/20 mm, Lit.[102] 116°C/20 mm

IR (neat): ν_{max} : 3300, 1020 cm^{-1}

^{1}H-NMR (100 MHz, $CDCl_3$): δ ppm : 2.7 (t, CH_2), 3.6(t, CH_2) 7.1(m, C_6H_5)and 1.4(d, CH)

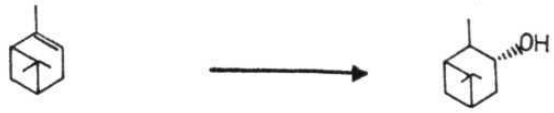
Isomeric 2-phenylethanol is present to the extent of 20% in this product.

Yield : 90% (4.0 g)

M.P. : 125°C, Lit.[104] 126°C

IR (neat): ν_{max} : 3350, 1130 cm^{-1}

^{13}C-NMR (25.0 MHz, $CDCl_3$): δppm : 74.2, 43.7, 41.7, 35.8, 34.2 28.1, 24.3



Yield	:	70% (4.3 g)
B.P.	:	98^{o}/10 mm, Lit.[102] 217^{o}/760 mm
IR (neat): ν_{max}	:	3350 cm^{-1}
^{13}C-NMR (25.0 MHz, $CDCl_3$): δppm	:	71.5, 47.9, 47.7, 41.8, 39.0, 38.2, 34.3, 27.7, 23.7, 20.8

Examination of the formation of BH_3 in the $CoCl_2/NaBH_4$ reagent system utilizing NEt_3

To a solution of $CoCl_2$(10 mmol, 1.30 g) in THF (60 ml) under nitrogen atmosphere, $NaBH_4$ (20 mmol, 0.8 g) was added in portions using a solid addition flask at $0^{o}C$ for 1h. The reaction mixture was stirred further for 1h at room temperature. Triethylamine (10 mmol) was added and the reaction mixture was stirred further for 3h at room temperature. The contents were poured into 3N HCl (50 ml) and organic layer was separated. The aqueous layer was extracted with ether (3x30 ml). The combined ether layer was washed with saturated sodium chloride solution and dried over anhydrous $MgSO_4$. The solvent was evaporated and the residue was separated by chromatography on a silice gel column to isolate Et_3NBH_3. IR spectrum of the Et_3NBH_3 isolated in this way exhibited strong >B-H absorptions at 2235, 2280, 2340 cm^{-1}.[105]

Reduction of 1-decene using $CoCl_2/NaBH_4/CH_3OH$ in THF

To a solution of $CoCl_2$ (10 mmol, 1.30 g) and CH_3OH (60 mmol, 1.9

g) in THF (60 ml) under nitrogen atmosphere, $NaBH_4$ (20 mmol, 0.8 g) was added in portions during 1h at 0^oC using a solid addition flask. 1-Decene (20 mmol, 2.8 g) was added and the reaction mixture was further stirred for 2h at 0^oC. The reaction mixture was poured into 3N HCl (50 ml) and saturated with solid sodium chloride. The organic layer was extracted with ether (3x30 ml). The combined ether extract was washed with water (10 ml), saturated sodium chloride solution (10 ml) and dried over anhydrous $MgSO_4$. The solvent was evaporated and the residue was distilled to isolate decane 2.27 g, 80%, b.p. $55^oC/10$ mm, Lit.[102] b.p. $58^oC/10$ mm.

IR (neat): ν_{max} : 2960, 2870, 1460, 720 cm^{-1}

^{1}H-NMR (100 MHz, $CDCl_3$): δ ppm : 0.9 (t,CH_3) 1.2 (m, CH_2)

^{13}C-NMR (25.0 MHz, $CDCl_3$): δ ppm : 14.0, 22.6, 23.6, 29.3, 29.6, 29.9, 31.9, 32.3

The above procedure utilizing $CoCl_2/NaBH_4/CH_3OH$ in THF for reduction was followed for the convertion of several olefins into the corresponding alkenes and the results are presented below.

$C_6H_5-CH=CH_2 \longrightarrow C_6H_5CH_2CH_3$

Yield : 65% (1.38 g)

B.P. : 136^oC, Lit.[102] $136^oC/760$ mm

IR (neat): ν_{max} : 3010, 1605 cm^{-1}

^{1}H-NMR (100 MHz, $CDCl_3$): δ ppm : 1.2 (t,CH_3), 2.6 (q,CH_2), 7.2 (m,C_6H_5)

trans-2-octene ⟶ **octane**

Yield : 70% (1.6 g)

B.P. : 123°C/760 mm, Lit.[102] 125.6°/760 mm

IR (neat): ν_{max} : 2870, 1460, 720 cm^{-1}

^{1}H-NMR (100 MHz, $CDCl_3$) : δppm : 0.9 (t, CH_3) 1.2 (m, CH_2)

Yield : 75% (2.0 g) column chromatographed product on a silica gel column using hexane as eluent.

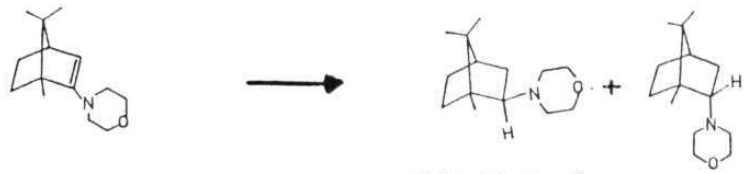
IR (neat): ν_{max} : 2870, 900 cm^{-1}

^{1}H-NMR (100 MHz, $CDCl_3$): δ ppm : 0.8 (d, CH_2) 0.9 (m, CH_2) 1.2 - 2.1 (m, CH_2) 5.3 (t, H)

Reduction of morpholine-enamine of camphor 7 using $CoCl_2/NaBH_4/CH_3OH$ in THF

To a stirred mixture of anhydrous $CoCl_2$ (20 mmol), CH_3OH (80 mmol) in THF, $NaBH_4$ (40 mmol) was added using a solid addition flask under nitrogen atmosphere at -10°C for 1h. The morpholine-enamine of camphor (10 mmol) was added and the contents were further stirred for 2h at -10°C under nitrogen atmosphere. Aqueous NaOH (3N, 20 ml) was added and the mixture was extracted with (3x30 ml). The combined organic layer was washed with 5N HCl (3x15 ml). The combined aqueous layer was treated with 5N NaOH (60 ml) to liberate the amine. The contents were extracted with ether (3x30 ml), washed with saturated sodium chloride solution

(10 ml), dried over anhydrous $MgSO_4$ and the solvent was evaporated. The residue on distillation under reduced pressure afforded a 4:1 mixture of bornyl and isobornyl morpholines.



Yield : 82% (3.6 g)

B.P. : 125°C/0.1 mm, Lit.[93] 85°C/0.05 mm

^{13}C-NMR (25.0 MHz, $CDCl_3$): δ ppm : 17.1, 18.7, 20.1, 27.4, 28.8, 36.4, 44.2, 48.1, 50.2, 53.9, 66.9, 77.1

In addition signals at 14.6, 19.6, 19.8, 28.9, 33.0 37.2, 44.9, 46.9, 49.6, 53.1, 67.4, 73.1 corresponding to the presence of isobornyl morpholine (~ 20%).

The above procedure utilizing $CoCl_2/NaBH_4/CH_3OH$ in THF system for reduction was followed for the conversion of several other imines to the corresponding amines in our laboratory (Table 2).

Camphor-anil was converted into the isomerically pure isobornyl aniline **6**following this method (Table 2).

Yield : 75% (3.4 g)

B.P. : 136°C/1 mm, Lit.[97] 131°C/1 mm.

^{13}C-NMR($CDCl_3$): δppm : 148.1, 129.1, 116.8, 112.6, 61.9, 48.6, 47.3, 45.0, 40.6, 36.6, 27.8, 20.9, 12.5

$[\alpha]_D^{25}$: -71.5° (C = 11.6, EtOH)
Lit[97].$[\alpha]_D^{10}$ = -89.1 (unverified)

Attempted carbonylation using $CoCl_2/NaBH_4/CH_3OH$ in THF

To a solution of $CoCl_2$ (10 mmol, 1.30 g) and CH_3OH (60 mmol) in THF (60 ml) under nitrogen atmosphere $NaBH_4$ (20 mmol, 0.8 g) was added in portions at 0°C. 1-Decene (20 mmol, 2.8 g) was added and carbon monoxide was bubbled through the reaction mixture for 3h at room temperature. The reaction mixture was poured into 3N HCl (50 ml). After usual workup, decane (1.0 g, 70%) was isolated. No product containing carbonyl or hydroxyl group was formed.

Hydrocobaltation - Carbonylation - Iodination - Methanolysis of 1-Decene

A mixture of $NaBH_4$ (20 mmol, 0.8 g) and PPh_3 (20 mmol, 5.2 g) was taken in a solid addition flask and added to the mixture of anhydrous $CoCl_2$ (10 mmol, 1.38 g) and 1-decene (20 mmol, 2.8 g) in anhydrous THF

(80 ml) in portions at $0^{o}C$ while bubbling carbon monoxide for 1h. Carbon monoxide was bubbled through the reaction mixture further for 4h with stirring at room temperature. I_2 in CH_3OH (6 g in 30 ml CH_3OH) was carefully added to the reaction mixture (gas evolution). After evolution of the gases had ceased, hexane (80 ml) was added followed by water (30 ml). The contents were filtered. The organic layer was separated and the aqueous layer was extracted with hexane (3x40 ml). The combined organic extract was washed successively with 20% $Na_2S_2O_3$ and sodium chloride solutions and dried over anhydrous $MgSO_4$. The solvent was evaporated. n-Pentane (10 ml) was added to the residue to precipitate out PPh_3BH_3 and $Ph_3P{=}O$ and most of the Ph_3P. The pentane solution was separated and the solvent was evaporated. The residue was distilled under reduced pressure to isolate 2-decene (cis/trans mixture, b.p. $50^{o}C$/8 mm, 0.86 g, 30%) and 1-undecanoicacid methyl ester (b.p. $70^{o}C$/8 mm, 1.0 g, 25%) (Spectrum no. 1). The residue left behind in the distillation flask was oxidised with H_2O_2/NaOH in THF to isolate 1-decanol (35%).

$$CH_3(CH_2)_7CH{=}CH_2 \longrightarrow CH_3(CH_2)_8CH_2COOCH_3$$

Yield : 25% (1.0 g)

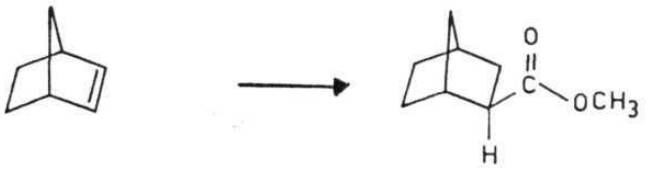
IR (neat): ν_{max} : 1740 cm^{-1}

^{1}HNMR (100 MHz, $CDCl_3$): δ ppm : 3.7 (s, CH_3) 2.3 (t, CH_3) 0.8 - 1.8 (m, remaining hydrogens)

^{13}C-NMR (25.0 MHz, $CDCl_3$): δ ppm : 173.9, 51.1, 34.1, 31.9, 29.5, 29.3, 25.0, 22.6, 13.9

The product contains ~5% of $CH_3(CH_2)_7CH(CH_3)COOCH_3$ (comparison of signals in ^{13}C-NMR spectrum).

The above procedure was followed for the conversion of norbornene and the corresponding ester was isolated by column chromatography on a silica gel column using 10% $CHCl_3$ in hexane as eluent (Spectrum 1).



Yield : 28% (0.86 g)

IR (neat): ν_{max} : 1740 cm^{-1}

^1H-NMR (100 MHz, $CDCl_3$): δ ppm : 3.6 (s, CH_3) 0.9-2.7 (m, remaining hydrogens)

^{13}C-NMR (25.0 MHz, $CDCl_3$): δ ppm : 176.1, 51.3, 40.9, 46.4, 34.2, 36.0, 29.5, 28.7, 36.4

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C H A P T E R 2

Studies on the reactivities of cobalt reagent generated utilizing $CoCl_2/NaBH_4$ system in the presence of Ph_3P

INTRODUCTION

Synthesis and Reactions of Transition Metal Hydride Complexes Containing Phosphine Ligands

The first example of a compound containing transition metal-hydrogen bond was reported as early as in 1844[1]. The early examples include CuH, CrH_3, FeH_2, CoH_2 and NiH_2 species.[2,3] However, the structures of these complexes were proved to be very complex.[2,3] The reasonably well defined hydride complexes of transition metals, $FeH_2(CO)_4$[4] and $HCo(CO)_4$,[5] were discovered in 1930's.[3] They remained as laboratory curiosities for a long time. However, it was later realized that some of these carbonyl hydrides are very important intermediates in catalytic addition of carbon monoxide and H_2 to olefin (eg. the oxo-process[6,7]).

The hydride complexes of transition metals constitute a very rich group of compounds with unusual structures, properties and reactivities.[8] Generally, hydride complexes are classified according to the nature of the other ligands bound to the metal atom: hydrometallates (only H is attached to the metal), tertiary phosphine hydrides, carbonyl hydrides, tertiary phosphine carbonyl hydrides, cyclopentadienyl hydrides, cyclopentadienyl carbonyl hydrides, cyanohydrides, organo-complex hydrides, amine hydrides and chloro hydrides.

As outlined in chapter 1, it was of interest to explore the reactivities of the $CoCl_2/NaBH_4$ reagent system in the presence of triphenyl-

phosphine. Accordingly, it will be helpful to briefly review the synthesis, structures and reactivities of transition metal hydrides containing only phosphine as other ligands. Syntheses of these types of transition metal hydride complexes are discussed in the order of group wise appearance of the metal in the periodic table. The reactions of these hydrides with organic substrates are also surveyed.

Group IIIA and IVA metals: (Sc, Y, La and Ti, Zr, Hf)

Hydride complexes of these early transition metals containing tertiary phosphines as other ligands are not common. These metals readily form hydride complexes containing cyclopentadienyl ligands [eg. $(Cp_2TiH)_2$,[9] $(Cp_2ZrH_2)_n$,[10] $Cp_2ZrCl(H)$[11,12]].

Group VA metals : (V, Nb, Ta)

Hydride complexes of this triad containing tertiary phosphine ligands are also not common. Tantalum hydride complex containing PEt_3 and cyclopentadienyl ligands, $Cp_2Ta(H)PEt_3$, has been prepared by heating Cp_2TaH_3 with PEt_3.[13]

Group VIA metals : (Cr, Mo, W)

The tungsten hydride, $H_6W(PMe_2Ph)_3$ has been prepared by $NaBH_4$ reduction of trans-$WCl_4(PMe_2Ph)_2$.[14] More conveniently, it can be prepared by Na/Hg reduction of $WCl_4(PMe_2Ph)_2$ in the presence of H_2.[15]

$$\text{trans-}[WCl_4(PMe_2Ph)_2] \xrightarrow{NaBH_4} H_6W(PMe_2Ph)_3$$

$$\text{trans-}[WCl_4(PMe_2Ph)_2] \xrightarrow[H_2/THF]{Na/Hg} H_6W(PMe_2Ph)_3$$

Hydride complexes of Cr and Mo containing carbonyl ligands have been synthesized by $NaBH_4$ reduction of the corresponding metal carbonyls.[16,17]

$$M(CO)_6 + NaBH_4 \xrightarrow{THF} HM_2(CO)_{10}^-$$

$$M = Cr, Mo,$$

Group VII A metals (Mn, Re, Tc)

The $HMn(PF_3)_5$ complex has been prepared from the reaction of $HMn(CO)_5$ and PF_3 in presence of UV light.[18] Several rhenium hydride complexes containing phosphine ligands have been synthesized.[19,20] These hydrides were obtained by $LiAlH_4$ reduction of various phosphine substituted chlorides, oxychlorides and alkoxychlorides of rhenium.[19,20]

$$\left.\begin{array}{l} ReOCl_3L_2 \\ \text{or} \\ ReCl_4L_2 \\ \text{or} \\ ReO(OR)Cl_2L_2 \end{array}\right\} \xrightarrow{LiAlH_4} H_7ReL_2$$

$$L = PPh_3,\ PEt_2Ph,\ PEtPh_2$$

$$ReCl_3L_3 \xrightarrow{LiAlH_4} H_5ReL_3$$

Treatment of H_5ReL_3 with $PPh_2CH_2CH_2PPh_2$ (diphos) gives the complexes H_3ReL_2 (diphos) and $H_3Re(diphos)_2$.[21] These complexes can be readily protonated to give the corresponding cationic complexes.[21] Treatment of trihydrides with halogens yields a mixture of dihydride and cationic tetrahydro species.[21] The complexes ReX_2L_2 (diphos) and $ReX_2(diphos)_2$ on prolonged treatment with complex hydrides give $H_2ReX(diphos)$.[21] The hydride ion is eliminated from ReH_9^{2-} ion on treatment with tertiary-phosphines.[22]

$$ReH_9^{2-} + L \longrightarrow H_8ReL$$

$$L = PPh_3,\ P^nBu_3,\ PEt_3$$

Group VIII Metals

(i) Iron sub-group (Fe, Ru, Os)

Reduction of $FeCl_2$ with $NaBH_4$ gives the tetrahydro species which can be heated to give coordinatively unsaturated complexes or can be heated with nitrogen to give the corresponding nitrogen complex.[23,24]

$$FeCl_2.H_2O + L \xrightarrow[EtOH]{NaBH_4} H_4FeL_3 \longrightarrow H_2FeL_3 + H_2$$

$$H_4FeL_3 \xrightarrow{N_2} H_2Fe(N_2)L_3$$

$$L = P(OEt)_3,\ P(OMe)_3,\ PEt_2Ph$$

When either $RuCl_3$ or $Ru(acac)_3$ is treated with $AlEt_3$ in the presence of PPh_3, the light yellow dihydride, H_2RuL_4, is obtained.[25]

$$RuCl_3 + PPh_3 \xrightarrow{Et_3Al} H_2Ru(PPh_3)_4$$

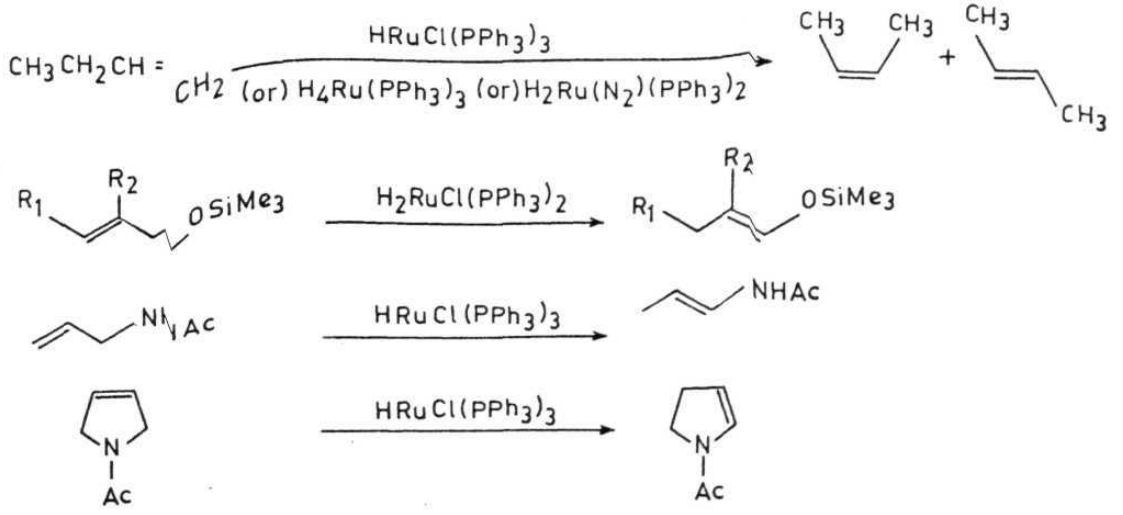
$$H_2Ru(PPh_3)_4 \xrightarrow{N_2} H_2Ru(N)_2(PPh_3)_3$$

The $H_2Ru(PPh_3)_3$ complex has been obtained in the reaction of PPh_3 and $H_4Ru(PPh_3)_3$.[25] The tetrahydro complex can be also prepared by the treatment of $HRuCl(PPh_3)_3$ with Et_3Al followed by hydrogenation with molecular hydrogen.[26]

$$H_4Ru(PPh_3) + PPh_3 \xrightarrow{Et_3Al} H_2Ru(PPh_3)_4$$

$$HRuCl(PPh_3)_3 \xrightarrow[H_2]{Et_3Al} H_4Ru(PPh_3)_3$$

These complexes are known to catalyse hydrogenation and isomerization of alkenes.[27-29]



The $HRuCl(PPh_3)_3$ complex was utilized as catalyst in hydrogenation of olefins and also for selective reduction of 1,3-dienes to terminal olefins.[30] The $HRuCl(PPh_3)_3$ complex can be obtained by the reaction of RuX_2L_2 with Et_3Al/H_2.[31]

$$RuX_2L_2 \xrightarrow{Et_3Al/H_2} HRuClL_3$$

$$X = Br, Cl \qquad L = PPh_3, P(OPh)_3$$

Tetrahydro complexes of osmium can be prepared by treating $OsCl_3L_3$ with $LiAlH_4$ or $NaBH_4$.[22,32]

$$OsCl_3L_3 \xrightarrow{LiAlH_4} H_4OsL_3$$

$$L = PMe_2Ph$$

$$OsCl_3L_3 + L \xrightarrow{NaBH_4} H_4OsL_3$$

$$L = PEt_2Ph$$

These complexes are also known to isomerize olefins.

(ii) Cobalt sub-group: (Co, Rh, Ir)

The chemistry of phosphine hydrides of this sub-group has been extensively studied. Many of these metal hydrides catalyse hydrogenations, isomerizations and other useful catalytic reactions.

Reduction of $CoCl_2$ with $NaBH_4$ in 1,2-dimethoxyethane at 0^oC in the presence of trimethylphosphite gives the corresponding $HCo[P(OMe)_3]_4$ complex.[33]

$$CoCl_2 + 4P(OMe)_3 \xrightarrow[1,2\ DME,\ 0^oC,\ 2h]{NaBH_4} HCo[P(OMe)_3]_4$$

Reduction of Co(II) salts, $Co(NO_3)_2.6H_2O$ or $CoCl_2.6H_2O$ with $NaBH_4$ in ethanol in the presence of triphenylphosphite gives the corresponding $HCo[P(OPh)_3]_4$.[34,35] This complex is also known to isomerise 1-hexenes into 2-hexenes and 3-hexenes.[34,35]

$$CoCl_2.6H_2O + 4P(OPh)_3 \xrightarrow{NaBH_4} HCo[P(OPh)_3]_4$$

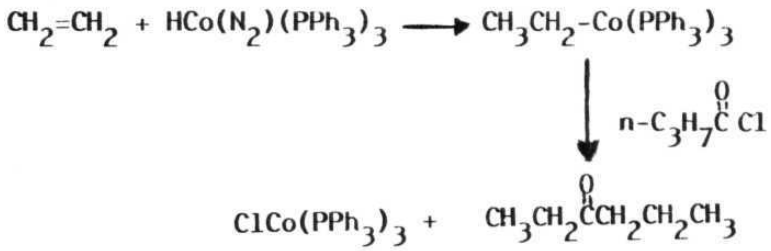
When a mixture of $Co(acac)_3$ and PPh_3 is treated with triisobutyl aluminium in diethyl ether under nitrogen atmosphere, the $HCo(N_2)(PPh_3)_3$ complex was obtained in 69% yield.[36]

$$Co(acac)_3 + PPh_3 \xrightarrow[N_2]{(^iBu)_3Al} HCo(N_2)(PPh_3)_3$$

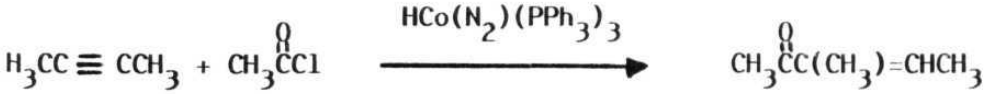
The $HCo(N_2)(PPh_3)_3$ converts ethylene to a mixture of butenes.[37]

$$CH_2{=}CH_2 \xrightarrow{HCo(N_2)(PPh_3)_3}$$ 

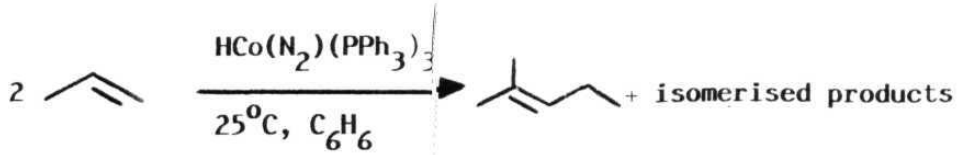
This complex has also been used in hydroacylation of olefin as illustrated in the preparation of 3-hexanones from ethylene and butyryl-chloride.[38]



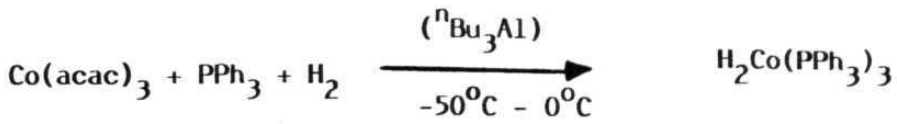
2-Butyne also undergoes the hydroacylation reaction but the yield is relatively poor.[38]



The $HCo(N_2)(PPh_3)_3$ complex has also been used in dimerization of propylenes and in isomerization reactions.[39]



When a mixture of $Co(acac)_3$ and PPh_3 was treated with triisobutyl-aluminum in the presence of hydrogen atmosphere, the $H_2Co(PPh_3)_3$ complex was obtained.[40]



The trihydride complex, $H_3Co(PPh_3)_3$, has been prepared by bubbling deoxygenated hydrogen gas through benzene solutions of $HCo(N_2)(PPh_3)_3$ for 1h at room temperature.[36]

$$HCo(N_2)(PPh_3)_3 + H_2 \xrightarrow[C_6H_6/1h]{25^oC} H_3Co(Ph_3P)_3$$

This trihydride complex can also be prepared by other methods. For example, reduction of $CoCl_2.6H_2O/CoX_2L_3$ with excess $NaBH_4$ under hydrogen atmosphere also gives the trihydride complex[41,42]

$$CoCl_2.6H_2O + PPh_3 \xrightarrow[EtOH,\ RT,\ H_2]{NaBH_4} H_3Co(PPh_3)_3$$

The $H_3Co(PPh_3)_3$ complex has also been utilized as a catalyst in isomerization and hydrogenation reactions.[36]

Several rhodium complexes containing phosphine and hydride ligands are known. Treatment of $RhCl_3$ with PF_3 and H_2 gives $HRh(PF_3)_4$ in good yields.[43] Treatment of $RhCl_3$ with Et_3Al in the presence of PPh_3 or $P(OPh)_3$ gives the corresponding $HRhL_4$ complex.[25]

$$RhCl_3 + L \xrightarrow{Et_3Al} HRhL_4$$

$$L \approx PPh_3, \quad P(OPh)_3$$

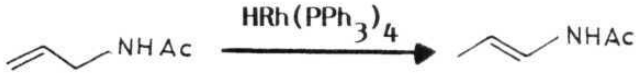
The $HRhL_4$ complexes can also be obtained from the corresponding phosphine carbonyl hydride.[44]

$$HRh(PPh_3)_3(CO) \xrightarrow{P(OPh)_3} HRh[P(OPh)_3]_4$$

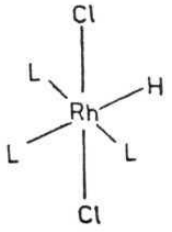
It has been reported that reduction of $RhCl(PMePh_2)_3$ with NH_2-NH_2 in the presence of $P(MePh_2)$ gives $HRh(PMePh_2)_4$.[45]

$$RhCl(PMePh_2)_3 \xrightarrow[NH_2NH_2]{L} HRh(PMePh_2)_4$$

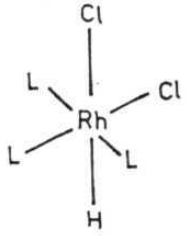
The $HRh(Ph_3P)_3$ complex has been utilized for isomerization of amide to enamides.[29]



Reduction of $RhCl_3.3H_2O$ in ethanol in the presence of tertiary-phosphines gives α - $HRhCl_2(P^nBuPh_2)_3$.[46] However, in the presence of H_3PO_4, β -$HRhCl_2(P^nBuPh_2)_3$ is obtained.[46]



α-form



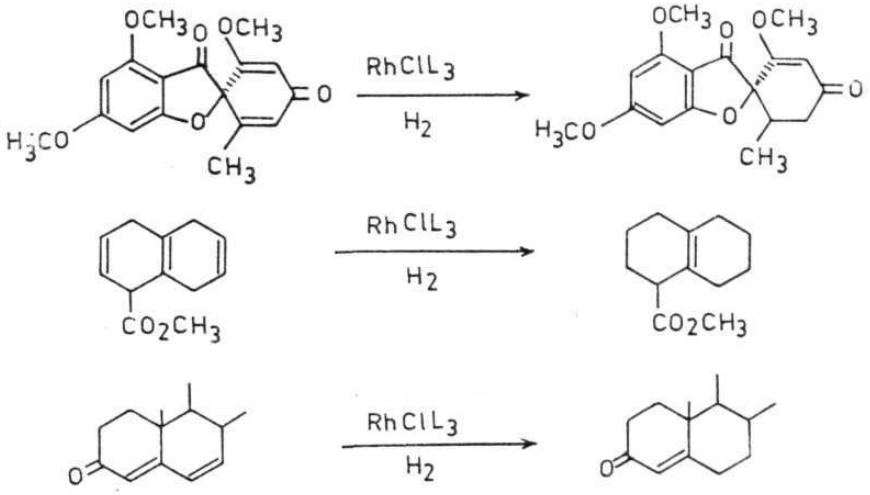
β-form

The Wilkinson catalyst,[47] $RhCl(PPh_3)_3$ in the presence of H_2 gives the corresponding dihydride.[46]

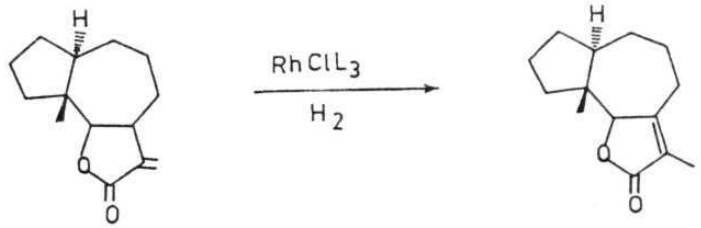
$$RhClL_3 + H_2 \longrightarrow H_2RhClL_3$$

$$L = PPh_3$$

The $RhCl(PPh_3)_3/H_2$ system has been utilized extremely for hydrogenation of alkenes.[48-50]

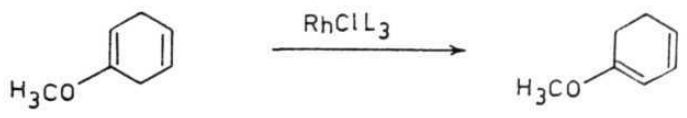


The α- methylene-lactone, I rearranges to II on treatment with $ClRh(PPh_3)_3$.[49]

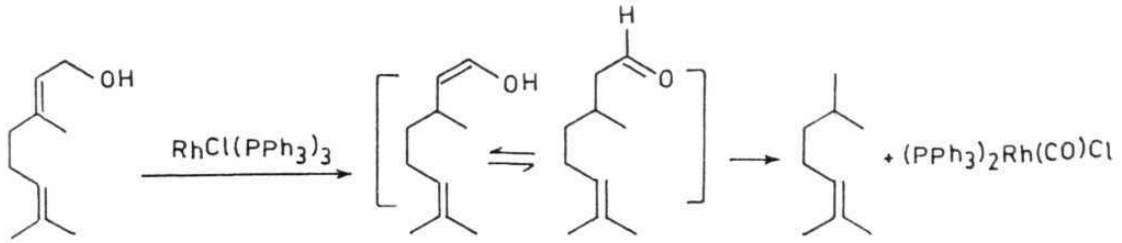


I II

The Wilkinson's catalyst also isomerizes olefins.[50]



It has been also utilized in decarbonylation reactions.[51]



Several iridium complexes containing phosphine and hydride ligands are known. The IrX_3L_3 complexes on heating with one equivalent of KOH gives $HIrX_2L_3$.[52]

$$IrX_3L_3 \xrightarrow{\text{1 eq. KOH}} HIrX_2L_3$$

$$L = PPh_3, PEt_3, \qquad X = Br, Cl$$

The corresponding iodide complex has been prepared by treating $HIrX_2L_3$ with NaI in acetone.[52]

$$HIrBr_2L_3 \xrightarrow[\text{acetone}]{\text{NaI}} HIrI_2L_3$$

Addition of HCl to $H_2IrCl(PMe_2Ph)_3$ also gives $HIrCl_2(PMe_2Ph)_3$.[53] The dihydride H_2IrClL_3 can be obtained by the reaction of $IrCl_3L_3$ with 2 eq. KOH.[52]

$$IrCl_3L_3 \xrightarrow{\text{2 eq. KOH}} H_2IrClL_3$$

$$L = Ph_3P$$

The trihydride of iridium can be obtained by the reduction $IrCl_3$ with $NaBH_4$ in the presence of Ph_3P in ethanol.[52] Reduction of the complex $IrCl_3L_3$ with $LiAlH_4$ gives H_5IrL_2.[52-54]

$$IrCl_3L_3 \xrightarrow{LiAlH_4} H_5IrL_2$$

$$L = PPh_3,\ PEt_3,\ PMe_3$$

(iii) Nickel sub-group metals : (Ni, Pd, Pt)

Nickel complexes containing phosphine or phosphite and hydride ligands can be prepared by protonation of the complexes of NiL_4 in strong acid.[55]

$$Ni[P(OEt)_3]_4 \xrightarrow{H_2SO_4} HNi[P(OEt)_3]_4^+$$

The five-coordinated cationic complex $[HNi(diphos)_2]^+$ was isolated on treatment of $Ni(diphos)_2$ with HCl.[56]

$$Ni(diphos)_2 + HCl \longrightarrow [HNi(diphos)_2]^+$$

$$diphos = Ph_2PCH_2CH_2PPh_2$$

Hydride complexes of nickel containing phosphine ligands can be prepared by reduction of the corresponding nickel complexes with $NaBH_4$.[57] The complex $(PCy_3)_2NiCl_2$ undergoes reduction with $NaBH_4$ in

THF-EtOH (4:1) mixture at room temperature to give the corresponding mono hydride complex.[57]

$$(PCy_3)_2NiCl_2 \xrightarrow[THF/EtOH]{NaBH_4} HNiCl(PCy_3)_2$$

The $NiCl_2(P^iPr_3)_2$ complex on reaction with $NaBH_4$ gives the hydrido tetrahydroborate complex containing phosphine and hydrogen as other ligands.[58]

$$NiCl_2(P^iPr_3)_2 \xrightarrow{NaBH_4} HNi(BH_4)(P^iPr_3)_2$$

The palladium complexes containing phosphine and hydride ligands have also been prepared by $NaBH_4$ reduction.[57]

$$PdCl_2L_2 \xrightarrow{NaBH_4} HPdClL_2$$

$$L = PCy_3 , \quad PEt_3 , \quad P^iPr_3$$

In some cases, the corresponding $HPd(BH_4)L$ complexes were also isolated.[57]

The platinum complexes containing phosphine and hydride as ligands can be prepared by reducing the corresponding platinum complex with hydrazine.[58]

$$L_2PtX_2 \xrightarrow[\Delta\ ,1h,\ HCl]{NH_2NH_2} HPtClL_2$$

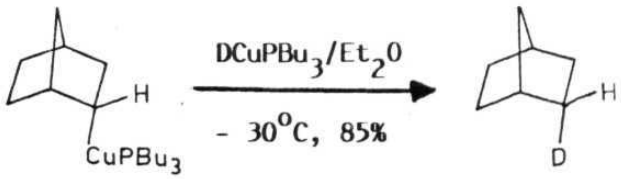
$$X = Cl,\ L = PPh_3,\ PPh_2Et,\ PPhEt_2,\ P^iPr_3,\ PEt_3,\ PMe_3$$

Group IB metals : (Cu, Ag, Au)

Copper(I) hydride was prepared by treating copper(I) bromide dissolved in pyridine with di-isopropylaluminum hydride at -50°C. The CuH species decomposes into Cu and H_2 above -20°C.[59]

$$CuBr \xrightarrow[-\ 50^oC]{(^iBu_2)AlH} CuH$$

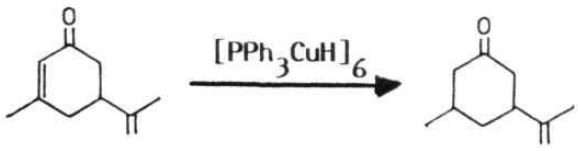
Tri-n-butylphosphine and CuH form a 1:1 complex. The high solubility of this complex in the solvent utilized has prevented its isolation.[59] The $HCuP^nBu_3$ complex prepared in Et_2O reduces primary, secondary, tertiary alkyl, vinyl and aryl Cu(I) compounds to the corresponding hydrocarbons in high yields under mild conditions.[59a]



The synthesis of copper(I) hydride cluster $[Ph_3PCuH]_6$ has been reported. It has been prepared by treating $(CuO^tBu)_4$ with Ph_3P under hydrogen atmosphere.[59b]

$$(CuO^tBu)_4 \xrightarrow[80\ psi\ H_2/RT/C_6H_6]{PPh_3} [Ph_3PCuH]_6$$

The copper(I) hydride cluster is effective for the selective conjugate hydride addition to α, β-unsaturated carbonyl compounds.[59c]



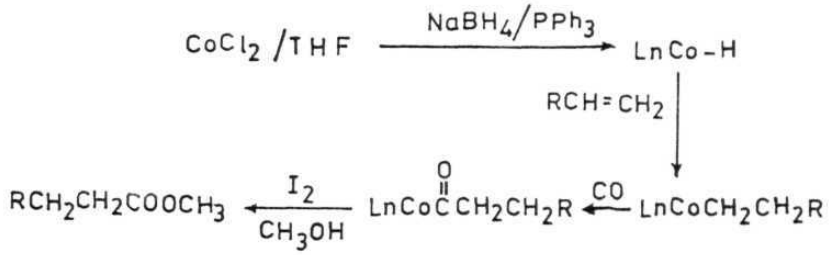
As outlined in chapter 1, the reactive LnCoH species generated utilizing the $CoCl_2/NaBH_4/PPh_3/CO$ reagent system in THF gives hydrometallation-carbonylation of olefins to give ~25% of one carbon homologated ester after treatment with I_2/CH_3OH. In order to examine the reactivity of the cobalt species generated utilizing the anhydrous $CoCl_2/NaBH_4$ system in the presence of PPh_3 in THF, we undertook the investigations described in this chapter.

RESULTS AND DISCUSSION

Isomerization of Alkenes Utilizing the $CoCl_2/Ph_3P/NaBH_4$ System

As outlined in chapter 1, addition of a mixture of $NaBH_4$ (20 mmol) and Ph_3P (20 mmol) to a mixture of $CoCl_2$ (10 mmol) and 1-decene (20 mmol) in THF (80 ml) in portions at 0^oC while bubbling carbon monoxide for 1h, further stirring for 3h at 0^oC followed by treatment with I_2/CH_3OH, affords methyl undecanoate in 20% yield (Spectrum no. 1) along with cis/trans mixture of 2-decenes (30%) (Scheme 1)

Scheme 1



As discussed previously, reaction of $CoCl_2$ with excess of Ph_3P and excess $NaBH_4$ in ethanol medium gives $H_3Co(PPh_3)_3$ which readily reacts with molecular nitrogen to give $H(N_2)Co(PPh_3)_3$.[41,42,60] As outlined earlier, both of these complexes are known to catalyse isomerization of 1-alkenes into 2-alkenes.[36] The $HCo(N_2)(PPh_3)_3$ complex has also been utilized in hydrocobaltation-acylation of some alkenes.[38] The present reaction conditions are very much different from the procedure utilized for the preparation of $H_3Co(PPh_3)_3$ and it is known that the $CoCl_2/NaBH_4$

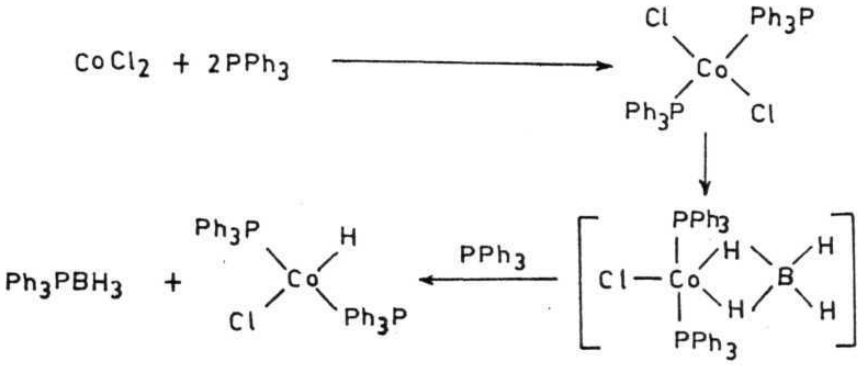
system gives different types of cobalt species depending on reaction conditions.[61] The nature of the reactive cobalt species generated under the present reaction conditions (Scheme 1) is not clearly understood. As outlined in chapter 1, in the absence of PPh_3 and CO, the $CoCl_2/NaBH_4$ system gives species which hydroborate or hydrogenate alkenes. Clearly, the presence of PPh_3 and CO give new type of reactivities for the system. It appeared that by proper choice of reaction conditions, it may be possible to generate different types of reagents which can be utilized for developing new synthetic methods. In this chapter, reactivities of the cobalt reagent generated utilizing the $CoCl_2/NaBH_4$ in the presence of PPh_3 towards alkenes and alkynes are described.

We have observed that the green coloured mixture prepared in situ under nitrogen by the addition of $NaBH_4$ (10 mmol) to a magnetically stirred suspension of $CoCl_2$ (10 mmol) and PPh_3 (30 mmol) in THF (80 ml) at $-10^{o}C$ during 15 minutes followed by further stirring for 15 minutes at $-10^{o}C$, isomerizes 1-decene (20 mmol) into a mixture of cis-2-decene and trans-2-decene (87:13) in 2h at $-10^{o}C$ (Table 1, Spectrum no. 2). However, by simply stirring the reaction mixture for 8h at $-10^{o}C$ after the addition of 1-decene, the product containing predominantly trans-2-decene (90:10) was isolated (Table 1, Spectrum no. 2). The percentage compositions were calculated from the intensities of the olefinic methyl group in the 270 MHz ^{1}H-NMR spectrum. The $CoCl_2/PPh_3/NaBH_4$ system gives cobalt complexes of various compositions in alcohol medium. For example, utilization of large excess of $NaBH_4$ gives $H_3Co(PPh_3)_3$ under argon atmosphere and $HCo(N_2)(PPh_3)_3$ under nitrogen atmosphere.[36,61] The $Co(BH_4)(PPh_3)_3$

complex has also been isolated.[36,61] Also, the reaction of $CoCl_2$ with $NaBH_4$ in the presence of tricyclohexylphosphine in toluene-ethanol mixture gives the stable $HCo(BH_4)PCy_3$.[62] Several of these cobalt complexes are known to isomerize olefins. For example, the cobalt(I) complex, $HCo(N_2)(PPh_3)_3$ isomerizes 1-butene to 2-butenes[37] and the cobalt(0) complex, $Co(N_2)(PPh_3)_3$, isomerises 1-hexene to 2-hexene.[63] Formation of such cobalt(I) and cobalt(0) species from cobalt(II) using $NaBH_4$ must involve hydrogen evolution. However, we have not observed any gas evolution under the present reaction conditions. Consequently, Co(I) or Co(0) species may not be the active species under the present reaction conditions.

Under the present reaction conditions, the Ph_3PBH_3 complex was isolated in 70-80% yields in several runs. Since most of the BH_3 comes out as Ph_3PBH_3 and there is no hydrogen evolution by decomposition of the metal hydrides (if any) produced, the amounts of reagents utilized would point out the stoichiometry outlined in Scheme 2, suggesting that the reactive species is the bis(triphenylphosphine)chloro-hydrido-cobalt(II), complex (A).

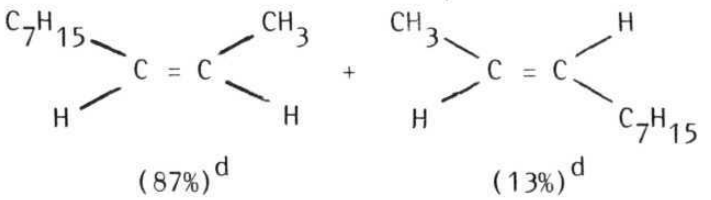
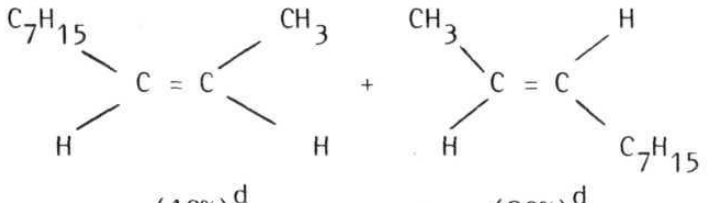
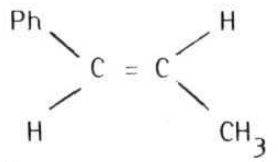
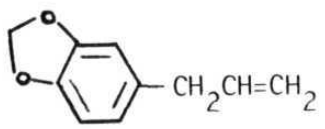
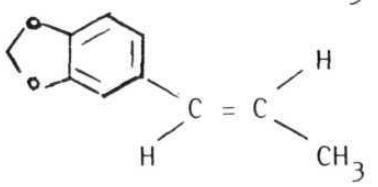
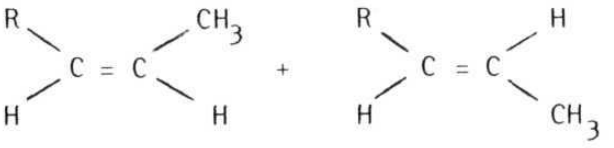
Scheme 2



We have attempted ESR studies for the $CoCl_2/PPh_3$ mixture and the $CoCl_2/PPh_3/NaBH_4$ mixture in THF prepared as above at 163^oK (frozen). However, both these systems failed to give detectable ESR signals.

In their independent studies, Kanai and his coworkers found that the cobalt halide complexes containing phosphine ligands such as $CoCl_2(PPh_3)_2$ react with $NaBH_4$ to give a green coloured homogeneous solution under conditions similar to the present reaction conditions.[64] They observed that the reagent generated in this way catalysed isomerization of 1-butene into a mixture of 2-butenes.[64] They have carried out a detailed kinetic studies on the isomerization and observed that the catalyst is more effective when the ratio of $(Ph_3P)_2CoCl_2/NaBH_4$ is 1:1.[64] They suggested that the $(Ph_3P)_2Co(H)Cl$ is the reactive species under their reaction conditions.[64] Kanai and coworkers have also found that the catalyst decomposes at higher temperatures (above 0^oC).

The most interesting observation in the present studies is the control of isomerization of 1-decene to the 2-decene mixture containing maximum amount of cis-2-decene (2h reaction at -10^oC) and to the mixture containing maximum amount of trans-2-decene (8h reaction at -10^oC) (Table 1). When the mixture was stirred further after 8h at -10^oC the product mixture showed an additional weak signal in the olefinic region of the ^{13}C-NMR spectrum indicating the presence of another olefinic product in addition to 2-decenes. Presumably, the trans-2-decene starts isomerizing into 3- and 4-decenes under prolonged reaction conditions. This possibility was not explored further. The results indicate that the

Substrate	Reaction time[b]	Product	Yield (%)[c]
$C_7H_{15}CH_2CH{=}CH_2$	2h	 (87%)[d] (13%)[d]	81
$C_7H_{15}CH_2CH{=}CH_2$	8h	 (10%)[d] (90%)[d]	78[e]
$PhCH_2CH{=}CH_2$	2h		81
	2h		80
cis,cis-1,5-Cyclooctadiene	8h	cis,cis-1,3-Cyclooctadiene	78
$R\text{-}CH_2\text{-}CH{=}CH_2$ $R = (CH_2)_6CO_2CH_3$	8h	 (50%) (50%)	72

[a] The reactions were carried out using anhydrous cobalt chloride (10 mmol), triphenylphosphine (30 mmol), sodium borohydride (10 mmol) and the olefinic substrate (20 mmol) in THF (80 ml) at -10°C (bath temperature) under nitrogen.

[b] Reaction time after the addition of the alkene following prepartion of the catalyst as described in the text.

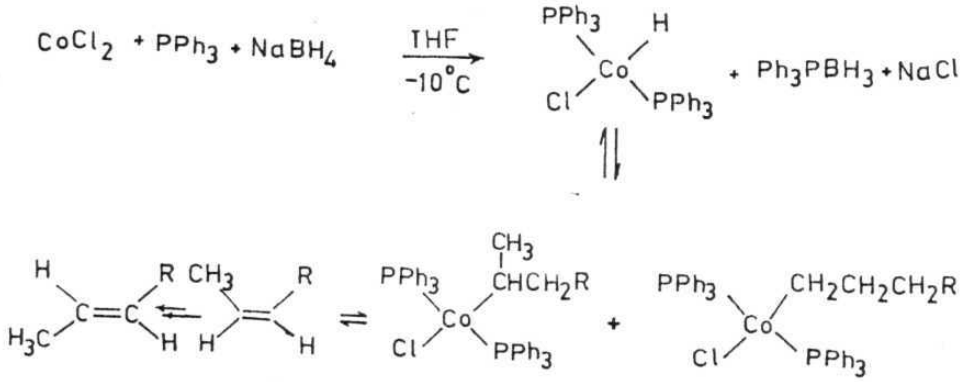
[c] Yields are of the isolated and distilled products. The yields are based on the olefinic substrate (20 mmol). When more than 20 mmol of the olefinic substrates were utilized a considerable amount of starting material remained in many cases. The products were identified from their spectral data (IR, ^{1}H-NMR and ^{13}C-NMR) and comparison with literature data.

[d] Percentage compositions were calculated from the intensities of the olefinic methyl group in the 270 MHz ^{1}H-NMR spectra.

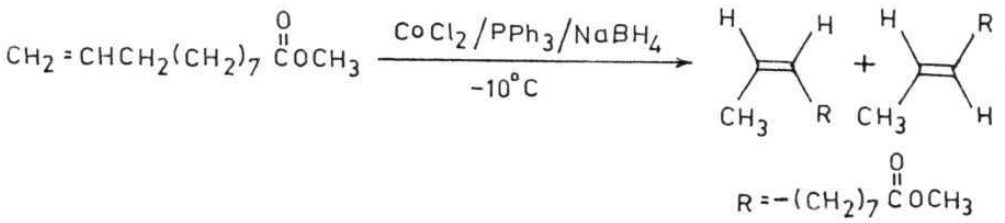
[e] A new ^{13}C-NMR signal begins to appear in the olefinic region at 129.5 ppm if the reaction mixture is stirred for a further 4h at -10°C; presumably as the double bond migrates along the carbon chain.

cis-2-decene is initially formed and then undergoes conversion into trans-2-decene. The ease of isomerization falls in the sequence: 1-decene > cis-2-decene> trans-2-decene. The isomerization observed here can be rationalised by the mechanism outlined in Scheme 3, involving hydrometallation-dehydrometallation equilibria.

Scheme 3

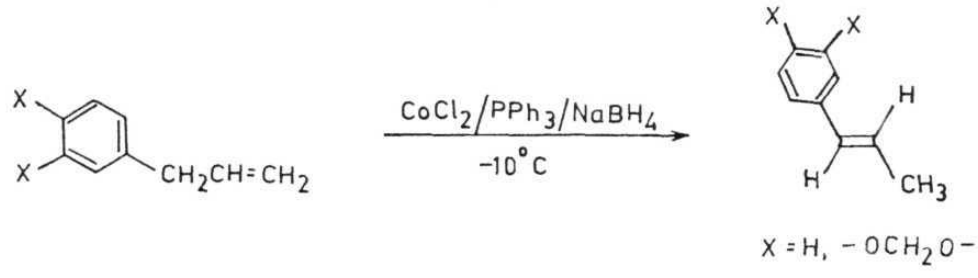


Methyl-10-undecenoate was isomerised into the corresponding mixture of cis/trans (50:50) methyl-9-undecenoate in 72% yield (Table 1) under the present reaction conditions. This result illustrates that the reagent system is able to isomerise olefins without affecting the carboxylic ester group.



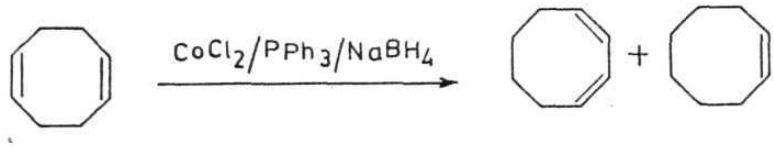
Allylbenzene and safrole gave only the corresponding trans-β-methyl styrenes and efforts to stop the reaction at cis-2-alkene stage were unsuccessful. In one run with allylbenzene, the experiment was carried out at -30^{o}C but no cis-product was isolated. Presumably, the cis-products

may be initially formed in these cases but get converted into trans-products in a fast manner. Alternatively, the trans-product may be formed directly without the intermediacy of the cis-isomer. These possibilities cannot be distinguished by the data available.

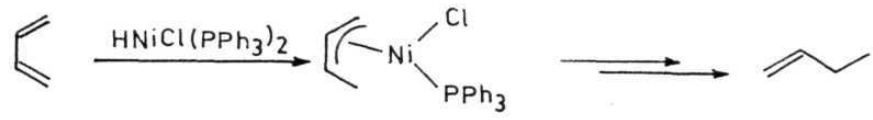


X = H, $-OCH_2O-$

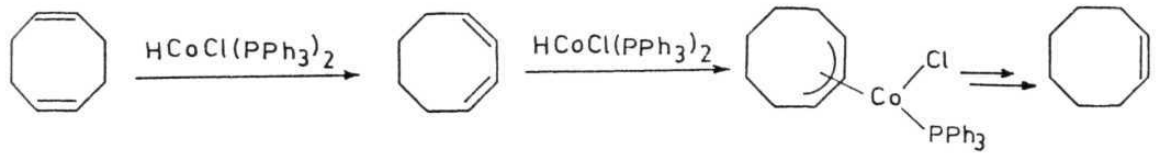
cis,cis-1,5-Cyclooctadiene gave cis,cis-1,3-cyclooctadiene in good yield (Table 1). In a run utilizing cis,cis-1,5-cyclooctadiene, when the reaction temperature was raised to room temperature during 2h after stirring the reaction mixture at -10°C for 8h, a small amount of (≃ 10%) cyclooctene was isolated along with cis,cis-1,3-cyclooctadiene.



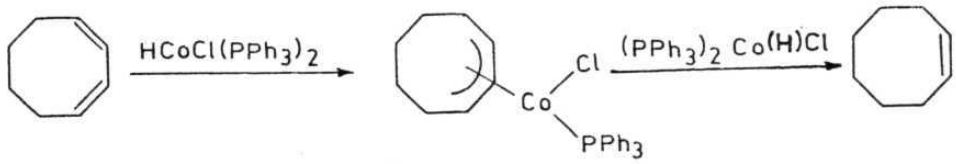
It has been reported that the $(PPh_3)_2)Ni(H)Cl$ reagent reduces butadiene to a mixture of butenes.[65] It was suggested that the reaction goes through the formation of corresponding allylnickel species.[65]



The formation of cyclooctene from cis,cis-1,5-cyclooctadiene under the present reaction conditions can be also explained by considering the formation of a similar allylcobalt intermediate.



In order to examine this possibility, we have carried out an experiment using cis,cis-1,3-cyclooctadiene (5 mmol) as follows: cis,cis--1,3-cyclooctadiene (5 mmol) was added to the $(Ph_3P)_2Co(H)Cl$ generated in THF at $-10^{o}C$ and the reaction temperature was raised to room temperature after stirring the reaction mixture for 8h at $-10^{o}C$ (see experimental section). The product obtained contains cyclooctene (~ 30%) besides cis,cis-1,3-cyclooctadiene (~ 70%). This further indicates the allylcobalt formation by the reaction of $(Ph_3P)_2Co(H)Cl$ with cis,cis-1,3-cyclooctadiene. However, when the reaction mixture was quenched with D_2O before workup, analysis of the product indicated that no deuterium incorporation had been taken place. In another run, the reaction mixture was treated with benzyl bromide at $-10^{o}C$ and stired further for 1h at room temperature, but no benzylated product was isolated. Presumably, the cyclooctene is formed from the reaction mixture before quenching with D_2O or coupling with benzyl bromide.

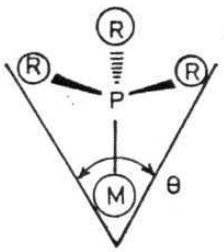


Such reductions of transition metal alkyl complexes with transition metal hydrides are known.[59a]

4-Vinylcyclohexene gave high boiling polymeric products under the present reaction conditions while limonene and 1-methylcyclohexene did not react at all. When more than 20 mmol of an olefinic substrate (Table 1) was utilized, considerable amount of starting materials remained unreacted under the present reaction conditions (8h, $-10^{o}C$). Furthermore, no isomerization of 1-decene occurs at $-40^{o}C$ and above $0^{o}C$ the catalyst decomposes. Theses results serve to indicate the scope and limilations of the present reagent. Although several catalytic systems are known to isomerize olefines,[66] the present system should be synthetically more attractive as the present catalyst system utilizes simple chemicals under mild conditions.

As visualized in Scheme 3, the isomerization involves the intermeadiacy of alkylcobalt species. It was of interest to examine whether the alkylcobalt species produced in this way can be carbonylated with carbon monoxide. The cobalt reagent $(PPh_3)_2Co(H)Cl$ was prepared as usual at $-10^{o}C$ and 1-decene was added and carbon monoxide was bubbled through the reaction mixture at various conditions ($-40^{o}C$ to $0^{o}C$, 1h to 8h). Workup (I_2/CH_3OH treatment etc.,) gave only 2-decenes and no carbonylated product was formed. Clearly, the β -elimination is the predominant reaction of the present alkylcobalt intermediates (Scheme 3). It was decided to examine the possibility of decreasing the steric effects of ligands around the cobalt metal in the coordination sphere in order to prevent β -elimination. It is well known that alteration of the substituents on tertiary phosphines can cause substantial changes in the chemical and physical properties of their transition metal complexes.[67] The bulky tertiary phosphine ligands distort the surrounding ligands and

markedly affect the chemistry of such phosphine complexes.[67] Such steric interactions influence the chemical properties such as the oxidative-addition reactions and β-elimination reactions. Tollman has proposed that the cone angle of a phosphine ligand can be used as a measure of its steric bulk.[67]



It appeared that it may be possible to prevent the β-elemination from the alkylcobalt species using ligands with less steric requirements. Cone angles of some phosphine ligands are listed below.

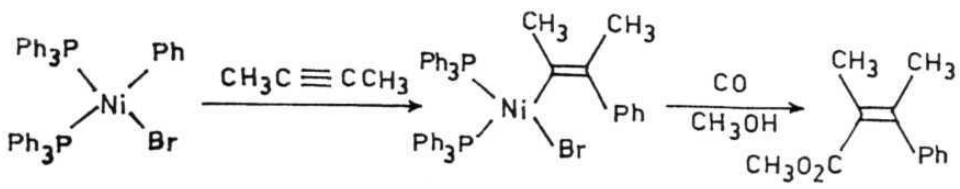
PR_3	θ	PR_3	θ
PMe_3 =	118^o	PPh_3 =	145^o
PEt_3 =	132^o	PCy_3 =	170^o
P^nBu_3 =	135^o	P^tBu_3 =	182^o

Trimethylphosphine appeared to be a less bulky ligand with relatively less cone angle. It exists as a gas and it is relatively difficult to handle *(ignites in air!)*. However, tri-n-butylphosphine is a readily accessible tertiary phosphine and it is relatively easy to handle. It has a Tollman cone angle of 135^o compared to the cone angle of 145^o for PPh_3.[67]

Surmizing in these lines, we carried out an experiment replacing PPh_3 by P^nBu_3. Upon addition of $NaBH_4$(10 mmol) to a magnetically stirred suspension of $CoCl_2$ (10 mmol) and P^nBu_3(30 mmol) in THF (60 ml) at 0^oC during 15 minutes followed by further stirring for 15 minutes at 0^oC, the colour of the reaction mixture remained blue with out any visible changes. The reaction mixture was stirred further for 1h at 0^oC and 1-decene (10 mmol) was added. The contents were further stirred for 4h at room temperature. After usual workup, 1-decene was recovered back quantitatively and no $^nBu_3PBH_3$ complex was formed. Clearly, the $NaBH_4$ does not react with the complex prepared using $^nBu_3P$ and $CoCl_2$. Presumably, the $^nBu_3P$, a stronger donor, changes the properties of the cobalt(II) dramatically and the resulting complex does not even react with $NaBH_4$.

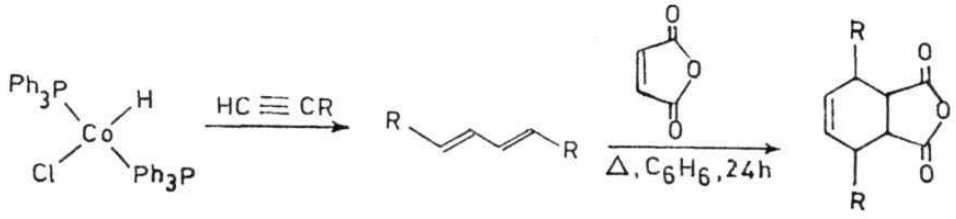
Hydrodimerization of 1-alkynes utilizing $CoCl_2/NaBH_4/PPh_3$ reagent system

As outlined above, our efforts on the carbonylation of organocobalt species obtained by hydrocobaltation of alkenes utilizing the $(Ph_3P)_2Co(H)Cl$ reagent system proved to be futile. It appeared that it may be possible to generate the corresponding vinylcobalt species by hydrometallation of alkynes. Such stable vinylcobalt species have not been synthesized in the past, but several stable nickel complexes have been prepared and carbonylated.[68,69]



In order to examine the reactivity of the present $(PPh_3)_2Co(H)Cl$ reagent towards alkynes, we carried out the following experiment. The $(PPh_3)_2Co(H)Cl$ reagent was prepared as usual using $CoCl_2$ (10 mmol), Ph_3P (30 mmol) and $NaBH_4$ (10 mmol). 1-Decyne (10 mmol) was added. The contents were stirred for 3h at -10^oC. After usual workup, it was found that 1-decyne had completely reacted. The major signals in the ^{13}C-NMR spectrum of the product correspond to 1,4-di-n-octyl-(E,E)-1,3-butadiene (70%). However, there were weak signals (small humps) in the olefinic region indicating that the sample is not pure. It appeared that the other impurity present may be polymeric in nature.

We have observed that the formation of the polymeric product can be prevented by carrying out the reaction at -20^oC utilizing 40 mmol of PPh_3. Under these conditions, 1-decyne was converted into 1,4-di-n-octyl-(E,E)-1,3-butadiene in 86% yield (Table 2). The product was identified by comparison of the ^{13}C-NMR spectral data with the data reported for similar (E,E)-1,3-dienes.[10] The diene obtained in the case of 1-heptyne following the present procedure, on treatment with maleic anhydride gave Diels-Alder adduct **III** (see experimental section)(Spectrum no. 3).



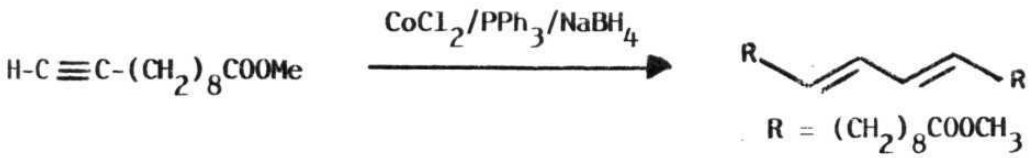
III

The above mentioned polymeric product may be formed through carbometallation of the alkyne with the vinylcobalt intermediate (Scheme 4).

Presence of excess PPh_3 would make the metal cordination sphere saturated and prevent the complexation of alkyne with the vinylcobalt intermediate. Alternatively, presence of excess PPh_3 may facilitate the decomposition of the vinylcobalt species into the (E,E)-1,3-dienes and hence the formation of polymeric product is prevented.

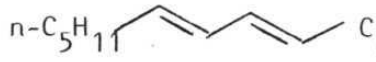
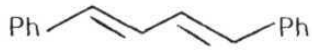
The hydrodimerization reaction was found to be a general one towards 1-alkynes (Table 2). 1-Octyne and 1-heptyne were converted into the corresponding (E,E)-1,3 dienes in 82% and 78% yields respectively (Table 2).

The methyl-10-undecynoate was converted into the corresponding hydrodimerized product in 69% yield (Table 2). This observation again illustrates that the present reagent is not affecting the ester group (Spectrum no. 4).



In the case of phenylacetylene when the experiment was carried out at -20°C, the polymeric product was also formed along with the 1,4-diphenyl-(E,E)-1,3-butadiene. However, when the cobalt reagent was prepared at -20°C as usual and phenyl acetylene was added after cooling the contents to -65°C and the mixture was stirred further for 3h at -65°C, 1,4-diphenyl-1,3-(E,E)-butadiene was isolated in 65% yield (Table 2), and the polymeric product was not formed (Spectrum no. 4).

Table 2: Hydrodimerization of terminal alkynes into (E,E)-1,3-dienes using $CoCl_2/PPh_3/NaBH_4$

Substrate[a]	Product[b]	Yield (%)
$n\text{-}C_8H_{17}C\equiv CH$		86
$n\text{-}C_6H_{13}C\equiv CH$		82
$n\text{-}C_5H_{11}C\equiv CH$		78
$PhC\equiv CH$		65
$RC\equiv CH$		69

$R=CH_2(CH_2)_7CO_2CH_3$

[a]The reactions were carried out using 10 mmol of alkyne, 10 mmol of anhydrous cobalt(II) chloride, 10 mmol of $NaBH_4$ and 40 mmol of Ph_3P in THF (80 ml). The reaction time and temperature were the same as those given in the text for all the substrates except phenylacetylene. In this case, the cobalt hydride reagent was prepared at -20^oC as given in the text and the phenylacetylene was added after cooling the contents -65^oC and the mixture was further stirred for 3h at this temperature before workup. In this case, polymeric products were also formed at -20^oC resulting in lesser yields of the trans, trans-1,4-diphenyl-1,3-butadiene.

[b]The products were isolated by chromatography on a silica gel column using hexane or hexane/$CHCl_3$ as eluent.

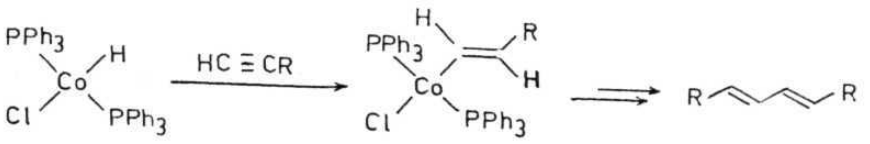
As discussed previously, the $(Ph_3P)_2Co(H)Cl$ reagent recduces, cis,cis-1,3-cyclooctadiene into cyclooctene (30%). However, the olefinic products derived from the 1,4-di-alkyl-1,3-dienes are not formed during the hydrodimerization of 1-alkynes. Presumably, the $(PPh_3)_2Co(H)Cl$ reagent does not react with the acyclic (E,E)-1,3-dienes in significant rate under the present reaction conditions.

The internal alkynes, diphenylacetylene, 1-phenyl-1-propyne, 5-decyne remained unreacted even after 12h under the present reaction conditions. Also, in addition to carboxylic ester group (Table 2), n-octyl cyanide, n-octyl bromide and cyclohexanone were also not affected by the present system.

We have observed that the $(Ph_3P)_2Co(H)Cl$ reagent, prepared utilizing $(Ph_3P)_2CoCl_2$ (1 eq), Ph_3P (2 eq) and $NaBH_4$ (1 eq) under the present reaction conditions, exhibits identical reactivities.

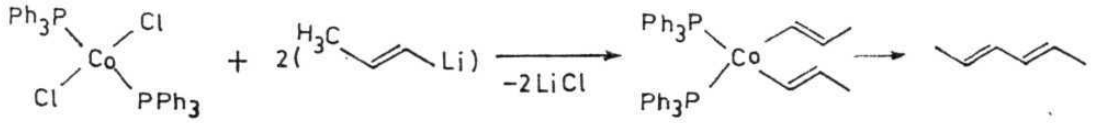
The formation of (E,E)-1,4-diphenyl-1,3-butadiene indicates that the hydrocobaltation of alkynes using the present reagent system takes place by the syn addition of the Co-H bond placing the cobalt at the terminal carbon atom (Scheme 4).

Scheme 4



Several mechanistic pathways are possible for the conversion of the vinylcobalt complex 2 into the corresponding (E,E)-1,3-dienes. Whitesides and his coworkers previously observed that treatment of trans-propenyl lithium (2.3 eq) with $(Ph_3P)_2CoCl_2$ (1 eq) gives the corresponding (E,E)-1,3-dienes in 98% yield with 96% retention of stereochemistry about the double bond.[71] They obtained similar results with several other transition metal complexes.[71] The authors indicated that no effort was made to characterize any transition metal organometallic intermediate generated under their reaction conditions and the optimum stoichiometries were not established. Their observation with the $(Ph_3P)_2CoCl_2$ system may tentatively be visualized as outlined in Scheme 5.

Scheme 5



The mechanistic studies of Whitesides and coworkers[71] are mainly concerned with the thermal decomposition of vinylcopper(I) and silver(I) organometallic compounds. However, these authors suggested that the thermal decompositions of other vinylorganometallics with high stereoselectivity are also subject to the same mechanistic constraints as are the thermal decompositions of vinylcopper(I) and silver(I) compounds.[71] They showed that the reaction cannot go through long lived free radicals since the vinyl radicals undergo inversion in a fast manner. Obviously, the formation of stereospecific dimerization in the present case cannot be explained by postulating the formation of free radical intermediates

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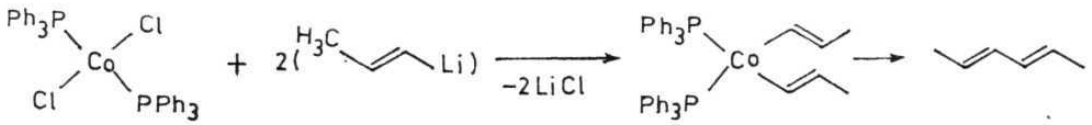
Scheme 5



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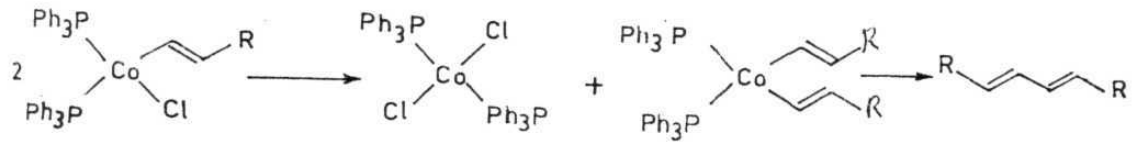
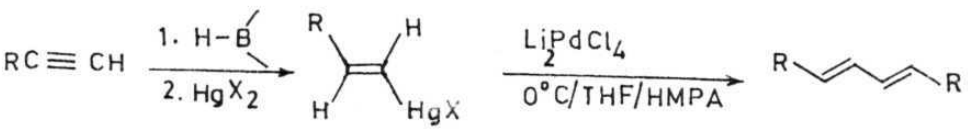
from the vinylcobalt species. A possibility is the disproportionation of the complex 2 (2 eq) into divinylcobalt species followed by the well-known reductive elimination process (Scheme 6).

Scheme 6



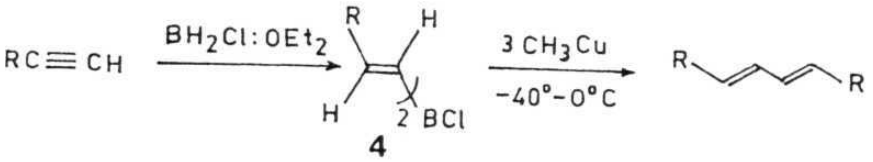
Such disproportionations and reductive elimination reactions are common in transition metal organometallic chemistry.[72] However, it should be pointed out that there is no data available at present to confirm this mechanistic proposal. Accordingly, the mechanistic pathway outlined (Scheme 4 and 6) for hydrodimerization of alkynes utilizing the present reagent system can serve only as a tentative working hypothesis.

There are several methods available for the conversion of 1-alkynes into the corresponding (E,E)-1,3-dienes.[73-75] For example, vinylmercuric chlorides 3, readily available through hydroboration-mercuration sequence, undergo reaction with palladium chloride and lithium chloride in HMPA at 0°C to give the corresponding (E,E)-1,3-dienes.[73]

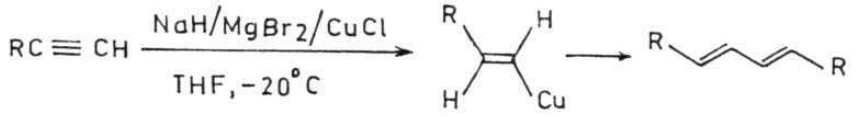


3

Dialkenylchloroboranes 4, readily available through hydroboration of alkynes with chloroborane-etherate, react with methylcopper to produce (E,E)-1,3-dienes.[74]



Very recently, it has been observed in our laboratory that the Cu(I) hydride species, prepared *in situ* in THF using $NaBH_4/MgBr_2/Et_3N/CuCl$ or $NaH/MgBr_2/CuCl$ reagent systems, converts alkynes into (E,E)-1,3-dienes.[75]



The present procedure of hydrodimerization of alkynes into the corresponding dialkyl-(E,E)-1,3-dienes is a good alternative method to the methods available in the literature since it utilizes simple chemicals under mild conditions.

Attempted carbonylations by bubbling carbon monoxide after the addition of 1-alkyne under the present reaction conditions (-65^{o} to $-20^{o}C$) did not yield any other product besides the (E,E)-1,3-dienes. Presumably, the vinylcobalt species decomposes instantaneously into (E,E)-1,3-dienes under the present conditions. The results indicate that the carbon monoxide is not able to intercept the alkyl or vinylcobalt(II) reagent generated utilizing the $(Ph_3P)_2Co(H)Cl$ reagent. Consequently, we turned our attention towards the effect of carbon monoxide on the reactivity of the $CoCl_2/NaBH_4$ reagent system (Chapter 3).

SUMMARY

The $(Ph_3P)_2Co(H)Cl$ reagent prepared using $CoCl_2/NaBH_4/PPh_3$ in THF isomerises 1-alkene into predominantly cis-2-alkenes or trans-2-alkenes. The $(Ph_3P)_2Co(H)Cl$ reagent also hydrodimerises 1-alkynes into the corresponding (E,E)-1,3-dienes. Attempted carbonylations of alkyl/vinylcobalt(II) intermediates generated utilizing the hydridocobalt(II) reagent were unsuccessful. Presumably, PPh_3 present in the complex does not allow carbon monoxide insertion.

EXPERIMENTAL

Several items given in the experimental section of chapter 1 are also applicable here. 1-Decyne and 1-octyne were prepared following a reported procedure[76]. 1-Heptyne and the olefins utilized were supplied by Fluka, Switzerland.

Preparation of methyl-10-undecynoate

10-Undecynoic acid was prepared following a reported procedure.[77] It was esterified following a procedure reported recently.[78] DBU (20 mmol, 3.0 g) was added to a magnetically stirred mixture of 10-undecynoic acid (20 mmol, 3.6 g) and CH_3I (25 mmol, 3.5 g) in benzene (15 ml). The reaction mixture was further stirred for 3h at 60°C. Ether (20 ml) was added to the reaction mixture and the solution was washed with 3N HCl (5 ml), water (10 ml), saturated sodium chloride solution (10 ml) and dried over anhydrous $MgSO_4$. The solvent was evaporated and the residue was distilled to isolate methyl-10-undecynoate 87%, 3.5g, b.p=120°/15 mm, Lit.[79] b.p. 121°/15 mm

IR (neat) : ν_{max} : 1740, 980, 900 cm^{-1}

Isomerization of 1-decene into cis-2-decene using $CoCl_2/NaBH_4/PPh_3$ system

$NaBH_4$ (10 mmol, 0.8 g) was added during 15 minutes to a magnetically stirred blue coloured suspension of $CoCl_2$ (10 mmol, 1.30 g) and PPh_3

(30 mmol, 7.8 g) in THF (80 ml) at -10°C under nitrogen atmosphere and the mixture was stirred further at -10°C for 30 minutes. (The colour of the solution turns to green colour) 1 Decene (20 mmol, 2.8 g) was injected and the mixture was stirred at -10°C for 2 h. Petroleum ether (200 ml) was added followed by 2N HCl (30 ml). The layers were separated and the aqueous layer was extracted with petroleum ether (2 x 25 ml). The combined organic extract was washed once with saturated sodium chloride solution (30 ml) and dried over anhydrous $MgSO_4$. The solvent was evaporated and pentane (10 ml) was added to the residue to precipitate the PPh_3BH_3 complex and most of the PPh_3. The solvent was evaporated from the filtrate and the residue was distilled to give cis-2-decene 2.3 g, 81%, b.p. 56°C/10 mm, Lit.[80] bp. 58°C/10 mm (Spectrum no. 2).

IR (neat): ν_{max} : 980, 900 cm^{-1}

^{1}H-NMR (270 MHz, $CDCl_3$): δppm : 0.9 (t, $-CH_3$), 1.5 (s, $-CH_2$) 1.8 (d, cis-CH_3) 1.9(d,trans-CH_3),2.3(1,$-CH_2$) 6.3 (m, -2H)

^{13}C-NMR (25.0 MHz, $CDCl_3$): δppm : 130.9, 123.5, 32.9, 32.2 29.8, 29.6, 27.1, 23.0, 14.2, 12.7.

In addition, small peaks at 131.8, 124.5, 17.9 characteristic of trans-2-decene were also present. The cis/trans ratio 87:13 (Table 1)

was calculated from the intensities of olefinic $-CH_3$ in the ^{1}H-NMR (270 MHz) spectrum.

Isomerization of 1-decene into trans-2-decene using $CoCl_2/NaBH_4/Ph_3P$

The reaction was carried out following the procedure outlined in the previous experiment except that the reaction mixture was stirred further for 8h after the additon of 1-decene at -10^oC. Workup as outlined in the previous experiment gave trans-2-decene. 2.26 g, 78%, b.p. $58^oC/10$ mm, Lit.[80] b.p. $58^oC/10$ mm (Spectrum no. 2)

IR (neat): ν_{max}	:	2960, 2850, 950 cm^{-1}
^{1}H-NMR (270 MHz, $CDCl_3$): δ ppm	:	0.9(t, $-CH_3$) 1.3(s, $-CH_2$) 1.8(d, cis-CH_3), 1.9(d, trans-CH_3) 2.3(q, $-CH_2$), 6.4(m, -2H)
^{13}C-NMR (25.0 MHz, $CDCl_3$): δ ppm	:	131.8, 124.5, 32.9, 32.3, 30.0 29.5, 23.9, 17.96, 14.2

In addition small peaks at 130.9, 123.5 and 12.7 characteristic of cis-2-decene were also present. The trans/cis ratio 90:10 was calculated from the intensities of olefinic $-CH_3$ group in the ^{1}H-NMR (270 MHz) spectrum.

The above procedure utilizing the $CoCl_2/NaBH_4/PPh_3$ system was followed for the isomerization of several other olefins (Table 1) and the results are presented below.

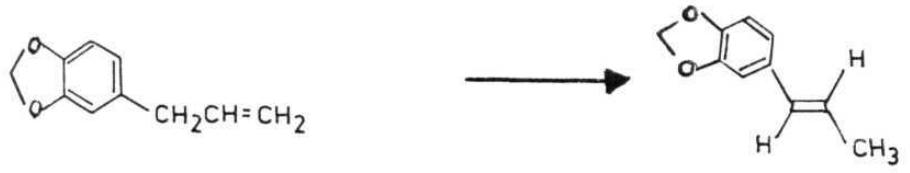
Yield : 81% (2.2 g)

B.P. : 70°C/9 mm, Lit.[80] b.p. 175°/760 mm

IR (neat): ν_{max} : 3010, 1600, 950, 740 cm^{-1}

^{1}H-NMR (100 MHz, $CDCl_3$): δppm : 1.7 (q, $-CH_3$), 6.1(m, $-CH_2$), 7.1 (m, C_6H_5)

^{13}C-NMR (25 MHz, $CDCl_3$): δ ppm : 139.8, 133.2, 130.1, 128.4, 127.7, 126.8, 20.0.



Yield : 80% (2.4 g)

B.P. : 120°/20 mm, Lit.[81] b.p. 111°/6 mm

IR (neat) : ν_{max} : 3010, 1600, 1240, 950 cm^{-1}

^{13}C-NMR (25.0 MHz, $CDCl_3$) : δppm : 146.4, 145.0, 131.9, 129.1, 121.9, 118.5, 106.5, 103.7, 99.2, 16.6

Yield : 78% (1.7 g)

B.P. : 55^{o}/25 mm, Lit.[80] b.p. 52^{o}/25 mm

^{13}C-NMR (25 MHz, $CDCl_3$): δ ppm : 131.0, 126.0, 28.3, 23.3

The product shows 1:1 correspondence (IR, NMR) to the authentic sample.

Isomerization of methyl-10-undecenoate to methyl-9-undecenoate using $CoCl_2/NaBH_4PPh_3$

The reaction was carried out following the procedure outlined in the previous experiment except that the reaction mixture was stirred for 8h after the addition of methyl-10-undecenoate. Workup as outlined in the previous experiment gave methyl-9-undecenoate.

Yield : 72% (3.1 g)

B.P. : 130^{o}/15 mm

IR (neat): ν_{max} : 1740, 980, 950, 900 cm^{-1}

^{1}H-NMR (270 MHz, $CDCl_3$): δppm : 1.6 (s, $-CH_2$), 1.9(d,cis-CH_3) 2.0(d,trans-CH_3), 2.4(q $-CH_2$) 2.75(t,$-CH_2$), 4.4(s $-OCH_3$), 6.5(m,-2H).

^{13}C-NMR (25.0 MHz, $CDCl_3$): δ ppm : 173.9, 132.2, 131.4, 125.2, 124.2, 51.6, 34.6, 33.4, 30.4, 30.0, 27.6, 25.8, 18.7, 13.2

Comparison of intensities of ^{13}C-NMR signals of olefinic carbon atoms indicates that the cis/trans isomers are present approximately in 1:1 ratio.

Examination of the nature of the cobalt species involved-Isolation of Ph_3PBH_3 Complex

$NaBH_4$ (10 mmol) was added under nitrogen atmosphere during 15 minutes to a magnetically stirred suspension of $CoCl_2$ (10 mmol) and Ph_3P (30 mmol) in THF at -10^oC and the reaction mixture was further stirred for 30 min at -10^oC. Petroleum ether (200 ml) was added and the aqueous layer was extracted with petroleum ether (2x25 ml). The combined extracts were washed with saturated sodium chloride solution and dried over anhydrous $MgSO_4$. The solvent was evaporated and the residue was chromatographed on a silica gel column (10% $CHCl_3$ in Hexane) to isolate Ph_3PBH_3, 2.2 g, 80%, m.p. 185^oC, Lit.[82] m.p. 189^oC.

Examination of the nature of cobalt species involved-Attempted E.S.R. studies

The complex prepared utilizing $CoCl_2$ (10 mmol), PPh_3 (40 mmol) and $NaBH_4$ (10 mmol) at -10^oC in THF was frozen to 163K and the ESR spectrum was recorded on a JEOL-Fe-3X spectrometer. However, no ESR signal was observed. The $CoCl_2$ (10 mmol) and Ph_3P (40 mmol) mixture in THF, frozen to 163K also did not show any ESR signal.

Reaction of cis,cis-1,3-cyclooctadiene with $CoCl_2/NaBH_4/PPh_3$ system

$NaBH_4$ (10 mmol) was added during 15 minutes into a magnetically stirred suspension of anhydrous $CoCl_2$ (10 mmol) and PPh_3 (30 mmol) in THF (80 ml) at -10°C under nitrogen atmosphere and the mixture was further stirred for 30 minutes. The cis, cis-1,3-cyclooctadiene (5 mmol) was injected and the reaction mixture was stirred further for 8h at -10°C. The temperature was raised to 25°C during 2h. After workup as outlined in the previous experiments, the crude product showed ^{13}C-NMR signals in the olefinic regions for cyclooctene (23.2, 28.1, 125.9, 128.4, 130.9) and cis,cis-1,3-cyclooctadiene (131.0, 126.0, 28.3, 23.3). Comparison of the ^{13}C-NMR signals indicates that these components are present approximately in the ratio 30:70. However, this can be only a crude estimate since the ^{13}C-NMR signals intensities are also affected by NOE.

In a run with cis,cis-1,3-cyclooctadiene, after stirring the reaction mixture for 8h at -10°C, D_2O (20 mmol) was added. After workup, analysis of the product indicated that no deuterium incorporation had taken place.

In another run, to the reaction mixture obtained after 8h at -10°C, benzyl bromide (5 mmol) was added and stirred for 2h but it was found that no benzylated product was formed.

Attempted carbonylation of 1-decene using $CoCl_2/PPh_3/NaBH_4$ system

$NaBH_4$ (10 mmol) was added under nitrogen atmosphere during 15 minutes to a magnetically stirred suspension of $CoCl_2$ (10 mmol) and PPh_3 (30 mmol) in THF (80 ml) at -10°C and the mixture was stirred at -10°C further for 30 minutes. The 1-decene (20 mmol) was added and carbon monoxide was bubbled through the reaction mixture for 4h at -10°C. Iodine in CH_3OH (5 gm in 20 ml) was added and the mixture was stirred for 1h. Petroleum ether (200 ml) was added to the reaction mixture followed by 2N HCl (30 ml). The layers were separated and the aqueous layer was extracted with petroleum ether (2x25 ml). The combined organic extract was washed with 10% $Na_2S_2O_3$ (10 ml) solution, followed by water (10 ml), saturated sodium chloride solution (10 ml) and dried over anhydrous $MgSO_4$. The solvent was evoporated. The crude product showed no carbonyl or hydroxyl absorption in IR. After distillation, a mixture of cis and trans-2-decenes (50:50) was isolated in 78% yield.

Reaction of 1-decene with $CoCl_2/NaBH_4/PPh_3$ at -40°C

$NaBH_4$ (10 mmol) was added under nitrogen atmosphere during 15 minutes into a magnetically stirred suspension of $CoCl_2$ (10 mmol) and Ph_3P (30 mmol) in THF (80 ml) at -10°C and the mixture was stirred further at -10°C for 30 minutes. The reaction mixture was cooled to -40°C and 1-decene was injected and the contents were further stirred for 8h at -40°C. After workup as outlined in previous experiments, 1-decene was recovered back quantitatively.

Preparation of tri-n-butylphosphine[83]

n-Butyl bromide (400 mmol) in ether (100 mmol) was added dropwise to magnesium turnings (10 g, 400 mmol) in anhydrous ether (150 ml) for 3h. The resulting solution of n-butylmagnesium bromide is cooled to $0^{o}C$ and a solution of redistilled PCl_3 (8.7 ml, 100 mmol) in anhydrous ether (50 ml) was added dropwise with stirring over a period of an hour. The mixture was refluxed for 30 minutes, cooled to $0^{o}C$ and treated with 250 ml of an ice cold aqueous saturated solution of ammonium chloride. After 30 minutes, ether (50 ml) was added and the organic layer was separated. The aqueous layer was extracted with ether (3x30 ml). The combined organic extract was dried over anhydrous $MgSO_4$. The solvent was evaporated and the residue was distilled to isolate tri-n-butylphosphine, 15.1 g, 57%, b.p. $149^{o}C/50$ mm, lit[83]. b.p. $115^{o}C/12$ mm. IR spectrum of the product was identical with the spectrum reported in the literature.[84]

Reaction of 1-decene $CoCl_2/NaBH_4/{}^{n}Bu_3P$ system

$NaBH_4$ (10 mmol) was added to a mixture of $CoCl_2$ (5 mmol) and ${}^{n}Bu_3P$ (30 mmol) in THF (80 ml) in portions for 1h at $0^{o}C$. 1-Decene (10 mmol) was added and the mixture was stirred further for 4h at $0^{o}C$. It was observed that the colour of the solution remained blue through out the experiment. Ether (70 ml) was added and the contents were poured into 3N HCl (20 ml). Solid sodium chloride was added and the organic layer was separated. The aqueous layers was extracted with ether (3x30 ml). The combined organic extract was washed with saturated sodium

chloride solution (30 ml) dried over anhydrous $MgSO_4$ and the solvent was evaporated. Distillation of the residue gave 1-decene and no other product was formed.

Hydrodimerization of 1-decyne with $CoCl_2/NaBH_4/PPh_3$

$NaBH_4$ (10 mmol) was added during 15 minutes into a magnetically stirred suspension of anhydrous $CoCl_2$ (10 mmol) and PPh_3 (40 mmol) in THF (80 ml) at -20°C (bath temperature) under nitrogen atmosphere and the mixture was further stirred for 45 minutes. 1-Decyne (10 mmol) was injected and the contents were further stirred for 3h at -20°C (CCl_4-liquid nitrogen bath). Petroleum ether (200 ml) was added at -20°C followed by addition of 2N HCl (30 ml). The layers were separated and the aqueous layer was extracted with petroleum ether (2x25 ml). The combined organic extract was washed once with saturated sodium chloride solution (30 ml) and dried over anhydrous $MgSO_4$. The solvent was evaporated and n-pentane (10 ml) was added to the residue to precipitate the PPh_3BH_3 complex and most of the Ph_3P. The solvent was evaporated and the residue was chromatographed on a silica gel column using hexane as eluent to isolate 1,4-di-n-octyl (E,E)-1,3-butadiene 1.2 g, 86%.

IR (neat) : ν_{max} : 2910, 2840, 950 cm^{-1}

^{1}H-NMR (100 MHz, $CDCl_3$): δppm : 0.9 (t, CH_3), 1.3(s, CH_2), 2.0(q, CH_2), 4.0(m, CH), 5.3-6.2(m, CH)

^{13}C-NMR (250 MHz, $CDCl_3$): δppm : 132.3, 130.5, 32.7, 32.0, 29.8, 29.6, 29.5, 22.8, 14.5

The above procedure utilizing $CoCl_2/NaBH_4/PPh_3$ system for hydrodimerization was followed for the conversion of several 1-alkynes into the corresponding (E,E)-1,3-dienes (Table 2).

Yield : 82% (0.9 g)

IR (neat): ν_{max} : 2910, 2840, 950 cm^{-1}

^{1}H-NMR (100 MHz, $CDCl_3$): δ ppm : 0.9(t, CH_3), 1.2(s, CH_2), 2.0(q, CH_2), 4.9(m, CH), 5.2-6.1(m, CH)

^{13}C-NMR (25.0 MHz, $CDCl_3$): δ ppm : 132.4, 130.7, 33.0, 29.0 22.7, 14.1.

Yield : 78% (0.8 g)

IR (neat) : ν_{max} : 2910, 2840, 950 cm^{-1}

^{1}H-NMR (100 MHz, $CDCl_3$): δ ppm : 0.9(t, CH_3), 1.2(s, CH_2), 2.0(q, CH_2), 4.8(m, CH), 5.1-6.1(m, CH)

^{13}C-NMR (25.0 MHz, $CDCl_3$): δ ppm : 132.4, 130.5, 32.8, 32.6, 32.1, 29.4, 22.8, 14.3.

Hydrodimerization of methyl-10-undecynoate utilizing $CoCl_2/NaBH_4/PPh_3$ system

The reaction was carried out following the procedure outlined in the previous experiment except the crude reaction product after work up was chromatographed on a silica gel column using 10% $CHCl_3$ in hexane as eluent.

Yield	:	69% (1.4 g)
M.P.	:	54°C, Lit.[73] m.p. 54.5°C, (mp. 40°C for trans, trans and cis, trans mixture).
IR (KBr): ν_{max}	:	2910, 2840, 1740, 950 cm^{-1}
^{1}H-NMR (100 MHz, $CDCl_3$): δ ppm	:	0.9(t, CH_3), 1.3(s,CH_2), 2.0(m, CH_2), 3.6(s, OCH_3), 5.0-6.3(m, CH)
^{13}C-NMR (25.0 MHz, $CDCl_3$): δ ppm	:	174.9, 132.0, 130.6, 51.0, 33.7, 32.0, 28.9, 24.7.

Reaction of di-1,4-n-pentyl (E,E)-1,3-butadiene with maleic anhydride

Maleic anhydride (10 mmol) was added into a magnetically stirred solution of di-1,4-n-pentyl -1,3-butadiene (10 mmol) in benzene (25 ml). The reaction mixture was refluxed for 24h. Water (10 ml) and ether (30 ml) were added and the layers were separated. The organic layer was washed with saturated sodium chloride solution, dried over anhydrous $MgSO_4$ and the solvent was evaporated. The crude product was purified by chromatography on a silica gel column using 10% ethyl acetate in hexane as eluent (70%, 2.0 g, mp = 124°C).

IR (KBr) : ν_{max} : 1820, 1760 cm^{-1}

^{13}C-NMR (25.0 MHz, $CDCl_3$: δ ppm : 177.8, 133.9, 44.9, 36.3, 31.6, 30.5, 27.6, 22.6, 13.9

Mass spectrum (m/e) : 292 (M^+)

Hydrodimerization of phenylacetylene with $CoCl_2/NaBH_4/PPh_3$ system

$NaBH_4$ (10 mmol) was added during 15 minutes into a magnetically stirred suspension of anhydrous $CoCl_2$ (10 mmol) and PPh_3 (40 mmol) in THF (80 ml) at -20°C under nitrogen atmosphere. The mixture was further stirred for 45 minutes. The contents were cooled to -65°C (bath temperature) and phenylacetylene (100 mmol) was injected. The contents wer further stirred for 3h at -65°C. After workup as outlined in previous experiments, the product was further purified by column chromatography on a silicagel column using 10% $CHCl_3$ in hexane as eluent. It was further purified by crystallization from ethylalcohol 65%, 0.7 g, mp = 150°C, Lit.[73] m.p. = 152.5°C.

IR (KBr) : ν_{max} : 1600, 950, 740 cm^{-1}

^{1}H-NMR (100 MHz, $CDCl_3$): δ ppm : 6.35-6.8(m, CH), 6.9-7.4 (m, C_6H_5)

^{13}C-NMR (25.0 MHz, $CDCl_3$): δ ppm : 137.3, 132.9, 129.4 128.8, 127.7, 126.5

Mass spectrum (m/e) : 206 (M^+)

Preparation of bis(triphenylphosphine) cobalt(II) chloride, $(PPh_3)_2CoCl_2$[85]

To a boiling solution of PPh_3 (40 mmol) in n-butanol (100 ml) was added a boiling solution of $CoCl_2.6H_2O$ (20 mmol) in n-butanol. The mixture was further boiled for 15 minutes. The $(PPh_3)_2CoCl_2$ separated out on cooling the solution. The complex was separated by filteration and recrystallised from the same solvent yield, 10.3 g, 74%.[85]

Hydrodimerization of 1-decyne utilizing $(PPh_3)_2CoCl_2/NaBH_4$ system

$NaBH_4$ (10 mmol) was added during 15 minutes into a magnetically stirred suspension of $(Ph_3P)_2CoCl_2$ (10 mmol) and PPh_3 (10 mmol) in THF (80 ml) at -20°C under nitrogen atmosphere and the reaction mixture was further stirred for 45 minutes. 1-Decyne (10 mmol) was injected and the contents were further stirred for 3h at -20°C. Workup as outlined in previous experiments gave 1,4-di-n-octyl (E,E)-1,3-butadiene 1.2 g, 86%. IR spectrum of the product showed 1:1 correspondence with the spectrum of the product obtained previously.

Attempted carbonylation of 1-decyne using $CoCl_2/NaBH_4/PPh_3$ system

The cobalt reagent was prepared at -20°C using $CoCl_2$ (10 mmol), PPh_3 (40 mmol) and $NaBH_4$ (10 mmol) in THF (80 ml) and 1-decyne (10 mmol) was injected. Carbon monoxide was bubbled through the reaction mixture for 4h at -20°C. I_2 in CH_3OH was added (5 g in 20 ml CH_3OH) and the mixture was stirred for 1h. The mixture was poured into the petroleum

ether (20 ml) and water (20 ml) was added. The layers were separated and the organic layer was washed with $Na_2S_2O_3$ solution (10%, 20 ml), water (20 ml), saturated sodium chloride solution (20 ml) and dried over anhydrous $MgSO_4$. After usual workup, as outlined in previous experiments, 1,4-di-n-octyl (E,E)-1,3-butadiene (76%) was isolated and no other product was formed.

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CHAPTER 3

Studies on the reactivities of cobalt reagents generated utilizing $CoCl_2/NaBH_4$ system in the presence of carbon monoxide

INTRODUCTION

Synthesis, structure and reactivity of organometallic compounds of the transition metals constitute the major portion of organometallic chemistry.[1-6] The organotransition metal compounds containing carbonyl ligands constitute the major class of organometallics of the transition metals.[1-6] Many transition elements form stable metal carbonyls, hydrido-metal carbonyl complexes and anionic metal carbonyl derivatives.[6] (Tables 1, 2 and 3). The metal carbonyl derivatives have a very rich chemistry and the subject has been extensively reviewed.[7,8]

In recent years, there is immense interest in the development of synthetic methods utilizing transition metal carbonyl derivatives.[9-13] As outlined in general introduction, many useful synthetic methods involving carbon-carbon bond formation reactions have been developed.[9-13] Inspite of these interesting developments by some research groups, there is not much interest on the metal carbonyl chemistry among the main stream synthetic chemists. This may be due to many reasons: The metal carbonyls are dangerous and it is difficult to handle them! They are not suitable for bench top preparations because the synthetic methods utilizing these carbonyls often requires carbon monoxide and undesirable reaction conditions (high temperature and high pressure). Finally, there are not many suppliers closer to the laboratories for these derivatives and hence the metal carbonyl derivatives are not readily accessible.

Table 1 : Metal carbonyls [6]

Group IV	Group V	Group VI	Group VI		Group VIII		Group IB
$Ti(CO)_6^*$	$V(CO)_6$	$Cr(CO)_6$	$Mn_2(CO)_{10}$	$Fe(CO)_5$	$Co_2(CO)_8$	$Ni(CO)_4$	$Cu(CO)_3^*$
$Ti(CO)_y^*$	$V(CO)_{1-5}^*$	$Cr(CO)_{3-5}^*$	$Mn_4(CO)_{16}$	$Fe_2(CO)_9$	$Co_4(CO)_{12}$	$Ni(CO)_{1-3}^*$	$Cu_2(CO)_6^*$
	$V_2(CO)_{10}^*$		$Mn(CO)_5^*$	$Fe_3(CO)_{12}$	$Co_6(CO)_{16}$		
		$Mo(CO)_6$	$Tc_2(CO)_{10}$	$Ru(CO)_5$	$Rh_2(CO)_8$	$Pd(CO)_{1-4}^*$	$Ag(CO)_{1-3}^*$
		$Mo(CO)_{3-5}^*$		$Ru_2(CO)_9$	$Rh_4(CO)_{12}$		$Ag_2(CO)_6^*$
				$Ru_3(CO)_{12}$	$Rh_6(CO)_{16}$		
	$Ta(CO)_{1-6}^*$	$W(CO)_6$	$Re(CO)_{10}$	$Os(CO)_5$	$Ir_2(CO)_8$	$[Pt(CO)_2]_n$	$Au(CO)_{1,2}^*$
		$W(CO)_{3-5}^*$		$Os_2(CO)_9$	$Ir_4(CO)_{12}$	$Pt(CO)_{1-4}^*$	

*Identified only by low-temperature matrix isolation.

Table 2: Metal carbonyl anions[6]

Group V	Group VI	Group VII		Group VIII	
$V(CO)_6^-$	$Cr(CO)_5^{2-}$	$Mn(CO)_5^-$	$Fe(CO)_4^{2-}$	$^*Co(CO)_4^-$	$^*Ni_2(CO)_6^{2-}$
$V(CO)_5^{3-}$	$Cr(CO)_4^{4-}$	$Mn(CO)_4^{3-}$	$Fe_2(CO)_8^{2-}$	$Co(CO)_3^{3-}$	$Ni_3(CO)_8^{2-}$
	$Cr_2(CO)_{10}^{2-}$	$Mn(CO)_9^{2-}$	$Fe_3(CO)_{11}^{2-}$	$Co_3(CO)_{10}^-$	$Ni_5(CO)_{9,12}^{2-}$
$Nb(CO)_6^-$	$^*Mo(CO)_5^{2-}$	$Tc(CO)_5^-$	$^*Ru(CO)_4^{2-}$	$^*Rh(CO)_4^-$	
	$Mo(CO)_4^{4-}$		$Ru(CO)_{11}^{2-}$	$Rh(CO)_3^{3-}$	
$Ta(CO)_6^-$	$^*W(CO)_5^{2-}$	$^*Re(CO)_5^-$	$^*Os(CO)_4^{2-}$	$^*Ir(CO)_3^{3-}$	$[Pt_3(CO)_6^{2-}]_n$
	$W(CO)_4^{4-}$	$Re(CO)_4^{3-}$	$Os_3(CO)_{11}^{2-}$	$Ir_4(CO)_{10}^-$	$n = 1 - 6$

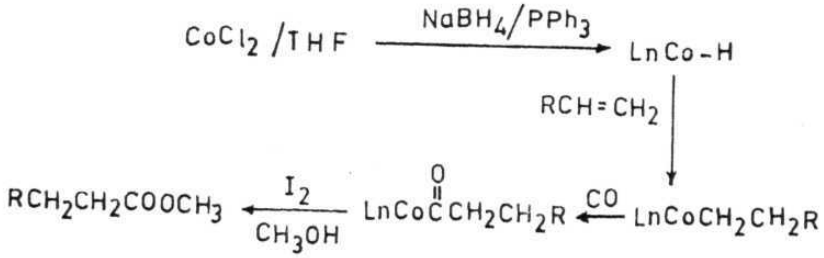
*Several other metal carbonyl anions have been reported but they are not common..

Table 3: Metal carbonyl hydrides[6].

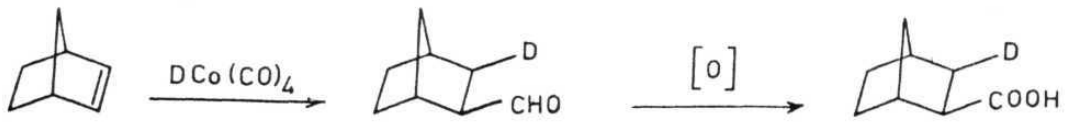
Group V	Group VI	Group VII		Group VIII	
$HV(CO)_6$	$H_2Cr(CO)_5$	$HMn(CO)_5$	$H_2Fe(CO)_4$	$HCo(CO)_4$	$H_2Ni_2(CO)_6$
$H_3V(CO)_3$		$H_2Mn_2(CO)_9$	$H_2Fe(CO)_8$	$HCo_3(CO)_9$	$H_2Ni_3(CO)_8$
		$H_3Mn_3(CO)_{12}$	$H_2Fe_3(CO)_{11}$		$H_2Ni_4(CO)_9$
		$HTc(CO)_5$	$H_2Ru(CO)_4^*$	$HRh(CO)_4$	
			$H_2Ru_3(CO)_{16}$		
		$HRe(CO)_5^*$	$H_2Os(CO)_4^*$	$HIr(CO)_4$	
		$H_3Re_3(CO)_{12}$	$H_2Os_2(CO)_8$	$H_2Ir_6(CO)_{15}$	

*Several other metal carbonyl hydrides have been reported but they are not common.

As outlined in chapter 1, we have observed that addition of $NaBH_4$/PPh_3 mixture to 1-decene and $CoCl_2$ in THF while bubbling carbon monoxide (atmospheric pressure) followed by treatment with I_2/CH_3OH give the corresponding one carbon homogolated ester in 20-25% yield. Clearly, the $CoCl_2/NaBH_4/PPh_3/CO$ system is able to hydrocarboxylate the 1-decene.



It has been reported that the $HCo(CO)_4$ exhibits similar reactivities.[14]



Accordingly, the present observations on the hydrocarboxylation of norbornene and 1-decene (Chapter 1) indicate the possibility of the synthesis of low valent metal carbonyl derivatives utilizing transition metal halides and simple reducing systems such as $NaBH_4$. Synthesis of the metal carbonyl derivatives <u>in situ</u> by such simple methods will be attractive for applications in organic synthesis since the difficulties involved in the utilization of metal carbonyls can be partly alleviated in this way.

As described in chapter 2, reactivity of the cobalt reagent prepared by the reaction of $CoCl_2/NaBH_4$ in the presence of PPh_3 is different from to the reactivity of the $CoCl_2/NaBH_4/Ph_3P/CO$ system which gives one carbon homologation (Chapter 1). We decided to explore the reactivities of the cobalt species generated by the reduction of $CoCl_2$ with $NaBH_4$ in the presence of carbon monoxide and in the absence of Ph_3P in order to investigate the problem further. It will be helpful for the discussion to briefly review the synthesis and reactivities of some known, widely utilized cobalt carbonyl reagents such as $Co_2(CO)_8$, $HCo(CO)_4$ and $Co(CO)_4^-$.

Synthesis of $Co_2(CO)_8$, $HCo(CO)_4$ and $MCo(CO)_4$

The stable dinuclear carbonyl, $Co_2(CO)_8$, is commercially available. Originally, it was synthesized by the reaction of cobalt metal, prepared by the reduction of cobalt oxalate with hydrogen, and carbon monoxide at high temperature and pressure.[15]

$$\text{Cobalt Oxalte} \xrightarrow[300^oC]{CO(40\ atm)/H_2(5\ atm)} Co_2(CO)_8$$

Most of the procedures for the preparation of $Co_2(CO)_8$ require high pressures and temperatures and the topic has been reviewed.[16] The most convenient high pressure synthesis involves a one step process in which cobalt acetate suspended in acetic anhydride is treated with a 1:4 mixture of H_2 and carbon monoxide at 160^o-180^oC at 200 atm pressure.[17]

$$Co(OAc)_2.4H_2O \xrightarrow[160^{\circ}C,\ (CH_3CO)_2O]{H_2/CO(1:4)\ 200\ atm} Co_2(CO)_8$$

A convenient laboratory synthesis requires the initial preparation of $K[Co(CO)_4]$ by passing carbon monoxide through an alkaline suspension of cobaltous cyanide[18,19] (eq. 1). On acidification, the initially formed $HCo(CO)_4$ decomposes thermally to give $[Co_2(CO)_8]$[18,19] (eq. 2). A low pressure direct synthesis using cobalt(II) iodide and zinc powder has been described[20] (eq. 3).

$$Co(CN)_2 + KOH \xrightarrow[H_2O,RT,\ 36\text{-}100h]{CO(1\ atm)} K[Co(CO)_4] \qquad ...(1)$$

$$K[Co(CO)_4] \xrightarrow{H^+} Co_2(CO)_8 \qquad ...(2)$$

$$CoI_2 + Zn \xrightarrow[t\text{-}BuOH,\ toluene]{CO,\ RT,\ 20h} Co_2(CO)_8 \qquad ...(3)$$

The dicobalt octacarbonyl is a very convenient starting material for the preparation of any cobalt carbonyl derivative as it is commercially available. The chemical reactions of $Co_2(CO)_8$ has been reviewed.[21]

The cobalt carbonyl hydride, $HCo(CO)_4$ and $MCo(CO)_4$ are the other promising cobalt carbonyl reagents. The $HCo(CO)_4$ is one of the first metal carbonyl hydrides discovered.[22] It is readily formed in a variety of reactions.[18,23,24] (a) direct synthesis from cobalt metal, carbon monoxide and H_2 at 250 atm pressure (b) disproportionation of $Co_2(CO)_8$ with N,N-dimethylformamide followed by acidification with HCl[25,26] or from $Co_2(CO)_8$ and hydrogen under pressure.[27] The laboratory synthesis involves acidification of salts containing the $\bar{C}o(CO)_4$ anion.[28] Good

yields are obtained from the hexapyridine-cobalt(II) salt prepared from $Co_2(CO)_8$.[28]

The $\bar{C}o(CO)_4$ anion is a product in the reaction of $Co_2(CO)_8$ with $\bar{O}H$.[28]

$$11Co_2(CO)_8 + 32\bar{O}H \longrightarrow 2Co^{2+} + 20\bar{C}o(CO)_4 + 8CO_3^{2-} + 16H_2O$$

Alcoholic solution or aqueous solutions of $\bar{C}o(CO)_4$ can be prepared by the reduction of cobalt(II) salts in alkaline sollution by carbon monoxide.[29]

$$CoCl_2.6H_2O + aq.KOH + aq.KCN + H_2O \xrightarrow[CO(1\ atm)]{RT,24\text{-}72h} KCo(CO)_4$$

Reduction of $Co_2(CO)_8$ with sodium-amalgam in ether solvents gives $NaCo(CO)_4$.[30]

$$2Na/Hg + Co_2(CO)_8 \xrightarrow[THF]{RT} 2NaCo(CO)_4$$

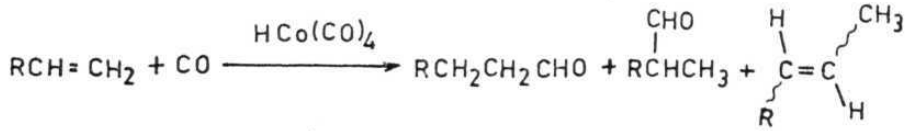
Several $MCo(CO)_4$ complexes have been prepared (Table 4).

Table 4: Synthesis of $MCo(CO)_4$ derivatives

Compound	Preparation	Reference
$LiCo(CO)_4$	$Li(BHEt_3) + Co_2(CO)_8$	31
$NaCo(CO)_4$	$NaOH + Co_2(CO)_8$	30
$KCo(CO)_4$	$KH + Co_2(CO)_8$	32
$AgCo(CO)_4$	$AgNO_3 + NaCo(CO)_4$	33
$HgCo(CO)_4$	$Hg(CN)_2 + \bar{C}o(CO)_4$	34
	$Hg + Co_2(CO)_8$	34
$MCo(CO)_4$	$M + HgCo(CO)_4$	35,36
M = Zn, Cd		
$MCo(CO)_4$	$M + Co_2(CO)_8$	37
M = Pd, Sn		

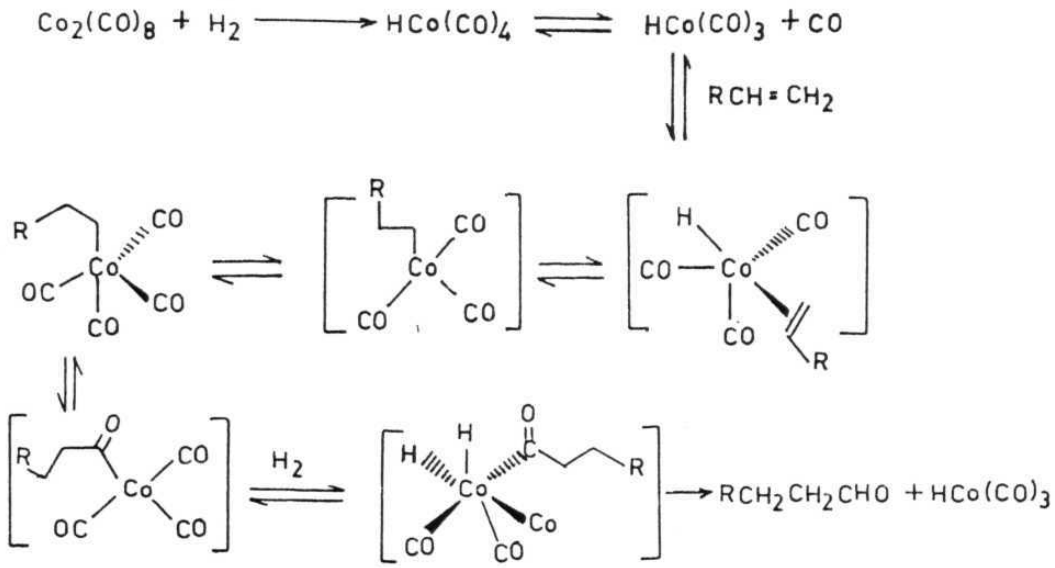
Reactions of $Co_2(CO)_8$ with organic substrates

Hydroformylation of olefins (oxo process) involves the synthesis of aldehydes from olefins, carbon monoxide and hydrogen in the presence of $Co_2(CO)_8$.[38,39] The alcohols and isomerized olefins are the side products.



The accepted mechanism of this important reaction is outlined in Scheme 1.[2,7,8,40]

Scheme. 1



The active catalyst in the reaction cycle is the four coordinate cobalt carbonyl hydride, $HCo(CO)_3$, formed from dissociative loss of CO from the saturated hydride, $HCo(CO)_4$, which hydrometallates the olefin.[40]

The resulting organocobalt species undergoes carbonylation followed by hydrogenation to yield aldehydes (Scheme 1).[40]

Alkene isomerization is often a side reaction in the hydroformylation reaction. This reaction goes through hydrocobaltation- β-elimination process as outlined below.[2,7,8,14,40]

$$Co_2(CO)_8 + H_2 \longrightarrow 2HCo(CO)_4$$

$$HCo(CO)_4 \rightleftharpoons HCo(CO)_3 + CO$$

$$HCo(CO)_3 + RCH{=}CH_2 \longrightarrow RCH{=}CHCH_3$$

(cis/trans mixture)

Several other organic substrates can be carbonylated at high temperature and pressure using $CO/Co_2(CO)_8$ or $H_2/CO/Co_2(CO)_8$ as outlined in Chart 1.

Dicobalt octacarbonyl forms stable complexes with alkynes.[54] The reactions can be conveniently carried out at room temperature.

$$R{-}C{\equiv}C{-}R^1 + Co_2(CO)_8 \longrightarrow$$

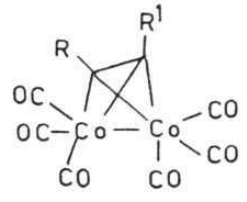
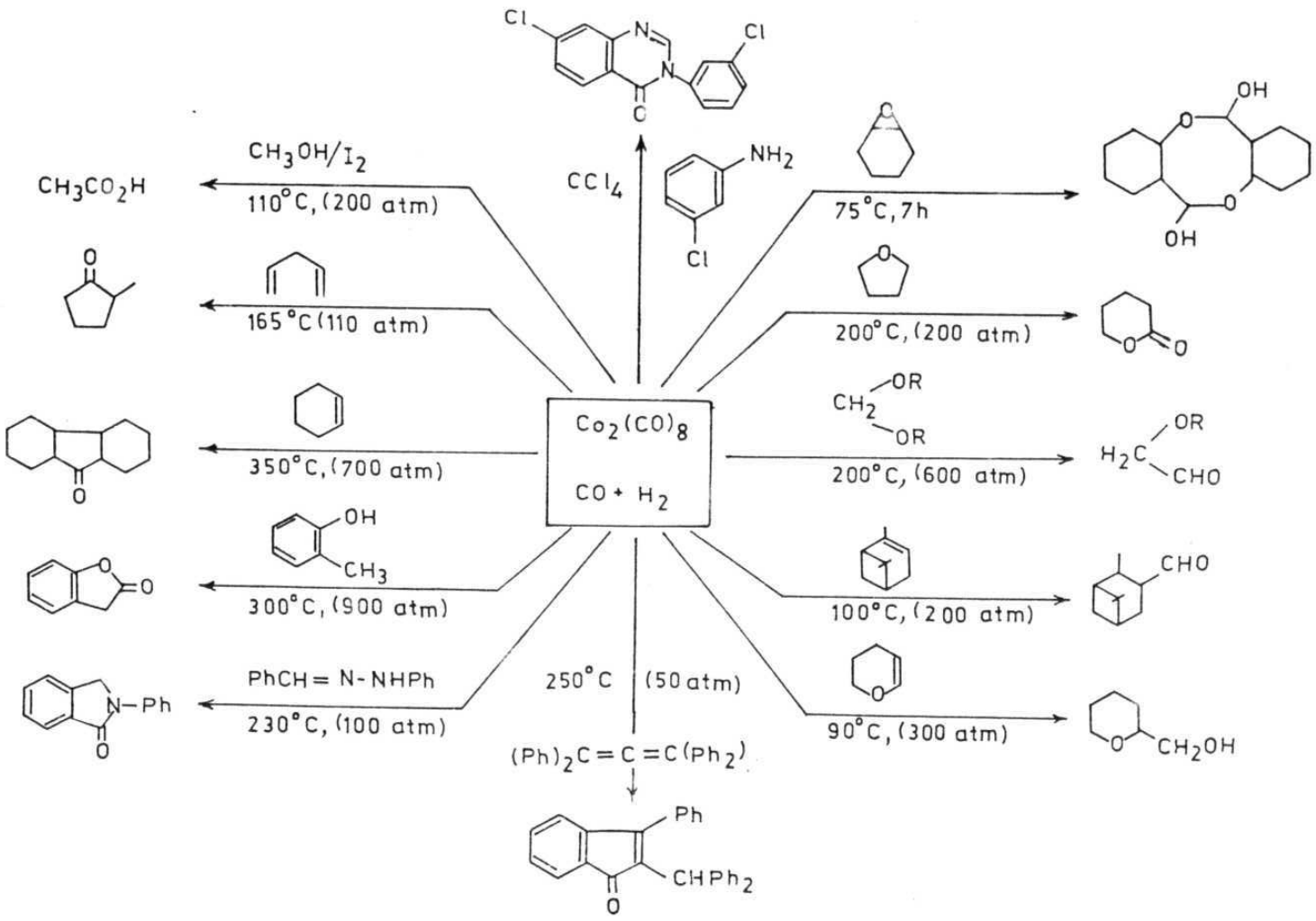
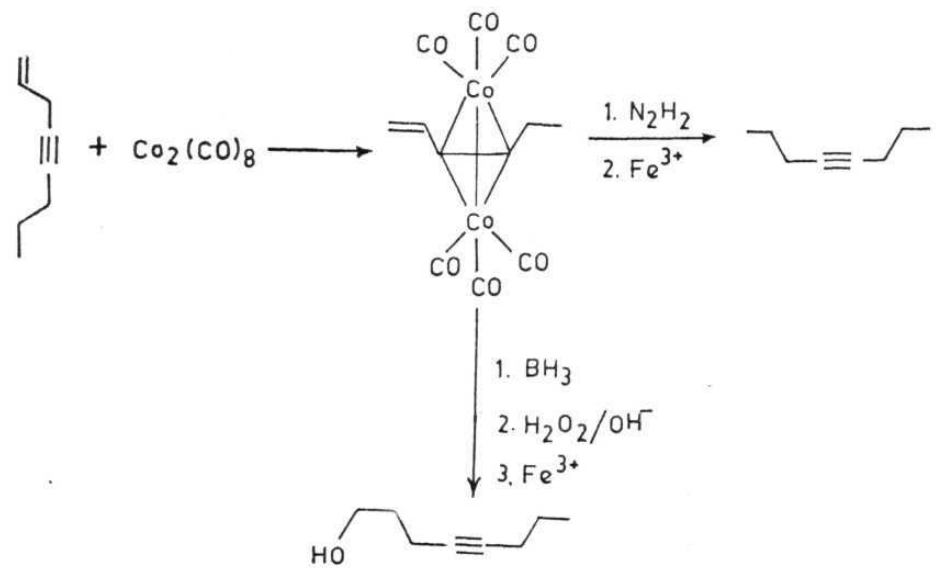


Chart 1


Cl
N
Cl
N
O
CCl4
NH2
Cl
CH3OH/I2
110°C, (200 atm)
CH3CO2H
165°C (110 atm)
350°C, (700 atm)
Co2(CO)8
CO + H2
300°C, (900 atm)
OH
CH3
PhCH = N-NHPh
230°C, (100 atm)
N-Ph
250°C
(50 atm)
(Ph)2C = C = C(Ph2)
Ph
CHPh2
75°C, 7h
OH
OH
200°C, (200 atm)
OR
CH2
OR
200°C, (600 atm)
OR
H2C
CHO
100°C, (200 atm)
CHO
90°C, (300 atm)
CH2OH

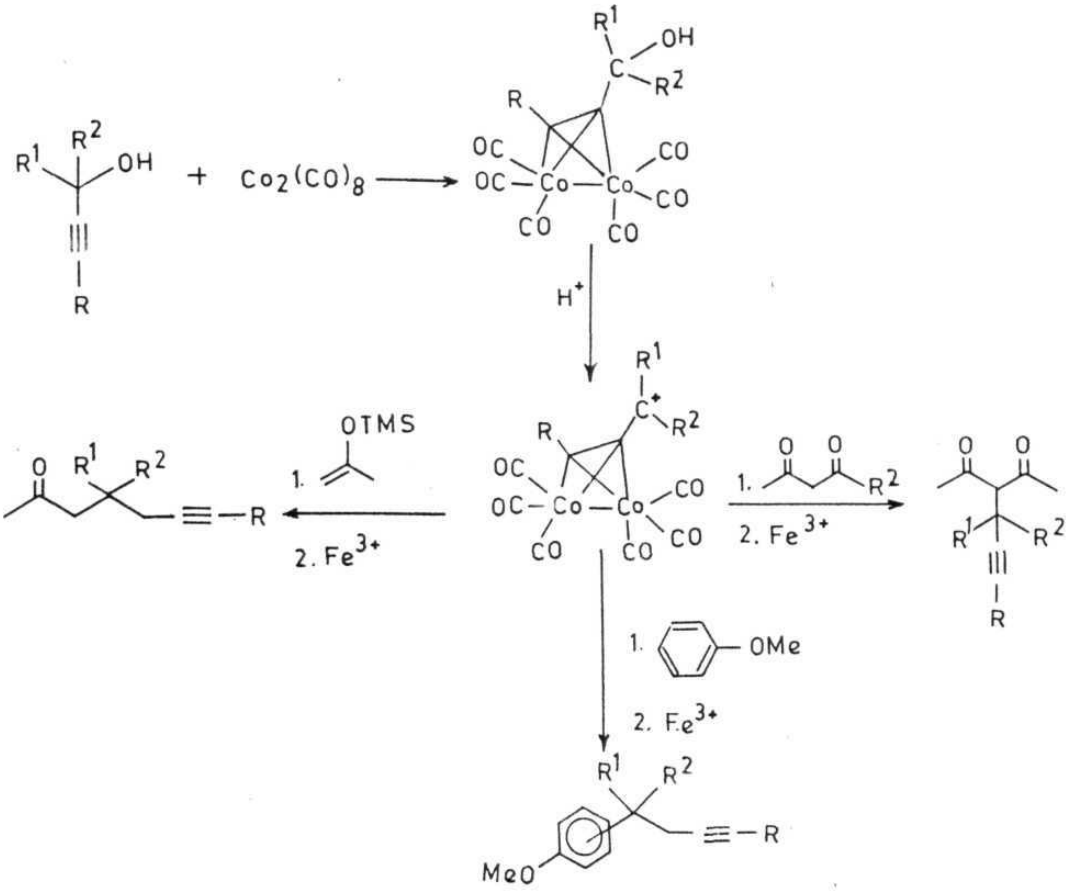
In these complexes, the alkyne bridges the two metals utilizing both of its π-bonding orbitals for complexation. As a consequence, the reactivity of the alkyne complexed in this fashion is drastically reduced. Infact, alkynes have been protected towards electrophilic addition and hydroboration reactions by complexation with $Co_2(CO)_8$.[5] The olefinic portion of an enyne can be selectively reduced or hydroborated after complexation of the alkyne with $Co_2(CO)_8$ (Scheme 2).[55] The organic product can be regenerated utilizing mild oxidizing agents.[55]

Scheme. 2



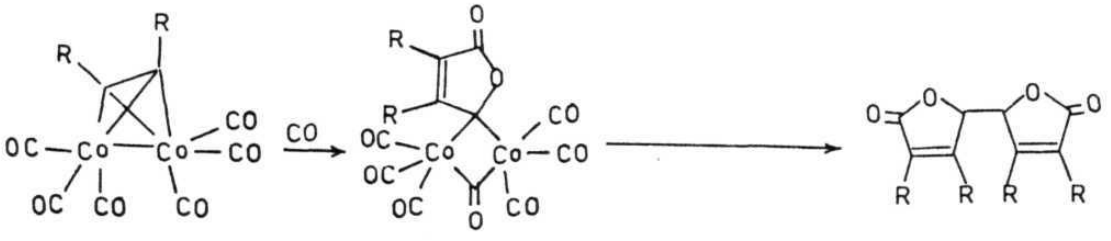
The complexed propargyl cations do not give undesirable rearrangements and the propargyl cationic moiety can be readily utilized in organic synthesis[56-58] (Scheme 3).

Scheme. 3

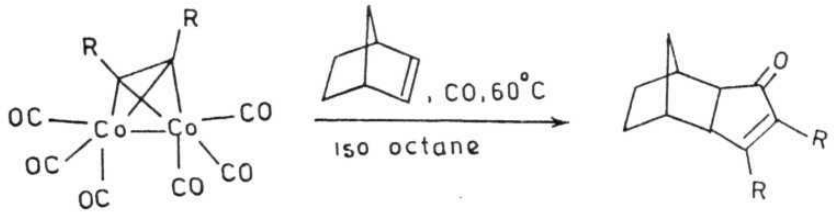


Although these cobalt-alkyne complexes are stable to electrophiles, they do undergo carbon monoxide insertions. Thus exposure of the alkyne complex of $Co_2(CO)_8$ to high carbon monoxide pressure (210 atm) at 75°C results in the formation of a lactone complex, with a net incorporation of two molecules of carbon monoxide (Scheme 4).[59]

Scheme. 4

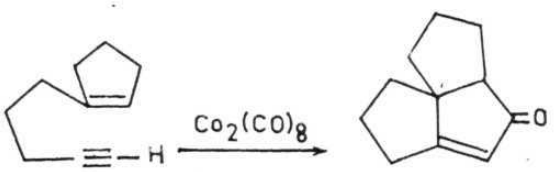


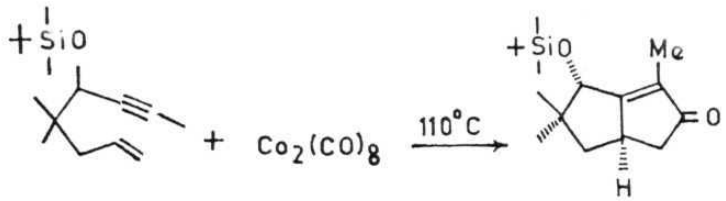
Pauson and Khand discovered that these acetylene complexes readily reacts with strained olefins to give the corresponding cyclopentenone derivatives.[9]



The reaction has been found to be a general one although the yields are poor with simple olefins.[9] There is an excellent review available for the Pauson-Khand reaction.[9] Intramolecular versions are known in literature (Scheme 5).[60,61]

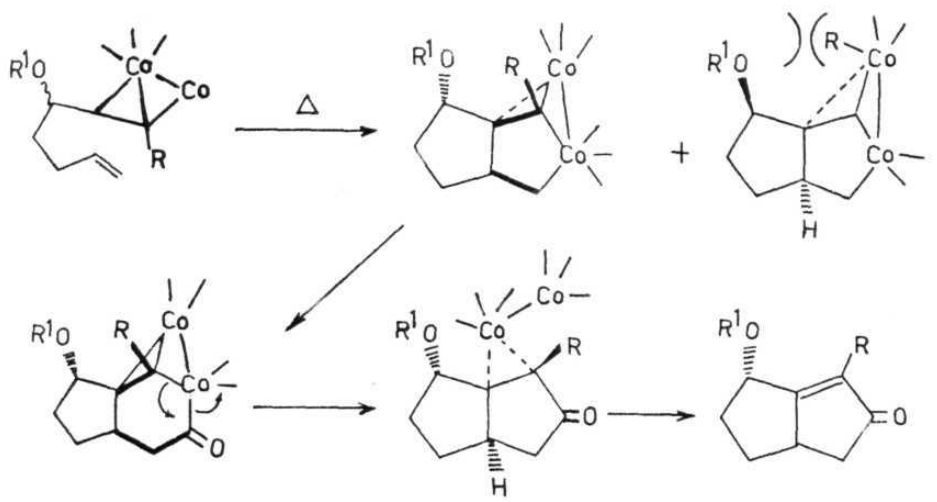
Scheme. 5





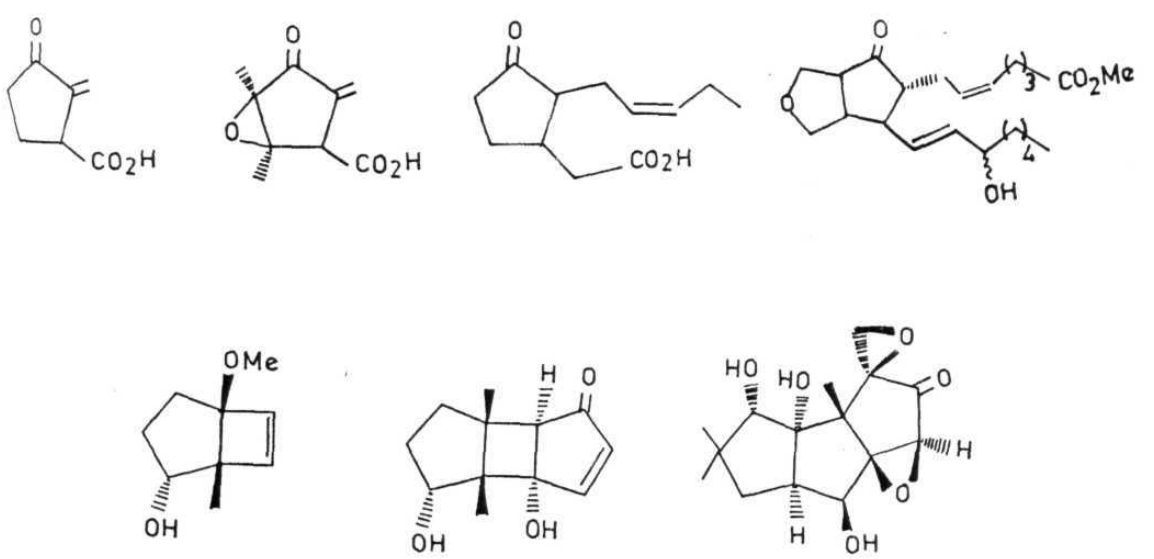
The mechanism outlined in Scheme 6 has been suggested for the intramolecular version.[60]

Scheme. 6



A variety of natural products (Chart 2) have been synthesized by utilizing the Pauson-Khand reaction in a crucial step in each case.[9]

Chart 2



Reactions of $HCo(CO)_4$ with organic substrates

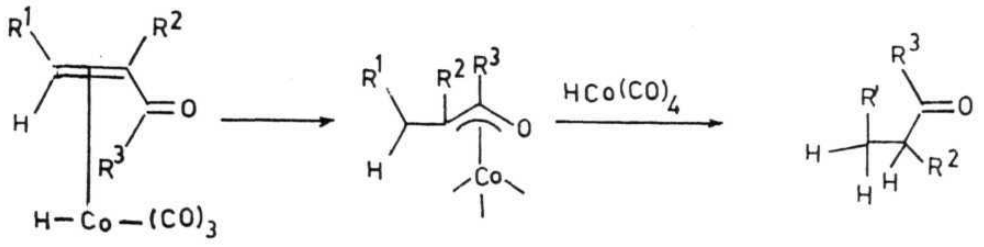
In the presence of catalytic amounts of $HCo(CO)_4$, alkenes react with H_2 and carbon monoxide to give the corresponding hydroformylated products and isomerized alkenes.[14] Similar reactivities have been observed with the $Co_2(CO)_8/H_2/CO$ system, indicating the intermediacy of $HCo(CO)_4$ in these reactions.[18-40]

$$RCH{=}CH_2 \xrightarrow{HCo(CO)_4} RCH_2CH_2CHO + \text{isomerized alkenes}$$

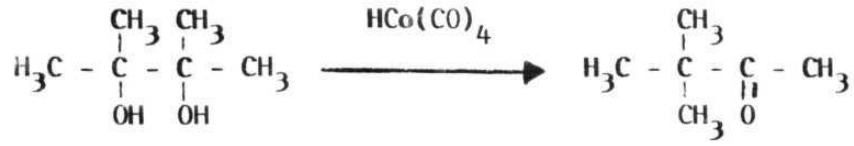
Similar products are also obtained when stoichiometric amounts of $HCo(CO)_4$ are utilized.[14,62] The catalytic cycle involves the formation and regeneration of $HCo(CO)_4$ (Scheme 1).[40] Under the stoichiometric reaction conditions, $HCo(CO)_4$ is the only source of hydrogen and carbon monoxide since the reaction can be carried out under nitrogen.[14]

As mentioned earlier, treatment of norbornene with $DCo(CO)_4$ followed by oxidation give the exo-3-D-exo-2-norbornyl carboxylic acid in 20% yield, indicating that the hydrometallation with this reagent takes place by cis addition of the LnCo-D bond to norbornene.[14]

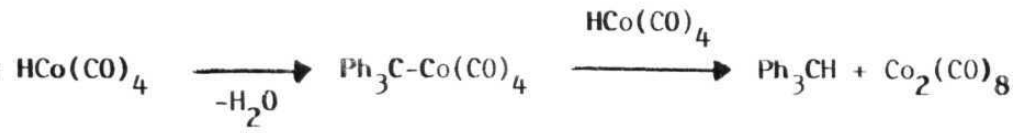
α, β-Unsaturated aldehydes and ketones are reduced to saturated aldehydes and ketones by $HCo(CO)_4$ at 25°C and atmospheric pressure.[14]



The $HCo(CO)_4$ reagent behaves like a strong acid.[14] This is revealed by its ability to catalyse pinacol-pinacolone rearrangement.[63]

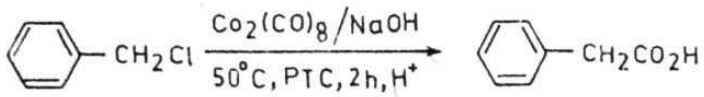


The property of $HCo(CO)_4$ as an acid is also revealed in several other reactions. For example, triphenyl carbinol on treatment with $HCo(CO)_4$ in acetone solution at room temperature gives triphenyl methane quantitatively.[64]



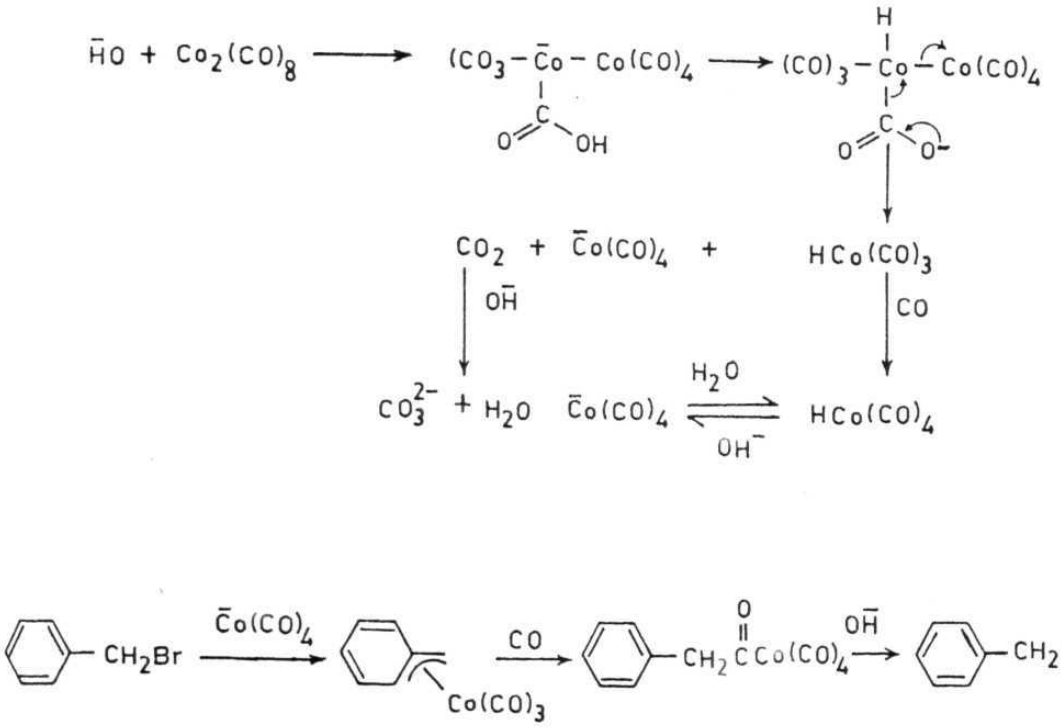
Reactions of $\bar{C}o(CO)_4$ with organic substrates

The $\bar{C}o(CO)_4$ species can be readily prepared from $Co_2(CO)_8$. Several methods were available in the literature (Table 4). Alper and his coworkers poineered in the utilization of the $\bar{C}o(CO)_4$ reagent in both catalytic and stoichiometric and stoichometric conditions. The subject has been extensively reviewed.[65-67] Alper and coworkers demonstrated the carbonylation of benzyl halides into the corresponding carboxylic acids, utilizing $\bar{C}o(CO)_4$ generated from $Co_2(CO)_8$/NaOH under phase transfer catalysis.[68]



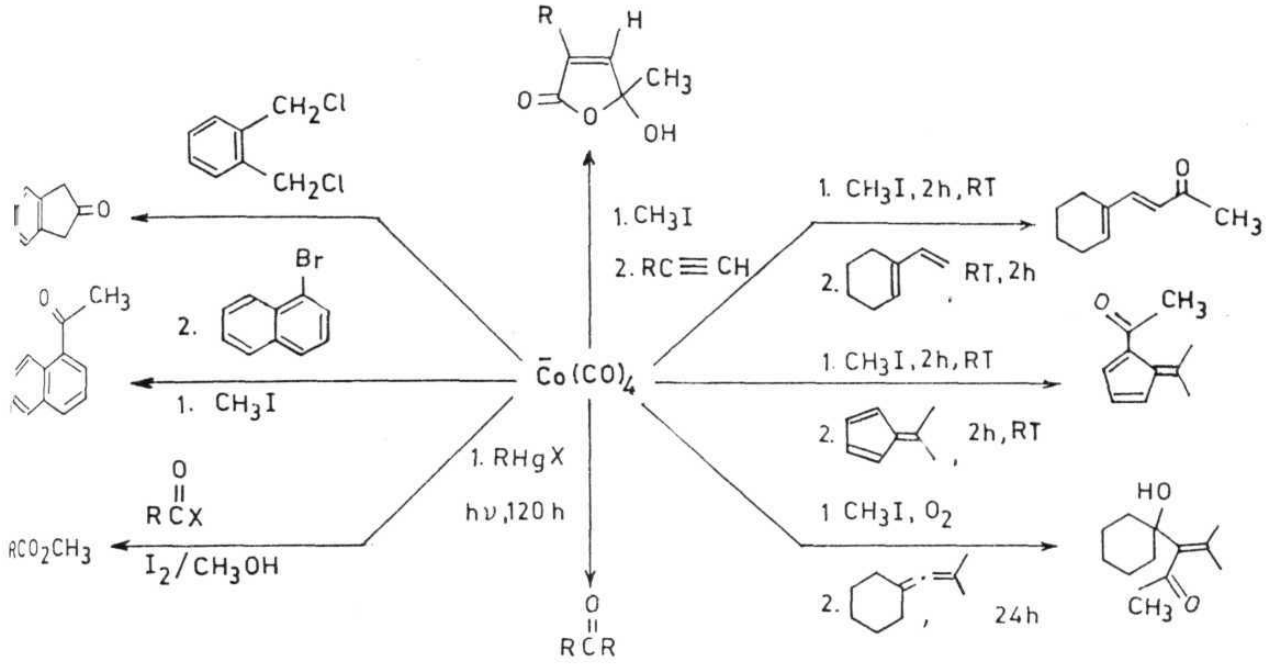
Under these reaction conditions, dicobalt octacarbonyl undergoes disproportion by the base (Scheme 7) to give $\bar{C}o(CO)_4$. Subsequent reaction of this anion with benzyl halides gives the π -allyl complex which in turn undergoes carbonylation followed by hydrolysis to give carboxylates (Scheme 7).[65]

Scheme. 7



Several other organic substrates can be carbonylated under mild conditions using $\bar{C}o(CO)_4$ as outlined in Chart 3.[64-76]

Chart 3



It was of interest to us to explore the reactivity of the cobalt species generated through $NaBH_4$ reduction of $CoCl_2$ under carbon monoxide atmosphere.

RESULTS AND DISCUSSION

Utilization of $\bar{C}o(CO)_4$ or its equivalent prepared *in situ* using the $CoCl_2/NaBH_4/CO/NaOH$ system

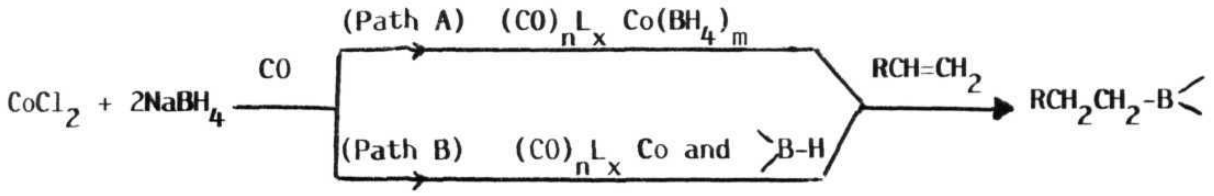
As described in chapters 1 and 2, the $CoCl_2/NaBH_4$ reagent system exhibits different reactivities towards alkenes and alkynes depending on the reaction conditions. Whereas the reagent prepared utilizing anhydrous $CoCl_2$ and $NaBH_4$ system hydroborates olefins, the reagent prepared in the presence of methanol gives hydrogenation of alkenes and some other substirates (Chapter 1). Treatment of alkenes with the $CoCl_2/PPh_3/NaBH_4/CO$ system gives products resulting from hydrometallation - carbonylation besides isomerized alkenes (Chapter 1). However, the reagent prepared by the addition of $NaBH_4$ into $CoCl_2/PPh_3$ mixture in THF isomerize some alkenes and hydrodimerize 1-alkynes into the corresponding (E,E)-1,3-dienes (Chapter 2).

In anticipation of developing cobalt carbonyl reagents utilizing the simple $CoCl_2/NaBH_4/CO$ system, it was decided to investigate the effect of cabon monoxide on the reactivities of anhydrous $CoCl_2$ with $NaBH_4$ in THF. It has been known for some time that anhydrous cobalt(II) halides react with alkali metal borohydrides at low temperatures (-80^oC) to give cobalt(II) borohydride, $Co(BH_4)_2$, which decomposes into black cobalt boride, B_2H_6 and H_2 on warming to room temperature.[77]

$$CoBr_2 + 2LiBH_4 \xrightarrow[-\ 80^{o}C]{Et_2O} Co(BH_4)_2 \xrightarrow{RT} "Co_2B" + B_2H_6 + H_2$$

We have observed that when $NaBH_4$ (20 mmol) was added to anhydrous $CoCl_2$ (10 mmol) in THF (80 ml) through which carbon monoxide was being bubbled at $0^{o}C$, no black cobalt boride was formed. Instead, the mixture was green in colour. Presumably, the carbon monoxide ligand is able to stablize the cobalt borohydride complex. Infrared spectrum of the mixture in THF exhibits a single, strong metal carbonyl absorption at 1910 cm^{-1} indicating the presence of metal carbonyl in the reaction mixture.

We have also observed that the green coloured reaction mixture obtained by the reaction of $NaBH_4$ with $CoCl_2$ in THF while bubbling carbon monoxide, hydroborates 1-decene. 1-Decanol was isolated as the only product after workup and oxidation with $H_2O_2/NaOH$. This observation indicates that either the cobalt carbonyl borohydride complex present in the mixture is able to supply the hydroborating species (Path A) or the contents contain the hydroborating species in addition to cobalt carbonyl species (Path B)



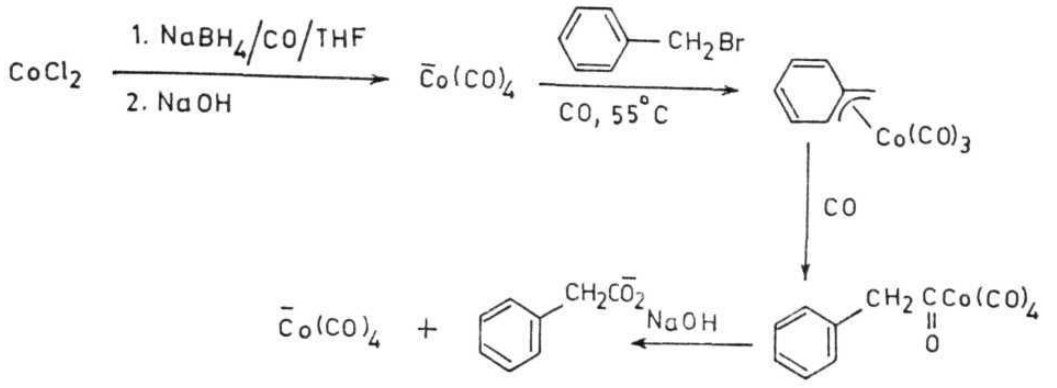
It has been reported that BH_3THF rapidly reacts with carbon monoxide to give trimethylboroxine in the presence of catalytic quantities of $NaBH_4$.[78] Accordingly, it is doubtful that the hydroborating species

such as BH_3THF not complexed with the cobalt reagent will survive under the present reaction conditions. It is possible that the olefin may strip off the $\rangle$B-H moiety from the cobalt borohydride complex. Since water (or hydroxylic solvents) destroys hydroborating species,[49] it may be surmized that the resulting species on treatment with H_2O would be $HCo(CO)_4$ species. If this is the case, addition of aqueous NaOH to the mixture would result in the formation of the corresponding anion, since the $HCo(CO)_4$ behaves like a strong acid.[14]

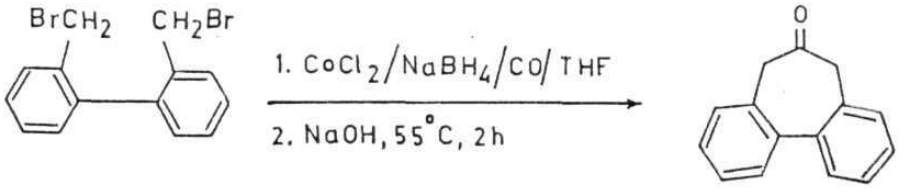
$$(BH_4)_mCo(CO)_nL_x \xrightarrow{H_2O} HCo(CO)_n \xrightarrow{O\bar{H}} \bar{C}o(CO)_n$$

As outlined earlier, the $\bar{C}o(CO)_4$ has been utilized in many synthetic applications (Chart 3).[65-67] This reagent catalyses the carbonylation of benzyl halides into the corresponding phenylacetic acids.[68] In order to examine the reactivity of the reagent generated by the aqueous NaOH treatment of the green coloured reaction mixture obtained as above, we have carried out the following experiment: $NaBH_4$ (20 mmol) was added during 15 minutes into a magnetically stirred suspension of $CoCl_2$ (10 mmol) in THF (60 ml) at 0^oC while bubbling carbon monoxide. The contents were further stirred for 1h at room temperature. During this time the colour of the contents turned from blue to green. Aqueous NaOH (5N, 10 ml) was carefully added. Benzyl bromide (10 mmol) in THF (10 ml) was added during 15 minutes and the contents were stirred further for 3h at 55^oC. After workup (experimental section), phenylacetic acid was isolated in 88% yield (Table 5). This clearly indicates the presence of $\bar{C}o(CO)_4$ or its equivalent in the reaction mixture. The transformation can be rationaized as outlined in Scheme 8.[68]

Scheme. 8



Several other substituted benzyl halides were converted into the corresponding substituted phenylacetic acids (Table 5). Under the present conditions the 2,2'-bis(bromomethyl)biphenyl can be cyclized into the corresponding ketone in 68% yield.



It may be of interest to note that this cyclic ketone was previously prepared in three steps starting from the corresponding bromomethyl derivative under relatively severe reaction conditions.[80]

The 1,2-bis(bromomethyl)benzene has been cyclized into 2-indanone using $\bar{C}o(CO)_4$ generated from $Co_2(CO)_8$ in benzene in the presence of KOH-crown ether complex.[81]

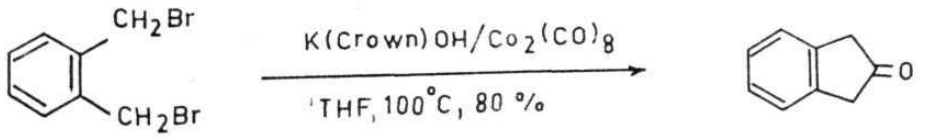
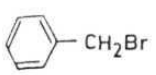
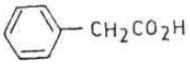
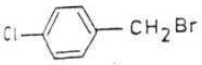
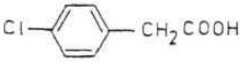
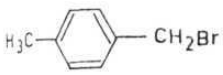
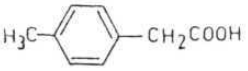
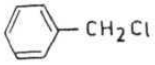
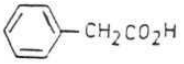
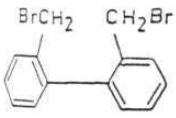
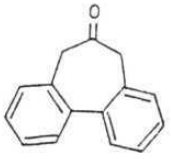


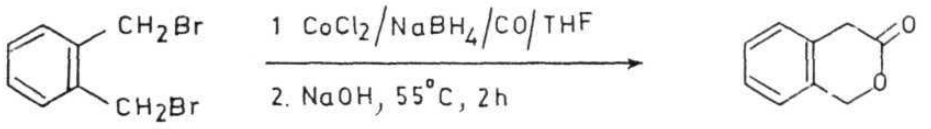
Table 5: Conversion of a benzyl halides into benzyl carboxylic acids and cyclic ketone.

Substrate[a]	Product	Yield [%]
		88
		78
		72
		70
		68[b]

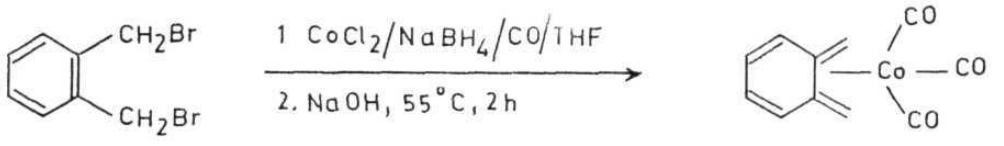
[a] The reactions were carried out using 10 mmol of benzyl halide, 10 mmol of anhydrous $CoCl_2$, 20 mmol of $NaBH_4$ and 10 ml of 5N NaOH. After the addition of the benzyl halide (10 mmol) the contents were stirred at 55°C for 3h for all substrates as given in the text. In order to examine the catalytic nature of the reagent, the reaction was also carried out using 50 mmol of benzyl bromide and 0.1 g of benzyl triethylammonium bromide for 3h at 55°C. In this case, phenylacetic acid was obtained in 79% yield.

[b] Product isolated by chromatography on a silica gel column using hexane/methanol eluent.

However, under the present conditions, this reaction was not clean and a complex product mixture was obtained. A minor product (5%) was identified as the corresponding lactone.



The difficulty may be due to the formation of intermediate diene-metal complex which may give a complex mixture of products under the present aqueous reaction conditions.



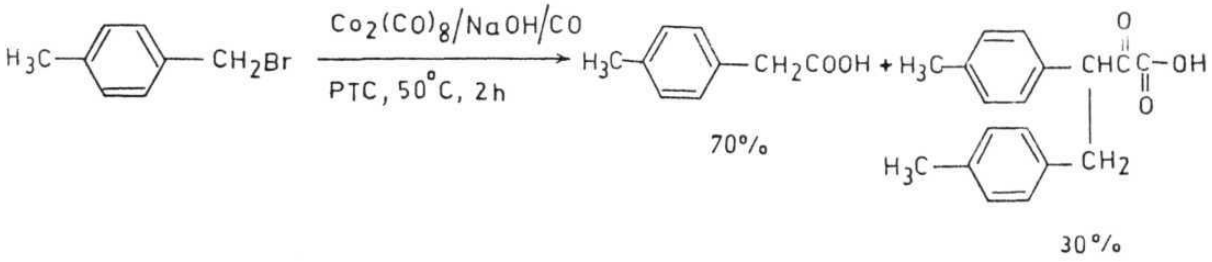
n-Octylbromide and bromobenzene were uneffected under present conditions. It has been reported that these substrates react with $\bar{C}o(CO)_4$ only under irradiation with UV light.[82]

3-Bromocyclohexene undergoes reaction to the extent of 30% under the present reaction conditions. However, the products are mixtures of carboxylic acids as indicated by the ^{13}C-NMR spectrum of the acidic residue (carboxylic carbon signals at 184.9, 177.8, 167.9 ppm).

The reactions with $\bar{C}o(CO)_4$ generated using $Co_2(CO)_8$ and NaOH are generally carried out in hydrocarbon solvents and aqueous NaOH system in the presence of a phase transfer catalyst.[68] Under the present reaction

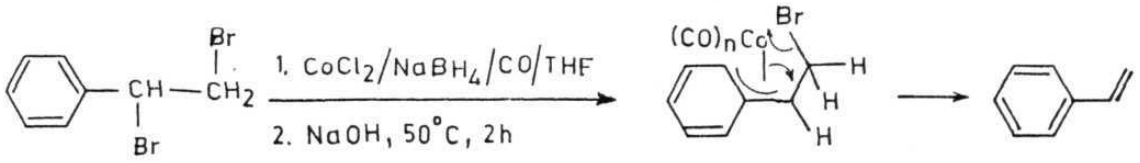
conditions, the reactions work equally well both in the absence and presence of a phase transfer catalyst although runs with excess benzyl bromide (50 mmol) require the addition of 0.1 g of benzyltirethylammonium bromide in order to complete the reaction in 3h at 55°C.

Under the present reaction conditions, 4-methylbenzylbromide gave a single product (Table 5) where as the reaction utilizing $\bar{C}o(CO)_4$ in dibenzylether/NaOH/PTC system has been reported to give two products.[83]



We have observed that under the present reaction conditions, styrene was obtained in 58% yield from styrene dibromide and no carbonylated product was formed. This result can be rationalized as outlined in Scheme 9.

Scheme 9



The present method of generation of $\bar{C}o(CO)_4$ reagent or its equivalent using simple reagents under atmospheric pressure of carbon monoxide for carbonylation of benzyl halides is a simple alternate method to the procedures available in the literature.[66]

Reactivities of the $CoCl_2/NaBH_4$ reagent with olefins utilizing various additives to prevent hydroboration

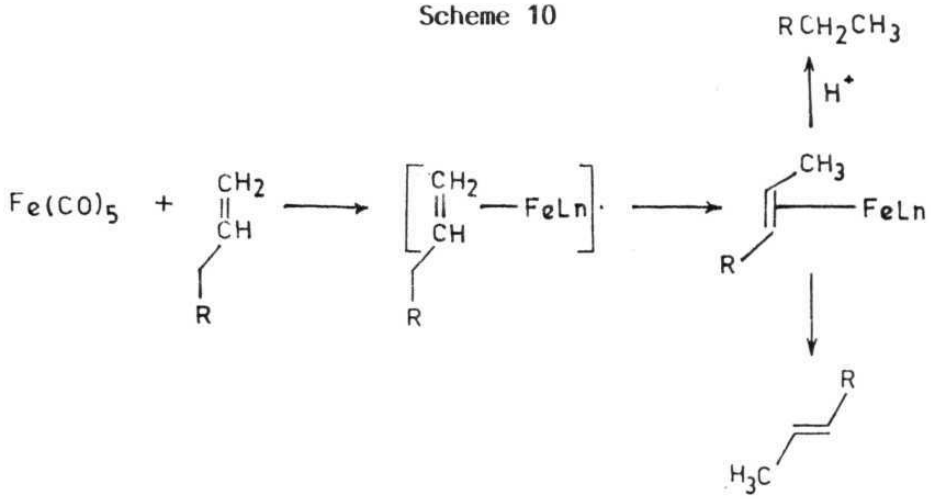
As described previously, the green coloured contents obtained from the reaction of $CoCl_2$ with $NaBH_4$ under carbon monoxide atmosphere hydroborates alkenes. Prevention of hydroboration is necessary for examining the reactivity of the cobalt carbonyl reagent system with alkenes. In order to examine the utilization of Ph_3P and Et_3N for preventing hydroboration, we have carried out the following experiments: $NaBH_4$ (20 mmol) was added during 15 minutes into a magnetically stirred suspension of $CoCl_2$ (10 mmol) in THF at 0^oC while bubbling carbon monoxide. The green coloured contents were stirred further for 1h and Et_3N (10 mmol) was added. 1-Decene (10 mmol) was added and the mixture was stirred for 3h under carbon monoxide atmosphere. After workup, 1-decene was recovered back quantitatively. Utilization of PPh_3 (10 mmol) in the place of Et_3N in this experiment also gave similar result. In both cases, Ph_3PBH_3 or Et_3NBH_3 were isolated.

As described in Chatper 1, the hydroboration reaction can be prevented by performing the reaction in the presence of alcohols. In order to examine utilization of alcohols to prevent hydroboration, we carried out the following experiment: $NaBH_4$ (20 mmol) in ethanol (15 ml) was added during 10 minutes into $CoCl_2$ (10 mmol) in THF (80 ml) under carbon monoxide at 0^oC. A black coloured reaction mixture was obtained. 1-Decene (10 mmol) was added and the mixture was stirred further for 2h at room temperature. After workup, 1-decene was recovered quanti-

tatively. However, when 1-decene (10 mmol) was used along with $CoCl_2$ (10 mmol) in THF, and $NaBH_4$ (20 mmol) in ethanol (15 ml) was added during 10 minutes 15 0^oC while bubbling carbon monoxide through the reaction mixture and the mixture was stirred for 30 minutes at room temperature, quenched by addition of hexane (100 ml) and water (15 ml), trans-2-decene was isolated in 86% yield.

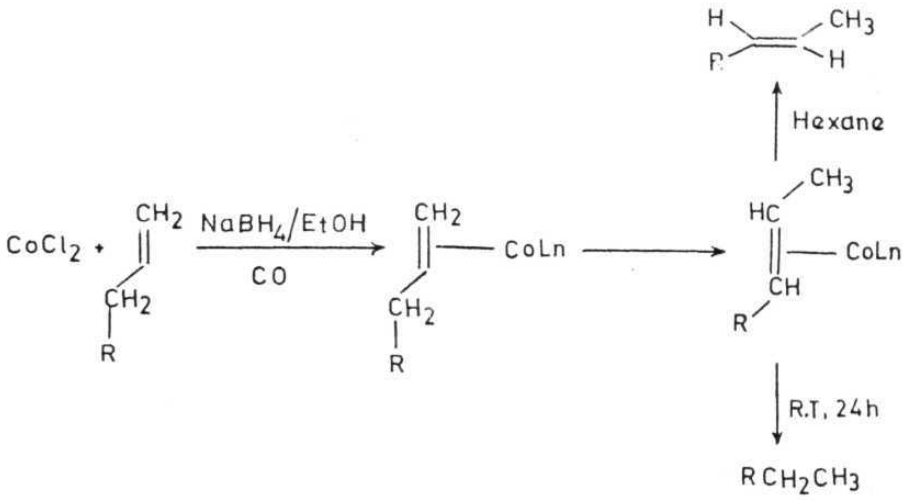
We have carried out several experiments in order to investigate this transformation. When concentrated HCl (12N, 5 ml) was added before workup and the mixture was stirred for 1h, decane was isolated in 89% yield. When the mixture was stirred for 12h after the $NaBH_4$ addition, decane was isolated in 82% yield even with out the addition of HCl. Protonolysis of olefin-$Fe(CO)_4$ complexes have been reported to yield the corresponding reduction products (Scheme 10).[84]

Scheme 10



In the present case, probably the 1-decene complexes with the reactive cobalt species generated *in situ* and is converted into the trans-2-decene cobalt complex which undergoes decomposition to give trans-2-decene or protonolysis by C_2H_5OH or HCl to give decene (Scheme 11).

Scheme 11

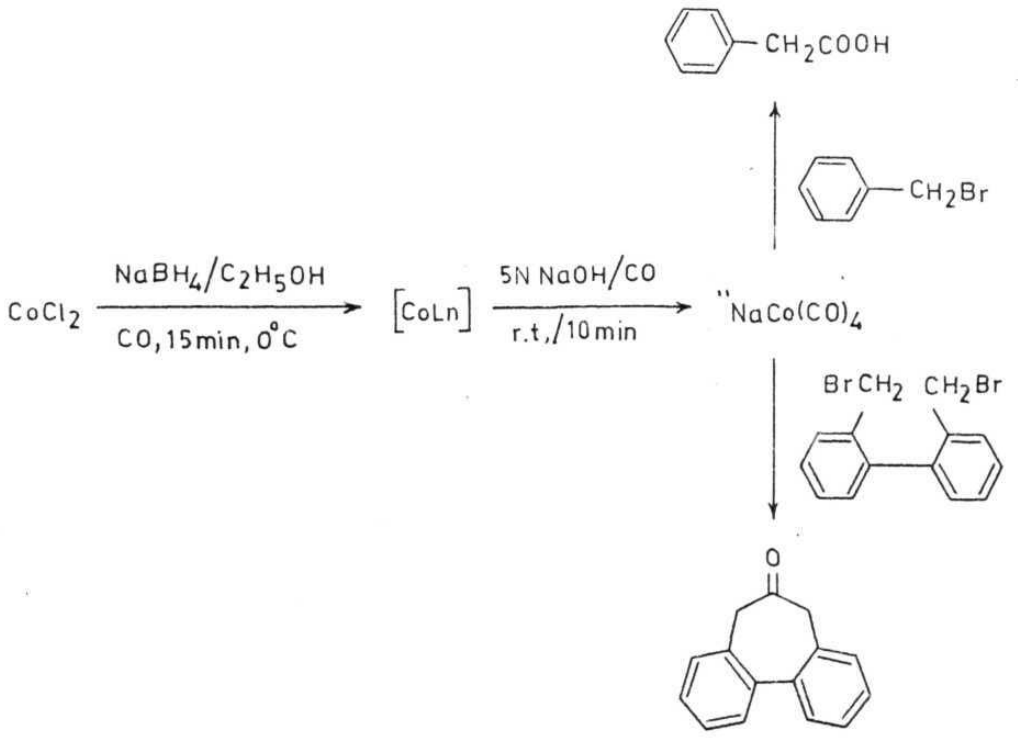


In order to find out whether the trans-2-decene is liberated during the course of the reaction and then reduced, we carried out an experiment involving additional of a further 10 mmol of 1-decene after the addition of $NaBH_4$ was complete and found that 10 mmol of 1-decene remained unchanged. In another run, we replaced this additional 1-decene by methyl-10-undecenoate (10 mmol) and stirred the mixture for 12h at room temperature. No 1-decene remained; decane was isolated 80% yield and the recovered methyl-10-undecenoate did not show ^{13}C-NMR signals corresponding to methyl undecanoate. These experiments show that the isomerization and reduction products are most probably formed from the alkene-CoLn complex (Scheme 11), and that there is no exchange of alkene with the alkenes added after the formation of the complex.

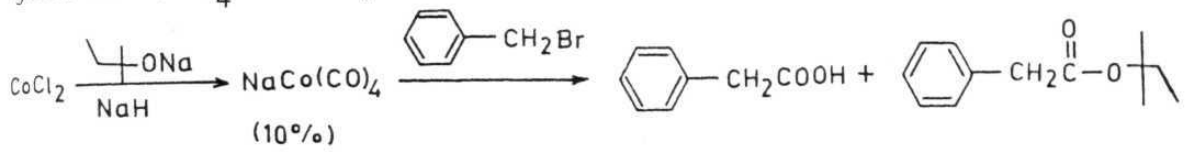
When allylbenzene was used in the place of 1-decene and the reaction was quenched with hexane and water as indicated for the isomerization of 1-decene (Scheme 11), n-propyl benzene was isolated in 84% yield. Presumably, protonolysis of the alkene-CoLn complex (Scheme 11) by the ethanol is very fast in this case.

We have also observed that $NaCo(CO)_4$ or its equivalent can be prepared by reducing $CoCl_2$ (10 mmol) with $NaBH_4$ (20 mmol) in ethanol (15 ml) in THF (80 ml) at 0^oC while bubbling carbon monoxide through, followed by treatment with aqueous NaOH. The formation of $NaCo(CO)_4$ or its equivalent is indicated by the carbonylation of benzyl bromide and 2,2'-bis(bromomethyl)biphenyl in the presence of catalytic amounts of benzyl trimethylammonium bromide (Scheme 12).

Scheme 12



It has been reported that the reduction of cobalt(II) haildes with NaH in the presence of sodium t-amyloxide under carbon monoxide gives $NaCo(CO)_4$ in 10% yield.[85]



As discussed previously, the green coloured mixture obtained by the reaction of $NaBH_4$ and $CoCl_2$ in THF in the presence of carbon monoxide, on treatment with aqueous NaOH gives $NaCo(CO)_4$ or its equivalent, as indicated by the reaction with benzyl bromide to give phenyl acetic acid. The present $CoCl_2/NaBH_4/C_2H_5OH/CO$ system would also give similar species. However, isomerization and reduction have not been observed with $NaCo(CO)_4$ or $Co_2(CO)_8$. The $HCo(CO)_4$ reagents is known to isomerize alkenes,[14] but gives a mixture of cis- and trans-2-alkenes and also 3-alkenes and 4-alkenes in some cases. Moreover, reactions utilizing $HCo(CO)_4$ have been carried out in hydrocarbon solvents and the isomerization reaction is catalytic with respect to the cobalt reagent. In the present system, even if the $HCo(CO)_4$ is formed at some stage it would not survive for long. Since it is highly acidic it would react with the H-B< species to give the corresponding LnCo-B< complex. Probably, in the present system, the alkene enters the coordination sphere of the cobalt along with CO ligands as the $CoCl_2$ is reduced with $NaBH_4/C_2H_5OH$, and then undergoes isomerization and reduction (Scheme 11).

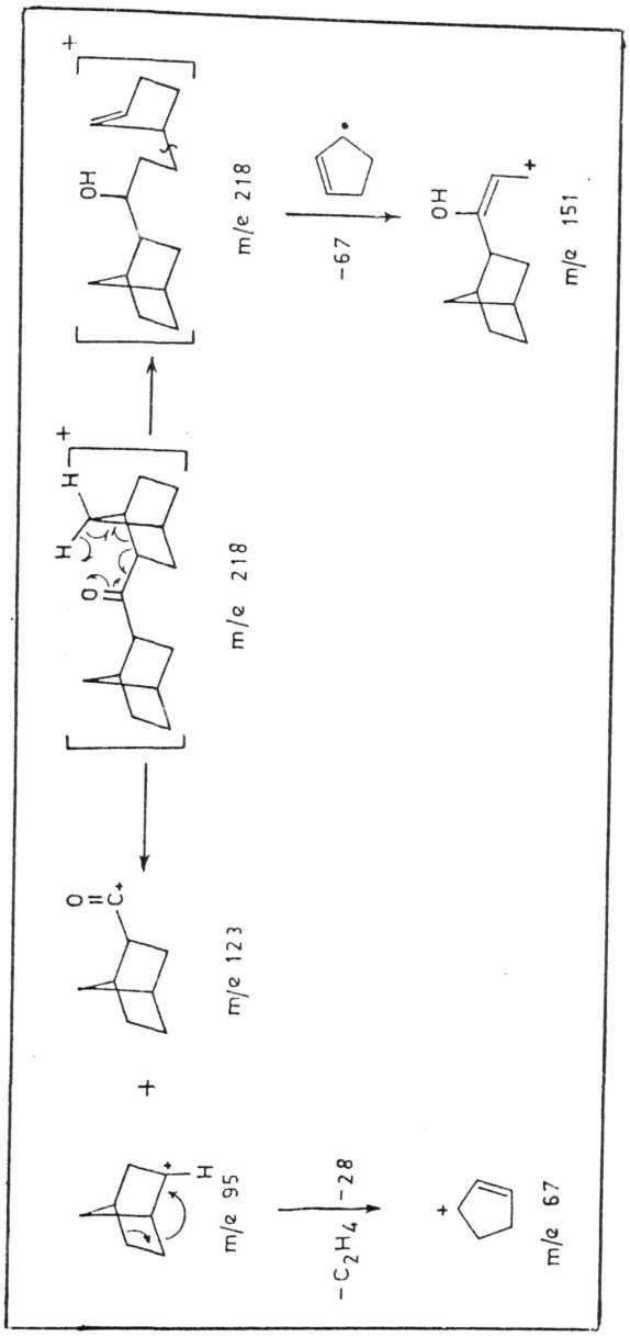
Reactivities of the cobalt reagent, generated in the presence of carbon monoxide utilizing $CoCl_2/NaBH_4/CH_3OH$, with norbornene and alkynes

As described previously, addition of $NaBH_4$ (20 mmol) in ethanol (15 ml) to a mixture of $CoCl_2$ (10 mmol) and 1-decene (10 mmol) in THF (80 ml) at 0^oC leads to isomerization or reduction of 1-decene. It was of interest to examine the reactivity of this system towards norbornene which cannot undergo such isomerizations. When the above experiment was carried out replacing 1-decene with norbornene, small amount of a mixture of products obtained after workup. The product residue exhibited a weak absorption in the carbonyl region of the IR spectrum, indicating the presence of a carbonyl product in the mixture. This encouraging result prompted us to investigate the reactivity of norbornene with the present reagent system further. Surmizing that the poor conversion in the above experiment with norbornene may be due to the presence of large excess of C_2H_5OH utilized to prevent hydroboration, we carried out an experiment utilizing calculated amount of methanol (6 eq to $CoCl_2$) to prevent hydroboration. $NaBH_4$ (20 mmol) was added during 15 minutes to a magnetically stirred suspension of $CoCl_2$ (10 mmol), CH_3OH (60 mmol) and norbornene (10 mmol) at 0^oC while bubbling carbon monoxide. The contents were stirred for 15 minutes at room temperature and the reaction mixture was stirred further for 3h at 60^oC. The crude product mixture obtained after workup exhibited carbonyl absorptions (two peaks at 1720 and 1780 cm^{-1}) in the IR spectrum along with absorptions similar to the presence of an organoboron compound (Chapter 1).

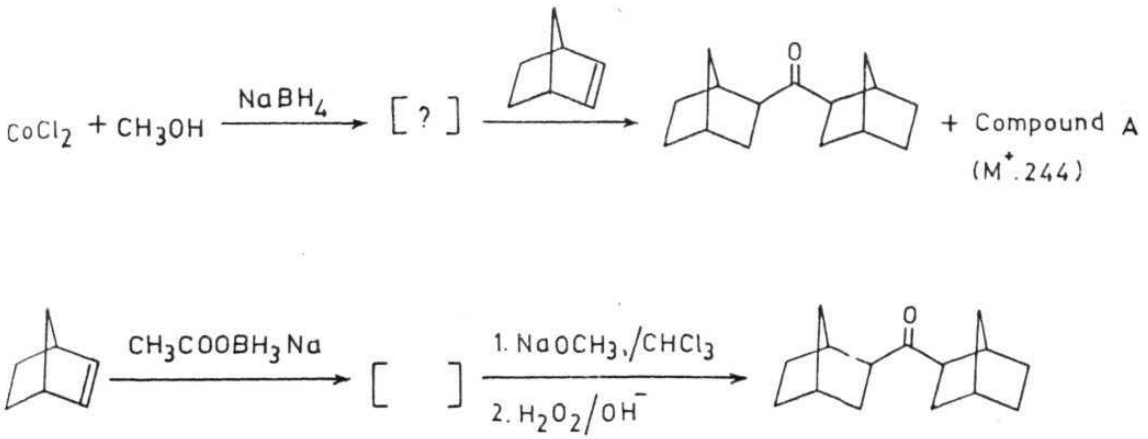
It was thought that the hydroboration reaction can be avoided by taking norbornene after the preparation of the reagent and also utilizing some more methanol. In order to examine this possibility, the following experiment was carried out: $NaBH_4$ (20 mmol) was added to a magnetically stirred suspension of $CoCl_2$ (10 mmol) and CH_3OH (100 mmol) at 0^oC while bubbling carbon monoxide. The contents were stirred for 30 minutes at room temperature and norbornene (10 mmol) was added and stirred for 15 minutes. The contents were stirred further for 2h at 60^oC while bubbling carbon monoxide. After workup (experimental section), the crude product mixture was chromatographed on a silica gel column using hexane/ethyl acetate as eluents. Ethyl acetate (5%) in hexane eluted 0.17 g of a compound, with M^+(m/e) 218. The IR and ^{13}C-NMR data (Spectrum no. 7) of this product was identical to the data of bis-exo-2-norbornyl ketone (Scheme 13), previously obtained in our laboratory by the hydroboration of norbornene with CH_3COOBH_3Na, carbenoidation using $NaOCH_3/CHCl_3$ followed by oxidation with $H_2O_2/O\bar{H}$.[86]

Mass spectrum (Spectrum no. 7) of this ketone exhibited major peaks at m/e, 218 (M^+), 151(M^+-67), 123(M^+-95), 95(M^+-123). The fragmentation pattern can be visualized as outlined in Chart 4 considering McLafferty rearrangements and α-cleavage processes. Similar fragmentation pattern has been reported for exo-acetyl norbornane.[87]

Chart 4



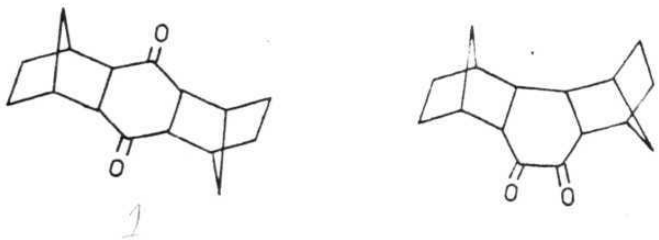
Scheme 13



Ethyl acetate (10%) in hexane eluted 0.7 g of an oily product (compound **A**) with M^+(m/e) 244 (Spectrum no. 8). The IR spectrum (Spectrum no. 6) of compound **A** shows two strong absorption at 1720 cm^{-1} and 1780 cm^{-1}. The decoupled ^{13}C-NMR spectrum of this compound is somewhat complex (Spectrum no. 8). Almost every signal has another signal very close to it, indicating the possibility of the presence of isomeric mixtures. The ^{13}C-NMR signals at 176.7, 142.7, 141.7, 120.0, 119.8 ppm indicate that the compound **A** contains olefinic and ester functional groups. Off-resonance decoupled spectrum of this compound indicates that there is no hydrogen attached to the olefinic and carbonyl carbon atoms. The precise structure of compound **A** could not be readily deduced from these data. Reaction mechanism should help to some extent in such cases but unfortunately the structure and reactivity of the cobalt species generated under the present conditions are also unknown. The bis-exo-norbornyl ketone is obtained as a side product in hydroformylation process under some conditions[88,89] but the formation of

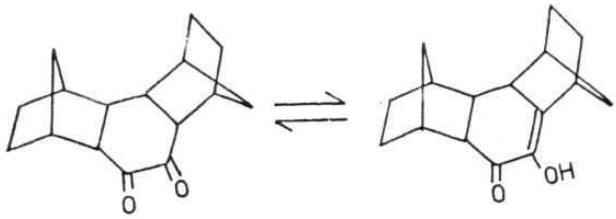
compound **A** has not been reported in the reaction of norbornene with either $Co_2(CO)_8$ or $HCo(CO)_4$.[7,8,14]

The compound **A** has a molecular weight of 244. This corresponds exactly to the presence of two norbornene units and two carbon monoxide units in the compound. One could think about the structures 1 and 2 as possibilities.



1

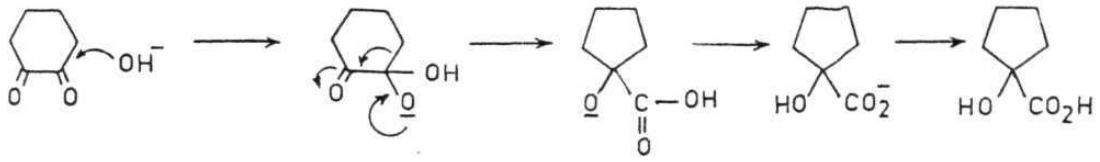
All the isomers of the 1,4-diketone **1** are known[90] and they are solid compounds, and hence structure **1** can be readily ruled out for compound **A**. Although the structure 2 may not fit into all the spectral data of compound **A**, initially we considered the possibility of this compound present as a tautomeric mixture *2* and **3**.



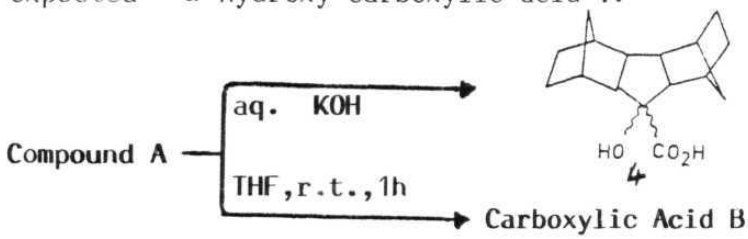
2 3

The α-diketones readily form quinoxaline derivatives on treatment with ortho-phenylenediamine. However, no quinoxaline derivative was formed on treating the compound **A** with ortho-phenylenediamine.

Cyclohexane-1,2-dione gives the corresponding α -hydroxy cyclopentane carboxylic acid on treatment with aqueous OH^- through benzyl-benzyllic acid type rearrangement.[91]



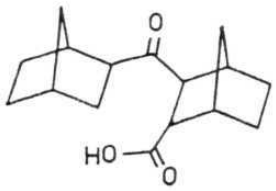
Treatment of compound **A** with aqueous KOH/THF mixture did give carboxylic acid product (**B**) after workup, but the product is not the expected α-hydroxy carboxylic acid **4**.



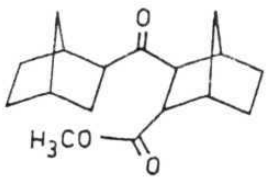
The carboxylic acid **B** was recrystallized from hexane (m.p. 130°C). Analytical data of this compound corresponds to the molecular formula $C_{16}H_{22}O_3$. The carboxylic acid **B** has M^+(m/e) peak at 262 (Spectrum no. 9). The ^{13}C-NMR signals (Spectrum no. 9) indicates the presence of keto carbonyl groups (211.6, 211.3) and carboxylic acid groups (181.53, 184.8) in the compound.

The methyl ester of the carboxylic acid can be readily prepared following the recently reported method for esterification utilizing DBU/CH_3I in THF at room temperature.[92] The IR spectrum of this ester shows two carbonyl absorptions at 1700 and 1730 cm^{-1} (Spectrum no. 6). In the mass spectrum of this ester, the M^+(m/e) peak appears at 276.

The ^{13}C-NMR spectrum of this ester (Spectrum no. 10) exhibits signals corresponding to the presence of ester carbonyl (175.5) and keto carbonyl (211.2). Comparison of this keto carbonyl signal and the aliphatic carbon signals at 51.6 and 52.9 ppm with those observed for the bis-exo-norbornyl ketone (Spectrum no. 7) indicates that the ester also should have the same skeleton as bis-exo-norbornyl ketone and all spectral data of the ester and acids can be readily accounted by assigning the structures **5** and **6** for the acid (compound **B**) and ester respectively.



5



6

Mass spectral fragmentation pattern of these compounds can be readily accounted by assigning these structures **5** and **6**, for the carboxylic acid **B** and the methyl ester as outlined in Chart 5 and Chart 6, considering CH_3OH elimination, McLafferty rearrangements and α-cleavage mechanisms,[93] reported in the literature for the aliphatic carboxylic acids and esters, exo-acetyl norbornane[87] and comparision of the fragmentation pattern observed for bis-exo-norbornyl ketone (Chart 4).

As discussed earlier, the IR and ^{13}C-NMR spectra of these compounds are in accordance with the assigned structures **5** and **6** for the carboxylic acid and the corresponding methyl ester.

Chart 5

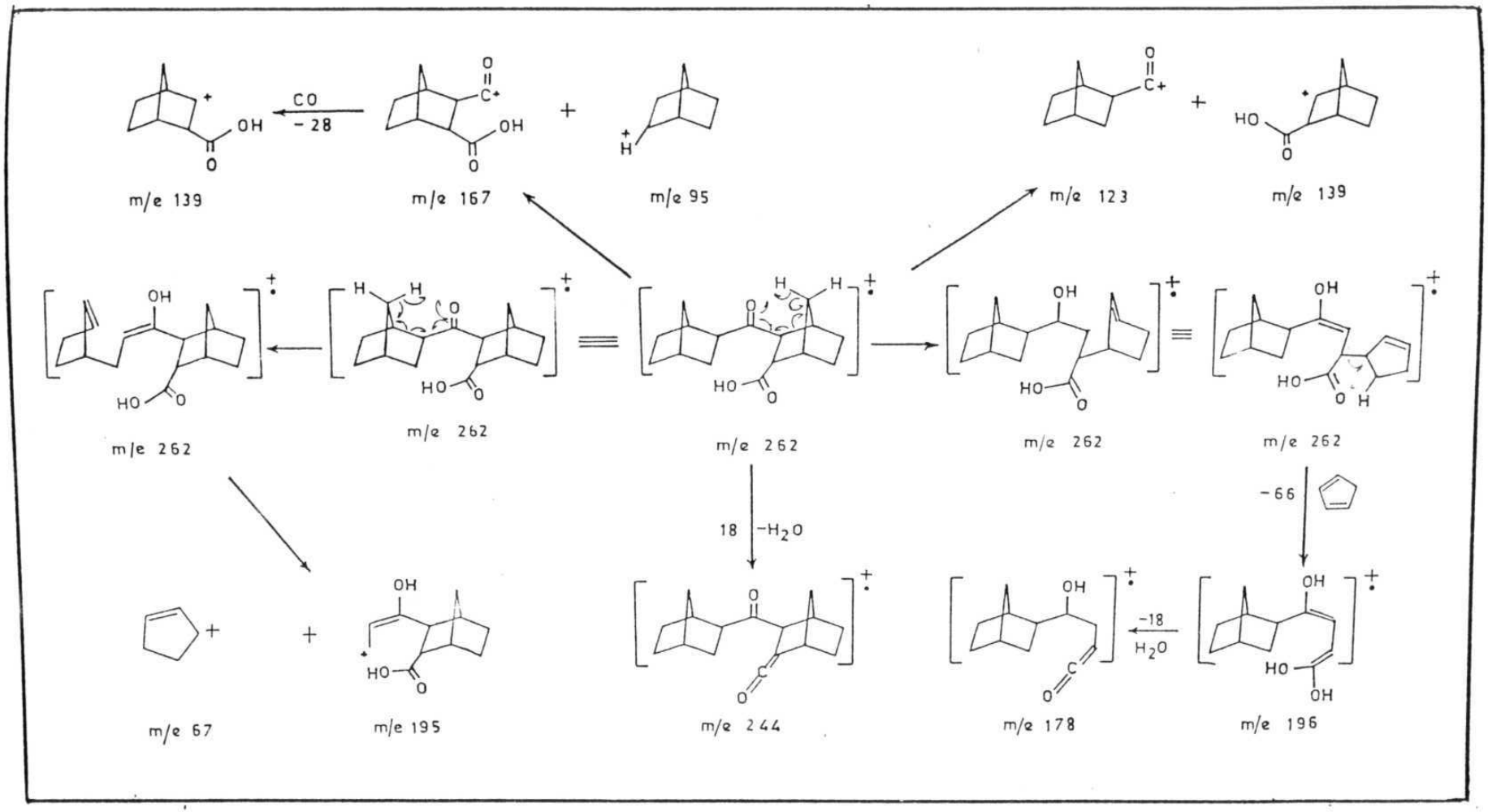
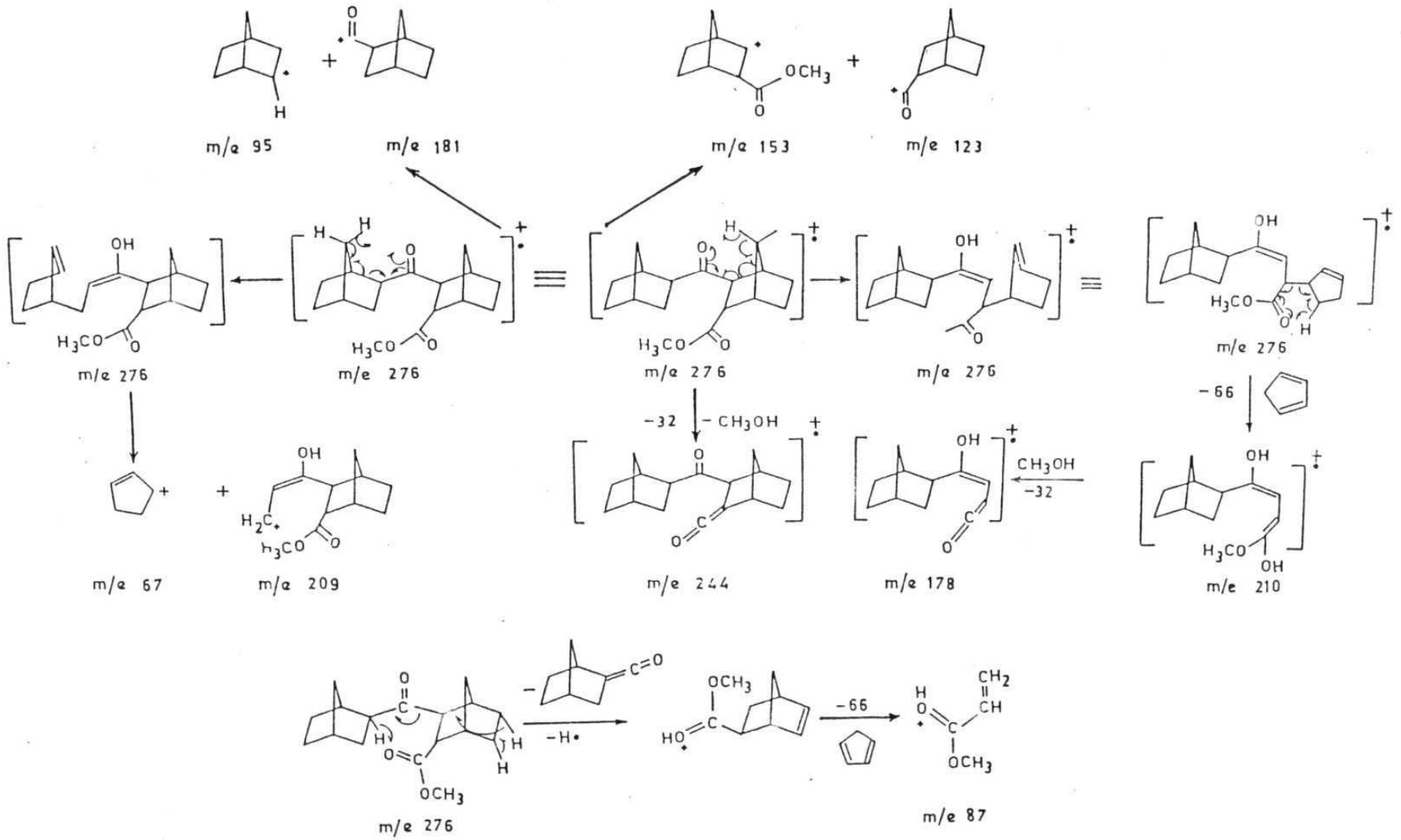
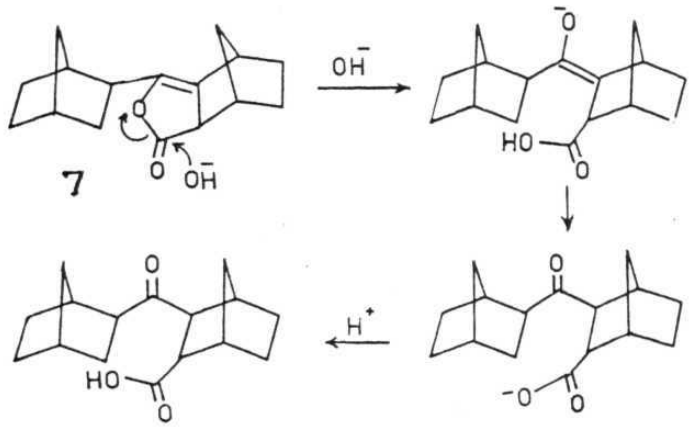

CO
- 28
m/e 139
m/e 167
m/e 95
m/e 123
m/e 139
m/e 262
m/e 262
m/e 262
m/e 262
m/e 262
18 -H2O
-66
-18
H2O
m/e 67
m/e 195
m/e 244
m/e 178
m/e 196

Chart 6


m/e 95
m/e 181
m/e 153
m/e 123
m/e 276
m/e 276
m/e 276
m/e 276
m/e 276
-32
- CH3OH
-66
m/e 67
m/e 209
m/e 244
m/e 178
CH3OH
-32
m/e 210
-H•
m/e 276
m/e 87

The carboxylic acid **B** can be easily formed from the compound **A** if the latter is the enolic lactone **7** (Scheme 14).

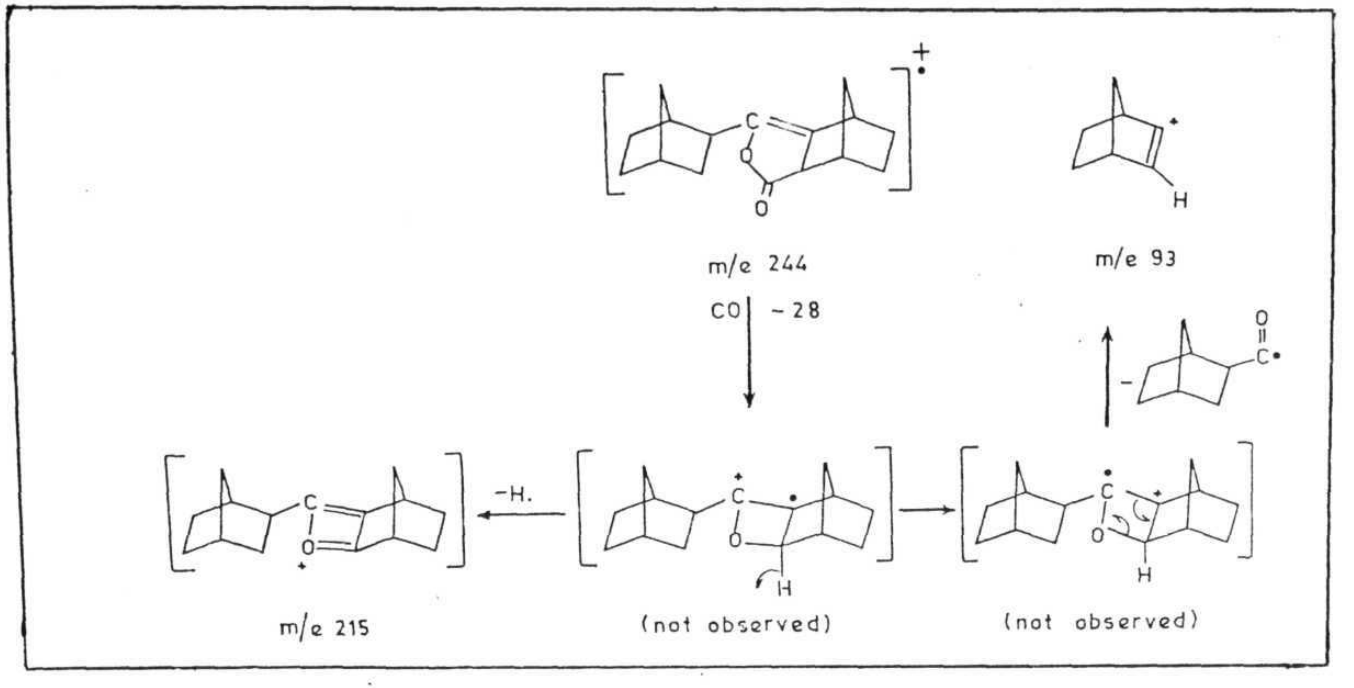
Scheme 14



All of the spectral data of compound **A** can be readily rationalized by structure **7.** Strong IR absorptions observed at 1720 and 1780 cm^{-1} will be expected for compound **7**, since enolic five membered lactones generally exhibits strong absorption at ~ 1700 cm^{-1} (C=C double bond) and ~ 1800 cm^{-1}.[94] The ester carbonyl and olefinic carbon signals which appear as singlets in the ^{13}C-NMR spectrum will be expected for this compounds. As mentioned earlier, every signal in the ^{13}C-NMR has another signal very close to it, indicating the possibility of the presence of isomeric/diasteriomeric mixture.

The major fragmentations of compound **A**, **7**, in the mass spectrum (Spectrum no. 8) appear at m/e, 244 (M^+), 215 (M^+-29) and 93[M^+-(28+123)]. The fragmentation pattern of this compound may be tentatively visualized as outlined in Chart 7, considering fragmetnation pattern reported in

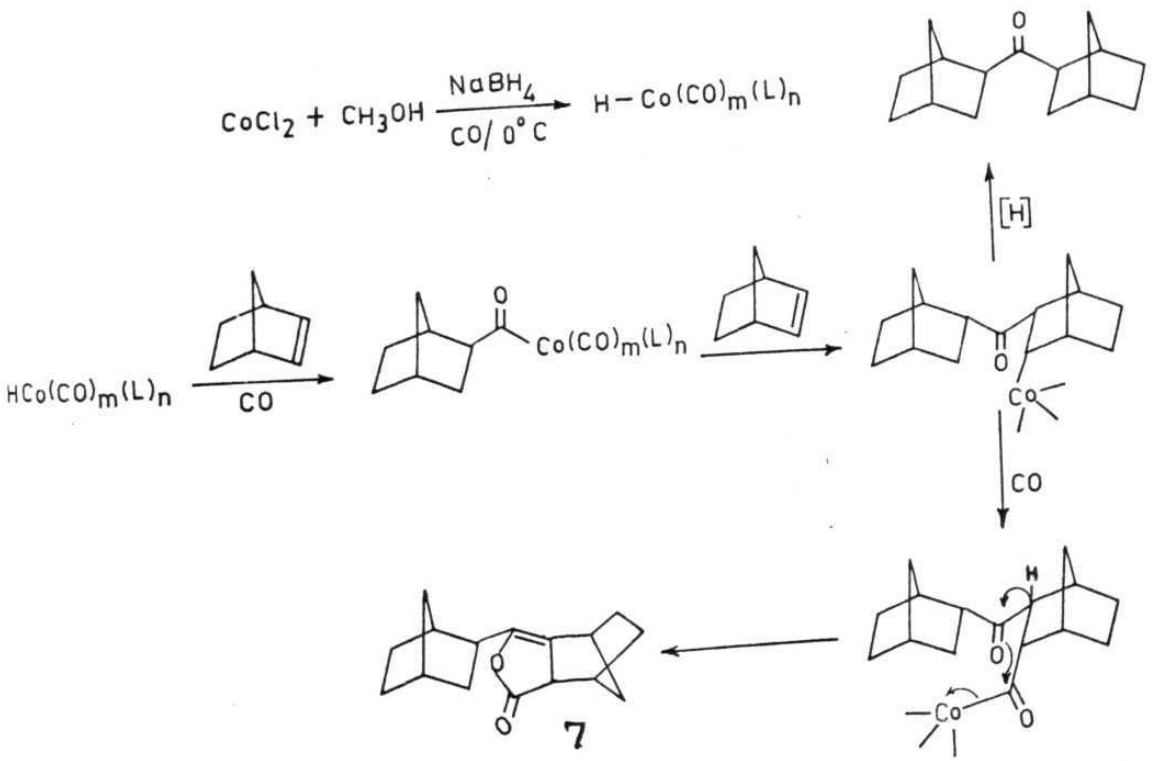
Chart 7



the literature for five membered lactones[95] and for some bornyl derivatives.[96]

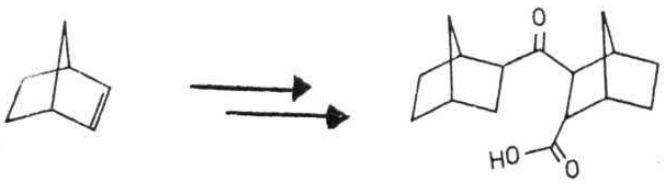
During the formation of compound **A**, **7**, a hydrogen is added to one of the norbornenes and a hydrogen is removed from another norbornene. Keeping this feature in mind, transformation of norbornene to compound **A**, **7**, and the bis-exo-norbornylketone can be visualised by the tentative mechanism outlined in Scheme 15, assuming a cobalt carbonyl hydride as an active species.

Scheme 15



As outlined earlier, the $HCo(CO)_4$ reagent has been reported to react with norbornene in hexane solvent at room temperature to give the corresponding aldehyde in 20% yield.[14] However, the transformation outlined in Scheme 15 has not been reported with the $HCo(CO)_4$ reagent.

When the reaction of norbornene (10 mmol) and the $CoCl_2$ (10 mmol)/ CH_3OH (100 mmol)/$NaBH_4$ (20 mmol) in THF was carried out as above (Scheme 15) and the reaction mixture was stirred with 5N aqueous KOH (20 ml) for 1h, the bis-exo-norbornyl ketone (10%) and the keto-carboxylic acid **5** (69%) were isolated.



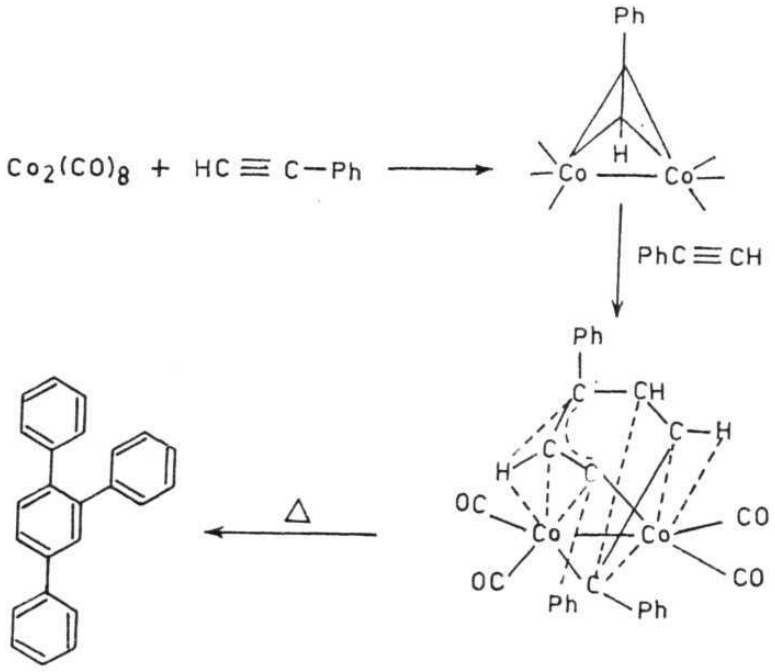
5

Whereas the 2,5-norbornadiene gave a complex mixture of products under the present reaction conditions, cyclopentene, cyclohexene and cyclooctene were converted to carbonyl compounds in very poor yields (~5% conversion) and the product mixture obtained in these cases were not characterized further. 1-Decene gave isomerized 2-decenes mixture containing trans-2-decene as major component (~ 90%).

Under the present reaction conditions, 1-decyne, phenylacetylene and diphenylacetylene took different course. Whereas 1-decyne gave a complex mixture of products, phenylacetylene gave 1,2,4-triphenyl benzene (58%) and diphenylacetylene gave a dark coloured complex containing cobalt carbonyl moiety.

It has been reported that treatment of $Co_2(CO)_8$ with phenylacetylene at 160°C gives 1,2,4-triphenyl benzene. The mechanism outlined in Scheme 16 was proposed.[9]

Scheme 16



Decomposition of the hydrido-cobalt carbonyl moiety (Scheme 15) into a dicobalt carbonyl which has reactivities similar to $Co_2(CO)_8$ would serve as a working hypothesis to explain the observation with phenylacetylene under the present reaction conditions.

In the case of diphenylacetylene, a complex containing cobalt carbonyl and diphenylacetylene, m.p. 86°C (dec), was obtained. This complex on treatment with I_2/THF gave diphenylacetylene. The $Co_2(CO)_6$-(Ph-C≡C-Ph) complex melts at 109.5°C.[97] Accordingly, although the

results indicate that a cobalt complex containing diphenylacetylene and carbonyl ligands has been isolated under the present reaction conditions, it is not the known $Co_2(CO)_6(PhC \equiv CPh)$ complex.

In order to examine the nature of the cobalt species generated in the above experiments, we carried out the ESR and IR studies of the mixture of $CoCl_2/CH_3OH/THF$ and $CoCl_2/NaBH_4/CO/CH_3OH/THF$ prepared at 0^oC. No ESR signal could be observed for these samples even at 163^oK. The reagent prepared utilizing $CoCl_2/NaBH_4/CO/CH_3OH/THF$ at 0^oC is also green in colour and IR spectrum of the solution shows a strong metal carbonyl absorption at $1910\ cm^{-1}$, similar to that observed for the green coloured $CoCl_2/NaBH_4/CO/THF$ system.

SUMMARY

The reagent, prepared *in situ* in THF under carbon monoxide atmosphere using $CoCl_2/NaBH_4/NaOH$ reagent system, converts benzyl halides into the corresponding carboxylic acids and 2,2'-bis(bromomethyl) biphenyl into the corresponding cyclic ketone in good yields. The low-valent cobalt species, prepared *in situ* in THF by the reduction of $CoCl_2$ with $NaBH_4/C_2H_5OH$ under carbon monoxide, isomerizes alkenes, reduces alkenes and carbonylates benzyl halides under appropriate conditions. The $CoCl_2/CH_3OH/NaBH_4/CO$ system cooligomerizes norbornene and carbon monoxide into bis-exo-norbonyl ketone, lactone **7** or keto acid **5**. Whereas the reaction of the $CoCl_2/CH_3OH/NaBH_4/CO$ reagent with phenylacetylene yields 1,2,4-triphenylbenzene, the reaction with diphenylacetylene gives a metal carbonyl-alkyne complex.

EXPERIMENTAL

Several items given in the experimental section of Chapter 1 are also applicable for the experiments outlined here. The 2,2'-bis(bromomethyl)biphenyl was prepared starting from phenanthrene: H_2O_2 oxidation of phenanthrene to the diphenic acid,[98] followed by the reduction of the acid with BH_3THF to alcohol,[99] and treatment of the alcohol with HBr gave the required dibromide.[98] The 1,2-bis(bromomethyl)benzene was prepared starting from phthalic acid following a similar route.[98,99] p-Methylbenzyl bromide and p-chlrobenzyl bromide were prepared from the corresponding carboxylic acids following the same route.[98,99] 1-Bromo--2-cyclohexene was prepared by bromination of cyclohexene.[98] The alkenes and alkynes utilized were supplied by Fluka, Switzerland.

Reaction of 1-decene with $CoCl_2/NaBH_4/CO$ system

$NaBH_4$ (20 mmol, 0.8 g) was added during 15 minutes into a magnetically strirred suspension of $CoCl_2$ (10 mmol, 1.30 g) in THF (60 ml) at 0^oC while bubbling carbon monoxide. The contents were further stirred for 1h at room temperature. During this time the colour of the contents turned from blue to green. 1-Decene (10 mmol, 1.4 g) was injected to this green coloured mixture and the contents were stirred for 3h at room temperature under carbon monoxide. The reaction mixture was poured in to 3N HCl (30 ml) and ether (100 ml) was added. The contents were saturated with solid sodium chloride and the ether layer was separated. The aqueous layer was extracted with ether (3x30 ml). The combined organic

ayer was washed with water (20 ml), brine (20 ml) and dried over anhydrous $MgSO_4$. The solvent was evoporated. The residue did not contain any 1-decene and the IR spectrum was similar to that observed for organoboran compounds (Chapter 1). To the organoboron residue, THF (25 ml) and NaOH (5 N, 10 ml) were added. The reaction mixture was cooled to 0^oC and H_2O_2 (16%, 10 ml) was added dropwise and the contents were stirred further for 3h. The reaction mixture was poured into 3N HCl (10 ml) and ether (30 ml) was added. The contents were saturated with solid sodium chloride and the organic layer was separated. The aqueous layer was extracted with ether (3x10 ml). The combined organic extract was washed with water (20 ml), brine (20 ml) and dried over anhydrous $MgSO_4$. The solvent was evaporated and distillation of the residue gave 1-decanol 70%, 1.0 g, b.p. $105^oC/7$ mm Lit.[100] b.p. $107^oC/7$ mm. The IR spectrum of this product was identical to the spectrum of 1-decanol obtained previously (Chapter 1).

Carbonylation of Benzyl bromide using $CoCl_2/NaBH_4/CO/NaOH$ system

$NaBH_4$ (20 mmol, 0.8 g) was added during 15 minutes into a magnetically stirred suspension of $CoCl_2$ (10 mmol, 1.30 g) in THF (60 ml) at 0^oC while bubbling carbon monoxide. The contents were further stirred for 1h at room temperature. Aqueous NaOH (5N, 10 ml) was carefully added (gas evolution). Benzyl bromide (10 mmol, 1.8 g) in THF (10 ml) was added during 15 minutes and the contents were stirred further for 3h at 55^oC under carbon monoxide atmosphere. The bubbling of carbon monoxide was stopped and the gas present above the surface of the reaction mixture

was flushed away by a stream of dry nitrogen. The contents were brought to room temperature and the precipitate was filtered off. The filtrate was diluted with water (20 ml) and the aqueous layer was separated. It was acidified with concentrated HCl and extracted with ether (3x30 ml). The ether layer was washed once with brine solution (30 ml) and dried over anhydrous $MgSO_4$. The solvent was evaporated. Recrystallization of the residue from water gave phenylacetic acid, 1.2 g, 88%, m.p. 76°C, Lit.[101] m.p. 76°C. IR spectrum of the compound showed 1:1 correspondence with the spectrum reported in the literature.[102]

The above experiment utilizing $CoCl_2/NaBH_4/NaOH/CO$ system for carbonylation of benzyl bromide was followed for other substituted benzyl halides and the corresponding substituted phenylacetic acids were isolated.

Yield	:	1.3 g, 78%
M.P.	:	104°C, Lit.[103] m.p. 105°C
IR (KBr): ν_{max}	:	3300-2500, 1710, 750, 700 cm^{-1}
^{1}H-NMR (100 MHz, $CDCl_3$): δppm	:	7.2(m, 4H), 3.6(s, 2H), 11.9(s, H)
^{13}C-NMR (25.0 MHz, $CDCl_3$): δppm	:	178.0, 133.5, 130.9, 129.0, 40.35

Yield : 1.0 g, 72%

M.P. : 89°C, Lit.[104] m.p. 91°C

IR (KBr): ν_{max} : 3300-2500, 1710, 750, 700 cm^{-1}

^{1}H-NMR (100 MHz, $CDCl_3$): δppm : 7.2(m,4H), 3.6(s,2H), 2.3(s,3H)
11.8 (s,1H)

^{13}C-NMR (25.0 NH_2, $CDCl_3$): δppm : 178.0, 129.47, 40.6, 21.0.

Yield : 1.1 g, 70%

M.P. : 76°C, Lit.[101] m.p. 78°C.

Cyclization of 2,2'-bis(bromomethyl)biphenyl using $CoCl_2/NaBH_4/CO/NaOH$ system

$NaBH_4$ (20 mmol, 0.8 g) was added during 15 minutes into a magnetically stirred suspension of $CoCl_2$ (10mmol, 1.30 g) in THF (60 ml) at 0°C while bubbling carbon monoxide. The contents were further stirred for 1h at room temperature. Aqueous NaOH (5N, 10 ml) was added carefully (gas evolution). 2,2'-Bis(bromomethyl)biphenyl (5 mmol, 1.7 g) in THF (10 ml) was added during 15 minutes and the contents were stirred further for 3h at 55°C under carbon monoxide atmosphere. The bubbling of carbon monoxide was stopped. The reaction mixture was bought to room temperature and ether (100 ml) was added. The ether layer was separated and

the aqueous layer was extracted with ether (3x30 ml). The combined ether extract was washed with water (20 ml), brine (20 ml) and dried over anhydrous $MgSO_4$. The solvent was evaporated. The residue was chromatographed on a silica gel column using hexane/CH_3OH mixture eluent. The product was crystalized from aqueous CH_3OH to isolate 6H-dibenzo (a,c)-5,7-dihydrocycloheptan-6-one, 1.4 g, 68% m.p. 75°C, Lit.[80] m.p. 78°C.

IR (KBr): ν_{max} : 1700, 750, 700 cm^{-1}

^{1}H-NMR (100 MHz, $CDCl_3$): δppm : 3.4(s, 2H), 7.1-7.5(m, 8H)

^{13}C-NMR (25.0 MHz, $CDCl_3$): δ ppm : 209.9, 138.9, 132.7, 129.1, 129.0, 127.7, 127.4, 48.7

Reaction of 1,2-bis(bromomethyl)benzene with $CoCl_2/NaBH_4$/NaOH/CO system

The procedure followed in the previous experiment has been followed utilizing $CoCl_2$ (10 mmol, 1.30 g), $NaBH_4$ (20 mmol, 0.8 g), NaOH (5N, 10 ml) and 1,2-bis(bromomethyl)benzene (5 mmol 1.3 g). After worukup as outlined in previous experiment, the residue was chromatographed using hexane $CHCl_3$ as eluent. Small amount of lactone (5%, 20 mg) was isolated besides small amounts of several unidentified products.

IR (KBr): ν_{max} : 3010, 1740, 750 cm^{-1}

^{13}C-NMR (25.0 MHz, $CDCl_3$): δppm : 140.5, 136.1, 131.6, 127.7, 127.0, 123.9, 52.2, 14.1

Carbonylation of benzylbromide (50 mmol) using $CoCl_2/NaBH_4$/CO/NaOH and benyl triethylammonium bromide as phase transfer catalyst

$NaBH_4$ (20 mmol, 0.8 g) was added during 15 minutes into a magnetically stirred suspension of $CoCl_2$ (10 mmol, 1.30 g) in THF (60 ml) at 0^oC while bubbling carbon monoxide. The contents were further stirred for 1h at room temperature. Aqueous NaOH (5N, 10 ml) was carefully added (gas evolution) followed by benzyl triethylammonium bromide (0.1 g). Benzyl bromide (50 mmol 8.6 g) in THF (20 ml) was added during 15 minutes and the contents were stirred further for 2h at 55^oC. After workup as outlined in previous experiments, phenylacetic acid m.p. 76, Lit.[101] m.p. 78^oC (55 g, 79%) was isolated.

Reaction of styrene dibromide with $CoCl_2/NaBH_4$ NaOH/CO system

The procedure followed in previous experiments was followed utilizing $CoCl_2$ (10 mmol), $NaBH_4$ (20 mmol), 5N NaOH (10 ml) and styrene dibromide (10 mmol). After workup, the crude product mixture was chromatographed on a silica gel column using hexane as eluent to isolate styrene, 0.6 g, 58% and styrene dibromide, 0.85 g, 32%.

Reaction of 1-decene with $CoCl_2/NaBH_4/CH_3OH$/CO system

$NaBH_4$ (10 mmol, 0.8 g) was added during 15 minutes into a magnetically stirred suspension of $CoCl_2$ (10 mmol, 1.30 g) in THF (60 ml) at 0^oC while bubbling carbon monoxide. The contents were further stirred

for 1h at room temperature. CH_3OH (100 mmol) was added (vigourous gas evolution). The contents became dark (black). 1-Decene (10 mmol, 1.4 g) was injected and the contents were stirred further for 3h at room temperature under carbon monoxide atmosphere. After workup, 1-decene was recovered back quantitatively.

The above experiment was carried out by replacing CH_3OH with PPh_3 (20 mmol), or H_2O (100 mmol), or NEt_3 (20 mmol) in separate runs. But in all runs 1-decene was recovered back quantitatively.

Isomerization of 1-decene using $CoCl_2/NaBH_4$/EtOH/CO system

$NaBH_4$ (20 mmol, 0.8 g) EtOH (15 ml) was added during 10 minutes into a magnetically stirred suspension of $CoCl_2$ (10 mmol, 1.30 g) and 1-decene (10 mmol, 1.4 g) in THF (60 ml) at 0^oC while bubbling carbon monoxide. The contents were further stirred for 30 minutes. Hexane (100 ml) was added to the reaction mixture followed by water (15 ml). The precipitate was filtered off. The organic layer was separated, washed with water (20 ml), dried over anhydrous $MgSO_4$ and the solvent was evaporated. Distillation of the residue gave trans-2-decene.

The IR spectrum of the sample showed 1:1 correspondence with the spectrum reported in the literature.[102] The ^{13}C-NMR spectrum (131.9, 124.6, 32.9, 32.2, 30.0, 29.5, 23.0, 17.96, 14.3) did not show signals corresponding to the cis-2-decene.

Reduction of 1-decene using $CoCl_2/NaBH_4$/EtOH/CO system

$NaBH_4$ (20 mmol, 0.8 g) in EtOH (15 ml) was added during 10 minutes into a magnetically stirred suspension of $CoCl_2$ (10 mmol, 1.30 g) and 1-decene (10 mmol, 1.4 g) in THF (60 ml) at 0^oC while bubbling carbon monixide. The contents were further stirred for 30 minutes. Concentrated HCl (12N, 5 ml) was added and the mixture was stirred for 1h. Hexane (100 ml) was added to the reaction mixture followed by water (15 ml). The precipitate was filtered off and the organic layer was separated, washed with water (20 ml), brine (20 ml) and dried over anhydrous $MgSO_4$. The solvent was evaporated and distillation of the residue gave decane (1.3 g, 89%), b.p. 60^oC/15 mm, Lit.[100] b.p. 63^oC/15 mm. The IR spectrum of the product showed 1:1 correspondence to the spectrum of the product obtained previsouly (Chapter 1).

Examination of the reactivity of the intermediate using additional amount of 1-decene after $NaBH_4$/EtOH addition

$NaBH_4$ (20 mmol, 0.8 g) in EtOH (15 ml) was added during 15 minutes to a mangetically stirred suspension of $CoCl_2$ (10 mmol, 1.30 g) and 1-decene (10 mmol, 1.4 g) in THF (60 ml) at 0^oC while bubbling carbon monoxide. The contents were stirred further for 30 minutes. 1-Decene (10 mmol) was injected and further stirred for 3h. Concentrated HCl (12N, 5 ml) was added and stirred for 1h. Hexane (100 ml) was added to the reaction mixture followed by water (15 ml). The perecipitate was filtered of and the organic layer was separated, washed with water

(20 ml), brine (20 ml) and dried over anhydrous $MgSO_4$. The solvent was evaporated and residue was distilled. GC analysis of the product (SE 30 column) indicated the presence of a 1:1 mixture of 1-decene and decane.

In another run, additional 1-decene was replaced by methyl-10-undecenoate (10 mmol, 1.8 g) and the mixture was stirred for 12 h at room temperature. After workup, distillation of the residue gave decane 1.1 g, 80% and methyl-10-undecenoate. The ^{13}C-NMR spectrum of the recovered methyl-10-undecenoate did not show signals corresponding to the presence of methyl undecanoate.

Reaction of allyl benzene with $CoCl_2/NaBH_4/CO$ system

$NaBH_4$ (20 mmol, 0.8 g) in EtOH was added during 15 minutes into a magnetically stirred suspension of $CoCl_2$ (10 mmol, 1.30 g) and allyl-benzene (10 mmol, 1.2 g) in THF (60 ml) at 0^oC while bubbling carbon monoxide. The contents were further stirred for 15 minutes. After workup as mentioned in previous experiments, distillation of the residue gave n-propyl benzene (1.0 g, 84% b.p. 158.0^oC, Lit.[100] b.p. 159.5^oC).

Carbonylation of benzyl bromide using $CoCl_2/NaBH_4$ in EtOH/CO/NaOH system

$NaBH_4$ (20 mmol, 0.8 g) in EtOH was added during 10 minutes into a magnetically stirred suspension of $CoCl_2$ (10 mmol) in THF (60 ml) at 0^oC while bubbling carbon monoxide. The contents were stirred further for 15 minutes. Aqueous NaOH (5N, 5 ml) was added to the reaction mxiture and 0.1 gm of benzyl triethylammonium bromide was added followed by

benzyl bromide (10 mmol, g). The contents were stirred further at 50°C under carbon monoxide for 2h. The contents were bought to room temperature and the precipitate was filtered off. The filtrate was diluted with water (20 ml) and the aqueous layer was separated. It was acidified with concentrated HCl and extracted with ether (3x30 ml). The ether layer was washed once with brine solution (20 ml) and dried over anhydrous $MgSO_4$. The sovlent was evaporated. Recrystallization of the residue from water gave phenylacetic acid (1.2 g, 89%, m.p. 76°C Lit.[100] m.p. 78°C).

Cyclization of 2,2'-bis(bromomethyl)biphenyl using $CoCl_2/NaBH_4$/EtOH/CO/ NaOH system

$NaBH_4$ (20 mmol, 0.8 g) in EtOH was added during 10 minutes into a mangetically stirred suspension of $CoCl_2$ (10 mmol) in THF (60 ml) at 0°C while bubbling carbon monoxide. The contents were stirred further for 15 minutes. Aqueous NaOH (5N, 5 ml) was added to the reaction mixture and 0.1 g of benzyl triethylammonium bromide was added followed by 2,2'-bis(bromomethyl)biphenyl (5 mmol, 1.7 g). The contents were stirred further at 50°C under carbon monixide for 2h. The contents were bought to room temperature and ether (100 ml) was added. The ether layer was separated and the aqueous layer was extracted with ether (3x30 ml). The combined ether extract was washed with water (20 ml), brine (20 ml), dried over anhydrous $MgSO_4$ and the solvent was evaporated. The residue was chromatographed on a silica gel column using hexane/CH_3OH mixture as eluent to isolate the cyclized product. The product was crysta-

llized from aqueous CH_3OH to isolate 6H-Dibenzo (a,c)-5,7-dihydro cyclo-heptane-6-one, 1.3 g, 63%, m.p. 75°C Lit.[80] m.p. 78°C. The IR spectrum of this product was identical to the specturm of the product obtained previously.

Reaction of Norbornene using $CoCl_2/NaBH_4$ in EtOH/CO system at room temperature

$NaBH_4$ (20 mmol, 0.8 g) in EtOH (15 ml) was added during 10 minutes into a magnetically stirred suspension of $CoCl_2$ (10 mmol, 1.30 g) and norbornene (20 mmol, 1.8 g) in THF (60 ml) at 0°C while bubbling carbon monoxide. The contents were further stirred at room temperature under carbon monoxide for 3h. Hexane (100 ml) was added to the reaction mixture followed by water (15 ml). The black precipitate was filtered off. The organic layer was separated and the aqueous layer was washed with 3N HCl (10 ml), water (20 ml), brine (20 ml) and dried over anhdyrous $MgSO_4$. Only a small amount of residue (50 mg) was left behind after evaporation. The product showed weak absorptions in the carbonyl region. The product was not further characterised.

Reaction of Norbornene with the $CoCl_2/CH_3OH/NaBH_4/CO$ reagent system

$NaBH_4$ (20 mmol, 0.8 g) was added during 15 minutes to a magnetically stirred suspension of $CoCl_2$ (10 mmol, 1.38 g) and CH_3OH (100 mmol)

at $0^{o}C$ while bubbling carbon monoxide. The contents were stirred for 30 minutes at room temperature. Norbornene (10 mmol, 1.0 g) was added and the mixture was further stirred for 15 minutes. The mixture was further stirred at $60^{o}C$ for 3h. It was bought to room temperature and hexane (100 ml) was added. The black precipitate was filtered off. The hexane layer was washed with 3N HCl (20 ml), water (20 ml), brine (20 ml) and dried over anhydrous $MgSO_4$. The solvent was evaporated. The product identified to be bis-exo-norbornyl ketone (see text) was isolated in 15% yield (0.17 g) by chromatography on a silica gel column using hexane/ethylacetate (5%) as eluent. Hexane/ethylacetate (10%) eluted 0.85 g (70%) of an oily product, identified to be compound 7 (see the text, yields are based on 10 mmol of norbornene utilized).

Spectral data of a bis-norbornyl ketone (Spectrum no. 7)

IR (neat): ν_{max}	:	1700, cm^{-1}
^{1}H-NMR (100 MHz, $CDCl_3$): δ ppm	:	0.9-1.9(m), 2.1-2.6(m)
^{13}C-NMR (25.0 MHz, $CDCl_3$): δppm	:	214.0, 213.8, 53.2, 52.9, 40.5, 39.9, 36.1, 35.8, 33.4, 32.8, 30.1, 29.8, 28.8

Mass (m/e): 218 (M^+), 151 (M^+-67), 23(M^+-95), 95 (M^+-123).

Spectral data of compound **7** (Spectrum no. 6 and 8)

IR (neat): ν_{max} : 1720, 1780 cm^{-1}

^{1}H-NMR (100 MHz, $CDCl_3$): δ ppm : 0.9-1.61(m), 1.9-2.7 (m)

^{13}C-NMR (25.0 MHz, $CDCl_3$): δ ppm : 176.8, 142.2, 141.8, 120.0, 119.9, 48.5, 48.4, 44.8, 44.6, 42.7, 40.3, 39.4, 39.8, 39.7, 39.0, 36.0, 33.7, 28.9, 28.8, 27.9, 27.7, 27.5, 27.4, 26.9, 27.0.

Mass (m/e) : 244(M^+), 215 (M^+-29), 93[M^+-(28+123)]

Reaction of compound 7 in THF with aqueous KOH

Aqueous KOH (5N, 5 ml) was added to the magnetically stirred solution of compound **7** (1.2 g, 5 mmol) in THF (10 ml). The reaction mixture was stirred for 1h at room temperature. The contents were acidified with concentrated HCl and ether (50 ml) was added. The ether layer was separated and the aqueous layer was extracted with ether (2x10 ml). The combined organic extract was washed with brine (10 ml) and dried over anhydrous $MgSO_4$. The solvent was evaporated. n-Pentane (10 ml) was added to the residue to precipitate out most of the keto-acid **5**. The white precepitate was filtered and recrystallized using hexane to isolate pure keto-acid 1.0 g, 76%, m.p. 130^{o}C. The filtrate was concentrated

and the residue on separation by column chromatography, gave an additional amount 0.13 g, 10%, of keto-acid **5**, on elution with 30% ethylacetate/hexane.

Spectral data of the keto acid **5** (Spectrum no. **6** and 9)

IR (KBr): ν_{max} : 3300-2500, 1700 cm^{-1}

^{1}H-NMR (100 MHz, $CDCl_3$): δ ppm : 1-1.8(m), 2.2-2.8(m), 2.9(t) 3.3(t), 3.5(t), 10.9 (broad,--COOH)

^{13}C-NMR (25.0 MHz, $CDCl_3$): δ ppm : 211.6, 211.3, 181.5, 181.4, 56.3, 55.8, 53.0, 46.9, 41.4, 41.2, 40.5, 39.2, 38.4, 36.0, 35.6, 34.6, 31.7, 30.2, 29.3, 28.7, 28.6, 23.9.

Mass (m/e) : 262(M^+), 196(M^+-66), 167(M^+-95), 139(M^+-123), 95(M^+-167)

Analysis : Calculated for $C_{16}H_{22}O_3$: C,73.3; H, 8.4

Found : C, 72.8; H, 8.3.

Reaction of compound 5 with CH_3I/DBU[92]

To a magnetically stirred suspension of compound **6** (1.3 g, 5 mmol) in THF (10 mmol), DBU (5 mmol) was added followed by CH_3I (5 mmol). The reaction mixture was stirred for 8h at room temperature. The contents were filtered off and the filtrate was concentrated in vacuum. To this

residue 6N HCl (5 ml) was added followed by ether (20 ml). The ether layer was separated and washed with water, brine and dried over anhydrous $MgSO_4$. The solvent was evaporated and the product identified to be compound **6** (keto-ester) was isolated by chromatography on a silica gel column using 5% ethylacetate in hexane as eluent. (1.25 g, 90%).

IR (neat): ν_{max}	:	1700, 1730 cm^{-1}
^{1}H-NMR (100 MHz, $CDCl_3$) : δppm	:	0.9-1.8(m), 2.1-3.0(m), 3.6(s)
^{13}C-NMR (25.0 MHz, $CDCl_3$) : δppm	:	211.2, 175.4, 56.2, 55.8, 52.9, 51.6, 46.7, 41.5, 41.0, 40.3, 38.7, 35.9, 35.4, 31.6, 28.6, 23.8

Reaction of Norbornene using $CoCl_2/CH_3OH/NaBH_4/CO$ system followed by aqueous KOH treatment

$NaBH_4$ (20 mmol, 0.8 g) was added during 15 minutes to a magnetically stirred suspension of $CoCl_2$ (10 mmol, 1.30 g) and CH_3OH (100 mmol) at 0^oC while bubbling carbon monoxide. The contents were stirred for 30 minutes at room temperature. Norbornene (10 mmol, 1 g) was added and the mixture was further stirred for 15 minutes. The contents were stirred further for 3h at 60^oC under carbon monoxide. The mixture was brought to room temperature and aqueous KOH (5N, 20 ml) was added. The contents were stirred further for 1h, 3N HCl (50 ml) was added followed by hexane (100 ml). The organic layer was separated. The aqueous layer was extracted

with hexane (3x30 ml). The combined organic layer was washed with water (20 ml), brine (20 ml) and dried over anhydrous $MgSO_4$. The solvent was evaporated. To the residue n-pentane (10 ml) was added and the keto-acid **5** (0.7 g, 59%) was filtered off and further purified by recrystallization from hexane. The filtrate was concentrated and chromatographed on a silica gel column using hexane/ethyl acetate as eluent to isolate an additional amount of the keto acid **5** (10%) and bis-exo-norbornyl ketone 0.25 g, 10%.

Reaction of $CoCl_2/NaBH_4/CH_3OH/CO$ system with other alkenes

$NaBH_4$ (20 mmol, 0.8 g) was added during 15 minutes to a magnetically stirred suspension of $CoCl_2$ (10 mmol, 1.30 g) and CH_3OH (100 mmol) at 0^oC while bubbling carbon monoxide. The contents were stirred for 30 minutes at room temperature. Cyclopentene (10 mmol, 0.68 g) was injected and the mixture was further stirred for 15 minutes. The contents were stirred further for 3h at 60^oC. After workup, as outlined in above experiments, a small amount (40 mg) of a product mixture which showed a weak absorptions in the carbonyl region was isolated. Attempts to isolate identifiable amount of the carbonyl product was unsuccessfull.

Similar results were obtained in runs with cyclohexene and cyclooctene.

Reaction of phenylacetylene with $CoCl_2/CH_3OH/NaBH_4/CO$ system

$NaBH_4$ (20 mmol, 0.8 g) was added during 15 minutes to a magnetically stirred suspension of $CoCl_2$ (10 mmol, 1.30 g) and CH_3OH (100 mmol) at 0^oC while bubbling carbon monoxide. The contents were stirred for 30 minutes at room temperature. Phenylacetylene (10 mmol, 1.0 g) was injected and the mixture was further stirred for 15 minutes. The contents were stirred further for 3h at 60^oC. Workup as outlined in the above experiment, gave a crude product mixture which showed no carbonyl absorption in the IR spectrum. Chromatography of the product on a silica gel column using hexane/5% ethyl acetate as eluent gave 1,2,4-triphenyl benzene, 0.53 g, 58%, m.p. 100^oC, Lit.[105] m.p. 100^oC.

IR (KBr): ν_{max} : 3010, 1600, 750, 700 cm^{-1}

^{1}H-NMR (100 MHz, $CDCl_3$): δ ppm : 7.1-73 (m)

^{13}C-NMR (25.0 MHz, $CDCl_3$): δ ppm : 147.7, 141.3, 141.2, 140.5, 139.7, 131.3, 130.3, 129.6, 129.0, 128.0, 127.6, 127.3, 126.8, 126.3.

Mass (m/e) : 306 (M^+) .

Reaction of diphenylacetylene with $CoCl_2/CH_3OH/NaBH_4/CO$ system

$NaBH_4$ (20 mmol, 0.8 g) was added to a magnetically stirred suspension of $CoCl_2$ (10 mmol, 1.30 g) and CH_3OH (100 mmol) at 0^oC while

bubbling carbon monoxide. The contents were stirred for 30 minutes at room temperature. Diphenylacetylene (10 mmol, 1.8 g) was added and the mixture stirred for 15 minutes. The reaction mixture was further stirred for 3h at 60°C. After workup as mentioned in the previous experiments, a violet coloured solid compound (3.1 g) was isolated. This solid compound was further purified by column chromatography on a silica gel column using hexane as eluent m.p. 86°C, reported, m.p. of $Co_2(CO)_6(PhC \equiv CPh)$, 109°C.[98]

IR (KBr): ν_{max} : 2000, 2010, 2030, 740, 680, cm^{-1}

To a solution of the above complex in THF, iodine (5 g) in THF (10 ml) was added. The mixture was stirred for 15 minutes. Ether (15 ml) was added followed by water (10 ml). The organic layer was separated and washed with $Na_2S_2O_3$ (5%, 20 ml), water (20 ml), brine (20 ml) and dried over anhydrous $MgSO_4$. The solvent was evaporated to isolate diphenyl acetylene (7 mmol, 1.2 g).

Spectral analysis of the $CoCl_2/NaBH_4/CO$ system in THF and the $CoCl_2/NaBH_4/CH_3OH/CO$ system in THF

The IR spectrum for the reagent prepared using $CoCl_2/NaBH_4/CO$ system as outlined in above procedures showed a single strong absorption at 1910 cm^{-1} corresponding to the presence of a metal carbonyl. The $CoCl_2/NaBH_4/CH_3OH/CO$ system also exhibited the absorption at 1910 cm^{-1} in the IR spectrum.

The ESR spectral studies for the $CoCl_2/NaBH_4/CO$ and $CoCl_2/NaBH_4/CH_3OH/CO$ reagents in THF (frozen) were attempted. However, no ESR signals were observed even at 163°K.

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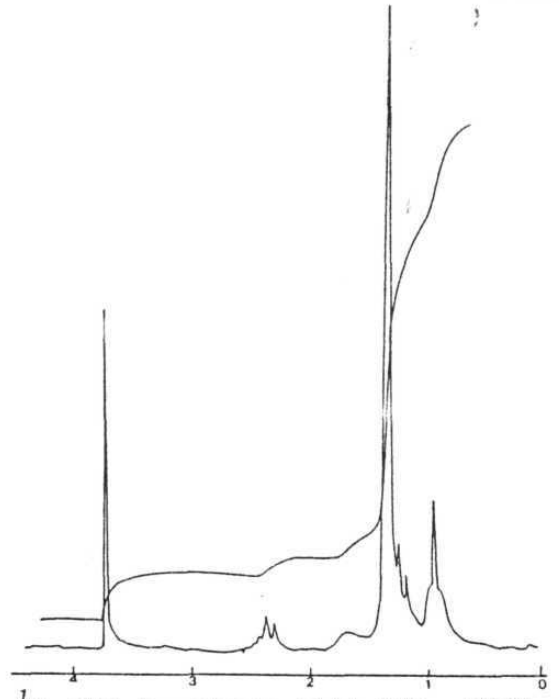
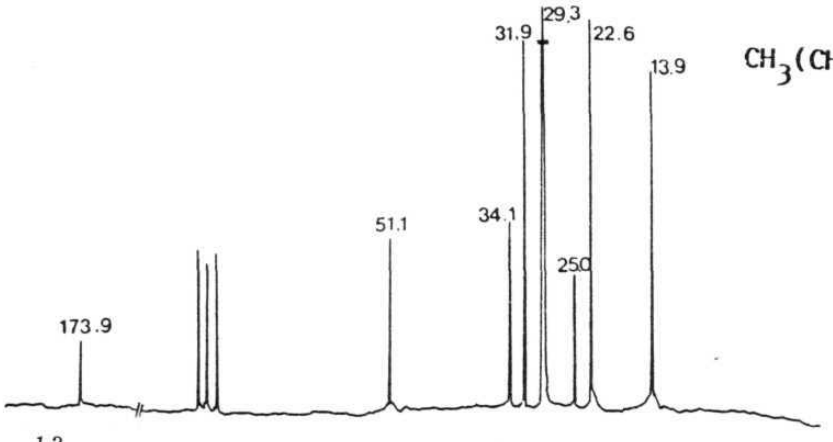
Spectrum number 1

$CH_3(CH_2)_8CH_2COOCH_3$



^1H NMR Spectrum (100 MHz, $CDCl_3$)

$CH_3(CH_2)_8CH_2COOCH_3$



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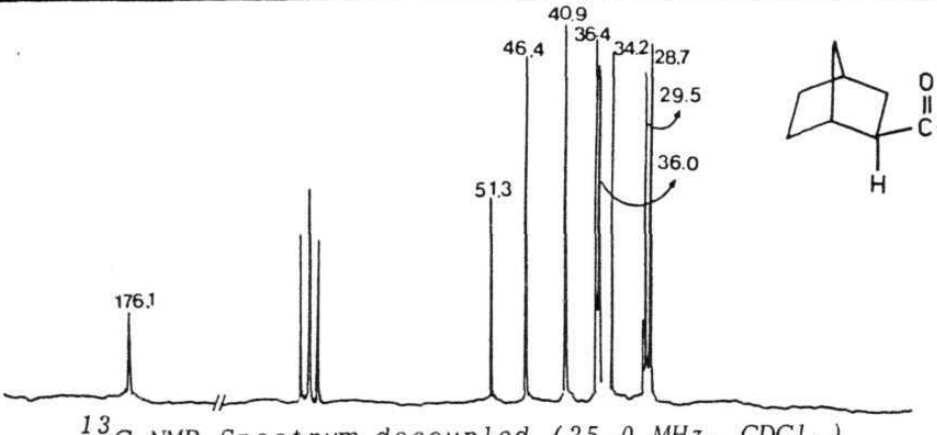

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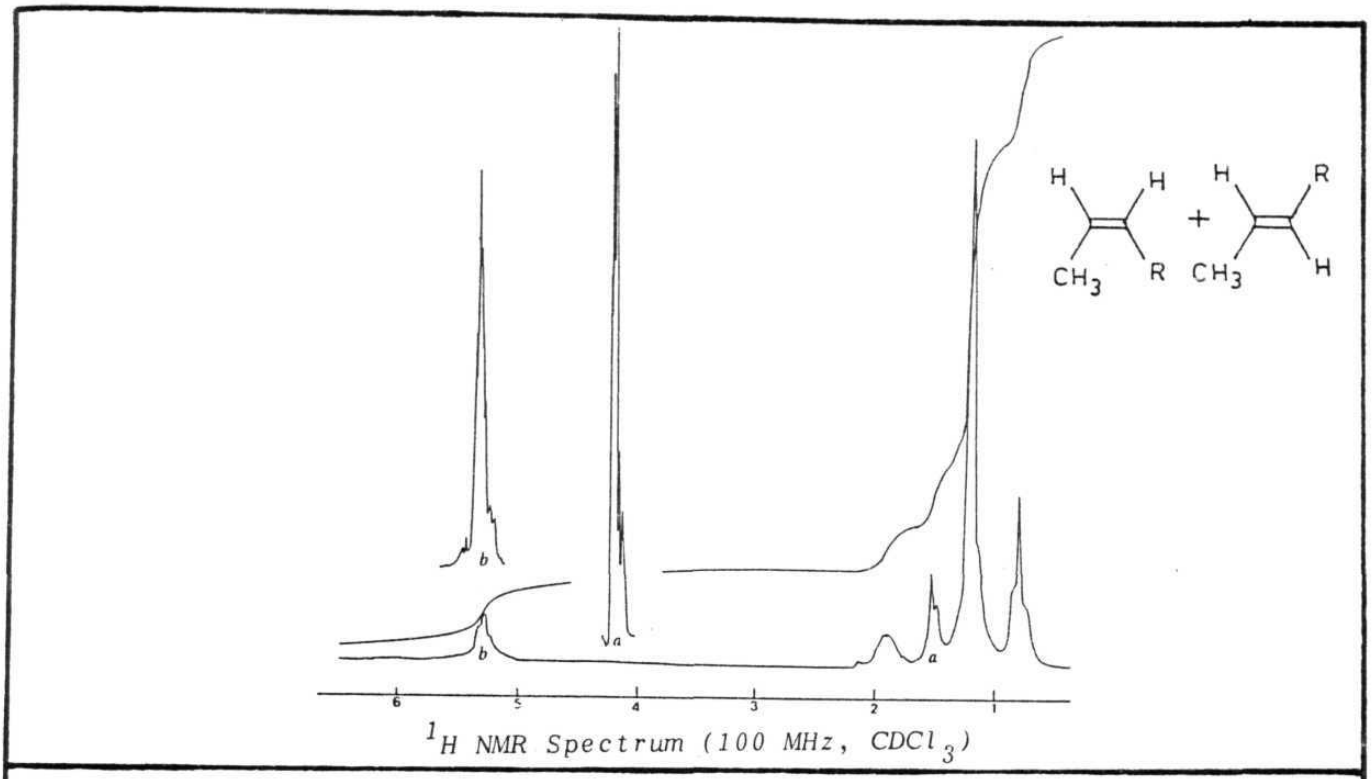

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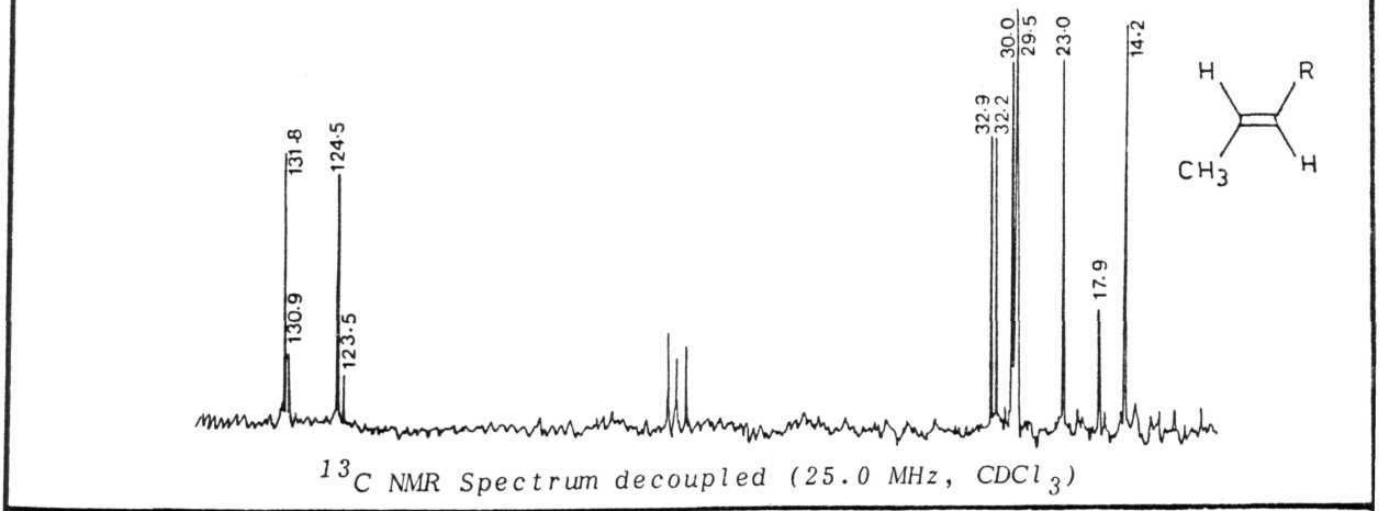

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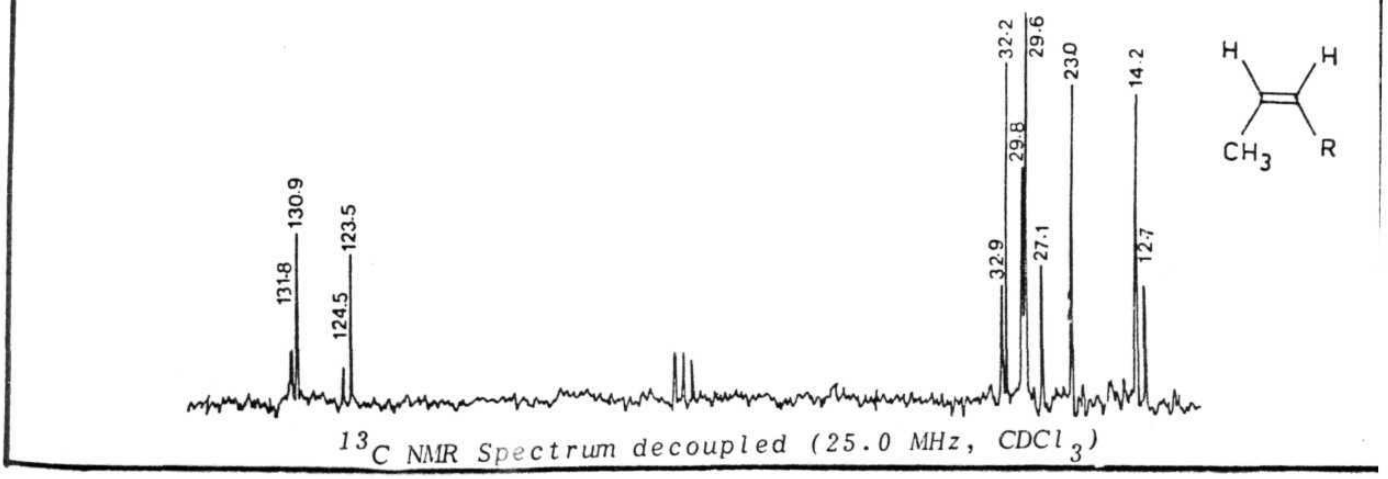

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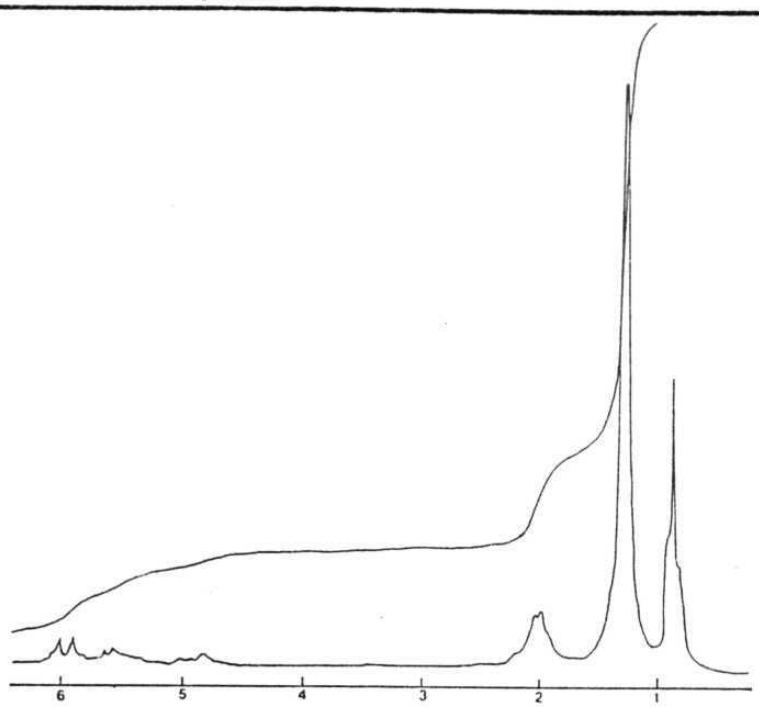
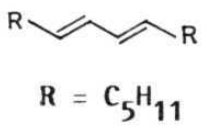
Spectrum number 3





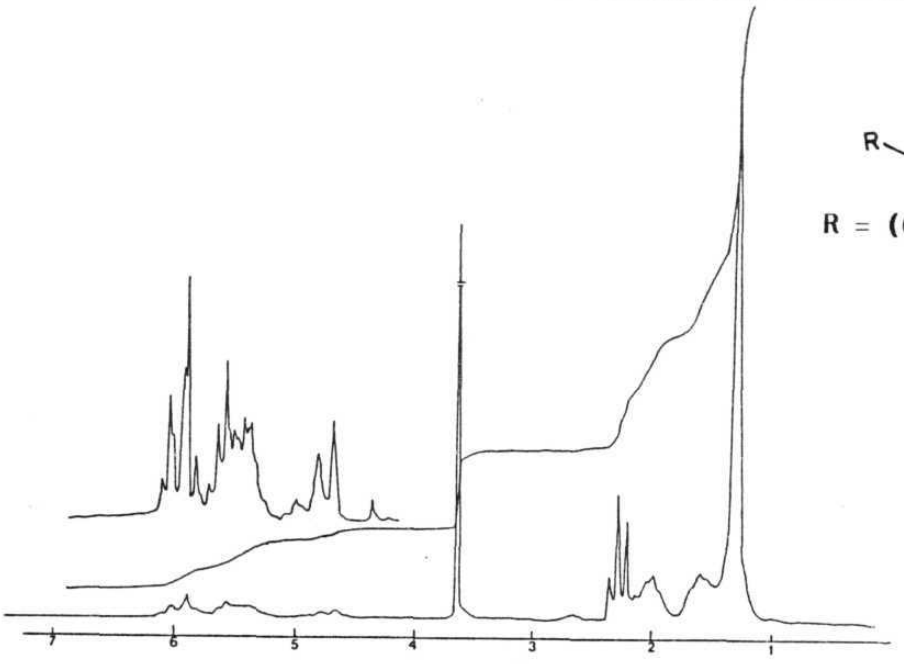
$R = C_5H_{11}$

^{1}H NMR Spectrum (100 MHz, $CDCl_3$)

^{13}C NMR Spectrum decoupled (25.0 MHz, $CDCl_3$)

^{13}C NMR Spectrum decoupled (25.0 MHz, $CDCl_3$)

Spectrum number 4



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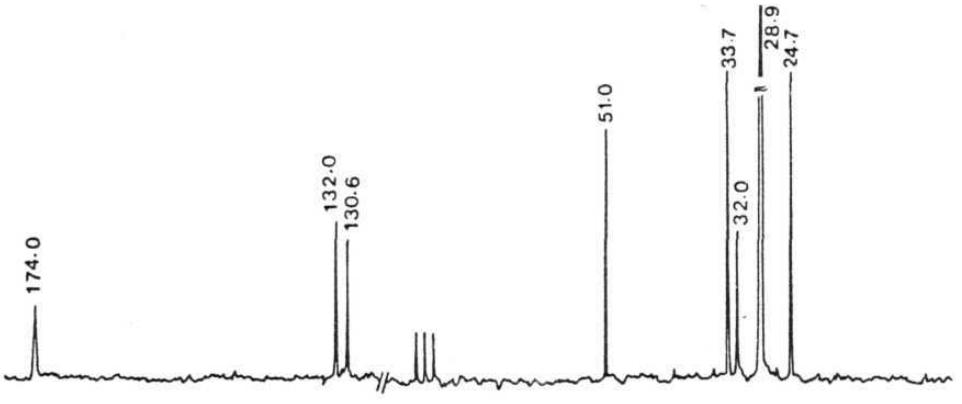

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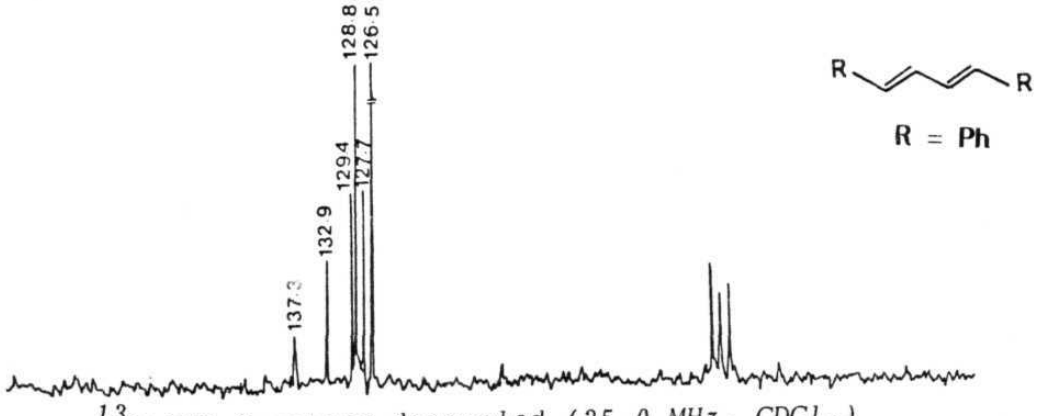

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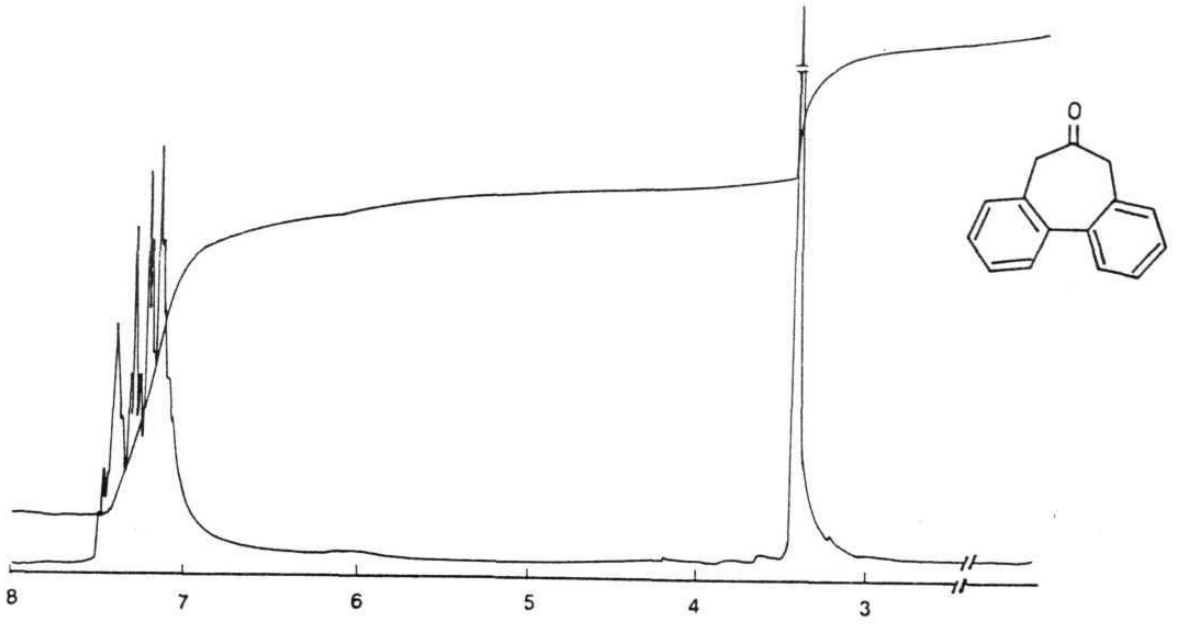
Spectrum number 5



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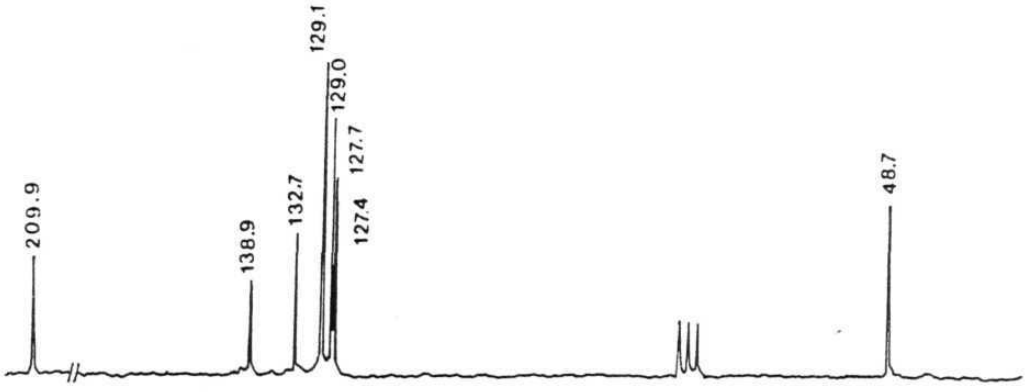
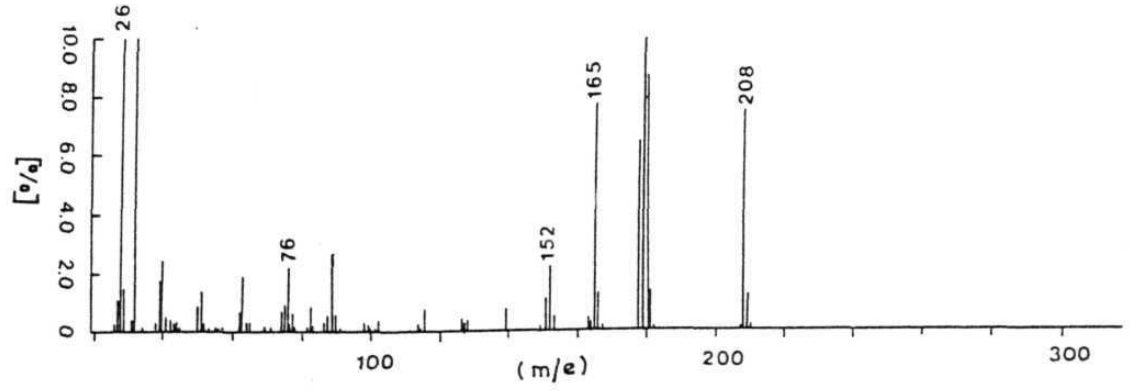
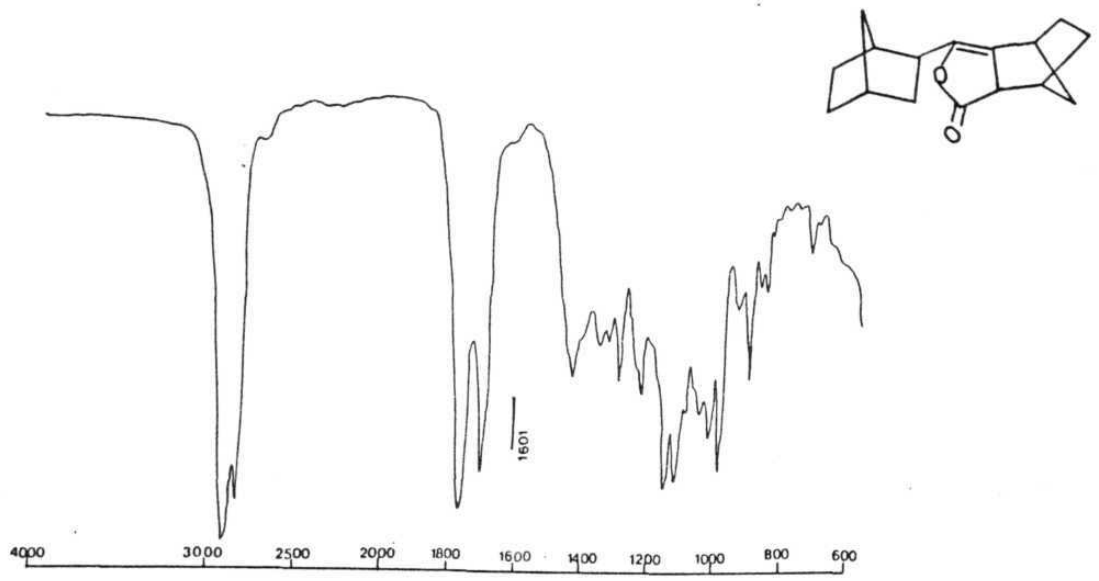


^{13}C NMR Spectrum decoupled (25.0 MHz, $CDCl_3$)

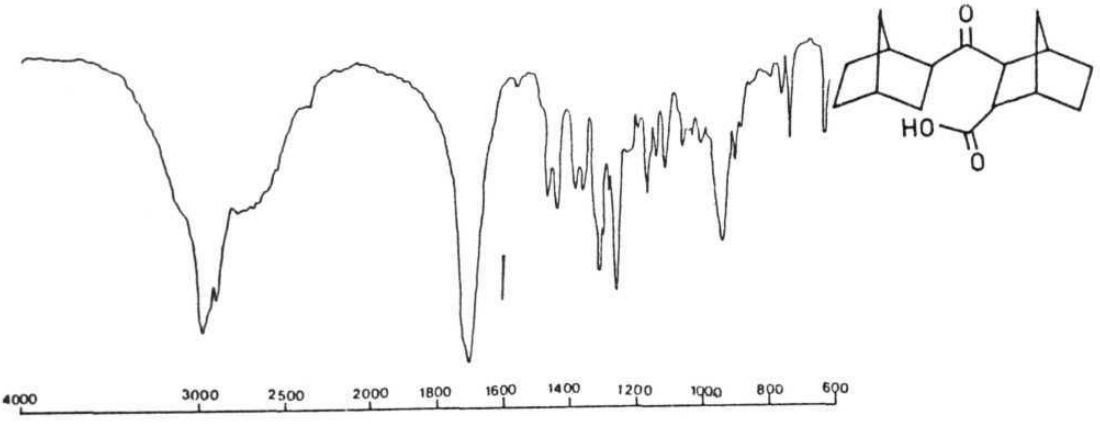


Mass Spectrum

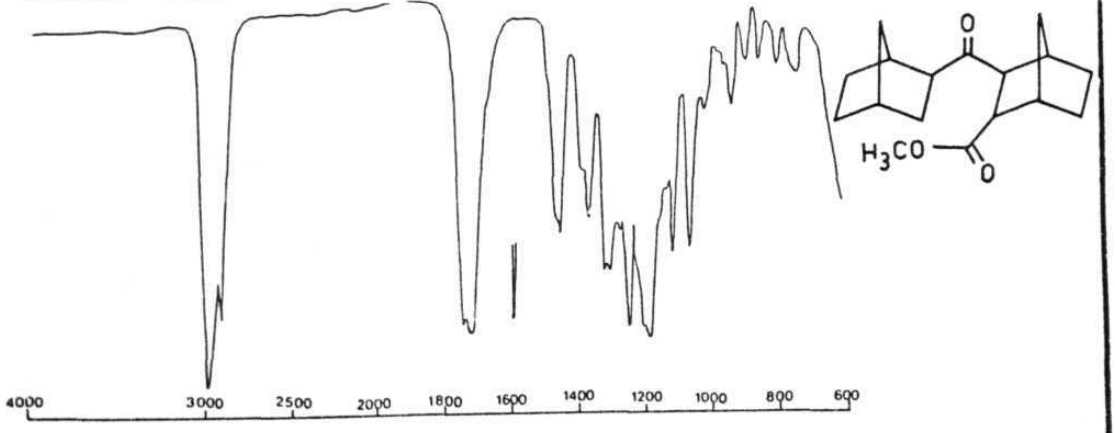
Spectrum number 6



Infrared Spectrum

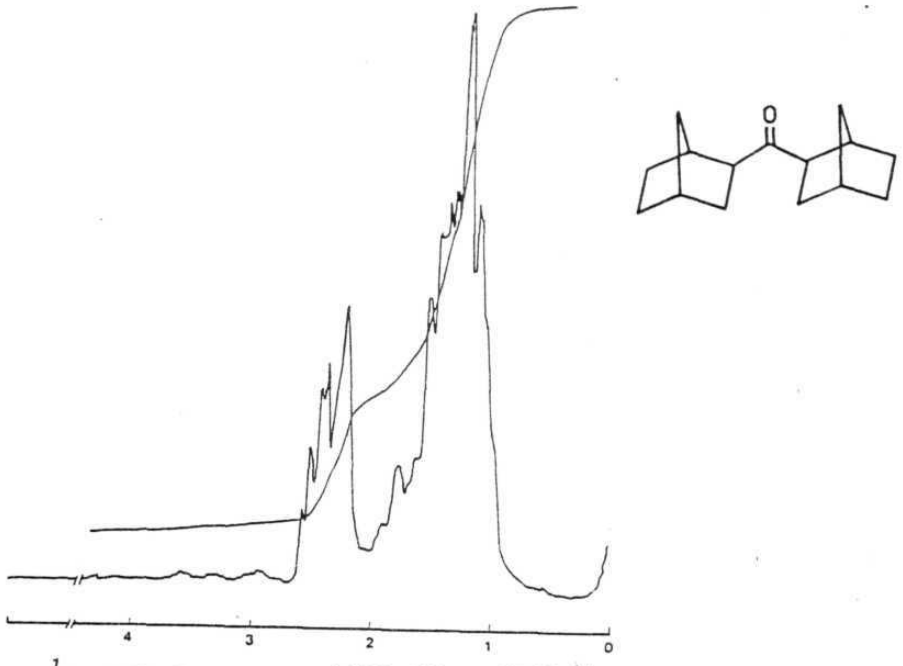


Infrared Spectrum

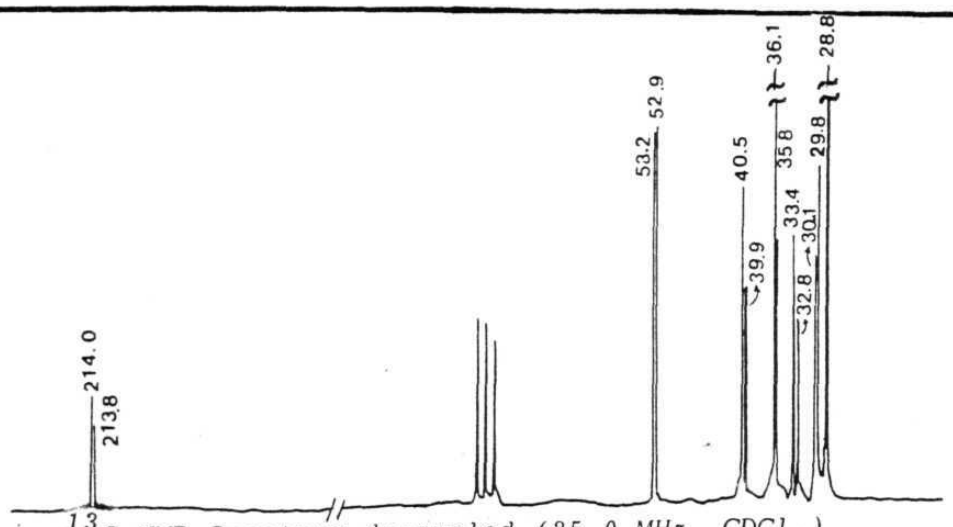


Infrared Spectrum

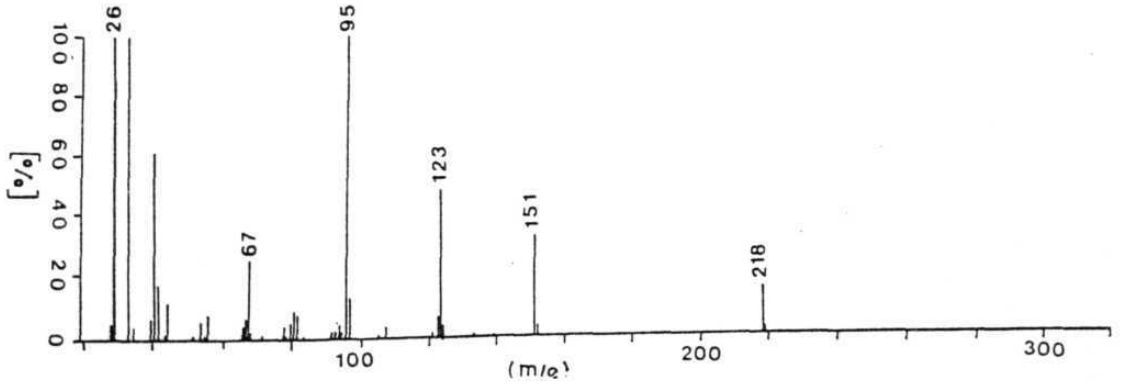
Spectrum number 7



^{1}H NMR Spectrum (100 MHz, $CDCl_3$)

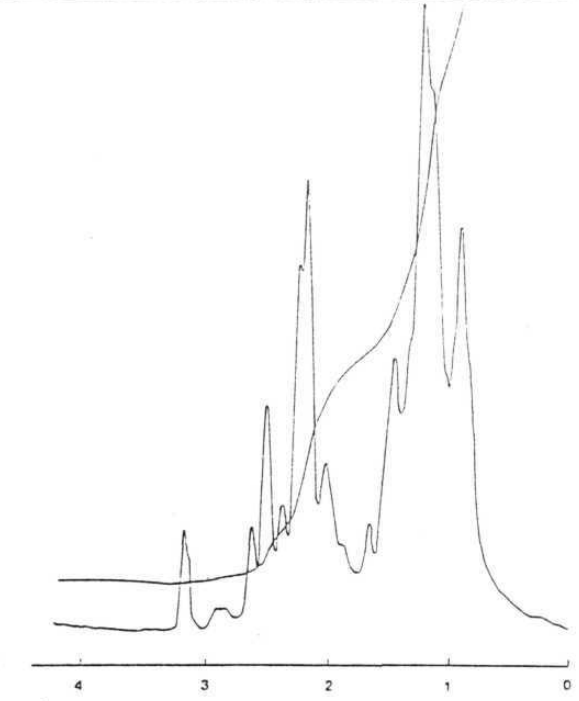


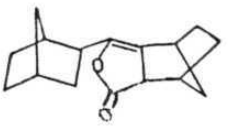
^{13}C NMR Spectrum decoupled (25.0 MHz, $CDCl_3$)



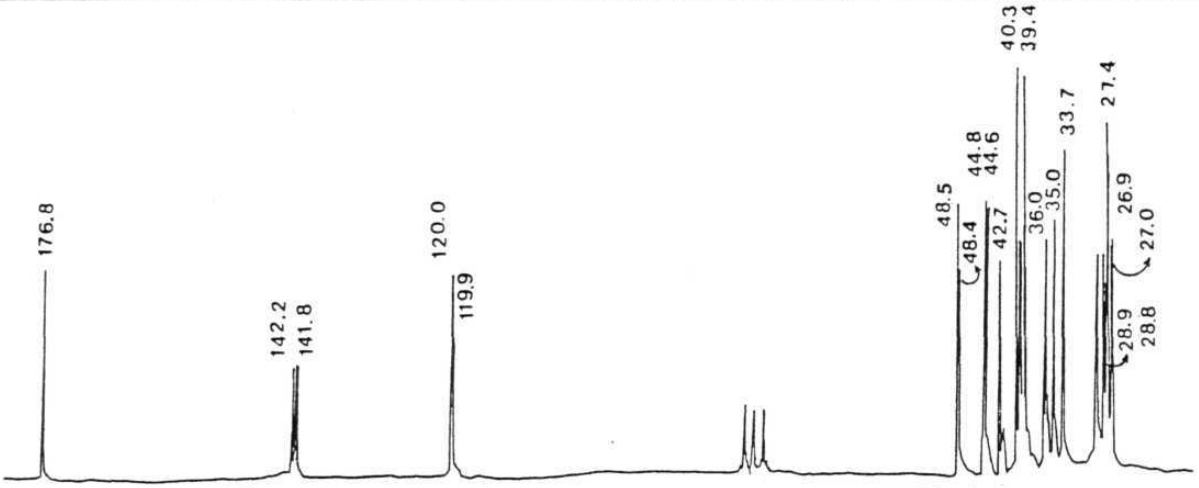
Mass Spectrum

Spectrum Number 8

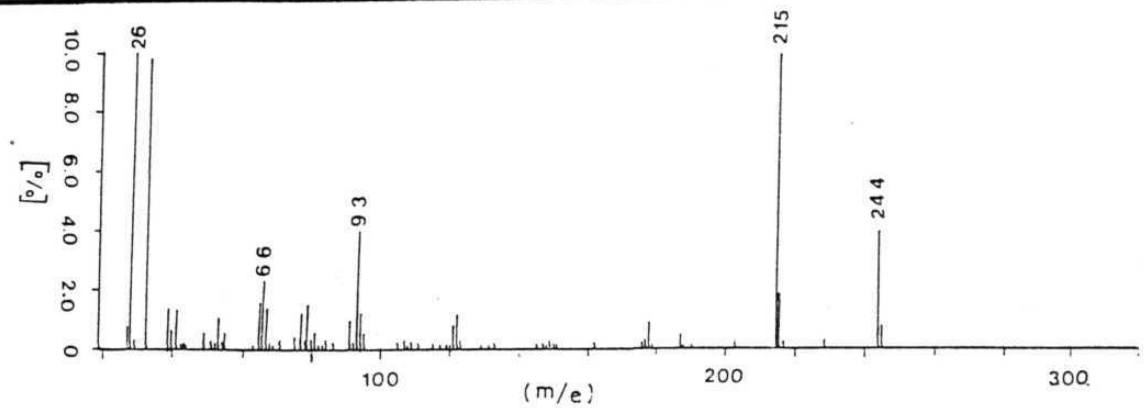




^{1}H NMR Spectrum (100 MHz, $CDCl_3$)

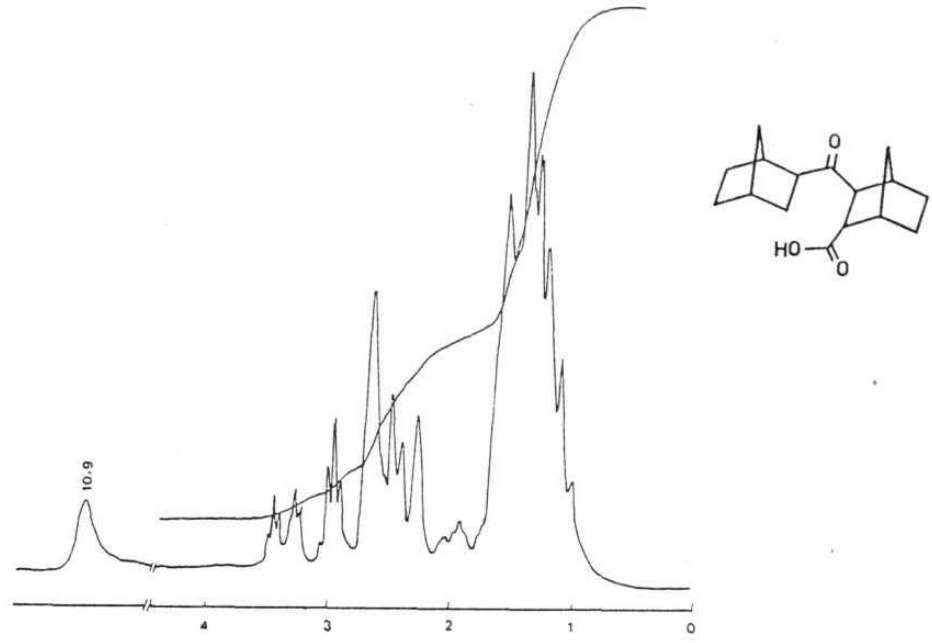


^{13}C NMR Spectrum decoupled (25.0 MHz, $CDCl_3$)

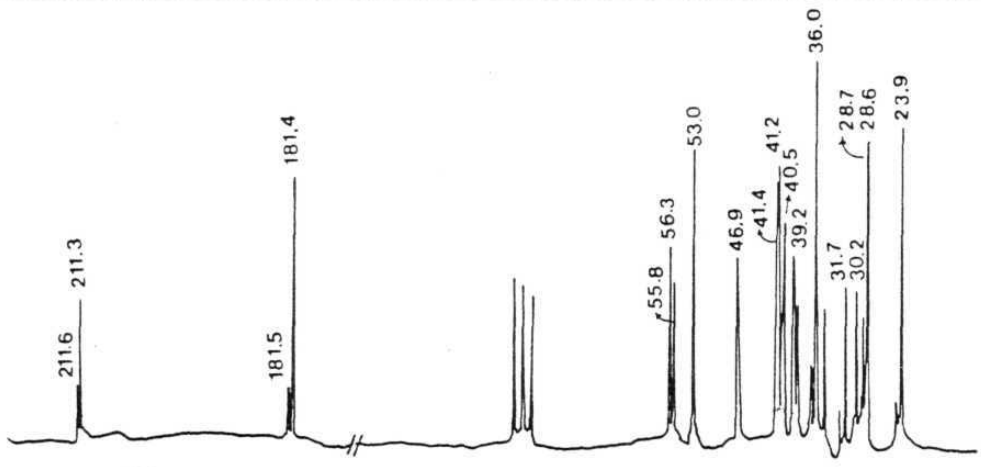


Mass Spectrum

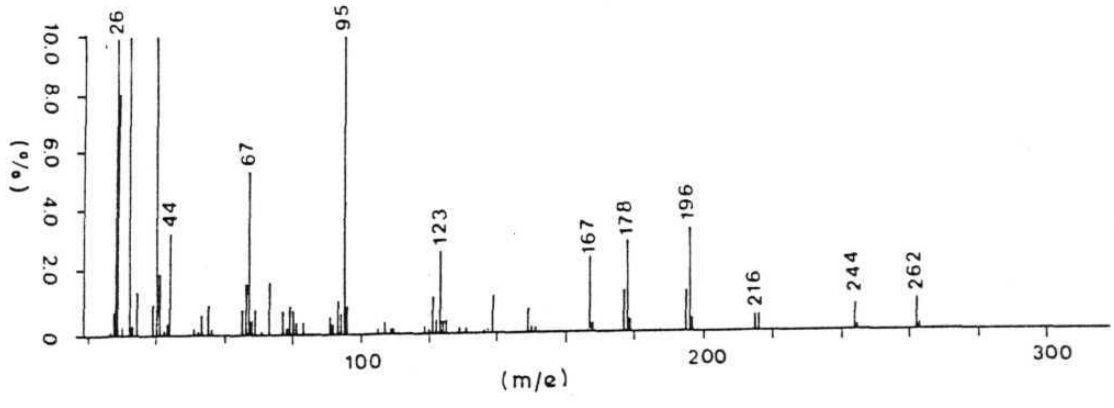
Spectrum number 9



^{1}H NMR Spectrum (100 MHz, $CDCl_3$)

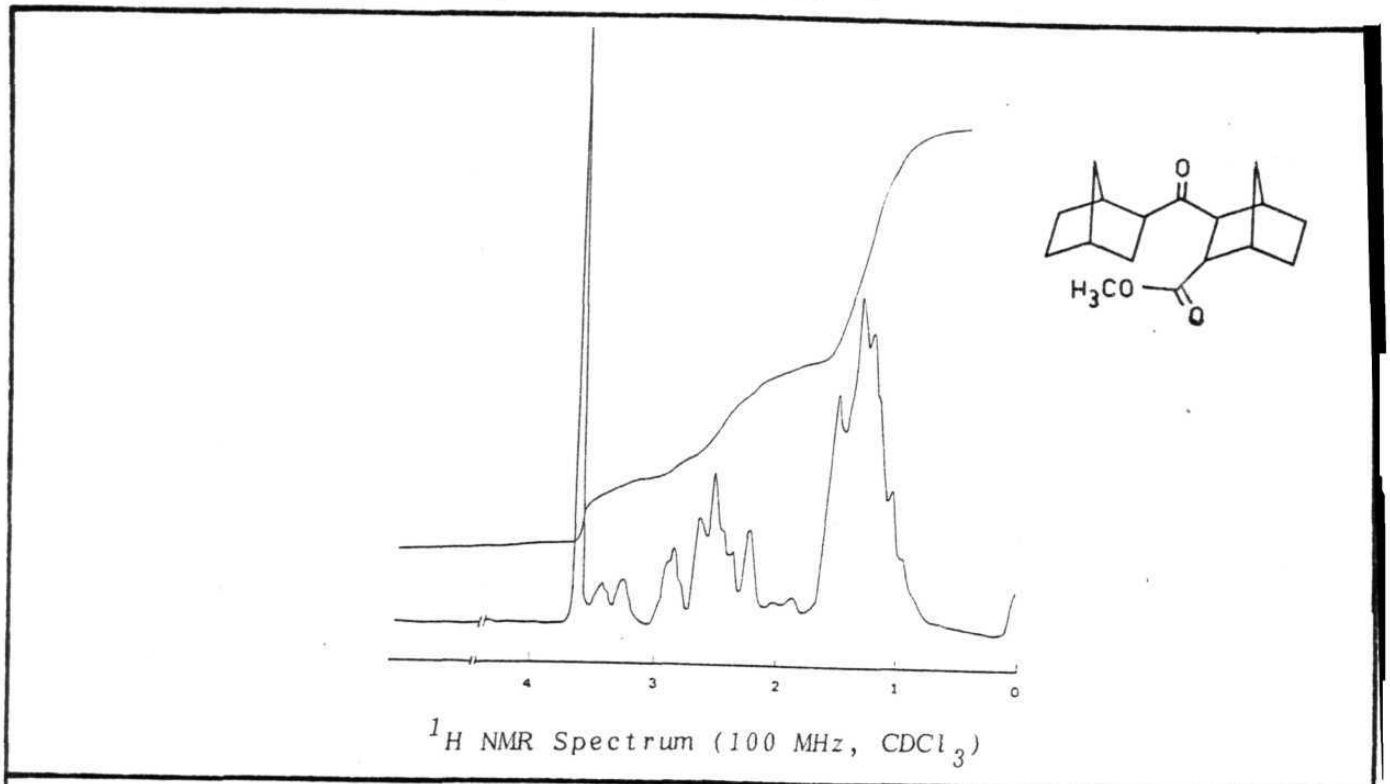


^{13}C NMR Spectrum decoupled (25.0 MHz, $CDCl_3$)

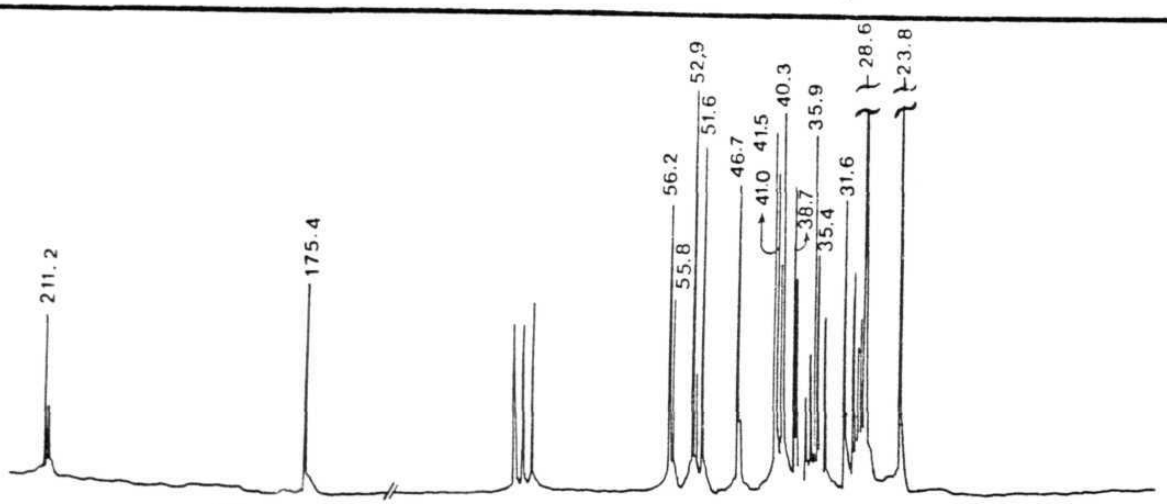


Mass Spectrum

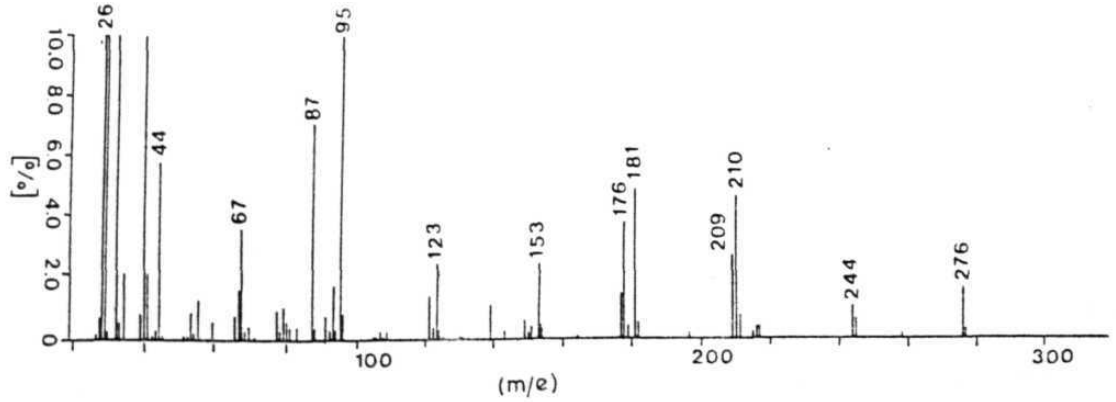
Spectrum number 10



^{1}H NMR Spectrum (100 MHz, $CDCl_3$)



^{13}C NMR Spectrum decoupled (25.0 MHz, $CDCl_3$)



Mass Spectrum

V I T A E

N. Satyanarayana was born on 20th June 1961 at Visakhapatnam (Andhra Pradesh). Following his early education at Anakapalle (Visakhapatnam Dist., Andhra Pradesh), he joined the A.M.A.L. College, Anakapalle and obtained a B.Sc. Degree from Andhra University. Later he received his M.Sc. Degree from School of Chemistry, University of Hyderabad (1981-83). He joined the Ph.D. Programme in the same School and presently continuing as a Senior Research Fellow. During the course of education, he was awarded the National Merit Scholarship and Junior and Senior Research Fellowship by the CSIR on the basis of CSIR National level test.

List of Publications :

1. Hydroboration or Hydrogenations of Alkenes with $CoCl_2/NaBH_4$.
   N. Satyanarayana and M. Periasamy, Tet., Lett., 25, 2501, **1984.**
2. Isomerization of Olefins Catalyzed by a $CoCl_2/Ph_3P/NaBH_4$ system.
   N. Satyanarayana and M. Periasamy, J. Organomet. Chem. 319, 113, **1987.**
3. A simple synthesis of trans, trans-1,3-dienes from terminal Alkynes using $CoCl_2/Ph_3P/NaBH_4$.
   N. Satyanarayana and M. Periasamy, Tet. Lett., 27, 6253, **1986.**
4. Carbonylation of Benzyl Halides using $CoCl_2/NaBH_4/CO/NaOH$ reagent system.
   N. Satyanarayana and M. Periasamy, Tet. Lett., 28, 2633, **1987.**
5. Novel Reactivities of Low Valent Cobalt Reagent Generated using $CoCl_2/NaBH_4/C_2H_5OH$ system in the presence of CO.
   N. Satyanarayana and M. Periasamy, J. Organomet. Chem. 333, C33, **1987.**

6. A Convenient Method for Reduction of Imines and Enamines with $MX_2/NaBH_4$(M= Co or Ni) under Mild Conditions.

   M. Periasamy, A. Devasagayaraj, N. Satyanarayana and C. Narayana, Communicated.

7. A Novel Carbonylation Reaction of Strained Alkenes Utilizing $CoCl_2/CH_3OH/NaBH_4/CO$ Reagent System.

   N. Satyanarayana and M. Periasamy,

   Communicated.