NEW SYNTHETIC METHODS VIA TRANSITION METAL ORGANOMETALLIC REAGENTS GENERATED UTILIZING COMBINATIONS OF MX_n - $NaBH_4$, MgH_2, RMgX AND MAGNESIUM

A THESIS
SUBMITTED FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY

By
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TO

MY MOTHER

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STATEMENT

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

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

31.8.88

S. ACHYUTHA RAO

CERTIFICATE

Certified that the work contained in this thesis entitled "NEW SYNTHETIC METHODS VIA TRANSITION METAL ORGANOMETALLIC REAGENTS GENERATED UTILIZING COMBINATIONS OF MX_n-$NaBH_4$, MgH_2, RMgX AND MAGNESIUM" has been carried out by Mr. S. Achyutha Rao, under my supervision and the same has not been submitted elsewhere for a degree.

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31/

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D E A N
SCHOOL OF CHEMISTRY

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S. ACHYUTHA RAO

ABBREVIATIONS

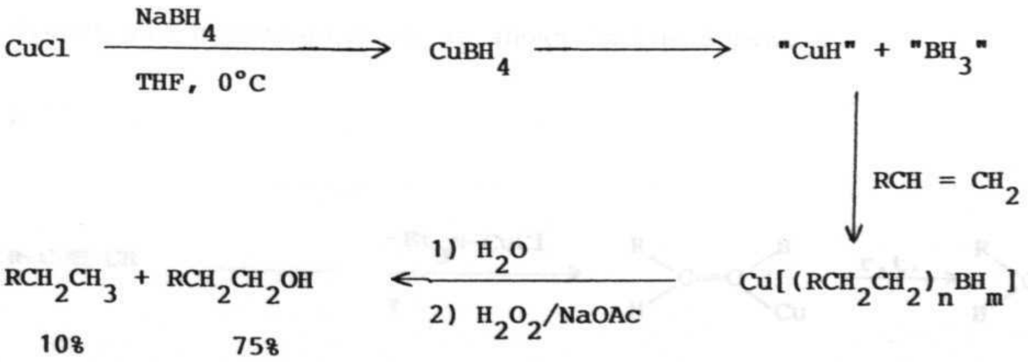
AcAc	acetylacetonate anion
Ac	acetyl
OAc	acetoxy
Am	amyl
NBS	N-bromosuccinimide
Bu	butyl
cat	catalyst
Cp	π-cyclopentadienyl, $n^5-C_5H_5$
C_5Me_5	π-pentamethyl cyclopentadienyl
DBE	1,2-dibromoethane
DME	1,2-dimethoxyethane
DMF	N,N-dimethylformamide
DMS	dimethyl sulfide
DMSO	dimethyl sulfoxide
DBU	1,5-diazabicyclo[5,4,0]undec-7-ene
EE	diethyl ether
Et	ethyl
HMPA	hexamethylphosphoric acid triamide
X	halide
i	iso
LAH	lithium aluminium hydride
L	any unidentate ligand
MeOH	methanol
M	Metal
Me	methyl
n	primary
Pr	propyl
s	secondary
TEA	triethyl amine
t	tertiary
THF	tetrahydrofuran

ABSTRACT

This thesis deals with the development of new synthetic methods via transition metal organometallic reagents, generated utilizing combinations of transition metal complexes with $NaBH_4$, MgH_2, RMgX and magnesium. It comprises of three chapters. Each chapter is subdivided into three parts: Introduction, Results and Discussion and Experimental section along with references. The work described in this thesis is exploratory in nature and the chapters are arranged in the order the investigations were executed.

The first chapter describes investigations on the hydrocupration and carbocupration reactions of alkynes. In the introduction part, various methods available for the preparation of organocopper reagents, some of their important applications and carbocupration of 1-alkynes are briefly discussed. Various methods available for the preparation of copper(I) hydride reagents and their applications are also briefly reviewed. It was observed that the reagent system, $CuCl/NaBH_4$ in the presence of olefin in THF provides a copper(I)alkylborohydride reagent via hydroboration-comproportionation (Scheme 1).

Scheme 1



$$\begin{tikzcd}
CuCl \arrow[r, "NaBH_4", "THF,\ 0^\circ C"'] & CuBH_4 \arrow[r] & \text{"CuH"} + \text{"BH}_3\text{"} \arrow[d, "RCH = CH_2"] \\
\underset{10\%}{RCH_2CH_3} + \underset{75\%}{RCH_2CH_2OH} & & Cu[(RCH_2CH_2)_nBH_m] \arrow[ll, "1)\ H_2O", "2)\ H_2O_2/NaOAc"']
\end{tikzcd}$$

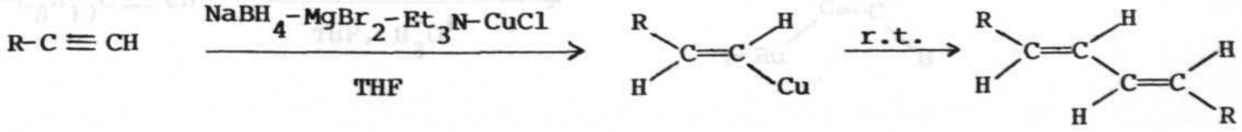
Formation of the reduced product after oxidation of the reaction mixture indicates that the reagent system is able to give copper(I)alkylborohydrides with alkenes. Utilization of the copper(I)alkylborohydride reagent, prepared as shown in Scheme 1, in the 1,4-alkylation of α,β-unsaturated esters afforded very low yields of alkylated ester along with some alkylated aldehyde (Scheme 2).

Scheme 2

$$\mathrm{Cu[(RCH_2CH_2)_nBH_m]} \xrightarrow[\text{2) } \mathrm{H_2O}]{\text{1) } \mathrm{CH_2{=}CHCO_2Me}} \underset{5\%}{\mathrm{R{-}CH_2CH_2CH_2CH_2CO_2Me}} + \underset{5\%}{\mathrm{RCH_2CH_2CH_2CH_2CHO}}$$

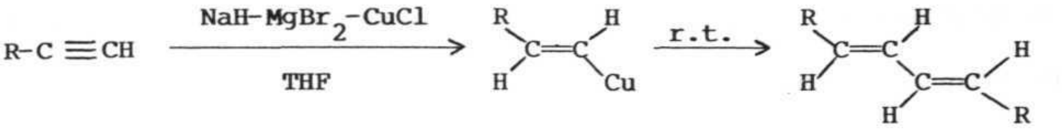
Attempts to optimize the conditions for obtaining better yields of the alkylated products were not successful under various experimental conditions. It is likely that the transfer of hydride dominates over that of the alkyl group in this case. Accordingly, we turned our attention towards efforts to utilize copper(I) hydride species, generated by the decomposition of $CuBH_4$, for direct hydrocupration of 1-alkenes and 1-alkynes. It has been observed that the reagent system $NaBH_4$-$MgBr_2$-Et_3N-CuCl, converts terminal alkynes into the corresponding (E,E)-1,3-dienes via hydrocupration as shown in the Scheme 3.

Scheme 3



It was also observed that the reagent system NaH-$MgBr_2$-CuCl, converts some terminal alkynes into the corresponding (E,E)-1,3-dienes which constitutes a simple method for the conversion of 1-alkynes into symmetrical (E,E)-1,3-dienes (Scheme 4).

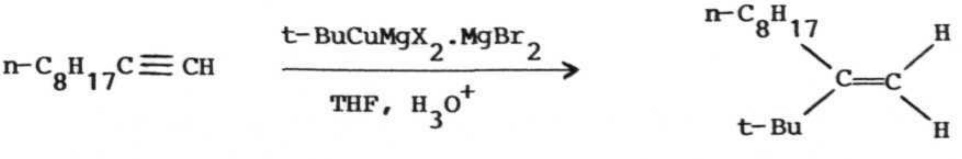
Scheme 4



However, attempts to utilize the vinylcopper intermediates for further transformations were unsuccessful since the hydrocupration does not take place at lower temperatures. Attempts to stabilize the vinylcopper intermediates at room temperature (∼25°C) were not successful.

During the course of the studies on hydrocupration, it has been observed that the less reactive 1-alkynes (eg.1-decyne) which do not undergo carbocupration with branched alkylcuprate reagents, can be made to undergo carbocupration with the reagent system RMgX/CuCl (1:1) (R=t-Butyl, t-amyl and isopropyl) in the presence of excess $MgBr_2$ (Scheme 5).

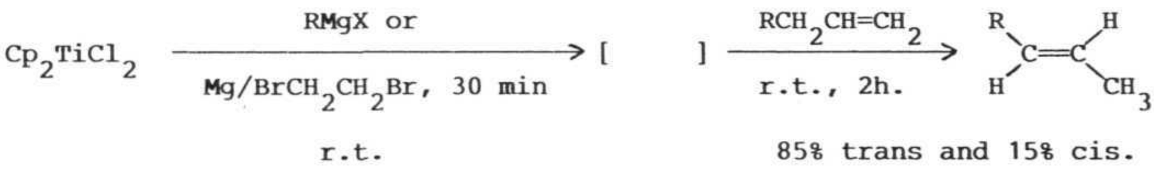
Scheme 5



The 2nd chapter describes the investigations on the reactivities of low valent titanium reagents generated utilizing the Mg/$BrCH_2CH_2Br$

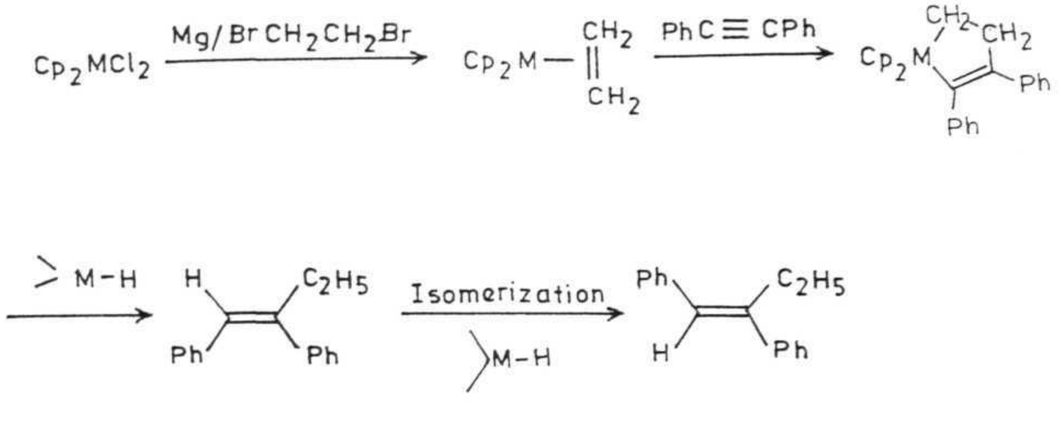
system. This investigation is an offshoot of the results outlined in the first chapter. The methods of generation of organotitanium reagents by the treatment of $TiCl_4$ and Cp_2TiCl_2 species with RM (or R_2M) and reducing agents such as alkali metals, alkalimetal naphthalenides and magnesium-amalgam, and the reactivities of these reagents with various organic substrates were discussed in the introductory section. "Titanocene" or its equivalent was generated in situ by the reaction of Cp_2TiCl_2 with iso-butyl or t-butylmagnesium halides or with Grignard grade magnesium and 1,2-dibromoethane in THF at room temperature. It has been observed that this system isomerizes 1-alkenes into predominantly trans-2-alkenes (Scheme 6).

Scheme 6



Later, it was found that the reduction of Cp_2MCl_2 (M=Ti, Zr) with Grignard grade magnesium and 1,2-dibromoethane in THF at 0°C gives the corresponding metallocene-ethylene complex along with the hydride species formed by the decomposition of "titanocene" or "zirconocene". Presence of these species are indicated by the reaction of this reagent with diphenylacetylene to give 1,2-diphenyl-(E)-1-butene (Scheme 7).

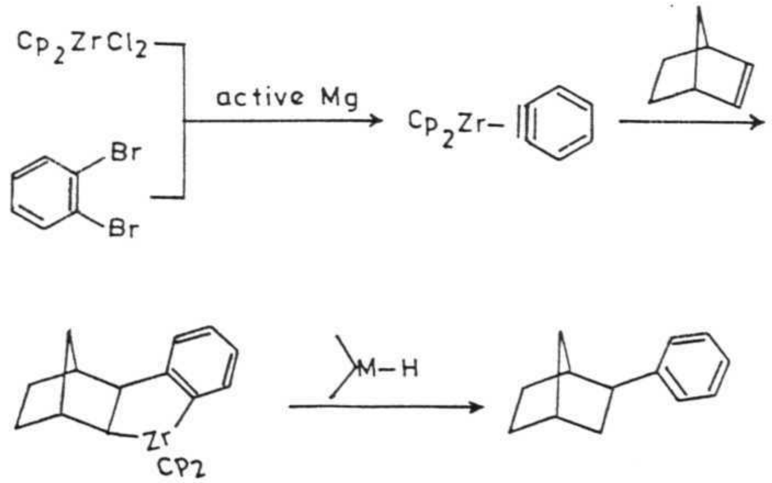
Scheme 7



Also, cis-stilbene isomerizes to trans-stilbene under the present reaction conditions.

Reduction of Cp_2ZrCl_2 with active magnesium in the presence of 1,2-dibromobenzene in THF at -24°C gives the corresponding zirconocene-benzyne complex as indicated by the incorporation of phenyl group into norbornene (Scheme 8).

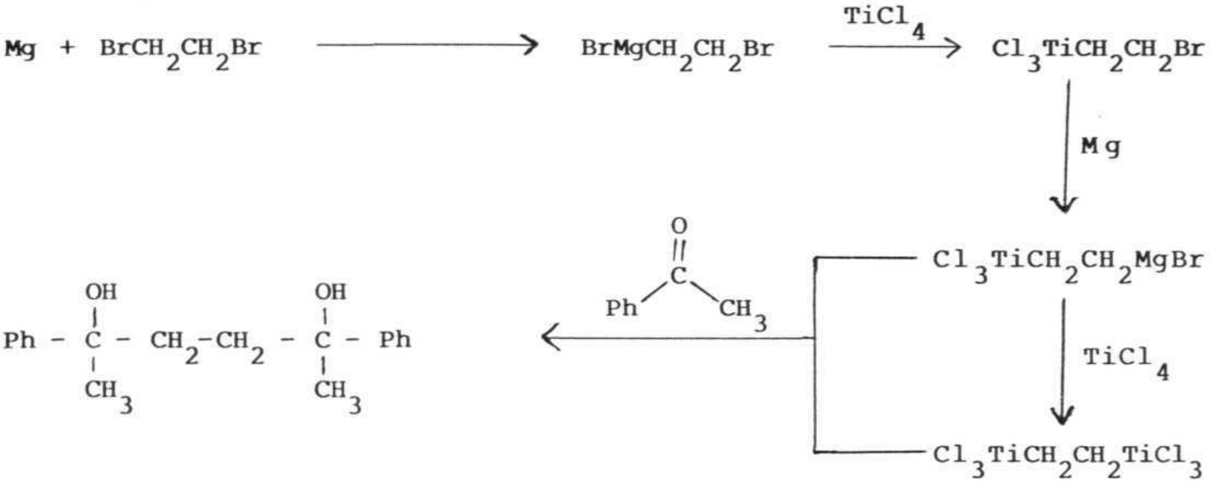
Scheme 8



Unfortunately, attempts to utilize the metallocycles prepared in this way in reactions with electrophiles (eg. D_2O) and CO were not successful since they undergo facile reductive cleavage to give the corresponding hydrocarbons.

It was of interest to study the reactivity of the $TiCl_4/Mg/BrCH_2CH_2Br$ system itself. It was observed that this system gives a 1,2-diorganometallic species which converts some ketones into the corresponding 1,4-diols (Scheme 9).

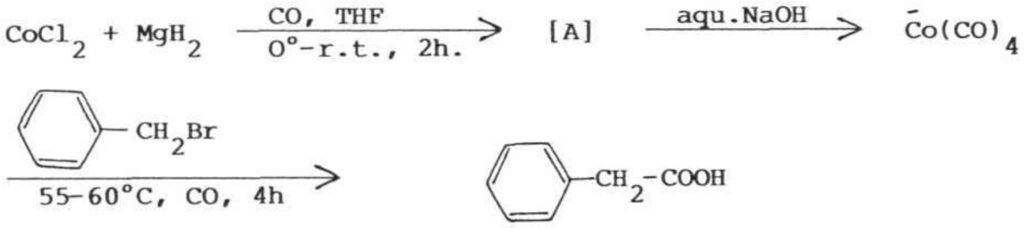
Scheme 9



The last chapter of the thesis deals with the exploratory studies on the reactivities of the reagent systems generated by the reaction of MgH_2 with some first row transition metal complexes towards alkenes and alkynes. This study was undertaken in order to have a broad view about the reactivities of these systems. The reports on the reactivities of the transition metal halides-$LiAlH_4$, transition metal complexes-NaH/NaOR and transition metal complexes-MgH_2 systems towards organic substrates were briefly reviewed in the introduction. It was observed that the reagent system generated utilizing MgH_2, prepared using $MgBr_2$ and NaH, and Cp_2MCl_2 (M=Ti, Zr), are capable of reducing 1-alkenes and 1-alkynes to the corresponding alkanes and/or 1-alkenes. The reagent systems generated utilizing MgH_2 and $CrCl_3$, $FeCl_3$, $CoCl_2$ and $NiCl_2$ are promising for the reduction of 1-alkenes to the corresponding alkanes although small amounts of 2-alkenes are produced in some cases. Several of these reagents polymerize 1-alkynes.

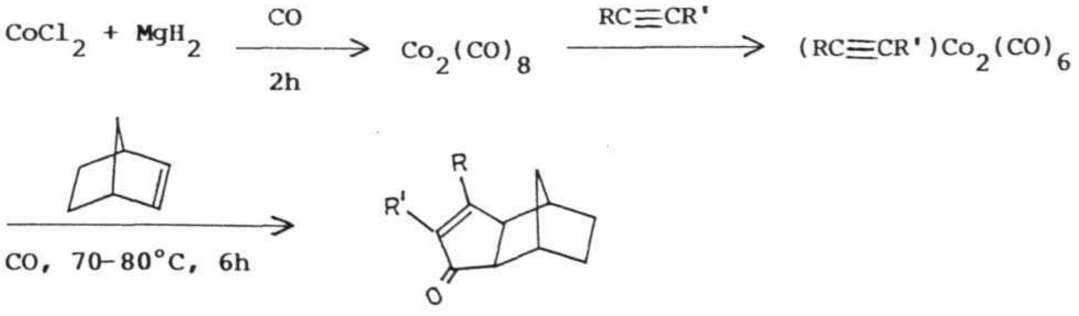
The reactivities of the MX_n ($CoCl_2$, $FeCl_3$, $CrCl_3$)/MgH_2 reagents prepared under carbon monoxide atmosphere also were examined. It was found that a cobalt carbonyl derivative (A) which reacts with aqueous NaOH to give $\bar{C}o(CO)_4$, is formed in the reaction of $CoCl_2/MgH_2$ system in THF under carbon monoxide atmosphere. The $\bar{C}o(CO)_4$ formation in this way was confirmed by the conversion of benzyl bromide into the corresponding phenylacetic acid (Scheme 10), a well-known reaction of $\bar{C}o(CO)_4$.

Scheme 10



The cobalt carbonyl "A", generated in this way readily forms a complex with 1-decyne. This was confirmed by i.r. spectral studies of the resulting complex and also the ability of the alkyne complex to undergo the Pauson-Khand cyclization with norbornene (Scheme 11).

Scheme 11



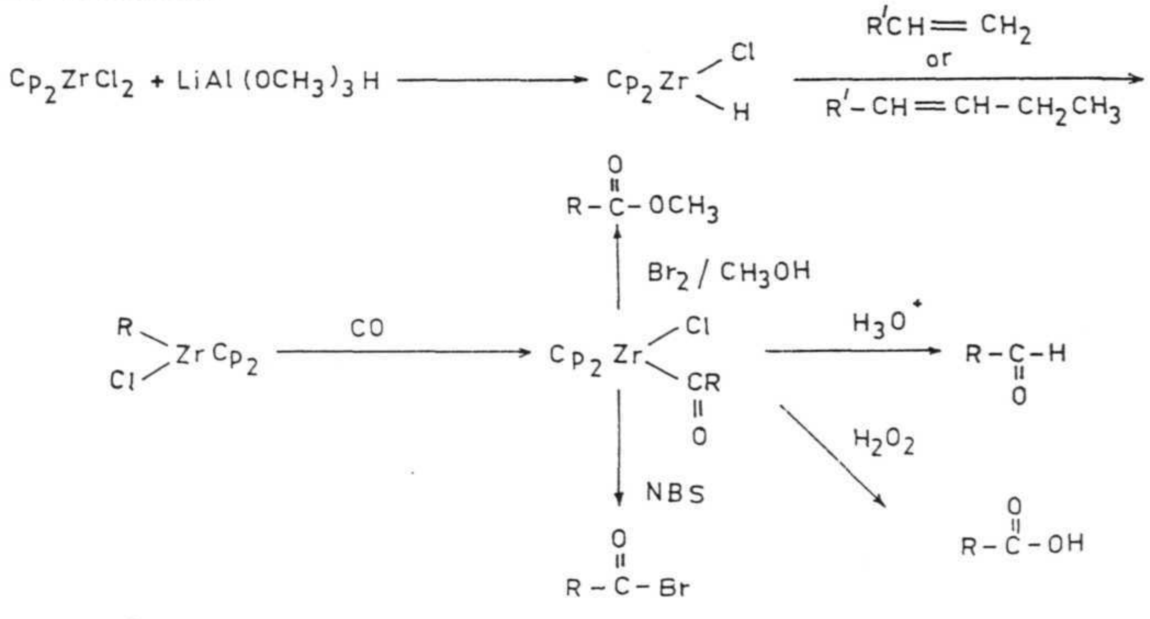
$R = R' = Ph, C_3H_7$

$R' = C_8H_{17}, Ph, R = H$

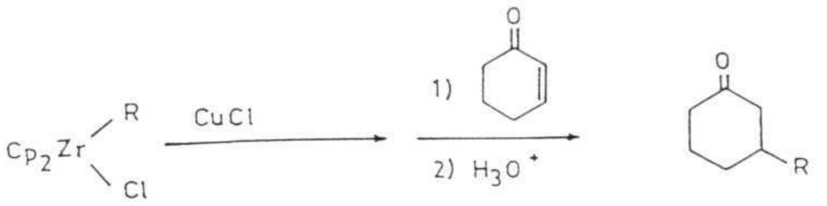
Although dicobalt octacarbonyl, $Co_2(CO)_8$, is commercially available, this simple one pot procedure for its preparation from the readily available bench-top chemicals should make this procedure attractive since the problems involved in the handling and storing of the metal carbonyls can be alleviated by preparing the reagents in situ in the reaction mixture. Infrared spectral studies of the products obtained with the $FeCl_3/MgH_2/CO$ and $CrCl_3/MgH_2/CO$ systems indicate that these systems also give metal carbonyl derivatives. However, these carbonyls failed to react with alkenes and alkynes.

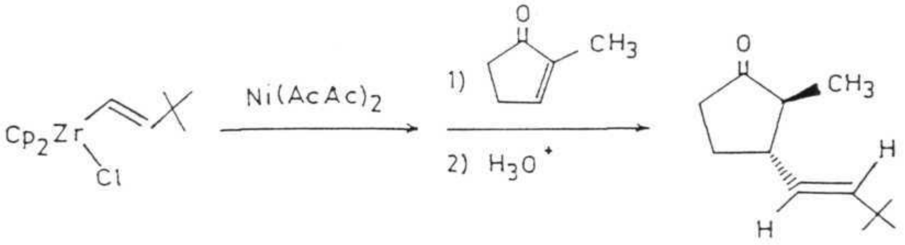
GENERAL INTRODUCTION

In recent years, there has been immense interest in the utilization of transition metal organometallic reagents for organic synthesis.[1] Several of these reagents can be readily generated in situ for utilization by the reaction of appropriate transition metal complexes with Grignard reagents, RMgX, or organolithium reagents, RLi.[1] It was of interest to explore the possibility of developing transition metal organometallic reagents without utilizing these somewhat carbanionic reagents. Several such methods have been developed in the last two decades. For example, the hydrozirconation of alkenes and alkynes with the $Cp_2Zr(H)Cl$ reagent, prepared utilizing Cp_2ZrCl_2 and $LiAlH_4$ or $LiAl(OCH_3)_3H$, readily gives organozirconium reagents which have a wide variety of applications in synthesis.[2]

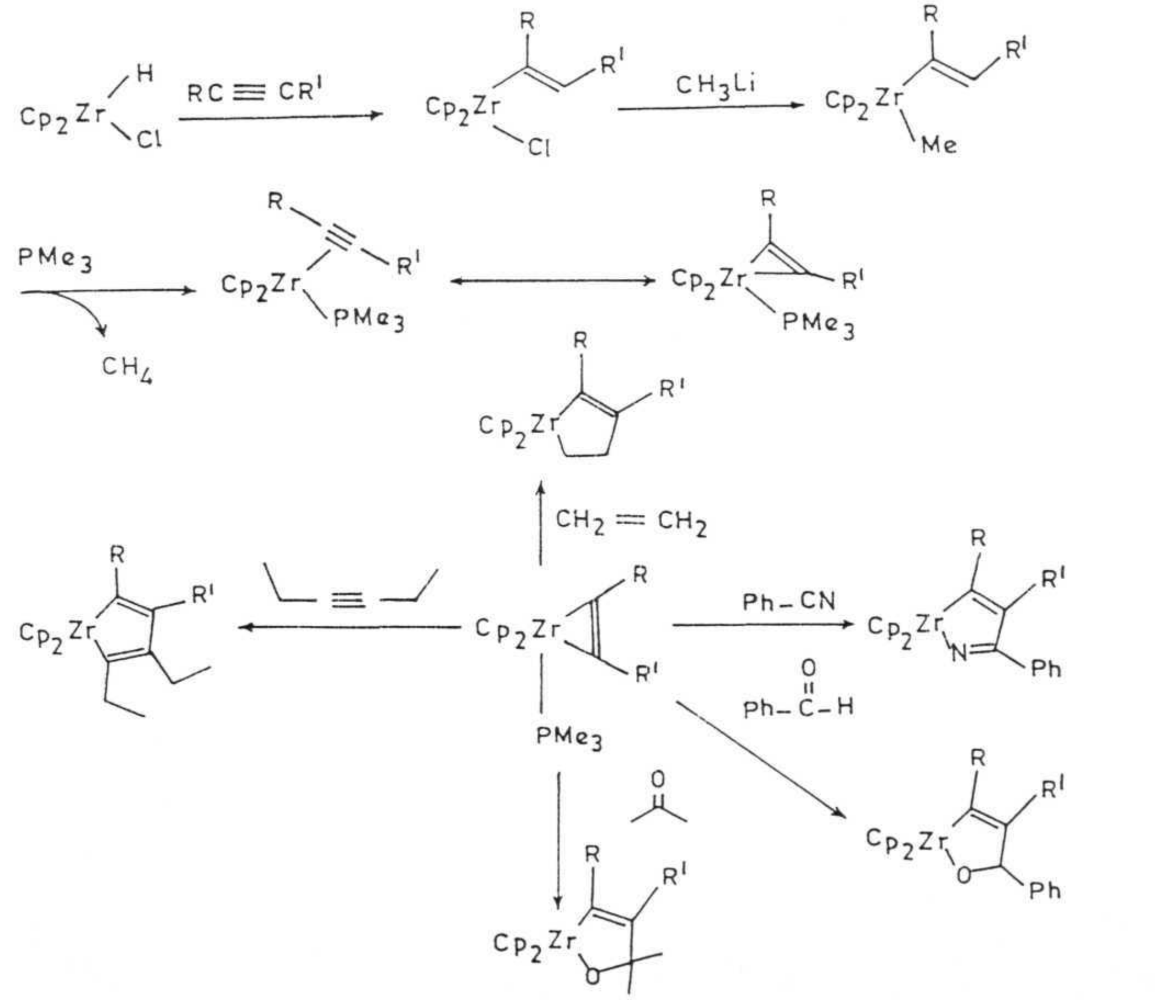


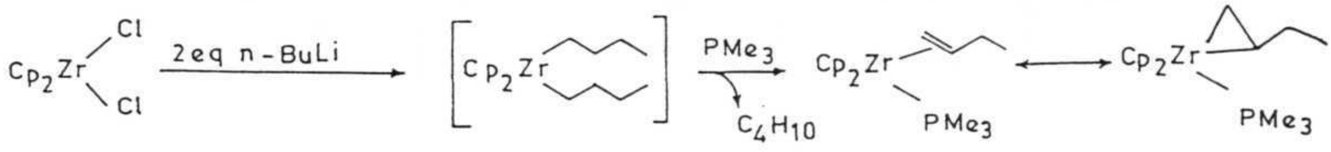
The alkyl group in the zirconium reagent can be readily transferred to copper and nickel complexes which in turn can be utilized for conjugate alkylations.[3,4]



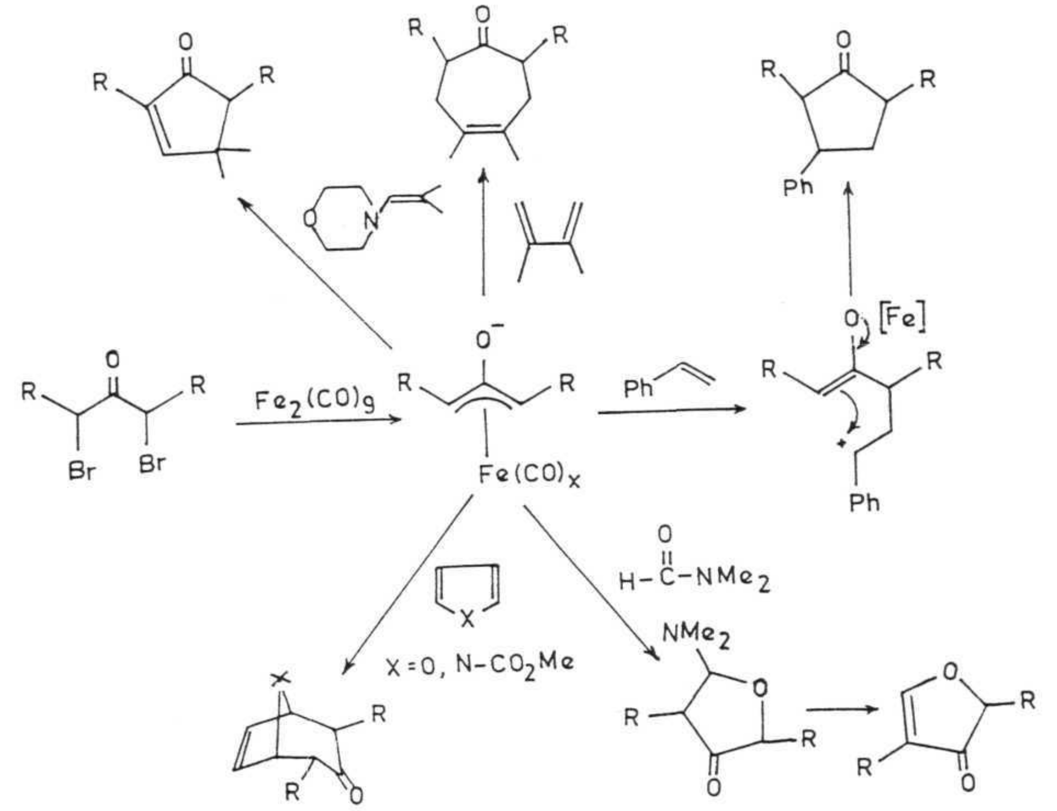


Recently, the organozirconium reagents prepared in this way have been utilized for the synthesis of the corresponding alkyne and alkene complexes which have been shown to undergo many interesting reactions.[5]

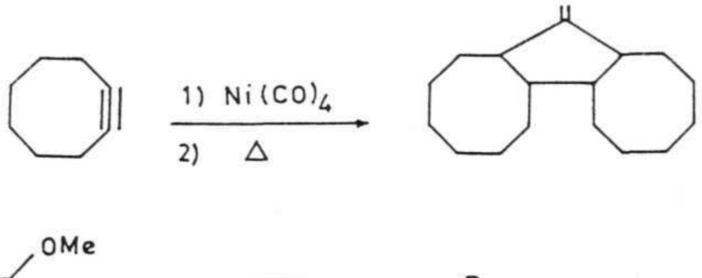


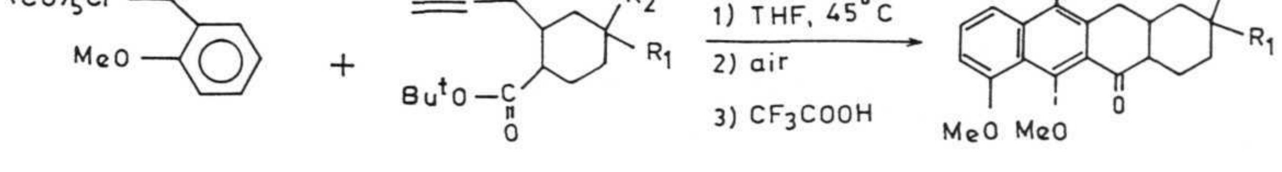


The carbonyl derivatives of Cr, Mn, Fe, Co and Ni have been shown to have many useful applications in organic synthesis.[1] For example, $Fe_2(CO)_9$ reacts with 1,3-dibromocarbonyl compounds to give a new complex which gives several interesting transformations.[6-9]

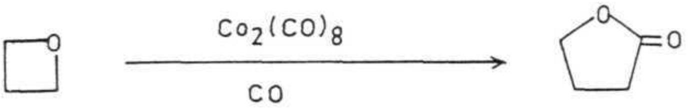


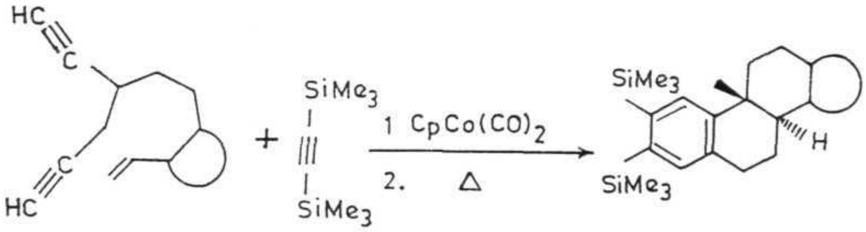
The carbonyl derivatives of nickel,[10,11] chromium,[12] manganese,[13] and cobalt[14,15] have been utilized in many useful transformations.[1]



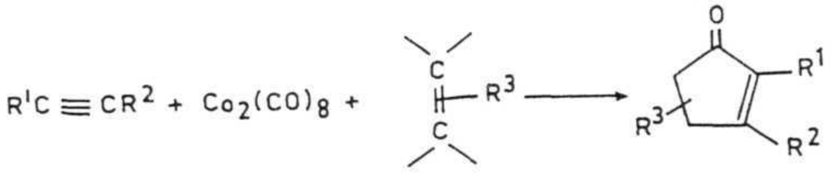


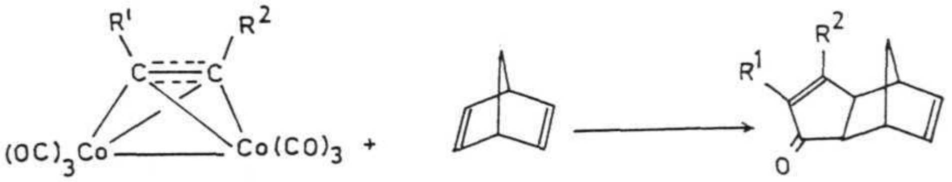
$$R-CH=CH_2 \xrightarrow[H_2/CO]{Co_2(CO)_8} R-CH_2-CH_2-CHO$$

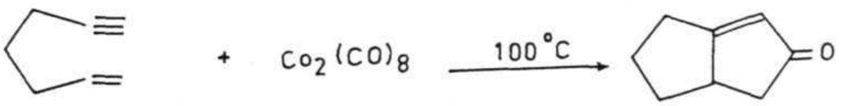




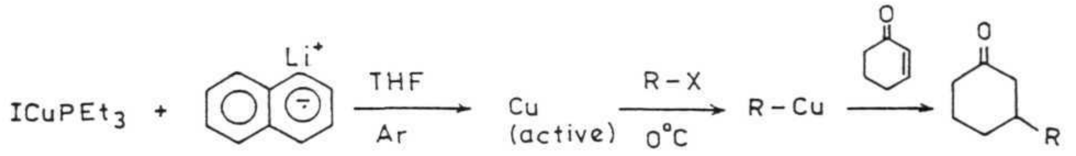
Dicobalt octacarbonyl, $Co_2(CO)_8$, readily complexes with alkynes which undergo the Pauson-Khand reaction with alkenes to give the corresponding cyclopentenones regio-selectively. This reaction has been also extensively utilized.[16-19]

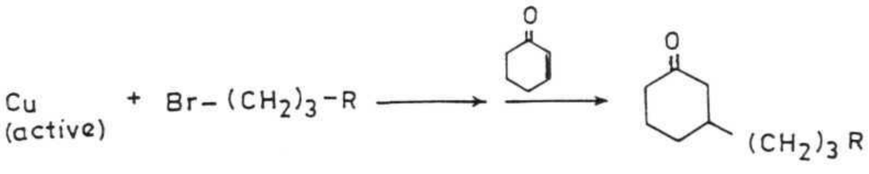




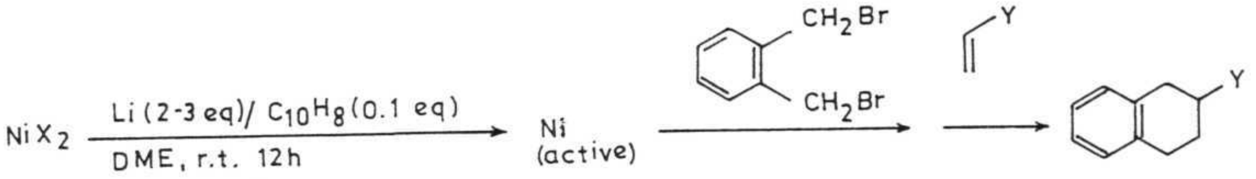


Rieke and coworkers published a series of papers on the direct synthesis of transition metal organometallic reagents by the reaction of highly reactive form of transition metals with alkyl halides.[20-22]



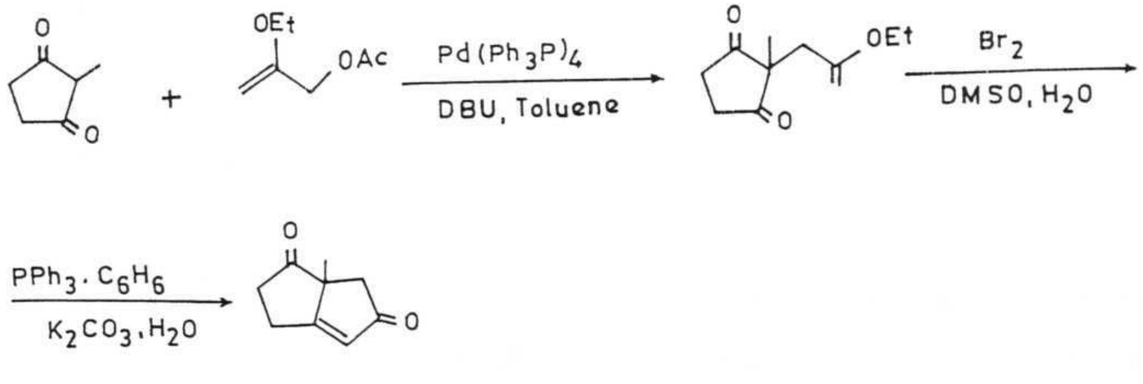


R = CO_2Et, CN, halogen.



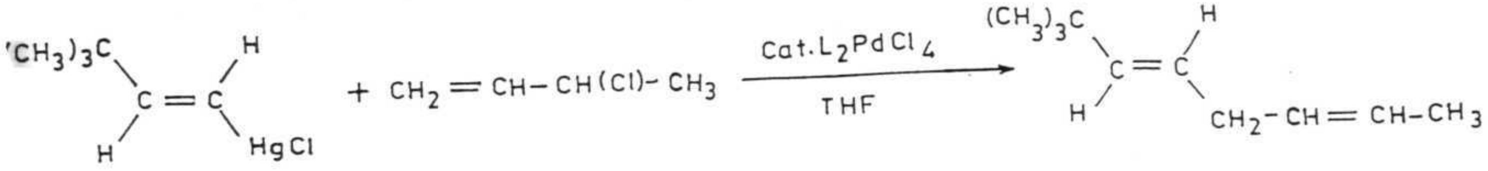
Y = CN, CO_2Me

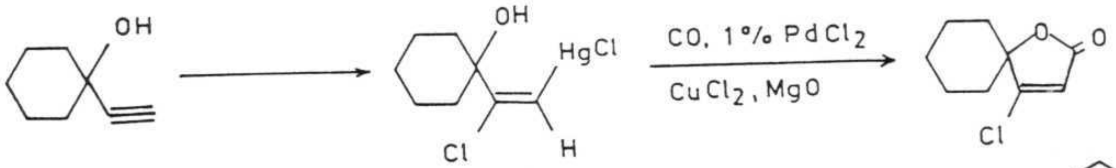
Organopalladium reagents can be readily prepared directly by the reaction of appropriate palladium complexes with organic substrates.[23-28] The palladium reagents have been extensively utilized and the subject has been reviewed.[29]

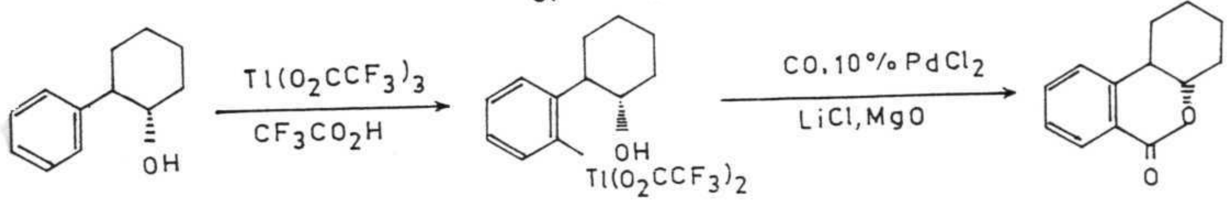


Larock and coworkers demonstrated that organopalladium compounds can be readily prepared in situ from the corresponding organomercurials and organothallium compounds for utilization in organic synthesis.[30-31]

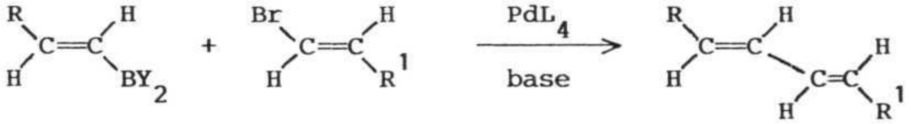
$$RHgX + PdX_2 + CH_2{=}CHY \longrightarrow RCH{=}CHY$$

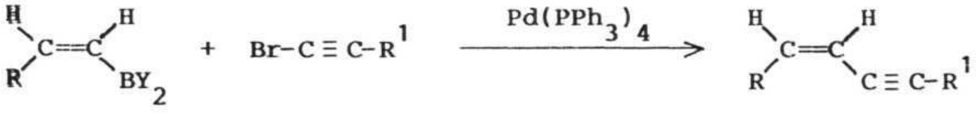




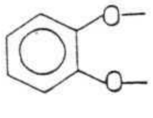


Organoboranes obtained through hydroboration of alkynes undergo coupling reactions on treatment with palladium complexes.[32-35] The reaction has been proposed to go through oxidative addition, transmetalation and reductive elimination.[32-35]

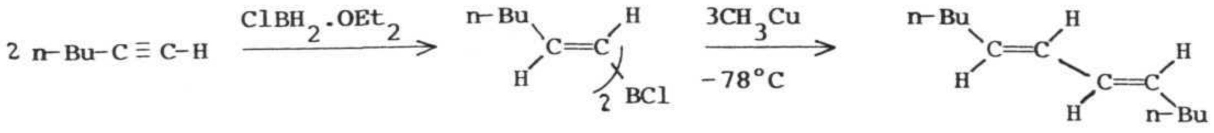




Y_2 = Bis(1,2-dimethylpropyl) or

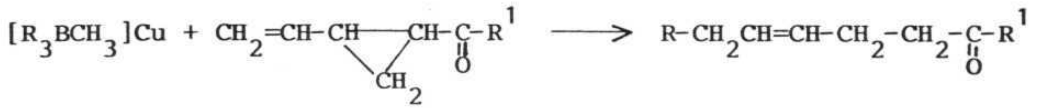


Yamamoto and coworkers found that some organoboron compounds can be made to achieve the reactivity of organocopper reagents on complexation with CH_3Cu.[36]

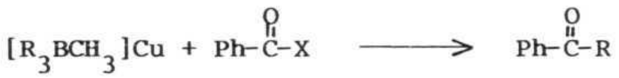


Suzuki and coworkers demonstrated that the complex prepared from R_3B, CH_3Li and CuX undergoes reactions characteristic of "RCu".[37]

$$3R^1CH{=}CH_2 \xrightarrow{BH_3.THF} R_3B \xrightarrow{CH_3Li} [R_3BCH_3]\,Li \xrightarrow{CuX} [R_3BCH_3]Cu$$



$$[R_3BCH_3]Cu + CH_2{=}CH\text{-}CN \longrightarrow R\text{-}CH_2\text{-}CH_2\text{-}CN$$



$$[R_3BCH_3]Cu + Ph\text{-}\overset{O}{\overset{\|}{C}}\text{-}X \longrightarrow Ph\text{-}\overset{O}{\overset{\|}{C}}\text{-}R$$

It was of interest to us to explore the possibilities of developing non-carbanionic pathways for the synthesis of organometallic reagents utilizing transition metal halides and simple reducing reagents such as $NaBH_4$ and MgH_2. We have also studied the development of some related synthetic methods involving RMgX and Mg. The results are described in Chapters 1,2 and 3. The chapters are arranged in the order in which the investigations were executed. Each chapter is divided into introduction, results and discussion and experimental sections. The literature references are listed at the end of each chapter.

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CHAPTER 1

Studies on the Hydrocupration and Carbocupration of Alkynes

INTRODUCTION

The organocopper reagents are the most widely utilized reagents among transition metal reagents.[1-3] Numerous natural products were synthesized employing these reagents in crucial steps.[1-3] Our interest is on the development of hydrocupration and carbocupration routes for the synthesis of these reagents. However, in order to facilitate the discussion of the results, we decided to briefly review various methods available for the preparation of organocopper reagents and their applications in conjugate alkylation, substitution reactions and carbocupration of alkynes. It will be also helpful to briefly review the various methods of preparation of copper(I) hydride reagents and their applications in synthesis.

Synthesis of Organocopper Reagents:

The alkylcopper reagents can be readily prepared by metathesis of an appropriate organometallic compound and a copper(I) salt at low temperature (0°C or below) in an inert atmosphere.

$$\text{R-Met} + \text{CuX} \longrightarrow \text{RCu} + \text{Met-X}$$

Met = Pb, Zn, Hg, Mg, Li, B, and Al.

The Grignard reagents and organolithium reagents are used most often in this reaction with CuI in diethyl ether.[4-6] Other metals such as lead,[7] zinc[8] and aluminium[5] can also be used. The use of CuX species complexed with ligands such as phosphines,[9,10,11] dimethyl sulfide[9] and amines[11] lead to the corresponding complexed alkyl copper species.

Lithium diorganocuprate(I) reagents can be generally prepared by the reaction of lithium alkyls (2 eq) with copper(I) salts at low temperature (0°C or below) in an inert atmosphere.[1-3]

$$2RLi + CuX \longrightarrow R_2CuLi + LiX$$

Magnesium diorgano- or monoorganocuprate(I) halide reagents can be prepared using Grignard reagents and copper(I) salts at low temperature in an inert atmosphere.[1-3]

$$RMgX + CuX \longrightarrow RCuMgX_2$$

$$2RMgX + CuX \longrightarrow R_2CuMgX$$

The reagent prepared utilizing CH_3Cu and n-equivalents of R_TMgBr or R_TLi (R_T=transferable alkyl group) are known as higher order cuprates.[12]

$$MeCu + nR_TMgBr \longrightarrow (R_T)_nMeCu(MgBr)_n$$

$$MeCu + nR_TLi \longrightarrow (R_T)_nMeCuLi_n$$

The original Kharasch reagent MeMgBr/1% CuCl is nothing but a higher order cuprate reagent.[13] The cyanocuprates are obtained when CuCN was utilized as the copper(I) reagent.[14]

$$CuCN + R_TLi \longrightarrow R_TCu(CN)Li$$

The Yamamoto reagent, $RCu.BF_3$, can be readily prepared by the reaction of alkylcopper reagents and $BF_3.OEt_2$ in THF at -70°C.

The alkylcopper reagents utilized can be readily prepared by the reaction of CuI and alkyl lithium in THF at -30°C.[15]

$$\mathrm{CuI + RLi \xrightarrow{-30°C} RCu + LiI}$$

$$\mathrm{RCu + BF_3.OEt_2 \xrightarrow[-70°C]{} RCu.BF_3}$$

Similarly, the Suzuki reagent $Cu[CH_3BR_3]$ can be prepared by the metal exchange reaction of lithium methyltrialkylborates with copper(I) halides. The $[R_3BMe]Li$ can be obtained from trialkylborane and methyllithium in THF at 0°C.[16]

$$\mathrm{R_3B + CH_3Li \longrightarrow [R_3BCH_3\text{-}Li \xrightarrow{CuX} [R_3BCH_3]Cu + LiX}$$

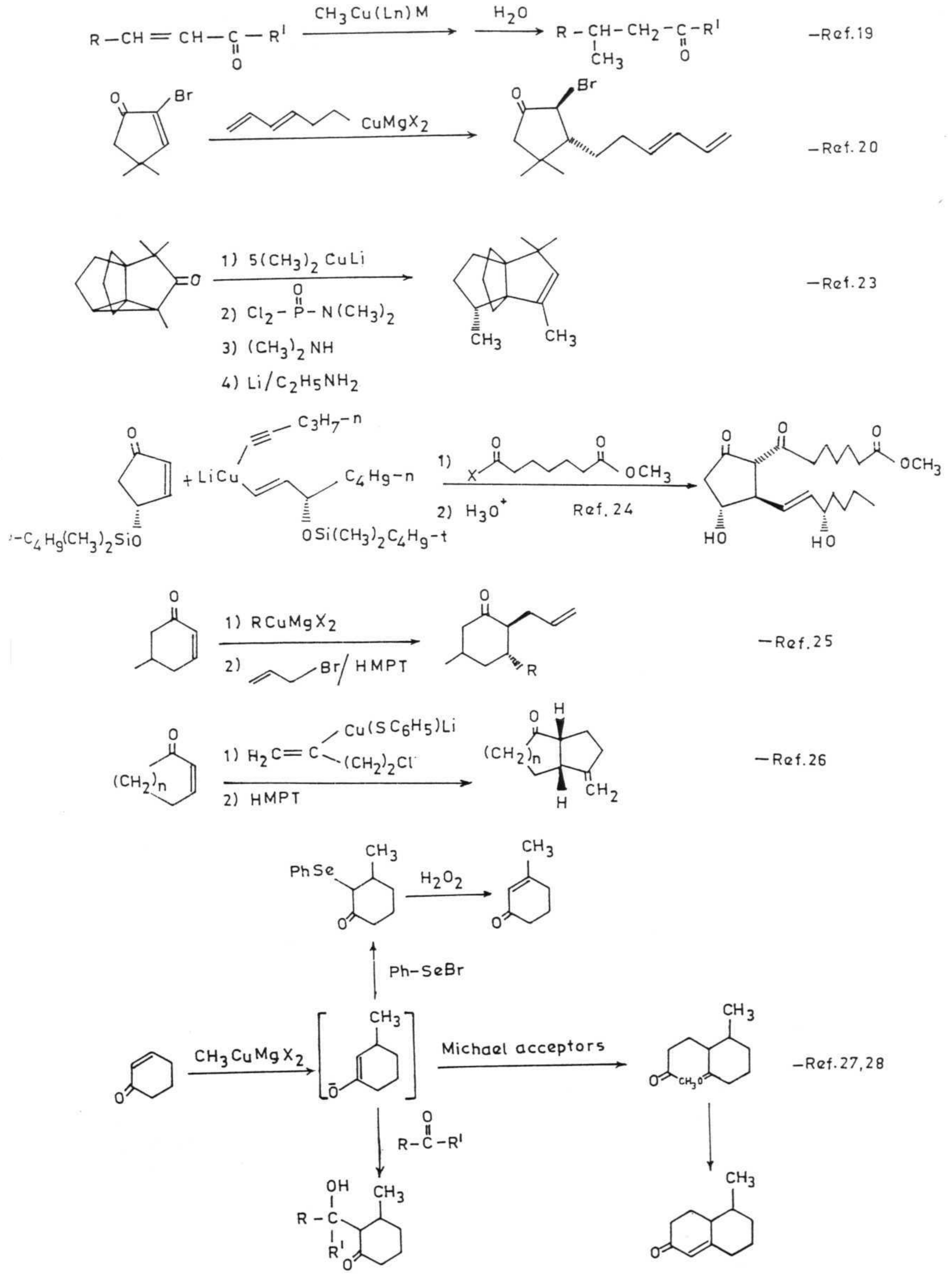
Silyl cuprates have been prepared by the reaction of dimethylphenylsilyllithium, generated from the corresponding chloride and lithium shot, with copper(I) cyanide at 0°C in THF.[17]

$$\mathrm{2Ph(CH_3)_2SiLi + CuCN \longrightarrow [Ph(CH_3)_2Si]_2CuCNLi_2}$$

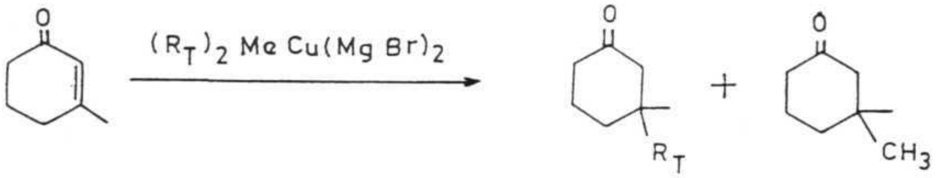
1,4-Alkylation of α,β-unsaturated carbonyl compounds using organocopper reagents:

This is the most important reaction of the organocopper reagents. The subject has been extensively reviewed.[1-3,18] Some representative examples are summarized in Chart 1.[19-33]

Chart 1



R—CH═CH—C(=O)—R'
CH3Cu(Ln)M
H2O
R—CH(CH3)—CH2—C(=O)—R'
—Ref.19
Br
CuMgX2
—Ref.20
1) 5(CH3)2CuLi
2) Cl2—P(=O)—N(CH3)2
3) (CH3)2NH
4) Li/C2H5NH2
CH3
CH3
—Ref.23
C3H7-n
+LiCu
C4H9-n
OSi(CH3)2C4H9-t
C4H9(CH3)2SiO
1) X—C(=O)(CH2)6C(=O)OCH3
2) H3O+
Ref. 24
OCH3
HO
HO
1) RCuMgX2
2) Br/HMPT
R
—Ref.25
1) H2C═C(Cu(SC6H5)Li)(CH2)2Cl
2) HMPT
(CH2)n
H
CH2
—Ref.26
CH3
PhSe
H2O2
Ph-SeBr
CH3CuMgX2
Michael acceptors
R—C(=O)—R'
OH
R'
—Ref.27,28



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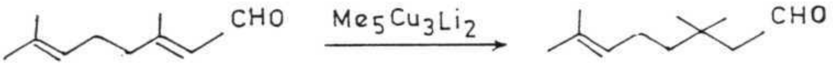

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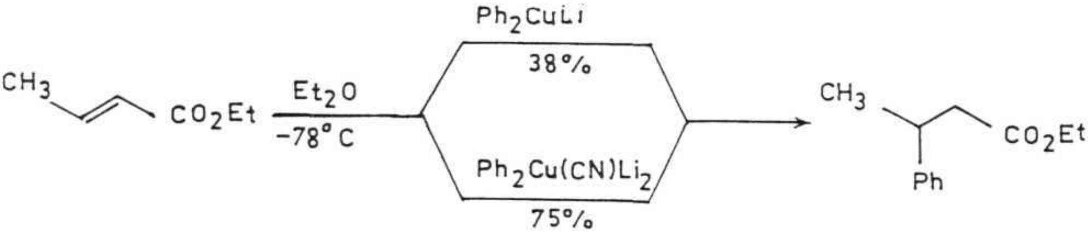

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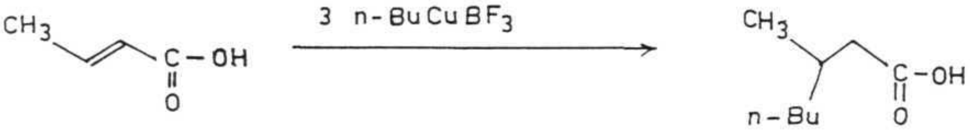

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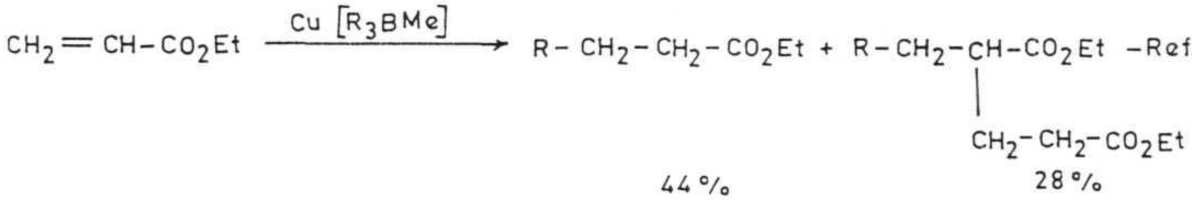

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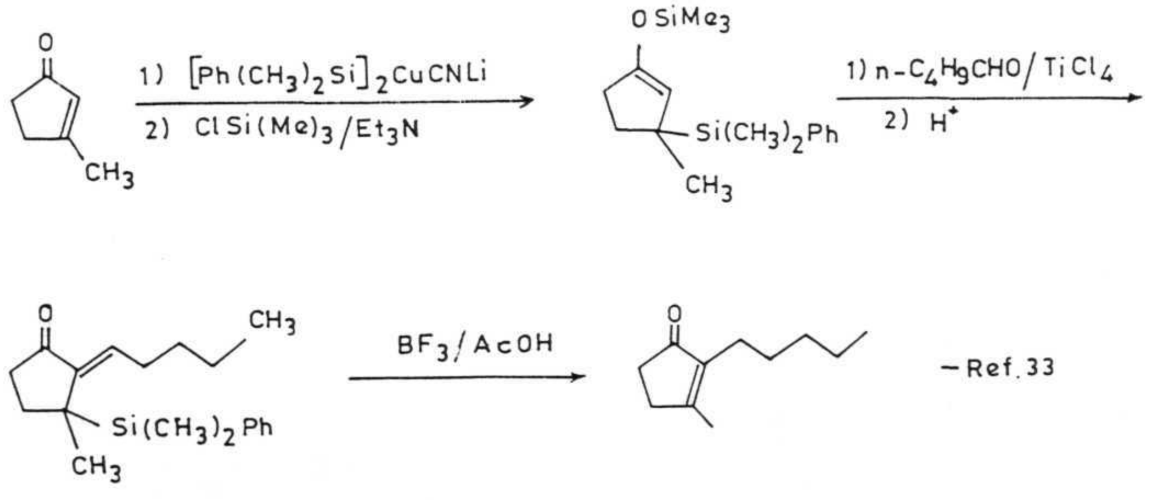

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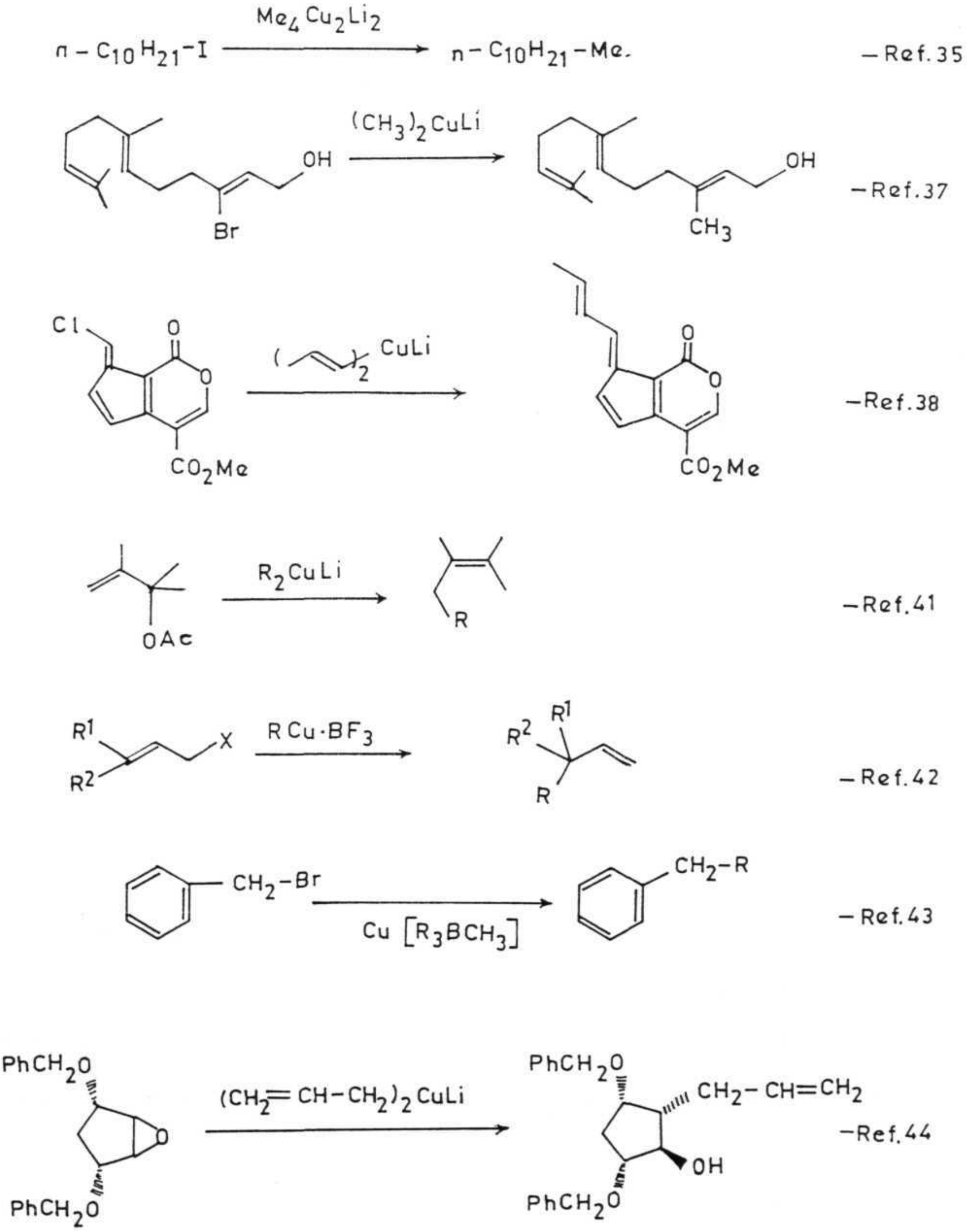
Substitution reactions using organocopper reagents:

The carbon-carbon bond formation using organocopper reagents and alkyl halides is an extremely useful reaction. An excellent review appeared on the topic.[3,34] Some typical transformations are outlined in Chart 2.[35-44]

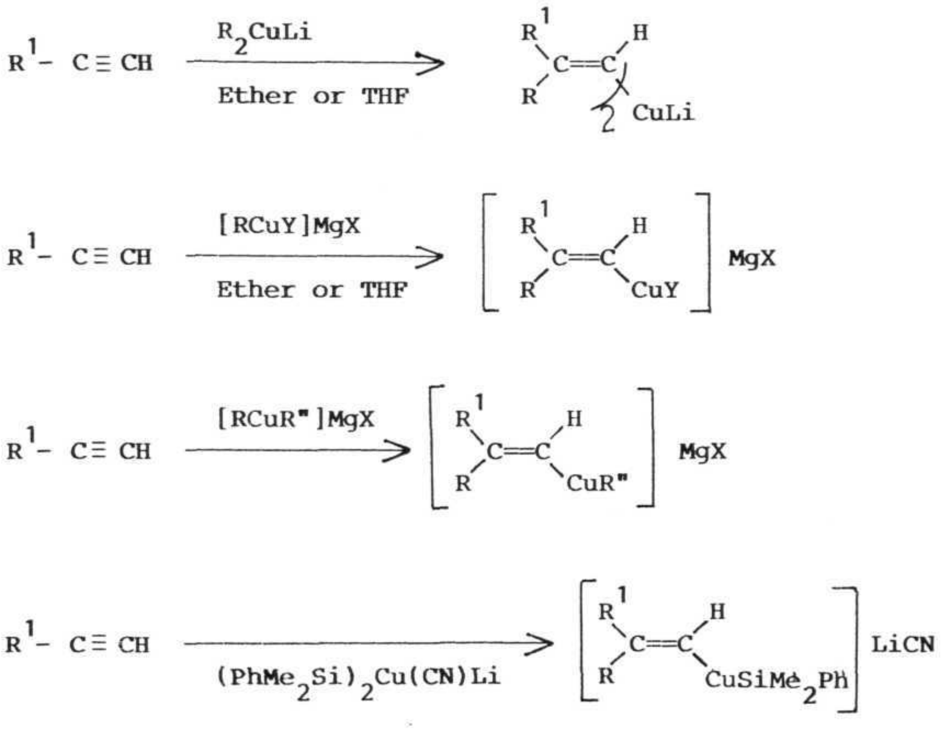
Chart 2



Carbometalation of Alkynes using organocopper reagents:

Normant and coworkers developed the carbometalation of alkynes using organocopper reagents (Scheme 1).[45-50]

Scheme 1



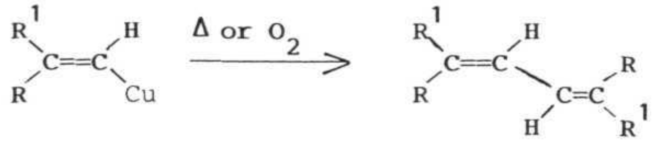
$R^1 = H, CH_3, Ph, alkyl$

R = alkyl

R" = R or $-C\equiv C-Bu$

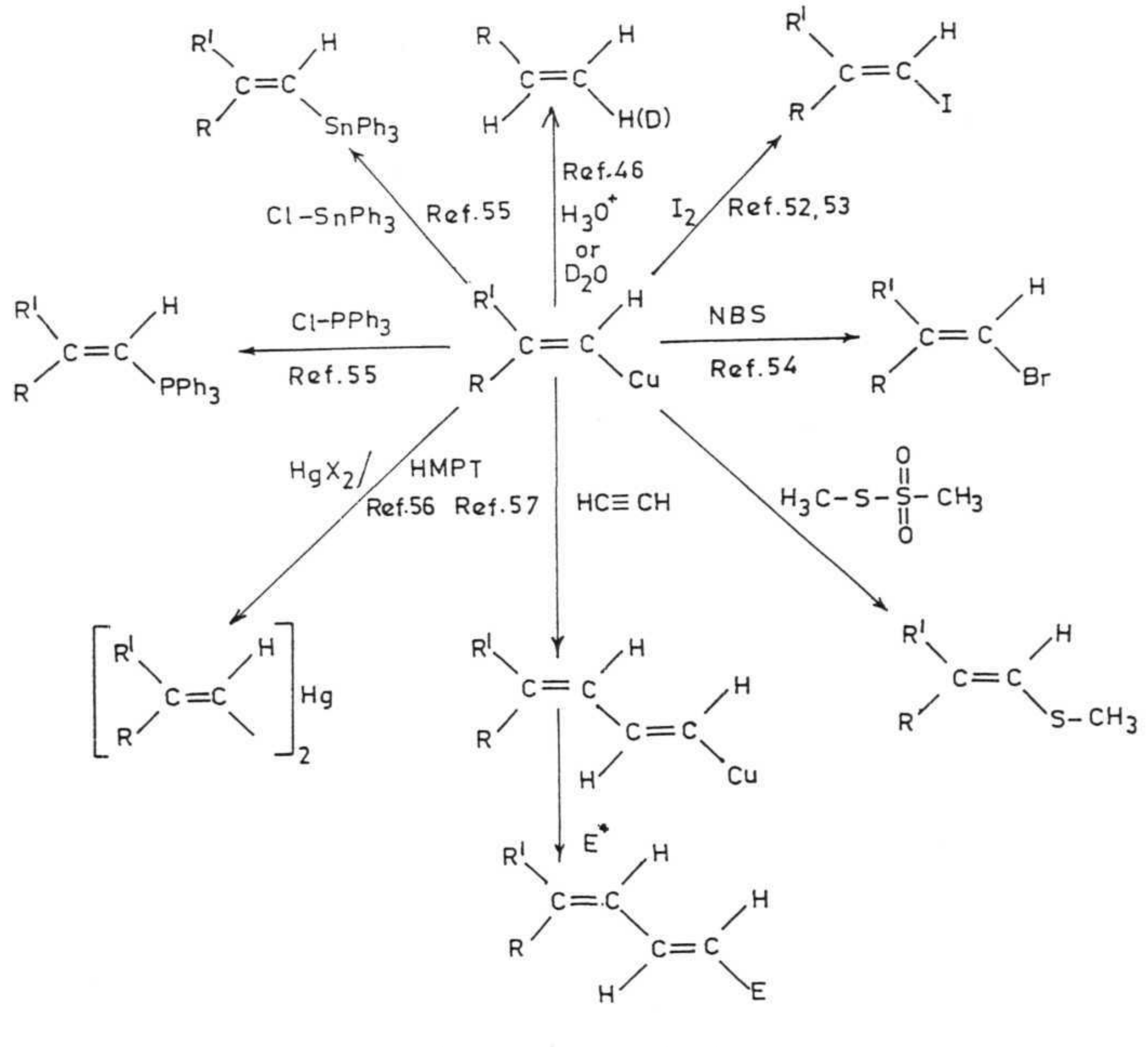
X = Cl or Br

The addition of "CuR" takes place in the syn-fashion and it is also regio- and stereo-specific.[46,48] The vinylcopper intermediates undergo thermal decomposition to the corresponding dienes.[51] Traces of oxygen also converts the vinylcopper intermediates into the dienes.[52]



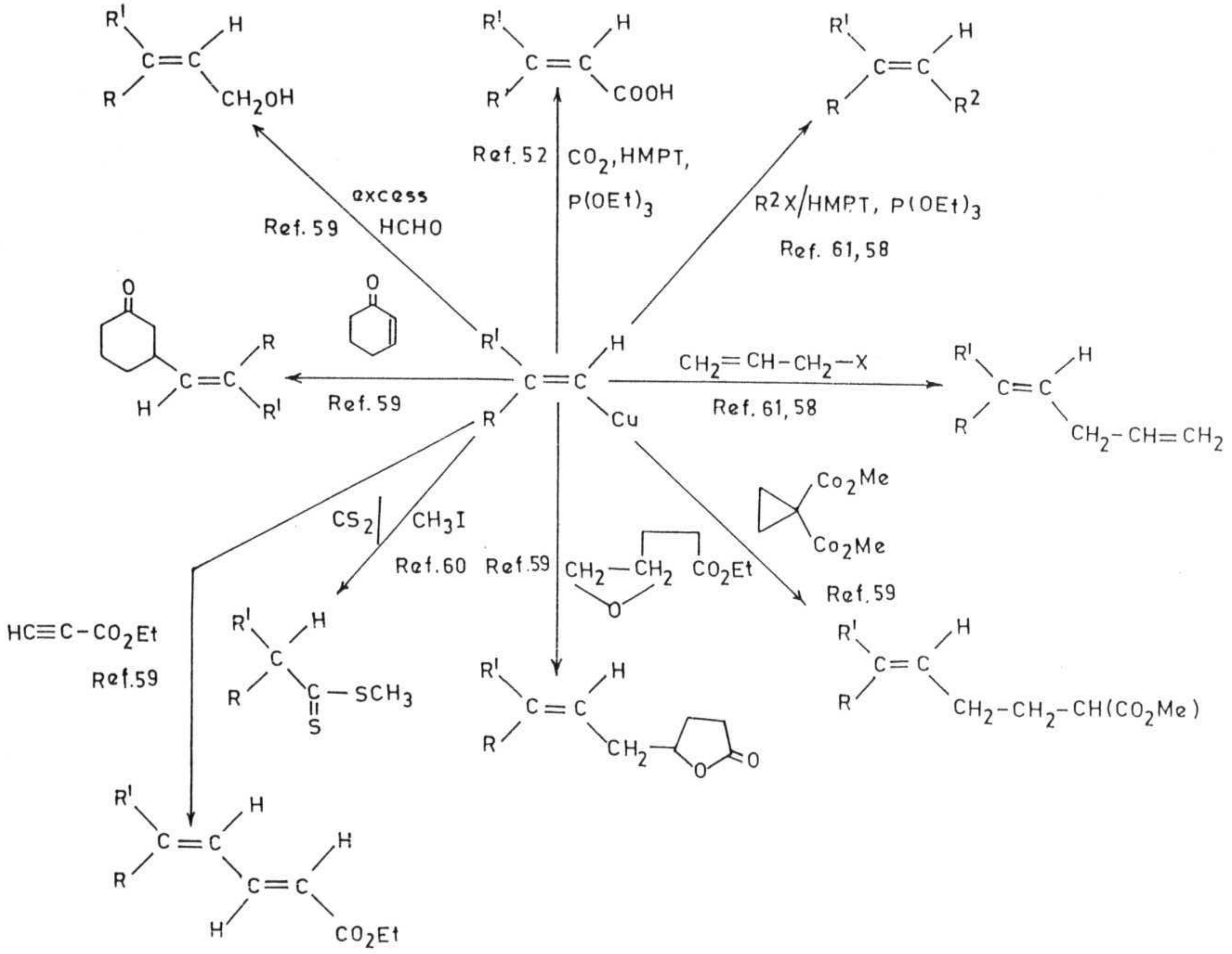
The vinylcopper intermediates are versatile reagents which can be converted into various unsaturated substrates by quenching with electrophiles (Chart 3,4).

Chart 3



$E = H^+, CO_2, R^I, CH_2{=}CH{-}CH_2{-}R$

Chart 4


excess
HCHO
Ref. 59
Ref. 52
CO2,HMPT,
P(OEt)3
R2X/HMPT, P(OEt)3
Ref. 61,58
Ref. 59
CH2=CH-CH2-X
Ref. 61,58
CS2
CH3I
Ref.60
Ref.59
CO2Et
Co2Me
Co2Me
Ref. 59
HC≡C-CO2Et
Ref.59
R¹
R
H
Cu
CH2OH
COOH
R2
SCH3
S
CH2-CH=CH2
CH2-CH2-CH(CO2Me)
CH2
O
CO2Et

Synthesis and reactions of copper(I) hydride reagents:

In 1844, Wurtz reported the formation of a red-brown copper hydride species in the reduction of an aqueous solution of copper(II) sulfate with hypophosphorous acid.[62]

$$2Cu^{+2} + 3H_2PO_2^- + 3H_2O \longrightarrow 2CuH + 3H_2PO_3^- + 4H^+$$

Copper hydride reagent was also prepared by the reduction of copper(II) salts using NaH_2PO_2.[63] It was suggested that the species form a complex with NaOH, probably CuH.NaOH. However, later it was shown that the copper hydride species prepared by the reduction of Cu(I) salts by complex hydride agents exhibit different properties compared to the copper hydride prepared in aqueous solutions. Accordingly, the nature of the hydride supposed to have been formed in aqueous solutions is not certain.

The reaction of lithium aluminium hydride with CuI in ether has been reported to give copper(I) hydride species.[64] The reaction in ether solution in the presence of pyridine has been found to have the following stoichiometry.[65]

$$4CuI + LiAlH_4 \xrightarrow{\text{Ether}} LiI + AlI_3 + 4CuH$$

Copper aluminium hydride complex, prepared by the reaction of Li_2CuBr_4 with $LiAlH_4$ at -80°C, decomposes above -80°C to Cu(0), CuH, Al and H_2.[66]

Lithium aluminium hydride reacts with 2 equivalents of CuI to give iodoaluminium hydride.[67]

$$LiAlH_4 + 2CuI \longrightarrow H_2AlI + LiI + Cu(0) + H_2$$

The H_2AlI reagent has been utilized for 1,4-reduction of α,β-unsaturated carbonyl compounds.[67]

The complex metal hydride of copper, $LiCuH_2$, has been prepared at low temperature by the reaction of $LiCuMe_2$ with $LiAlH_4$ in ether.[68] This complex is also stable as an etherate. The complex metal hydride of copper obtained in this way is stable at room temperature for several days.[68]

$$MeLi + CuI \longrightarrow MeCu + LiI$$

$$MeCu + MeLi \longrightarrow LiCuMe_2$$

$$LiCuMe_2 + LiAlH_4 \longrightarrow LiCuH_2 + LiAlMe_2H_2$$

Following this methodology, Ashby and coworkers prepared a series of stable complex metal hydrides of copper with composition Li_nCuH_{n+1} (n=1-5), analogous to higher order cuprates,[12] by the reaction of $LiAlH_4$ with the corresponding lithium dimethylcuprates in diethyl ether at -78°C. They showed that these complexes convert alkyl halides, tosylates, enones and cyclic ketones to the corresponding reduced products both in Et_2O and THF.[69]

$$(n+1)\ CH_3Li + CuI \xrightarrow[-78^{\circ}C]{Et_2O} Li_nCu(CH_3)_{n+1} + LiI$$

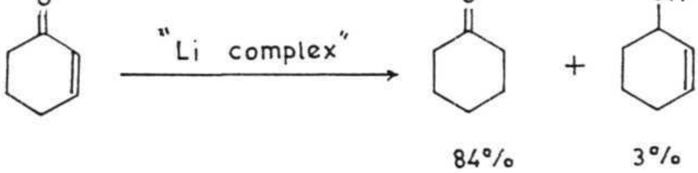
$$Li_nCu(CH_3)_{n+1} + (\frac{n+1}{2})LiAlH_4 \xrightarrow[-78^\circ C]{Et_2O} Li_nCuH_{n+1} + (\frac{n+1}{2})\ LiAlH_2(CH_3)_2$$

A mixture of $LiAlH(OCH_3)_3$ (8 eq) and CuI (1 eq) gives a dark brown mixture in THF which has been considered to contain hydride "ate" complexes of Cu.[70] This reagent has been utilized for reductive removal of halo groups with retention of configuration, mesyloxy group with inversion of configuration and reductive cleavage of epoxides into alcohols.[70]

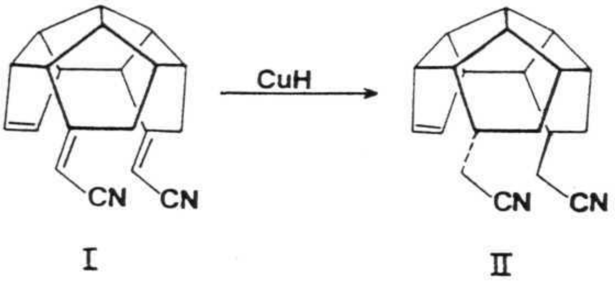
The copper hydride reagents, prepared by the reaction of CuBr with $LiAlH(OCH_3)_3$ and $NaAlH_2(OCH_2CH_2OCH_3)_2$ in THF at 0°C, as a brown-black suspension has been found to be useful for several synthetic transformations.[71]

$$2\ LiAlH(OCH_3)_3 + CuBr \xrightarrow[0^\circ C]{THE} \text{"Li complex"}$$

$$NaAlH_2(OCH_2CH_2OCH_3)_2 + CuBr \xrightarrow[0^\circ C]{THF} \text{"Na complex"}$$



The copper hydride reagent prepared from cuprous bromide, vitride and sec-butanol in THF was utilized for selective reduction of double bond α- to the nitrile group in **I** in a 1,4-fashion to obtain the required regioisomer of hexaquinane **II**.[72]

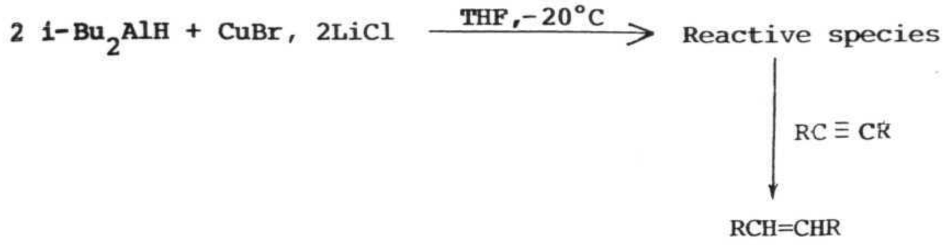


Whitesides and coworkers have prepared copper(I) hydride species by the reaction of $(Bu^i)_2AlH$ with CuBr in pyridine at -50°C.[73]

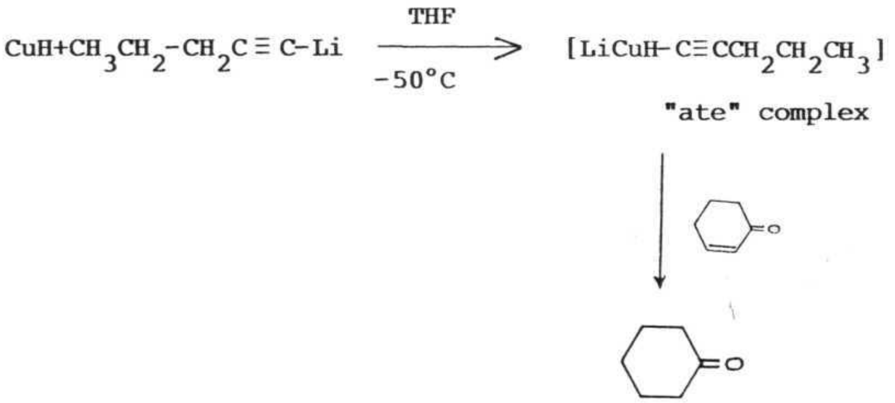
$$CuBr + (Bu^i)_2AlH \xrightarrow[-50°C]{Pyridine} CuH + (Bu^i)_2AlBr$$

The copper hydride precipitates on dilution with excess ether. The hydride obtained in this way was found to be relatively pure compared to that obtained following other methods.[65] The sample is indefinitely stable at -78°C and decomposes above -20°C. It forms 1:1 complex with PBu_3. The resulting hydrido(tri-n-butylphosphine) copper(I) has been utilized for the reduction of RCu and ArCu reagents into the corresponding hydrocarbons.[73]

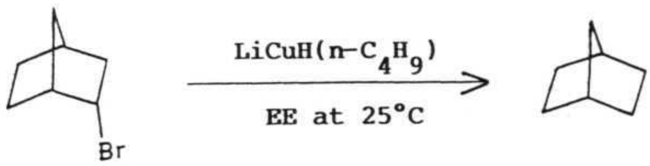
The copper(I) hydride reagent, prepared following the above procedure, reduces the internal alkynes into the corresponding cis-alkenes in a syn fashion in the presence of LiCl.[73]



The "ate" complexes of copper, LiCuHR [R=1-pentyne, -OBu^i, -SPh], analogous to diorganocuprates, can be obtained in THF solution by the reaction of lithio-1-pentyne with CuH prepared by Whitesides procedure at -50°C.[74] These "ate" complexes have been employed for 1,4-reduction of α,β-unsaturated enones, aldehydes and esters. The yields are very high when the reaction was carried out in the presence of HMPT.[74]



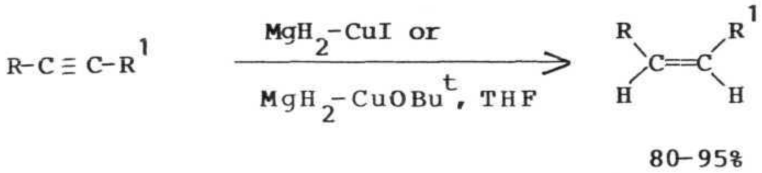
It was found that the regio-selectivity and functional selectivity are very high in this case. The "ate" complexes are also effective for reductive removal of halo and mesyloxy groups.[75]



$$CH_3(CH_2)_6CH_2OMs \xrightarrow[\text{EE at 25°C}]{\text{LiCuH(n-}C_4H_9\text{)}} CH_3\text{-}(CH_2)_6\text{-}CH_3$$

The MgH_2-CuI and MgH_2-$CuOBu^t$ reagent systems are capable of reducing some 1-alkynes into the corresponding 1-alkenes. Internal alkynes gave cis-alkenes with high stereospecificity. It was proposed that the composition of the CuI/MgH_2 reagent system is CuH-HMgI, analogous to the Normant's carbocupration reagents $RCuMgX_2$.[76]

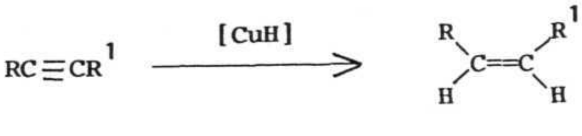
$$R-C\equiv CH \xrightarrow[MgH_2-CuOBu^t,\ THF]{MgH_2-CuI\ or} \underset{80-90\%}{R-CH=CH_2}$$



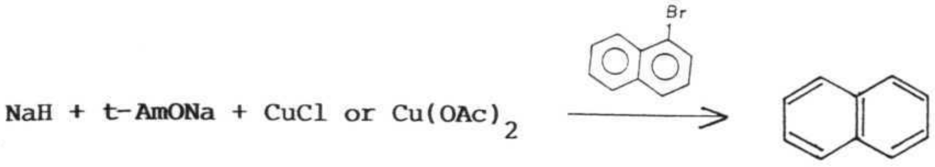
It has been reported that the 1-alkenes were not affected by these reagents.

The CH_3CH_2MgX/CuBr, n-BuMgX/CuBr and i-PrMgX/CuBr reagents in diethyl ether reduce some internal alkynes into cis-alkenes. The intermediacy of copper(I) hydride species, formed by the β-hydride elimination of the RCH_2CH_2Cu species, was invoked.[77]

$$RCH_2CH_2Cu \xrightarrow{-RCH=CH_2} [CuH]$$



The complex reducing agents (CRA), developed by Caubere and coworkers, utilizing copper(I) salts, NaH and t-AmONa, were utilized for the reduction of 1-halogenonaphthalenes into naphthalene.[78]



A novel reactive hydride species of copper was obtained by the addition of 2 eq. of potassium tri-sec-butylborohydride, $KBu^{s}_{3}BH$ to CuI in THF.[79]

$$KBu^{s}_{3}BH + CuI \xrightarrow[-50^{\circ}C]{THF} (KCuH_2)_n$$

raised to r.t. over 2h

This reagent, presumably $KCuH_2$, is effective for the reduction of alkyl halides, alkenyl halides and 1-halo-1-alkynes, which are not reduced using several other reducing reagents of copper.[69,75] Saturated ketones and esters were also reduced to the corresponding alcohols. The reagent system also reacts with 5-decyne to produce 5-decenes (Z:E = 88:12).

Bright red crystals of the $H_6Cu_6(PPh_3)_6$ cluster were obtained on cooling the mixture of $[PPh_3CuCl]_4$ and sodium trimethoxyborohydride in DMF solution in an ice bath for 30 min.[80]

$$[PPh_3CuCl]_4 + NaB(OCH_3)_3H \xrightarrow{DMF} H_6Cu_6(PPh_3)_6$$

This reagent is useful for catalytic 1,4-reduction of enones.

Sodium borohydride reacts with Cu(I) salts in the presence of triphenylphosphine to give $(Ph_3P)_2CuBH_4$.[81] This reagent has been utilized extensively. For example, it has been found to be effective for the reduction of 2-adamantyl tosylhydrazone into the corresponding hydrocarbon in good yields.[82]

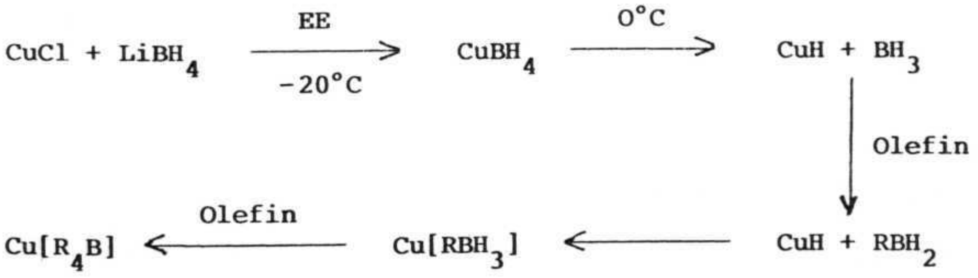
Lithium borohydride reacts with CuCl to give $CuBH_4$ at -20°C in ether solvent.[83] The $CuBH_4$ prepared in this way decomposes to Cu, H_2 and B_2H_6 at 0°C.[83] It was suggested that the reaction goes through the intermediacy of CuH species. Surprisingly, this simple system was not studied further. We decided to investigate the $CuX/\overset{-}{B}H_4$ system further.

RESULTS AND DISCUSSION

Investigations on the reactivities of the CuCl/NaBH$_4$ system:

As outlined in the introductory section, Suzuki and coworkers reported that copper(I)methyltrialkylborates, Cu[CH$_3$BR$_3$], prepared by the reaction of methyllithium with trialkylboranes followed by treatment with copper(I) halides,[16] undergo a variety of reactions characteristic of organocopper reagents.[43,84] It was reported that the CuCl/LiBH$_4$ system in diethylether at -20°C gives the corresponding CuBH$_4$, which decomposes into copper metal, H_2 and B_2H_6 through 'CuH' and 'BH$_3$' intermediates at 0°C.[83,85] It seemed to us that if this were the case, then it should be possible to prepare the copper(I)alkylborates by carrying out the reaction in the presence of olefins to initiate a hydroboration-comproportionation sequence. Such a method should be very attractive, since the synthesis of the copper(I)alkylborates would be achieved without the use of carbanionic organometallic reagents such as RLi and RMgX (Scheme 1).

Scheme 1

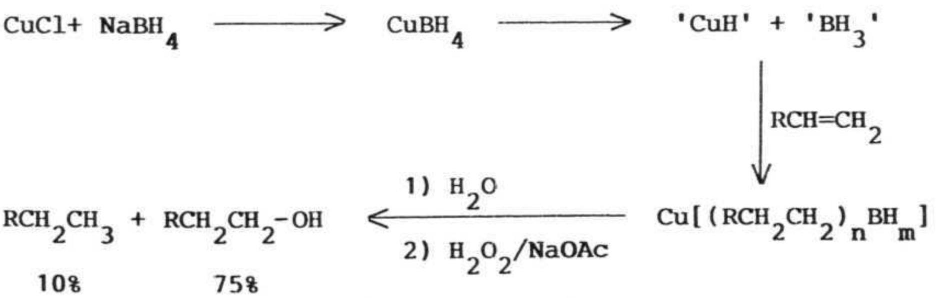


In order to examine this possibility, we carried out the following experiment: A mixture of CuCl (10 mmol) and 1-decene (20 mmol) in THF

(80 ml) was cooled to -10°C (ice-salt bath) and $NaBH_4$ (10 mmol) was added under nitrogen atmosphere. The temperature was raised to 25°C during 2 h and the mixture was stirred at this temperature for 12 h. (If the temperature is immediately raised to 25°C, considerable decomposition of the hydride takes place, as indicated by evolution of hydrogen.) Hydrolysis of the reaction mixture at 0°C and oxidation with $H_2O_2/NaOOCCH_3$[86] gave 1-decanol in 75% yield besides 1-decane in 10% yield (Table 1).

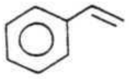
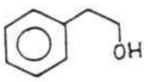
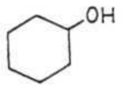
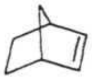
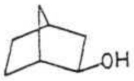
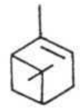
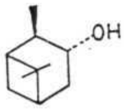
In the reaction with methyl-10-undecenoate, methyl undecanoate (15%) was isolated besides methyl-11-hydroxyundecanoate (70%) (Table 1). These observations can be rationalized in terms of the formation of copper(I) alkylborohydride species via hydroboration and subsequent complexation of the resulting organoboron intermediates with CuH species (Scheme 2).

Scheme 2



The reaction was found to be a general one and many other olefins can be hydroborated and oxidised following this procedure. The regio- and stereo-selectivities observed with this system are similar to those obtained utilizing the $BH_3.THF$ reagent. The results are summarized in Table 1.

Table 1: Reaction of the $CuCl/NaBH_4$ reagent with alkenes.[a]

Substrate	Product[b]	Yield (%)[c]
$CH_3(CH_2)_7CH = CH_2$	$CH_3(CH_2)_7CH_2CH_2OH$	$75^{d,e}$
		75^{f}
		65
		68^{d}
		60^{d}
$CH_2{=}CH(CH_2)_8COOCH_3$	$HOCH_2(CH_2)_9COOCH_3$	$70^{d,g}$

a) The reactions were carried out by the addition of $NaBH_4$ (10 mmol) to a mixture of CuCl (10 mmol) and alkene (20 mmol) in THF (80 ml) under nitrogen atmosphere. The reaction temperature and time 24 h (except 1-decene 12 h) are the same for all reactions.

b) Products isolated after hydrolysis at 0°C and oxidation with H_2O_2/NaOAc. The products were identified by spectral data (IR, ^1H 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 ^{13}C NMR spectrum of the distilled product does not show signals corresponding to the isomeric/epimeric alcohols; thus the amount of the isomeric alcohol (if any) cannot exceed 5%.

e) Decane (10%) was also isolated; the yield in this case is based on the assumption that only one equivalent of the alkene or hydride in the borate complex would undergo hydrolysis.

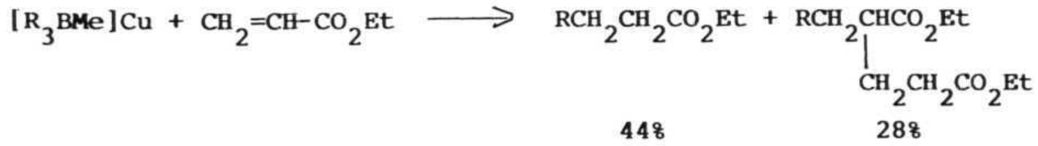
f) Up to 17% of the isomeric 1-phenylethanol is present (^1H NMR).

g) Methyl undecanoate (15%) was also isolated: the products were isolated by chromatography (silica gel, hexane/$CHCl_3$).

Unreacted olefin remained when more than 20 mmol of olefins were utilized indicating that the system does not give the tetraalkylborates. It is not certain that the reaction gives the dialkylborate species cleanly. Moreover, the copper(I) alkylborohydride may be polymeric rather than the discrete species shown in Scheme 2.

It was observed that the addition of water at 0°C to the copper(I) alkylborohydride species also gives the same reduction products: 10% of decane in the run with 1-decene and 15% of methyl undecanoate in the run with methyl-10-undecenoate. Organoboranes are relatively stable towards water under the reaction conditions (0°C), but the tetraalkyl organoborates would undergo hydrolytic cleavage of one of the alkyl-boron bonds.[87] Thus the formation of the reduction products indicate that the CuCl/NaBH$_4$ reagent system gives copper(I) alkylborohydrides with alkenes.

It has been reported that copper(I) methyltrialkylborate reacts with ethyl acrylate to give the corresponding 1,4-adduct.[16]



$$[R_3BMe]Cu + CH_2{=}CH{-}CO_2Et \longrightarrow \underset{44\%}{RCH_2CH_2CO_2Et} + \underset{28\%}{RCH_2\underset{\displaystyle CH_2CH_2CO_2Et}{\underset{|}{C}}HCO_2Et}$$

In order to examine the reactivity of the copper(I) alkylborohydrides, the following experiments were carried out. The copper(I) decylborohydride was prepared by adding NaBH$_4$ (10 mmol) to a mixture of 1-decene (20 mmol) and CuCl (10 mmol) in THF (80 ml) at -10°C (bath temperature). The reaction mixture was stirred further for 8 h at this temperature and methyl acrylate (10 mmol) was added. The mixture was further stirred for 2 h at -10°C. After hydrolysis, oxidation with $H_2O_2/NaOOCCH_3$ and work-up, methyl tridecanoate (5%) and tridecanal (5%) were isolated by chromatography on a silica gel column (hexane/chloroform as eluent) along with polymeric materials containing ester and decyl groups.

$$\mathrm{Cu[H_mB(RCH_2CH_2)_n]} \xrightarrow[2)\ \mathrm{H_2O}]{1)\ \mathrm{CH_2{=}CH{-}CO_2CH_3}} \underset{5\%}{\mathrm{RCH_2CH_2CO_2CH_3}} + \underset{5\%}{\mathrm{RCH_2CH_2CHO}}$$

$m + n = 4$

The yields of the conjugate addition products in the present experiment are very low compared to the yields (45-70%) obtained with the Suzuki's reagent, $Cu[CH_3BR_3]$. It is possible that the transfer of the hydride dominates over that of the alkyl group in the present case. It seemed possible that if the "borane" unit could be separated using Bu_3P as unreactive alkylborane-PBu_3 complex, then alkyl transfer reaction might be favoured. However, when the conjugate addition was carried out after addition of Bu_3P (10 mmol), only a 1/1 mixture of eicosane (RR) and decane (RH) were isolated along with Bu_3P-borane complexes (B-H, strong IR absorption at 2350 cm^{-1}).

$$\mathrm{Cu[H_mBR_n]} \xrightarrow{\mathrm{Bu_3P}} \underset{\text{mixture}}{\mathrm{Bu_3PBH_xR_y}} + \underset{20\%}{\mathrm{RR + RH}}$$

It has been reported that $[PBu_3]_nCuR$ complexes readily decompose to give RR and RH species[88] and so our results can be rationalized in terms of the formation of $(Bu_3P)_nCuR$. All our efforts to improve the yields of the addition products by carrying out the reaction under various conditions (i.e. different time, temperature, solvent, utilization of CuBr, $Zn(BH_4)_2$ and $LiBH_4$) were unsuccessful.

It has been reported that diborane reacts with copper(I) chloride in ether solvent to give Cu, H_2 and BCl_3.[89] It appeared that it may be possible to prepare monochloroborane and dichloroborane reagents using appropriate amounts of CuCl in ether solvent. These chloroborane reagents have many useful synthetic applications[90] and we decided to explore the possibilities of the preparation of monochloroborane reagent using $NaBH_4$ and CuCl.

$$\mathbf{NaBH_4 + 2CuCl \longrightarrow NaCl + ClBH_2 + Cu + H_2}$$

Trial experiments indicated that it is necessary to solubilize the $\bar{B}H_4$ in Et_2O using $ZnCl_2$. The $Zn(BH_4)_2$ (5 mmol) was prepared in ether solvent at r.t. using $ZnCl_2$ (5 mmol) and $NaBH_4$ (10 mmol)[90] and CuCl (20 mmol) was added at 0°C. The reaction mixture was brought to 25°C and stirred further for 2 h. 1-Decene (30 mmol) was added and the mixture was stirred for 12 h. The mixture was hydrolysed with methanol (20 ml) and the organoborane species was oxidized with $NaOH/H_2O_2$. After usual work-up and distillation, 1-decene (9 mmol) and 1-decanol (18 mmol) were isolated. Recovery of unreacted 1-decene (1 eq) clearly indicates that the reagent system gives monochloroborane species, which reacts with only 2 equivalents of 1-decene (Scheme 3).

Scheme 3

$$NaBH_4 + ZnCl_2 \xrightarrow[r.t.]{EE} Zn(BH_4)_2 \xrightarrow[0°C]{CuCl} CuBH_4 + ZnCl_2$$

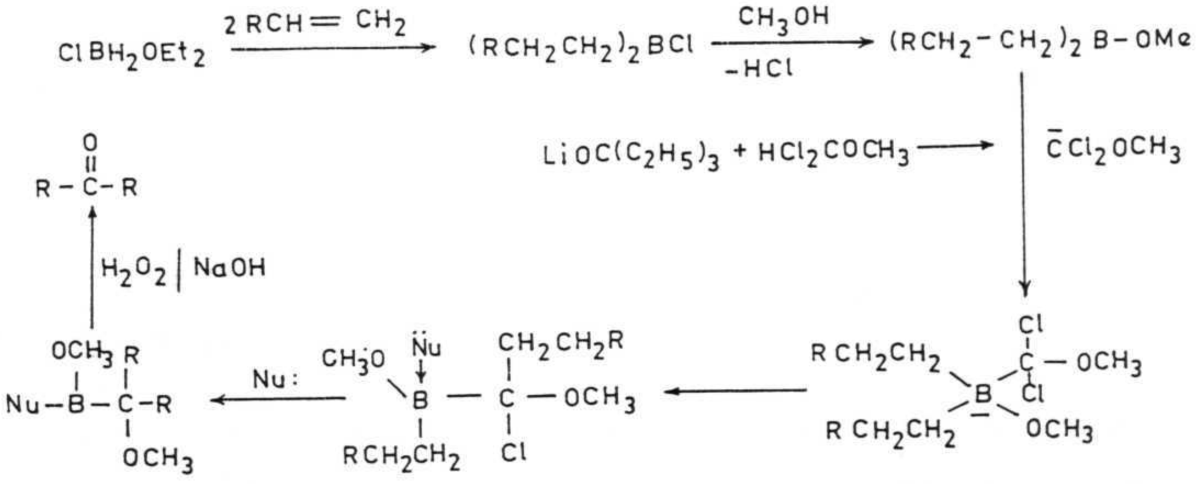
$$CuBH_4 \xrightarrow[EE]{r.t.} Cu + H_2 + \text{'}BH_3\text{'} \xrightarrow{CuCl} ClBH_2$$

$$ClBH_2 + \text{1-decene} \xrightarrow{EE} BR_2Cl \xrightarrow{CH_3OH} R_2BOMe$$

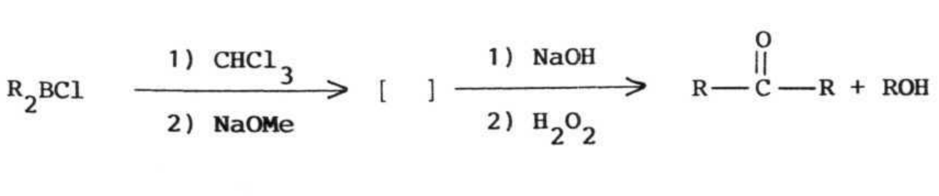
$$R_2BOMe \xrightarrow{NaOH/H_2O_2} 2ROH$$

It has been reported that dialkylborane species such as R_2BOMe, prepared by hydroboration of 1-alkenes with chloroborane followed by methanolysis, reacts with the carbenoid reagent, generated from dichloromethylmethyl ether and lithium triethylcarboxide to give the corresponding dialkyl ketone after oxidation (Scheme 4).[91]

Scheme 4



Recently, in our laboratory, a new and simple carbenoidation procedure utilising $CHCl_3/NaOCH_3$ system was developed for the conversion of R_2BOMe, prepared via hydroborations using $RCOO\bar{B}H_3$ reagent in THF, into dialkyl ketone in 80% yield.[92] In order to examine the formation of dialkylchloroborane species in the reaction utilizing CuCl (2 eq) and $NaBH_4$ (1 eq) and 1-decene (2 eq), we have carried out the carbenoidation reaction as follows. To the organoborane, using 2 equivalents of 1-decene, chloroform (10 ml) was added followed by $NaOCH_3$ (40 mmol) from a solid addition flask during 20 min at room temperature. The contents were further stirred at 55°C for 4 h. The reaction mixture was hydrolysed with water (2 ml) after bringing to r.t. The organoboron compound was oxidised with $NaOH/H_2O_2$. After work-up and chromatography over a silica gel column, di-1-decyl ketone (60%) and 1-decanol (35%) were isolated (the yields are based on the amount of 1-decene utilized). The yields of the di-1-decyl ketone is somewhat less in the present case. However, it should be noted that the conditions are somewhat different from the previously reported procedure (i.e. Et_2O is used as solvent instead of THF).[92] Also, disproportionation of the $ClBH_2/R_2BCl$ into R_3B and $RBCl_2$ species would also decrease the yield of the ketone. It has been found that the R_3B and $RB(OCH_3)_2$ reagents give 1-decanol as the major product after carbenoidation with $NaOCH_3/CHCl_3$ followed by oxidation.[91,92]



$$R_2BCl \xrightarrow[\text{2) NaOMe}]{\text{1) } CHCl_3} [\quad] \xrightarrow[\text{2) } H_2O_2]{\text{1) NaOH}} R-\overset{\overset{\displaystyle O}{\|}}{C}-R + ROH$$

Since there are several other methods available for the preparation of $ClBH_2$ species,[90] we turned our attention to the utilization of the "CuH" species generated in the decomposition of $CuBH_4$ (Scheme 1).

Hydrocupration of 1-alkynes with the $NaBH_4$-$MgBr_2$-Et_3N-CuCl or NaH-$MgBr_2$-CuCl reagent systems in THF:

As outlined in the introductory section, it has been reported that the $CuBH_4$ reagent, prepared from $LiBH_4$ and copper(I) salts, decomposes to 'BH_3' and 'CuH'.[83] The resulting copper(I) hydride is not stable above 0°C and decomposes into copper metal and hydrogen.

$$CuCl + LiBH_4 \xrightarrow[EE]{-20^\circ C} CuBH_4 + LiCl$$

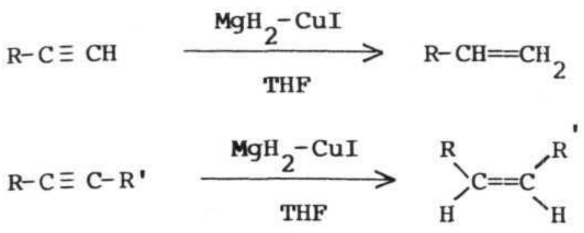
$$CuBH_4 \xrightarrow{0^\circ C} \text{'CuH'} + \text{'}BH_3\text{'}$$

It was of interest to utilize the copper(I) hydride reagent, generated by the decomposition of $CuBH_4$, for the hydrocupration of 1-alkenes and 1-alkynes in order to obtain alkyl and vinylcopper reagents. In order to examine this possibility, we carried out the following experiment in the presence of triethylamine to prevent hydroboration.[93] $NaBH_4$ (10 mmol, purified by recrystallization from 1,2-dimethoxy ethane) was added to a mixture of 1-decene (10 mmol), Et_3N (12 mmol) and anhydrous CuCl (10 mmol) in THF (60 ml) under nitrogen atmosphere at 0°C and stirred for 12 h at room temperature. After work-up only triethylamine-borane complex and unreacted 1-decene were isolated. When the above experiment was carried out using 1-decyne (10 mmol) in the place of 1-decene, the starting material was recovered quantitatively. Clearly, the copper(I) hydride, generated under the present reaction conditions, does not react with either 1-decene or 1-decyne.

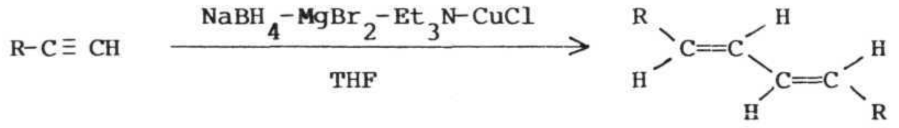
Normant, Alexakis and coworkers usually write the composition of the reagent system as $RCu.MgBr_2$ in their carbocupration reports.[45] However, Ashby and coworkers have found that this reagent actually exists in tetrahydrofuran (THF) as aggregates whose composition is dependent on the time and temperature of the reaction.[94] They also reported that the yields of the addition product of the 'RCu' species with phenylacetylene increase with excess of $MgBr_2$ in some cases.[94] It appeared that it may be possible to make the 'CuH' species more reactive by carrying out the reaction in the presence of $MgBr_2$. In order to examine this possibility we carried out the following experiment.

Magnesium bromide (20 mmol) was prepared in THF (50 ml) using Mg (40 mmol, excess) and 1,2-dibromoethane (20 mmol). This solution was then added to $NaBH_4$ (10 mmol) in THF (50 ml) under nitrogen, and the reaction mixture was stirred for 2 h at room temperature and cooled to -20°C. CuCl (15 mmol) and Et_3N (12 mmol) were added followed by 1-decene (5 mmol). The contents were stirred at -20°C for 2 h and at room temperature for 40 h. After work-up and chromatography only unreacted 1-decene was isolated. This is not surprising since it has been reported that the complexed copper(I) hydride reagent, generated using $LiAlH_4$ and CuI react with 1-octene to give only very low yields (5%) of 1-octane.[95]

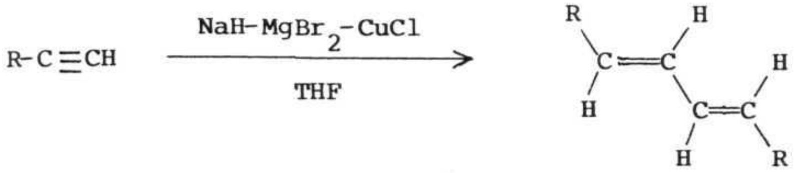
It has been reported that the reagent system, CuH-HMgI, generated by mixing of MgH_2 and CuI, is capable of reducing 1-alkynes and internal alkynes to the corresponding alkenes.[76]



Accordingly, we have examined the reactivity of the $NaBH_4/MgBr_2/CuCl/NEt_3$ reagent using 1-decyne instead of 1-decene. After work-up and chromatography on a silica gel column using hexane as eluent, (E,E)-9,11-eicosadiene was isolated in 60% yield. The formation of symmetrical 1,3-diene indicates that 1-decyne undergoes hydrocupration with $CuH-MgX_2$ (X=Br or Cl) reagent.



If the function of the triethylamine in this experiment is just to strip off the "BH_3" moiety as the corresponding unreactive amine-borane complex, it should possible to utilize NaH as the hydride source in the place of $NaBH_4$. The following experiment was carried out, replacing $NaBH_4$ with NaH and using 10 mmol of 1-heptyne in the absence of triethylamine. $MgBr_2$ (20 mmol) was prepared in THF (80 ml) using Grignard grade magnesium (40 mmol) and 1,2-dibromoethane (20 mmol). This solution was transferred to oil free NaH (~ 30 mmol) under nitrogen using a double ended needle. The mixture was stirred for 2 h at room temperature and cooled to -20°C. CuCl (15 mmol) and 1-heptyne (10 mmol) were added and stirred for 2 h at -20°C. The mixture was brought to room temperature and stirred further for 40 h at r.t. After work-up and chromatography on a silica gel column using hexane as eluent, (E,E)-6,8-tetradecadiene was isolated in 70% yield. The product was identified by comparison of the spectral data with the data reported for similar (E,E)-1,3-dienes previously.[96] Several other 1-alkynes were converted into the corresponding (E,E)-1,3-dienes following this procedure (Table 2).



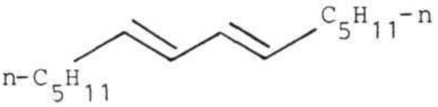
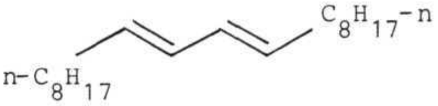
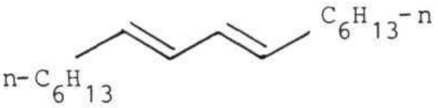
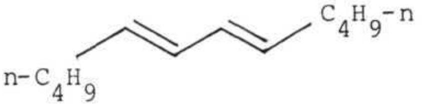
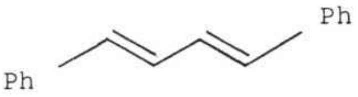
When the experiment was carried out utilizing methyl 10-undecynoate, the ester group was cleaved and only 10-undecynoic acid (15%) and unreacted methyl 10-undecynoate (70%) were isolated. However, the hydrocupration of 1-octyne was not prevented when the reaction was carried out in the presence of 1-decyl acetate. Here, the ester group cleaved product 1-decanol was isolated along with the (E,E)-7,9-hexadecadiene (55%). This indicates that the hydrocupration is prevented only when the substrate contains both the ester group and the acetylenic moiety in the same molecule and this behaviour is not clearly understood.

$$HC\equiv C\text{-}(CH_2)_8\text{-}COOMe \xrightarrow[\text{THF}]{\text{NaH-MgBr}_2\text{-CuCl}} \xrightarrow{H_3O^+} HC\equiv C\text{-}(CH_2)_8COOH$$

It was found that internal alkynes, diphenylacetylene and 5-decyne remained unreacted under the reaction conditions. Also, n-octyl cyanide and n-octyl bromide were not affected by the present system.

The ^{13}C-NMR spectra of the (E,E)-1,3-dienes obtained following the present method do not show signals corresponding to the (E,Z) or

Table 2: Conversion of terminal alkynes into (E,E)-1,3-dienes using $NaH-MgBr_2-CuCl$.

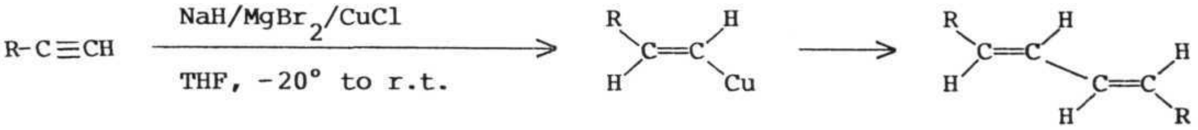
Substrate[a]	Product[b]	Yield (%)
$n-C_5H_{11}C\equiv CH$		70
$n-C_8H_{17}C\equiv CH$		77
$n-C_6H_{13}C\equiv CH$		73
$n-C_4H_9C\equiv CH$		70
$Ph-C\equiv CH$		60

a) The reactions were carried out using 10 mmol of alkyne, 15 mmol of anhydrous CuCl, 30 mmol of NaH in THF (80 ml). The reaction time and temperature were the same as those given in the text for all the substrates.

b) The products were isolated by chromatography on a silica gel column using hexane as eluent.

(Z,Z)-1,3-dienes or other isomers (if any). Accordingly, these isomers cannot be present in significant amounts in the (E,E)-1,3-dienes obtained following the present method. This indicates that the hydrocupration of 1-alkynes using the CuH/MgX_2 reagent system is highly regio- and stereospecific (Scheme 5).

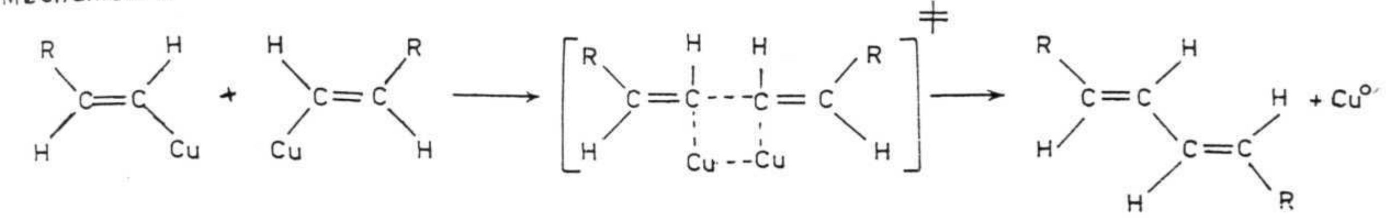
Scheme 5



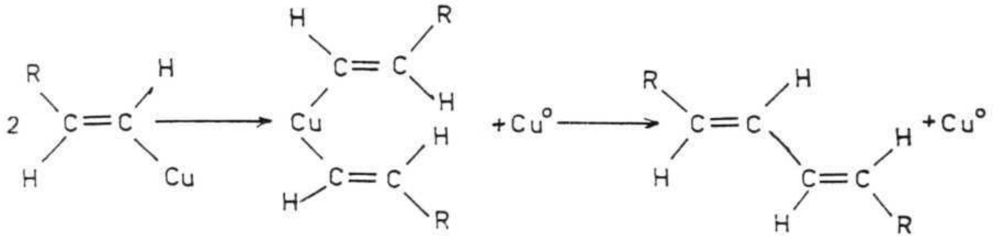
Presumably, the NaH reacts with $MgBr_2$ to give the magnesium hydride species[97,98] which in turn reacts with CuCl to give the reactive CuH-MgX_2 (X=Cl or Br) aggregates. The hydrocupration of the 1-alkynes by this reagent would result in the formation of (E)-alk-1-enylcopper species. Thermal decomposition of these vinylcopper intermediates would give the corresponding (E,E)-1,3-dienes. Whitesides and coworkers observed that the (E)-prop-1-enylcopper decomposes in diethyl ether at 25°C to give the corresponding (E,E)-1,3-diene with retention of stereochemistry about the double bond.[99] It was demonstrated that free radicals are not intermediates in this reaction and they suggested several other mechanistic pathways. It was concluded that two mechanisms are compatible with the results (Scheme 6). Mechanism A involves a four-center transition state and Mechanism B involves disproportionation of two molecules of the vinylcopper(I) reagent to a copper(0) atom and a copper(II) organometallic intermediate which give the diene by reductive elimination.

Scheme 6

Mechanism A



Mechanism B



The present results may be rationalised by the formation of vinylcopper intermediates (Scheme 5) by the addition of copper hydride species to the triple bond which in turn undergoes thermal decomposition to give the corresponding 1,3-diene by one of the mechanistic pathways suggested by Whitesides and coworkers (Scheme 6).

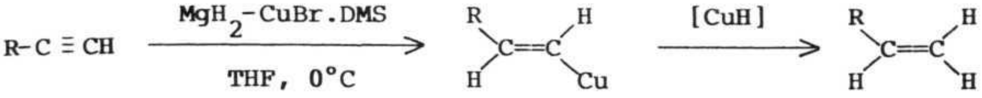
As outlined in the introductory section, vinylcopper(I) intermediates are versatile intermediates which can be transformed into various useful compounds by treating with electrophiles. We have carried out several experiments in order to examine the utilization of the vinylcopper intermediates produced in the present case.

It was thought that the decomposition into the 1,3-diene takes place due to longer reaction period at room temperature. It has been reported that the reaction of NaH with $MgBr_2$ in THF gives MgH_2 slurry in 48 h.[97,98] We prepared the MgH_2 slurry by mixing of NaH and $MgBr_2$

in THF and stirring the contents for 36 h before utilization and utilized the more soluble anhydrous CuBr and carried out the reaction as follows. To the MgH_2 slurry, CuBr (15 mmol) and 1-decyne (10 mmol) were added at -10°C (ice-salt) and the contents were stirred for 12 h at 0°C. After work-up the 1,3-diene (55%) and 1-decene (25%) were isolated.

House and coworkers reported a method for preparing the dimethylsulfide-copper bromide complex in a highly pure form, free of the copper(II) salt contaminents which is generally responsible for the decomposition of organocopper compounds.[100] We have purified the $CuBr.SMe_2$ complex in the same way and utilized in the following experiment: Dimethylsulfide-copper bromide complex was added to a MgH_2 slurry in THF at -10°C (ice-salt) followed by 1-decyne. The contents were stirred for 12 h at -10°C. After work-up and chromatography on a silica gel column using hexane as eluent, a mixture containing the 1,3-diene (50 %) and 1-decene (50 %) was isolated. The experiment was run under several conditions in order to avoid diene formation but these efforts were not successful.

It is known that deuterium incorporated product was obtained when the alkenylcopper intermediate was quenched with D_2O before work-up.[48] However, the 1-decene, obtained after treatment of the reaction mixture with D_2O before work-up in the runs with DMS-CuBr complex at 0°C, did not contain any deuterium. Clearly, the 1-decene is formed from vinylcopper intermediate before work-up. Surprisingly, the 1-decene was not formed in runs with CuCl. Presumably, the CuBr gives more soluble 'CuH' aggregates facilitating the reductive cleavage of vinylcopper intermediates into 1-decene. It may be of interest to note that it has been reported that the CuI/MgH_2 system also converts alkynes to alkenes.[76] Whitesides and coworkers reported that the CuH reagent converts CuR species into the corresponding hydrocarbons.[73]



Recently, Seyferth and coworkers reported that the alkylcopper(I) or alkenylcopper(I) intermediates undergo carbonylation with carbon monoxide to give acylcopper intermediates[101] which can be converted into acids and esters by treating with H_3O^+ and I_2/MeOH respectively. However, attempted carbonylations by bubbling carbon monoxide at 0°C in the experiments with $CuBr.SMe_2$ complex did not yield any other product besides the (E,E)-1,3-diene and 1-decene mixture. Presumably, the vinylcopper species undergo competitive dimerization and reductive cleavage reactions spontaneously in the present case.

In order to examine whether the diene formation can be prevented by utilizing other copper(I) salts, we have run similar experiments using CuI and CuCN in the place of CuBr.DMS complex in individual runs. However, the diene was isolated as a major product along with 1-decene (~25%) in these cases.

It has been reported that the vinylcopper intermediates produced by carbocupration of 1-alkynes are relatively stable in the presence of excess LiBr.[48] However, we have found that in the above runs with $CuBr.SMe_2$ complex, the results are the same both in the presence and absence of LiBr.

It was thought that it may be possible to prevent the diene formation by carrying out the hydrocupration reaction at low temperatures (-50°C to -20°C). However, when the experiment utilizing CuBr.DMS and 1-decyne was carried out at -20°C, only unreacted 1-decyne was recovered after work-up and chromatography. It is clear that the hydrocupration takes place only between 0°-room temperature.

It has been reported that alkenes and alkynes can be hydrometalated with MgH_2 in the presence of catalytic amount of Cp_2TiCl_2.[102] It was suggested that it involves hydrotitanation-transmetalation sequence (Scheme 7).

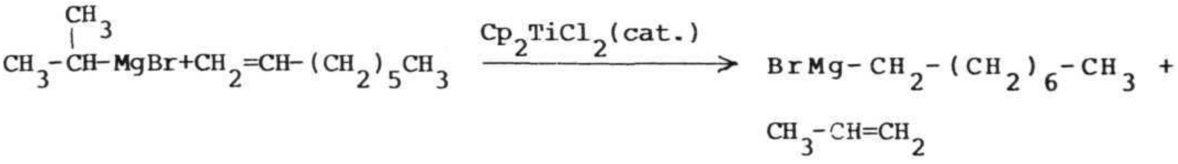
Scheme 7

$$CH_2{=}CH{-}(CH_2)_5CH_3 \xrightarrow[1\%\ Cp_2TiCl_2]{MgH_2} CH_3{-}(CH_2)_6{-}CH_2{-}MgX \xrightarrow{H_3O^+} CH_3{-}(CH_2)_6{-}CH_3$$

$$HC{\equiv}C{-}(CH_2)_5CH_3 \xrightarrow[1\%\ Cp_2TiCl_2]{MgH_2} XMg{-}CH{=}CH{-}(CH_2)_5CH_3 \xrightarrow{H_3O^+} CH_2{=}CH{-}(CH_2)_5CH_3$$

It was of interest to examine the possibility of preparing vinylcopper(I) reagent via hydrotitanation-transmetalation to MgX_2 (Scheme 7) and then to CuX. In order to examine this possibility, we carried out the following experiment. The MgH_2 slurry in THF (80 ml) was prepared in the usual way. To this, Cp_2TiCl_2 (2 mmol) was added under nitrogen atmosphere at -10°C. CuBr.DMS (15 mmol) and 1-decyne (10 mmol) were successively added. The reaction mixture turned to black color. It was stirred for 10 h at 0°C. After usual work-up and chromatography, an yellow product mixture was isolated. GC analysis of this compound indicated the presence of 1-decene (30%), (E,E)-9,11-eicosadiene (30%) and an unidentified oligomeric compound in the mixture.

We have also attempted another way to synthesize vinyltitanium derivatives and transmetalate to CuX. It is known that titanium hydride species (see Chapter 2) is the intermediate in the exchange of isopropylmagnesium bromide to 1-octylmagnesium bromide.[103]

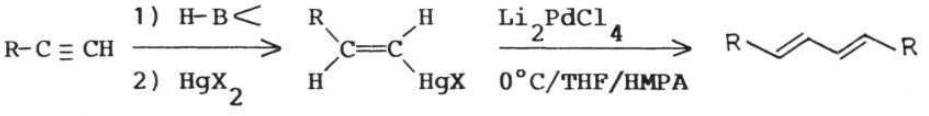


$$CH_3-\overset{CH_3}{\overset{|}{CH}}-MgBr+CH_2{=}CH-(CH_2)_5CH_3 \xrightarrow{Cp_2TiCl_2(cat.)} BrMg-CH_2-(CH_2)_6-CH_3 + CH_3-CH{=}CH_2$$

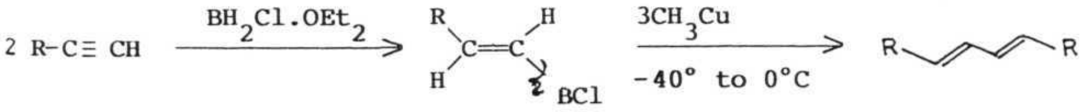
It was of interest to examine the possibility of utilizing titanium hydride species produced in this way for hydrotitanation of acetylenes and transmetalate to CuX. The following experiment was carried out in order to examine this possibility. t-BuMgBr was prepared by the addition of 1,2-dibromoethane to the Grignard grade magnesium and t-BuCl in THF (80 ml). To this, catalytic amount of Cp_2TiCl_2 (2 mmol) and CuCl (15 mmol) were added at -20°C. After 2 h stirring, 1-decyne was added. The contents were brought to r.t. during 2 h and stirred further for 12 h at r.t. After work-up and chromatography, only a polymeric compound was isolated. It did not distill even at 300°C under 0.5 mm Hg pressure. This oligomeric product was not characterized further. The reagent system gave isomerized 2-decenes with 1-decene. The polymeric material was also obtained when the reaction was carried out in the absence of CuCl. 1-Decene was also isomerized into 2-decenes in the absence of CuCl. The results indicate the formation of a titanium species capable of oligomerizing 1-decyne and isomerizing 1-decene. Further investigations of this system is described in chapter 2.

Our attempts to utilize the vinylcopper intermediates generated using the $CuCl/MgH_2$/1-alkyne system were unsuccessful. However, the present work does provide a simple method for the conversion of 1-alkynes into the corresponding 1,3-dienes.

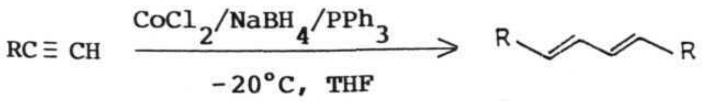
Vinylmercury compounds, obtained through hydroboration of acetylenes and transmetalation to mercury, on treatment with palladium chloride and lithium chloride in HMPA at 0°C give the corresponding (E,E)-1,3-dienes.[104]



Hydroboration of 1-alkynes with chloroborane-etherate provides a convenient method for the preparation of dialkenylchloroboranes which on treatment with methylcopper produce (E,E)-1,3-dienes.[105]



The $CoCl_2/NaBH_4/PPh_3$ reagent system was utilized in our laboratory for hydrodimerization of 1-alkynes to the corresponding (E,E)-1,3-dienes.[96]



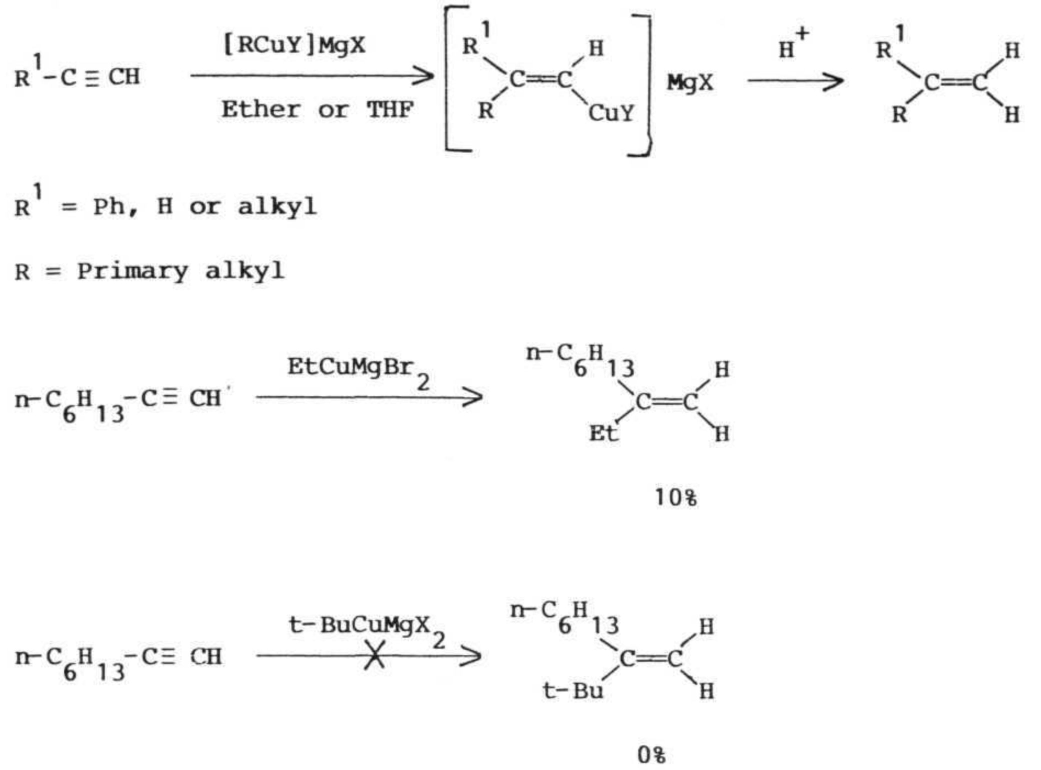
In addition to providing a reagent system for the hydrocupration of 1-alkynes, the present method also serves as a relatively simple alternate procedure to the methods available for the conversion of 1-alkynes into the corresponding (E,E)-1,3-dienes.

Carbocupration of 1-alkynes with branched alkyl heterocuprates ($RCuMgX_2$) in the presence of excess $MgBr_2$:

As outlined in the introductory section, organocopper reagents prepared from CuI and a primary Grignard reagent (eg. n-BuMgBr) in Et_2O are capable of reducing internal alkynes into the corresponding cis-alkenes in a stereoselective manner.[77] A mechanism involving the in situ generation of a copper(I) hydride species has been proposed.[77] It has been reported that the organocopper reagent derived from t-BuMgBr decomposed more rapidly as anticipated but no reduction was observed.[77] In the course of our efforts to utilize the copper hydride species, generated by the decomposition of t-$BuCuMgX_2$ in THF, for the hydrocupration of terminal alkynes into vinylcopper intermediate we have obtained the corresponding carbocupration product. This is unexpected since the branched alkylcuprates are relatively unreactive towards less reactive 1-alkynes such as 1-decyne. Accordingly, we have decided to investigate this further. A brief survey of literature on the subject will be helpful.

It has been reported that heterocuprates ($RCuMgX_2$ or RCuLiX, R=primary alkyl, X=Br, I or SPh) obtained from CuX and RMgX, can be readily added to reactive 1-alkynes ($RC \equiv CH$; R = Ph, H, Me) (Scheme 8).[46,48,52,53] However, carbocupration of less reactive 1-alkynes (eg. 1-octyne) using branched alkyl heterocuprates (eg. tert-$BuCuMgX_2$) was not successful (Scheme 8).

Scheme 8



R^1 = Ph, H or alkyl

R = Primary alkyl

As mentioned above, we have found that the branched alkylcopper reagents readily add to the less reactive 1-alkynes under the present reaction conditions. Presumably, presence of excess $MgBr_2$ (~20 mmol) facilitates the reaction, similar to the observations with the CuCl/MgH_2 system. The experiment was carried out as follows: to a mixture of Grignard grade magnesium (60 mmol) in THF (80 ml) containing t-BuCl (20 mmol), 1,2-dibromoethane (20 mmol) was added during a period of 10 min at r.t. under nitrogen atmosphere and the mixture was stirred for 3 h. The contents were cooled to -24°C (liq.N_2 and CCl_4 bath) and CuCl (20 mmol) was added. The mixture was stirred for 2 h at -24°C and 1-decyne (10 mmol) was added. The black reaction mixture was brought to r.t. during a period of 3 h and stirred for further 12 h. After usual work-up and chromatography on a silica gel column, 2-tert-butyl-1-decene (65%) and unreacted 1-decyne (30%) were isolated.

In order to examine the stability of the vinylcopper intermediates produced in the present case, the reaction mixture was treated with D_2O before work-up and stirred for 1 h in a run with t-amyl chloride. Mass spectral data of the isolated alkene revealed that the deuterium was incorporated to the extent of 75% (M^+ peak at m/e 211 and M^+-1 peak at m/e 210 are in 3:1 ratio) and the recovered 1-decyne did not contain any deuterium.

The reaction was found to be a general one and the results obtained using different branched alkylcuprates with 1-decyne and 1-octyne are summarized in Table 3.

The literature reports indicate that when the addition of heterocuprates to alkynes were carried out at temperatures above -15°C, the terminal alkenes obtained after hydrolysis were contaminated with variable amounts of the 1,3-dienes, resulting from the consecutive thermal dimerization of the vinylcopper intermediates. However, in the present case the vinylcopper intermediate is somewhat stable even at r.t. as indicated by deutorolysis with D_2O. It has been reported that excess LiBr exhibits a favourable influence on the thermal stability of the vinylcopper intermediates and the thermal dimerization was absent in the presence of excess LiBr at higher temperatures.[48] Such solutions are even stable at room temperature. Presumably, the $MgBr_2$ also has similar effect. In addition, the vinylcopper intermediate formed in the present case would be highly hindered. This aspect may also help in the unusual stability of the vinylcopper intermediates in the present case since the formation of the Whitesides (Scheme 6) transition state or intermediate A and B would be difficult when the alkyl groups are bulky.

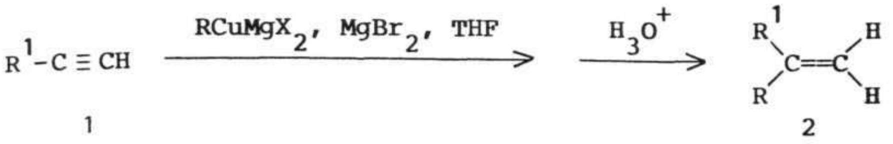


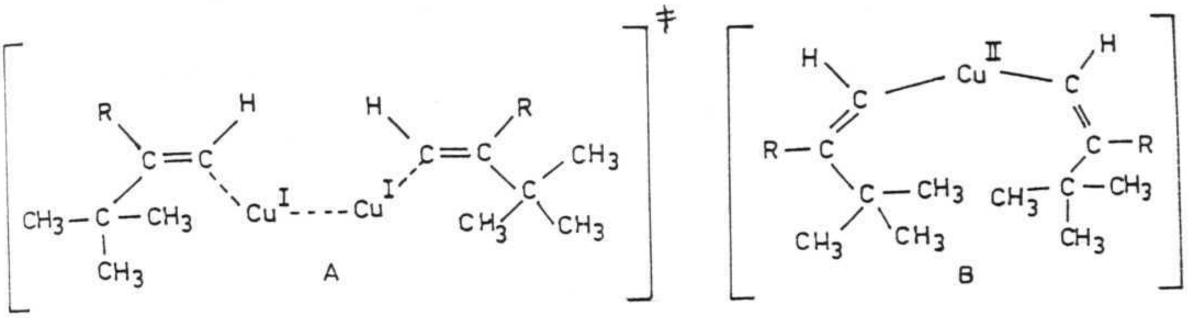
Table 3: Conversion of 1-alkynes into 2,2-dialkyl olefins.

Entry	R' in 1 (10 mmol)	R in RMgX/CuCl/MgBr$_2$[a] (20/20/20 mmol)	Yield (%)[b] 2	Recovered 1-alkyne (%)[c]
1	n-C_8H_{17}	t-Bu (X=Cl)	65	30
2	n-C_6H_{13}	t-Bu (X=Cl)	60	35
3	n-C_8H_{17}	iso-propyl (X=Br)	57	35
4	n-C_8H_{17}	t-amyl (X=Cl)	40	50
5	n-C_6H_{13}	t-amyl (X=Cl)	40	52

a) All the reactions were carried out under the same conditions of temperature and time using 10 mmol of 1-alkyne, 20 mmol of CuCl, 20 mmol of RMgX and 20 mmol of $MgBr_2$. Further increase in the amount of $MgBr_2$ did not have any affect and only small amount (5%) of addition product was isolated without $MgBr_2$.

b) All yields are of isolated products by chromatography on a silica gel column using hexane as eluent and are based on the amount of 1-alkyne initially taken. The actual yields will be higher if the amount of recovered 1-alkynes are taken into account. The products were identified by IR, ^{1}H NMR, ^{13}C NMR and mass spectral data.

c) Yields are of recovered starting alkynes.



This might also explain the thermal instability of the relatively less hindered vinylcopper species produced by the reaction of CuCl/MgH_2 system (Scheme 5).

Another problem in the carbocupration of 1-alkynes with secondary or tertiary alkylcuprates is the abstraction of the acetylenic proton.[46,47] It has been found that such proton abstractions were suppressed completely by carrying out the addition in the presence of LiBr.[48] In the present case also the $MgBr_2$ seems to suppress proton abstraction since the recovered 1-decyne did not contain any deuterium when the reaction mixture was treated with D_2O before work-up.

We have observed that the conversion is very low when the reaction was carried out in diethyl ether solvent. For example, in runs with 1-decyne, only 10% of the carbocuprated products were isolated besides unreacted starting material.

Control experiments clearly indicate that the addition of branched alkylcuprate requires the presence of excess $MgBr_2$. Only small amount (~5%) of addition product was isolated without using $MgBr_2$ and it is well-known that the acetylenic proton abstraction is the only reaction in the absence of Cu(I) salts.

In order to examine the effect of copper(I) salt on the carbocupration of 1-alkynes, we carried out individual runs using CuBr.DMS complex in the place of CuCl. The 1-decyne was recovered quantitatively in all cases. This is highly unexpected since the CuBr.DMS is more soluble in the medium. We do not have any explanation for this since the nature of the reactive species is not clearly understood.

SUMMARY

The $CuCl/NaBH_4$ reagent system was utilized for the preparation of copper(I) alkylhydroborates, $Cu[BH_mR_n]$, in the presence of olefins, to initiate a hydroboration-comproportionation sequence. Although this attempt is conceptually pleasing, only low yields of alkyl transferred products were isolated when alkylation of methyl acrylate was carried out with this reagent. The $NaBH_4/CuCl/NEt_3$ was utilized for the hydrocupration of 1-alkynes in the presence of $MgBr_2$. Utilizing NaH as the hydride source, a simple method for hydrodimerization of 1-alkynes into the corresponding (E,E)-1,3-dienes was developed. As an offshoot of the efforts on hydrocupration of 1-alkynes, a method for the carbocupration of less reactive 1-alkynes with branched alkylcuprates was developed.

EXPERIMENTAL

All 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-FX-100 Spectrometer with chloroform-d as a solvent and TMS as reference (δ = 0 ppm). Elemental analysis 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 ionisation 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's silica gel (100-200 mesh).

All glassware was predried in an air oven, assembled at hot conditions 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.[106] Glove bag techniques were followed for handling sodium hydride under a stream of nitrogen gas. Reagents prepared <u>in situ</u> in solvents were transformed using double ended stainless steel (Aldrich) needle under a stream of nitrogen whenever required.

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 dry solvents were distilled from appropriate drying agents just before use. As a routine all organic extracts were washed with saturated sodium chloride solution and 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 gr) supplied by LOBA-Cheme, India and Fluka, Switzerland were utilized and were kept under nitrogen in a dessicator after opening the bottle. Sodium hydride (55-60% dispersion in oil) supplied by Fluka, Switzerland was utilized and stored in a dessicator under nitrogen atmosphere. Commercial Grignard grade magnesium, supplied by Fluka, Switzerland was utilized. 1,2-Dibromoethane, supplied by BDH, England was utilized. The olefins utilized were commercial samples supplied by Fluka, Switzerland. 1-Decyne, 1-octyne and phenylacetylene were prepared following a reported procedure.[107] 1-Heptyne and 1-hexyne utilized were supplied by Fluka, Switzerland.

Anhydrous CuCl utilized was prepared from $CuCl_2.2H_2O$ and Na_2SO_3.[108] It was dried further at 100°C for 3 h under vacuum. t-Butyl chloride and t-amyl chloride were prepared following a reported procedure.[109]

Sec-butyl bromide and iso-propyl bromide supplied by Fluka, Switzerland were utilized.

Hydroboration of 1-decene using CuCl/$NaBH_4$ in THF:

A mixture of CuCl (10 mmol, 1.0 g) and 1-decene (20 mmol, 2.8 g) in THF (80 ml) was cooled to -10°C (ice-salt bath) and $NaBH_4$ (10 mmol, 0.4 g) was added in portions during 15 minutes using a solid-addition flask under nitrogen atmosphere. The temperature was raised to 25°C during 2 h and the mixture was stirred at this temperature for 12 h (24 h in the case of other olefins). The excess hydride (if any) was destroyed by adding water (2 ml). 3N NaOH (10 ml) was added carefully at 0°C and H_2O_2 (20 ml, 16%) was introduced dropwise. The contents were stirred for 3 h 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 (30 ml), saturated sodium chloride solution (30 ml) and dried over anhydrous $MgSO_4$. The solvent was evaporated and the residue was chromatographed on a silica gel column. The product eluted with hexane was identified as decane (0.142 g, 10%). The product eluted with $CHCl_3$ was identified as 1-decanol (2.37 g, 75%). IR spectra of these products showed 1:1 correspondence with the spectra reported in the literature.[110]

Spectral data for 1-decanol

IR (neat): ν_{max}: 3350, 1140 cm^{-1}.

B.P. 110°C/10 mm, Lit[111], 120°/12 mm.

^{1}H NMR (100 MHz, $CDCl_3$): δ ppm 5.3 (br-s,-OH), 3.6 (t,-CH_2), 1.2 (m,other
-CH_2 hydrogens), 0.9 (t,-CH_3).

^{13}C NMR (25.0 MHz, $CDCl_3$): δ ppm 62.6, 32.7, 31.9, 29.6, 29.4, 29.2,
25.9, 22.6, 13.9.

Signals due to the isomeric 2-decanol were not observed in the ^{13}C NMR spectrum which indicates that the isomeric 2-decanol (if any) cannot be present more than 5%. Several other olefins were hydroborated following the above procedure and the resulting organoboranes were oxidised with H_2O_2/ $\bar{O}H$. In these cases, we have not attempted the isolation of the volatile reduction product. The hydroboration-oxidation results are summarized below.

Styrene ⟶ 2-phenyl-1-ethanol

Yield: 75% (1.8 g).

B.P. 90-92°C/10 mm, Lit.[112] 100-106°/12 mm.

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

^{1}H NMR (100 MHz, $CDCl_3$): δ ppm 7.3-7.1 (m,-C_6H_5), 4.7 (q,CH-O-), 3.6
(t,-CH_2-O), 2.8 (br,s,OH), 2.7 (t,-CH_2),
1.4 (d,-CH_3).

^{13}C NMR (25.0 MHz, $CDCl_3$): δ ppm 138.7, 128.8, 128.2, 127.1, 126.1,
125.3, 65.9 ($\underline{C}$HOH), 63.3, ($\underline{C}H_2OH$),
35.1 ($\underline{C}H_2$-Ar) 24.9 ($\underline{C}H_3$).

^{1}H and ^{13}C NMR signals showed that upto 17% of the isomeric 1-phenylethanol is present.

Cyclohexene $\longrightarrow$ cyclohexanol

Yield: 65% (1.3 g).

B.P. 60°C/10 mm, Lit.[113] 157°/760 mm.

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

^{13}C NMR (25.0 MHz, $CDCl_3$): δ ppm 69.0 ($\underline{C}HOH$), 34.6, 25.0, 23.7.

Norbornene $\longrightarrow$ exo-norborneol

Yield: 68% (1.5 g).

M.P. 125°C, Lit.[114] 127-8°.

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

^{1}H NMR (100 MHz, $CDCl_3$): δ ppm 3.6 (br-s,OH), 2.0 (br-m,-CH), 1.5-1.1 (m,-CH protons), 1.0-0.7 (m,$-CH_2$ protons).

^{13}C NMR (25.0 MHz, $CDCl_3$): δ ppm 74.6 ($\underline{C}HOH$), 44.1, 42.2, 35.4, 34.3, 28.2, 24.5.

The ^{13}C NMR data were identical to the data reported in the literature.[114a]

α-Pinene $\longrightarrow$ isopinocampheol

Yield: 60% (1.9 g).

B.P. 98°C/10 mm, Lit.[115] 217°/760 mm.

IR (neat): ν_{max}: 3350 cm^{-1}

^{13}C NMR (25.0 MHz, $CDCl_3$): δ ppm 71.7 ($\underline{C}H-OH$), 48.2, 48.0, 47.8, 42.1, 38.3, 34.1, 27.9, 23.8, 20.8.

The ^{13}C NMR data were identical to the data reported in the literature.[115a]

The above hydroboration procedure was followed for methyl-10-undecenoate. In this case, the $H_2O_2/NaOOCCH_3$ system was utilized for oxidation. The methyl undecanoate (0.3 g, 15%, the yield in this case is based on the assumption that only one equivalent of the alkyl or hydride in the borate complex form would undergo reduction) and methyl-11-hydroxy-undecanoate (3.1 g, 70%) were isolated by column chromatography using hexane/$CHCl_3$ as eluent.

$$CH_2{=}CH{-}(CH_2)_8COOMe \longrightarrow \underset{70\%}{HO{-}CH_2{-}(CH_2)_9COOMe} + \underset{15\%}{CH_3{-}(CH_2)_9COOMe}$$

Spectral data for methyl-11-hydroxyundecanoate

Yield: 70% (3.1 g).

B.P. 130°C/1 mm, Lit.[116] 156-159°/3 mm.

IR (neat): ν_{max}: 3350, 1720 cm^{-1}.

^{13}C NMR (25.0 MHz, $CDCl_3$): δ ppm 174.2 ($\underline{C}OOMe$), 63.1 ($\underline{C}H_2OH$), 51.3 ($O\underline{C}H_3$), 37.2, 32.9, 29.7, 29.5, 29.4, 29.2, 25.8, 25.1.

Examination of the formation of $Cu[(RCH_2CH_2)_nBH_m]$ species via hydroboration-comproportionation sequence with CuH generated in situ using CuCl/$NaBH_4$ and 1-decene system by hydrolysis

$NaBH_4$ (10 mmol, 0.4 g) was slowly added for 15 minutes to a precooled (-10°C) solution of CuCl (10 mmol, 1.0 g) and 1-decene (20 mmol, 2.8 g) in THF (80 ml) under nitrogen atmosphere. The temperature of the reaction mixture was brought to 25°C during 2 h and the contents were stirred for further 12 h. The reaction mixture was hydrolysed with water (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 ether extract was washed with saturated sodium chloride solution and dried over anhydrous $MgSO_4$. The solvent was evaporated and the residue was chromatographed to isolate decane (0.142 g, 10%) using hexane as eluent. The IR spectrum was superimposable with the reported IR spectrum.[110]

Yield: 10% (0.142 g).
B.P. 56-57°C/10 mm, Lit.[117] 63°/15 mm.
^{13}C NMR (25.0 MHz, $CDCl_3$): δ ppm 31.9, 29.7, 29.4, 22.7, 14.0.

The above procedure was followed in a run with methyl-10-undecenoate and the methyl undecanoate (0.3 g, 15%) was isolated by column chromatography using 50% chloroform in hexane as eluent.

B.P. 72°C/1 mm, Lit.[113] 70-2°/1 mm.
^1H NMR (100 MHz, $CDCl_3$): δ ppm 3.5 (s,$-OCH_3$), 2.1 (t,$-CH_2$), 1.17 (m, all other CH_2 hydrogens), 0.8 (t,$-CH_3$).
^{13}C NMR (25.0 MHz, $CDCl_3$): δ ppm 174.0 ($\underline{C}OOCH_3$), 51.2 ($O\underline{C}H_3$), 34.2, 31.9, 28.5, 28.2, 28.0, 25.0, 22.7, 14.0.

Attempted conjugate alkylation of methyl acrylate using copper(I) decylborohydride prepared from CuCl/$NaBH_4$ and 1-decene:

The copper(I) decylborohydride was prepared by adding $NaBH_4$ (10 mmol, 0.4 g) to a mixture of CuCl (10 mmol, 1.0 g) and 1-decene (20 mmol, 2.8 g) in THF (80 ml) at -10°C (bath temperature). The reaction mixture was stirred further for 8 h at this temperature and methyl acrylate (10 mmol, 0.86 g) was added. The mixture was further stirred for 2 h at -10°C. The contents were hydrolysed with water (2 ml) and the organoboron product was oxidised with sodium acetate (20 ml, 3N) and H_2O_2 (20 ml, 16%) at 0°C. The mixture was brought to room temperature and stirred further for 3 h. The contents were poured into dil.HCl (50 ml, 3N) and the organic layer was separated. The aqueous layer was extracted with ether (3x30 ml). The combined organic extract was washed with water (50 ml), brine (50 ml) and dried over anhydrous $MgSO_4$. The residue obtained after removal of the solvent was subjected to column chromatography (hexane/chloroform as eluent) to isolate methyl tridecanoate (0.115 g, 5%) and tridecanal (0.10 g, 5%) along with polymeric materials containing ester and decyl groups.

Spectral data for methyl tridecanoate

IR (neat): ν_{max}: 1740 cm^{-1}.

^{1}H NMR (100 MHz, $CDCl_3$): δ ppm 3.6 (s,$-OCH_3$), 1.5 (t,$-CH_2$),1.2 (m,$-CH_2-$ hydrogens), 0.8 (t,$-CH_3$).

Mass spectrum (m/e): 228 (M^+).

Spectral data for tridecanal

IR (neat): ν_{max}: 2720, 1725 cm^{-1}.

^{1}H NMR (100 MHz, $CDCl_3$): δ ppm 9.67 (t,$-\overset{O}{\overset{\|}{C}}-H$), 2.27 (q,$-CH_3$), 1.19 (m,$-CH_2-$ hydrogens), 0.8 (t,$-CH_3$).

Attempted conjugate alkylation of methyl acrylate using copper(I) decylborohydride prepared from CuCl, $NaBH_4$ and 1-decene in the presence of PBu_3:

The preparation of copper(I) decylborohydride is outlined in the above experiment. To this PBu_3 (15 mmol, 3.0 g) was added at 0°C followed by methyl acrylate (10 mmol, 0.86 g). The reaction mixture was stirred for 3 h at 0°C and hydrolysed. The organic layer was separated. The aqueous layer was extracted with ether (3x30 ml). The combined organic extract was washed with brine solution (50 ml) and dried over anhydrous $MgSO_4$. The solvent was evaporated and the residue was chromatographed on a silica gel column. The mixture of eicosane and decane (0.52 g, 30%) in 1:1 ratio were eluted with hexane and the Bu_3P-alkylborane complex was eluted with $CHCl_3$. The ratio of eicosane and decane was determined by GC analysis. Strong B-H absorption at 2350 cm^{-1} was observed in the IR spectrum of the Bu_3P-alkylborane complex.

Examination of the possibility of $ClBH_2:OEt_2$ synthesis using the reagent system $ZnCl_2$, $NaBH_4$ and CuCl (0.5:1:2) in EE solvent:

To a solution of $ZnCl_2$ (5 mmol, 0.68 g) in EE (80 ml), $NaBH_4$ (10 mmol, 0.4 g) was added under nitrogen atmosphere at room temperature. The mixture was stirred for 2 h and CuCl (20 mmol, 2.0 g) was added to this solution at 0°C (bath temperature). The reaction mixture was brought to 25°C and stirred further for 2 h. 1-Decene (30 mmol, 4.2 g) was added and the mixture was stirred for 12 h. The mixture was hydrolysed with MeOH (2 ml) and the organoborane was oxidised with $NaOH/H_2O_2$.

The reaction mixture was poured into HCl (50 ml, 3N) and the organic layer was separated. The aqueous layer was extracted with ether (3x30 ml). The combined organic extract was washed with water (50 ml), brine (50 ml) and dried over anhydrous $MgSO_4$. The residue obtained after removal of the solvent was distilled to isolate 1-decene (9 mmol, 1.2 g) and 1-decanol (18 mmol, 2.8 g). The IR spectra of these compounds were found to be superimposable with the reported IR spectra.[110]

Further examination of the formation of dialkylchloroborane species by the carbenoidation reaction with $NaOCH_3/CHCl_3$:

To the monochloroborane species, prepared from $ZnCl_2$ (5 mmol, 0.68 g), $NaBH_4$ (10 mmol, 0.4 g) and CuCl (20 mmol, 2.0 g) in EE (conditions mentioned in the above experiment), 1-decene (20 mmol, 2.8 g) was added at room temperature and the mixture was stirred for 12 h. To the reaction mixture chloroform (10 ml) was added followed by NaOMe (40 mmol, 2.16 g) from a solid addition flask during 20 minutes. The contents were further stirred at 55°C for 4 h. The mixture was brought to room temperature and water (2 ml) was added. The organoboron compound was oxidised with H_2O_2/NaOH. The contents were neutralized with 2N HCl and extractd with ether (3x30 ml). The combined ether extract was washed with saturated sodium chloride solution (50 ml), dried over anhydrous $MgSO_4$ and the solvent was removed. The residue was chromatographed on a silica gel column (hexane-chloroform as eluent) to yield di-1-decylketone (1.8 g, 60%) and 1-decanol (1.0 g, 35%) (yields are based on the amount of 1-decene utilized).

Spectral data for di-1-decylketone

Yield: 60% (1.8 g).

IR (neat): ν_{max}: 1710 cm^{-1}.

M.P.64°C, Lit.[118] m.p. 64°C.

^{1}H NMR (100 MHz, $CDCl_3$): δ ppm 3.4 (t,$-CH_2-$), 1.75 (m,$-CH_2-$), 1.5 (m,$-CH_2-$), 1.25 (m, other $-CH_2-$ hydrogens), 0.9 (m,$-CH_3$).

^{13}C NMR (25.0 MHz, $CDCl_3$): δ ppm 211.0 ($-\overset{O}{\overset{\|}{C}}-$), 42.9 ($CO-\underline{C}H_2$), 32.1, 29.4, 24.1, 22.8, 14.1.

Attempted hydrocupration of 1-decene using the $NaBH_4/CuCl/Et_3N$ system:

To a mixture of CuCl (10 mmol, 1.0 g), 1-decene (10 mmol, 1.4 g), triethylamine (12 mmol, 6 ml, standard solution prepared by taking 100 mmol (10.1 g) of Et_3N in 50 ml THF) in THF (80 ml), $NaBH_4$ (10 mmol, 0.4 g, purified by recrystallization from 1,2-dimethoxy ethane) was added in portions during 15 min at 0°C (ice bath) under nitrogen atmosphere. The contents were brought to room temperature during 1 h and stirred for 12 h. The reaction mixture was poured into water (50 ml). Solid sodium chloride was added to saturate the mixture and the organic layer was separated. The aqueous layer was extracted with ether (3x30 ml). The combined organic extract was washed with water (50 ml), brine (50 ml) and dried over anhydrous $MgSO_4$. The solvent was removed and the residue was chromatographed on a silica gel column to isolate unreacted 1-decene (1.25 g, 90%) and $Et_3N:BH_3$ (90%). IR spectrum of the $Et_3N:BH_3$ complex exhibited strong B-H absorptions at 2235, 2280 and 2340 cm^{-1}.

The above experimental procedure was followed for the hydrocupration of 1-decyne using the $NaBH_4/CuCl/Et_3N$ reagent system. Only unreacted 1-decyne and $Et_3N:BH_3$ complex were isolated after chromatography on a silica gel column.

Hydrocupration of 1-decyne using $NaBH_4/MgBr_2/Et_3N/CuCl$ reagent system in THF:

The $MgBr_2$ (20 mmol) solution was prepared in THF (50 ml) using Mg (40 mmol, 1.0 g excess) and 1,2-dibromoethane (20 mmol, 3.7 g) under nitrogen atmosphere at room temperature. This solution was transferred into another flask containing purified $NaBH_4$ (10 mmol, 0.4 g) in THF (50 ml) using a double ended needle under nitrogen atmosphere. The contents were stirred for 2 h at room temperature and cooled to -20°C (bath temperature). CuCl (15 mmol, 1.5 g) and Et_3N (12 mmol, 6 ml) were added followed by the addition of 1-decyne (5 mmol, 0.7 g). The contents were stirred at -20°C for 2 h and at room temperature for 40 h. The resulting black mixture was poured into dil.HCl (3N, 100 ml). The 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 (50 ml), saturated sodium chloride solution (50 ml) and dried over anhydrous $MgSO_4$. The solvent was evaporated and the residue was chromatographed on a silica gel column using hexane as eluent to isolate a compound which was identified as (E,E)-9,11-eicosadiene (60%) (the spectral data are given later).

Hydrocupration of 1-heptyne using NaH/$MgBr_2$/CuCl reagent system in THF:

To a suspension of Mg (40 mmol, 1.0 g) in THF (100 ml), 1,2-dibromoethane (20 mmol, 3.7 g) was added during 10 min under nitrogen atmosphere and stirred for 2 h at room temperature to obtain $MgBr_2$ in THF solution. The NaH (30 mmol, 1.5 g in oil) was taken in another flask under nitrogen atmosphere using glove bag and the oil was washed with dry THF (2x10 ml). The $MgBr_2$ solution was transferred into the flask containing oil free NaH and the mixture was stirred for 3 h at room temperature and cooled to -20°C (bath temperature). CuCl (15 mmol, 1.5 g) was added followed by 1-heptyne (10 mmol, 0.96 g). The mixture was brought to room temperature during 3 h and stirred further for 48 h. The black reaction mixture was poured into HCl (3N, 100 ml). The mixture was saturated with solid sodium chloride and the layers were separated. The aqueous layer was extracted with ether (3x30 ml). The combined organic solution was washed with water (50 ml) followed by brine solution (50 ml) and dried over anhydrous $MgSO_4$. The ether extract was evaporated and the residue was subjected to chromatography on a silica gel column using hexane as eluent to isolate (E,E)-6,8-tetradecadiene.

Spectral data for (E,E)-6,8-tetradecadiene

Yield: 70% (0.68 g).

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

^1H NMR (100 MHz, $CDCl_3$): δ ppm 6.1-5.1 (m,-CH), 4.8 (m,-CH), 2.0 (br,-CH_2), 1.2 (m,-CH_2- hydrogens), 0.9 (t,-CH_3).

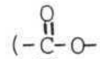
^{13}C NMR (25.0 MHz, $CDCl_3$): δ ppm 132.4, 130.5, 32.8, 32.6, 32.1, 29.4, 22.8, 14.3. **(spectrum No. 1)**

The spectral data of the (E,E)-6,8-tetradecadiene were identical to the data of the sample previously obtained in the reaction of n-$C_5H_{11}C\equiv CH$ and $(Ph_3P)_2Co(H)Cl$ in our laboratory.[96,119] It was further characterized by the preparation of the maleic anhydride adduct.

Spectral data of the maleic anhydride adduct prepared from (E,E)-6,8-tetradecadiene

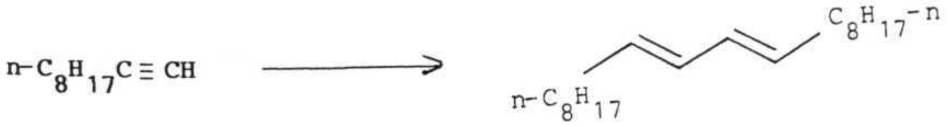
M.P. 124°C.

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

^{13}C NMR (25.0 MHz, $CDCl_3$): δ ppm 177.8  $(-\overset{O}{\overset{\|}{\underline{C}}}-O-)$, 133.90 $(-\underline{C}=\underline{C}-)$, 44.9, 36.3, 31.6, 30.5, 27.6, 22.6, 13.9. **(spectrum No. 1A)**

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

The procedure outlined in the previous experiment was followed for the conversion of several 1-alkynes into the corresponding (E,E)-1,3-dienes utilizing the NaH/$MgBr_2$/CuCl reagent system in THF solvent.



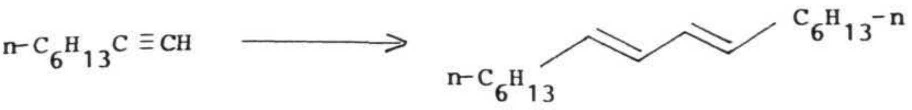
Yield: 77% (1.06 g).

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

^{1}H NMR (100 MHz, $CDCl_3$): δ ppm 6.2-5.3 (m,-CH), 4.0(m,-CH), 2.0 (br,-CH_2), 1.3 (m,-CH_2- hydrogens), 0.99 (t,-CH_3).

^{13}C NMR (25.0 MHz, $CDCl_3$): δ ppm 132.2, 130.6, 32.8, 32.1, 29.7, 29.5, 29.2, 22.8, 14.2.

The spectral data of the (E,E)-9,11-eicosadiene were found to be identical to the data of the sample previously obtained in the reaction of n-$C_8H_{17}C\equiv CH$ and $(PPh_3)_2Co(H)Cl$ in our laboratory.[96,119]



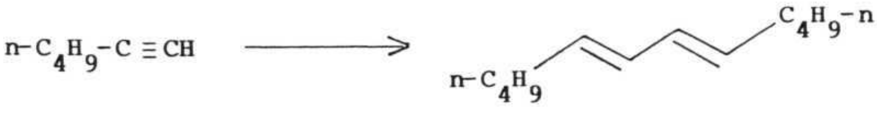
Yield: 73% (0.8 g).

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

^1H NMR (100 MHz, $CDCl_3$): δ ppm 6.1-5.2 (m,-CH), 4.4 (m,-CH), 2.0 (br,-CH_2-), 1.2 (m,-CH_2- hydrogens), 0.9 (t,-CH_3).

^{13}C NMR (25.0 MHz, $CDCl_3$): δ ppm 132.2, 130.6, 32.8, 32.0, 29.7, 29.1, 22.8, 14.1.

The spectral data of the (E,E)-7,9-hexadecadiene were identical to the data of the sample previously obtained in the reaction of n-$C_6H_{13}C\equiv CH$ and $(PPh_3)_2Co(H)Cl$ in our laboratory.[96,119]



Yield: 70% (0.58 g).

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

^1H NMR (100 MHz, $CDCl_3$): δ ppm 6.2-5.1 (m,-CH), 4.7 (m,-CH), 2.0 (br,-CH_2), 1.2 (m,-CH_2- hydrogens), 0.9 (t,-CH_3).

^{13}C NMR (25.0 MHz, $CDCl_3$): δ ppm 132.0, 130.7, 32.2, 31.9, 30.0, 22.5, 14.0.

The spectral data of (E,E)-5,7-dodecadiene were identical to the sample previously obtained in the reaction of n-$C_4H_9C\equiv CH$ and $(PPh_3)_2Co(H)Cl$ in our laboratory.[96,119]

Hydrocupration of phenylacetylene utilizing the NaH/$MgBr_2$/CuCl reagent system:

The reaction was carried out following the procedure outlined in the previous experiment. After work-up the product was purified by column chromatography on a silica gel column using 10% $CHCl_3$ in hexane as eluent. It was further purified by crystallization from ethyl alcohol.

Yield: 60% (0.65 g).

M.P. 150°C, Lit.[120] m.p. 152.5°C.

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

^1H NMR (100 MHz, $CDCl_3$): δ ppm 7.4-6.9 (m,-C_6H_5), 6.8-6.3 (m,-CH).

^{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^+).

Hydrocupration of methyl-10-undecynoate utilizing NaH/$MgBr_2$/CuCl reagent system:

The procedure outlined in the previous experiment was followed for carrying out this experiment. After work-up, unreacted methyl-10-undecynoate (1.37 g, 70%) and 10-undecynoic acid (0.27 g, 15%) were isolated by column chromatography using 50% chloroform in hexane as eluent.

Selective hydrocupration of 1-alkynes with NaH/$MgBr_2$/CuCl reagent system in the presence of other functional groups:

The procedure for the hydrocupration of 1-octyne in the presence of 1-decyl acetate is representative.

The procedure outlined in the previous experiments were followed. 1-Octyne (6 mmol, 0.66 g) and 1-decyl acetate (6 mmol, 1.2 g) were added. After stirring the mixture for 72 h at room temperature and work-up, the residue obtained after evaporating the solvent was subjected to chromatography on a silica gel column using hexane and chloroform as eluent to isolate (E,E)-7,9-hexadecadiene (0.4 g, 55%), 1-decanol (0.6 g, 65%) and 1-decyl acetate (0.12 g, 10%).

Similar experiments were carried out by taking 1-decyne along with 1-decene, octyl cyanide, and octyl bromide. In these cases, only the diene derived from 1-decyne was isolated besides the starting additives and no other product was isolated.

Hydrocupration of 1-decyne utilizing NaH/$MgBr_2$/CuBr.DMS complex system in THF at 0°C:

The $MgBr_2$ (20 mmol) in THF solution, prepared from Mg (40 mmol, 1.0 g) and 1,2-dibromoethane (20 mmol, 3.7 g) was transferred to a flask containing NaH (30 mmol) under nitrogen atmosphere using double ended needle. The mixture was stirred for 36 h at room temperature. The resulting MgH_2 slurry was cooled to -10°C (ice-salt bath) and CuBr.DMS complex (15 mmol, 3.1 g) was added. 1-Decyne (10 mmol, 1.4 g) was injected. The contents were stirred at 0°C for 10 h, quenched with D_2O (2 ml) and stirred for 30 min. The black reaction mixture was poured into saturated ammonium chloride solution (10 ml). After stirring for 1 h to decompose the CuBr.DMS complex, the organic layer was separated and the aqueous layer was extracted with ether (3x30 ml). The combined ether extract was washed with water (50 ml), brine (50 ml) and dried over anhydrous $MgSO_4$. The solvent was evaporated and the residue was distilled to isolate 1-decene (0.56 g, 40%) and (E,E)-9,11-eicosadiene (0.65 g, 23%). The ^{1}H NMR and ^{13}C NMR signals of this diene are superimposable with the data of the diene obtained previously.

Spectral data for 1-decene

B.P. 57°C/10 mm, Lit.[121] 75-78°/30 mm.

^{13}C NMR (25.0 MHz, $CDCl_3$): δ ppm 139.1, 114.0, 33.7, 31.8, 29.4, 29.2, 22.5, 13.9.

Analysis of the olefinic signal ($=CH_2$) indicates that the compound does not contain deuterium.

Attempted carbonylation of vinylcopper intermediate by bubbling carbon monoxide:

The MgH_2 slurry was prepared from $MgBr_2$ (20 mmol) and NaH (-30 mmol) as mentioned in the above experiment. CuBr.DMS complex (15 mmol, 3.1 g) was added to this slurry at -10°C followed by 1-decyne (10 mmol, 1.4 g). The reaction mixture was stirred for 10 h at 0°C and carbon monoxide was bubbled through the reaction mixture for 6 h at room temperature. After usual work-up, (E,E)-9,11-eicosadiene (25%) and 1-decene (40%) were isolated and no other product was formed.

Examination of the possibility of stabilization of alkenylcopper intermediates in the presence of LiBr:

The MgH_2 slurry was made in THF (80 ml) solution under nitrogen atmosphere using $MgBr_2$ (20 mmol) and NaH (~30 mmol) in the usual way. It was cooled to -10°C (ice-salt bath). To this CuBr.DMS complex (17 mmol, 3.5 g) dissolved in EE (25 ml) and DMS (25 ml) were added under nitrogen atmosphere using double ended needle. 1-Decyne (10 mmol, 1.4 g) and LiBr (25 mmol, 2.0 g, dissolved in 25 ml THF) were successively added. During 1 h the mixture was brought to room temperature and stirred for 24 h. The black reaction mixture was poured into aqueous ammonium chloride solution (100 ml) and the organic layer was separated. The aqueous solution was extracted with ether (3x30 ml). The ether extract was washed successively with water (50 ml), then with brine solution (50 ml) and dried over anhydrous $MgSO_4$. The residue was obtained after removing the solvent. The crude product was chromatographed on a silica gel column using hexane as eluent to isolate both 1-decene and diene as a mixture (0.9 g). Comparison of the ^{13}C NMR signals in the olefinic region of this sample with those observed for pure sample of the diene indicates that the 1-decene is a major contaminant (~ 50%) in the present sample. However, this can be only a very crude estimate since the ^{13}C signals concerned will be affected by different NOE factors.

Examination of the use of CuCN instead of CuCl for hydrocupration:

To a slurry of MgH_2 in THF, prepared in the usual way, CuCN (15 mmol, 1.35 g) was added at -10°C (ice-salt bath) under nitrogen atmosphere followed by 1-decyne (10 mmol, 1.4 g). After raising of the reaction temperature within 2 h from -10°C to 25°C and the mixture was stirred for 15 h at room temperature. The black reaction mixture was poured into HCl (3N, 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 ether layer was washed successively with water (50 ml), brine (50 ml) and dried over anhydrous $MgSO_4$. The ether solvent was evaporated and the crude residue was chromatographed on a silica gel column using hexane as eluent to obtain a mixture of 1-decene and (E,E)-9,11-eicosadiene in a 1:3 ratio. The ratio of both the compounds is only a very crude approximation since it is based on the intensities of the ^{13}C-signals which will be affected by different NOE factors.

Examination of the question whether the reagent system $NaH/MgBr_2/Cp_2TiCl_2/$ CuBr.DMS system gives stable alkenylcopper intermediate via transmetalation after hydrotitanation of 1-alkynes in THF

To a suspension of MgH_2 in THF (80 ml), Cp_2TiCl_2 (2.0 mmol, 0.5 g) was added under nitrogen atmosphere at -10°C (ice-salt bath). CuBr.DMS (15 mmol, 3.1 g) and 1-decyne (10 mmol, 1.4 g) were successively added. The reaction mixture turned to black colour via brown. It was stirred for 10 h at 0°C (ice bath). The black reaction mixture was hydrolysed with aqueous ammonium chloride solution (100 ml) and the organic layer was separated. The aqueous layer was extracted with ether (3x30 ml). The combined ether extract was washed with water (50 ml), brine solution (50 ml) and dried over anhydrous $MgSO_4$. The crude product, remained after evaporation of the solvent, was subjected to chromatography on a silica gel column using hexane as eluent to isolate a yellow compound. GC (SE-30 column) analysis of this mixture indicated the presence of 1-decene (30%), (E,E)-9,11-eicosadiene (30%) and an unidentified oligomeric compound (30%).

Examination of the question whether the reagent system Mg/DBE/t-BuCl/Cp_2TiCl_2/CuCl will give stable vinylcopper intermediate via hydrotitanation-transmetalation sequence in THF:

To a mixture of Grignard grade magnesium (50 mmol, 1.25 g) and t-BuCl (16 mmol, 1.5 g) in THF (80 ml), 1,2-dibromoethane was added at room temperature under nitrogen atmosphere. The contents were stirred for 3 h and cooled to -20°C (liq.N_2 and CCl_4 bath). Cp_2TiCl_2 (2 mmol, 0.5 g) and CuCl (15 mmol, 1.5 g)was added successively. After 2 h 1-decyne (10 mmol, 1.4 g) was added. The reaction mixture was brought to r.t. during 2 h and stirred for 12 h. After usual work-up, the solvent was evaporated and the residue was chromatographed on a silica gel column using hexane as eluent to isolate a polymeric yellow compound. This was not characterised further.

Examination of the question whether the reagent system Mg/DBE/t-BuCl/CuCl will give stable alkenylcopper intermediate via hydrocupration of 1-alkynes in THF:

To a suspension of Mg (80 mmol, 2.0 g) and t-BuCl (30 mmol, 2.76 g) in THF (80 ml), 1,2-dibromoethane (30 mmol, 5.4 g) was added dropwise at room temperature under nitrogen atmosphere and stirred for 4 h at room temperature. The Grignard reagent was cooled to -24°C (liq.N_2 and CCl_4) and CuCl (30 mmol, 3.0 g) was added. The reaction mixture turned to black colour within 10 min. It was stirred further for 1 h at this temperature. 1-Decyne (10 mmol, 1.4 g) was added and the temperature was raised during 2 h from -24°C to 25°C. Stirring was continued for 15 h at room temperature. The black reaction mixture was poured into dil. HCl (3N, 50 ml) and solid sodium chloride was added to saturate the aqueous layer. The organic layer was separated and the aqueous layer was extracted with ether (3x30 ml). The combined organic extract was washed successively with water (50 ml), brine solution (50 ml) and dried over anhydrous $MgSO_4$. The solvent was evaporated and the residue was chromatographed on a silica gel column using hexane as eluent to isolate 2-t-butyl-1-decene (0.9 g, 50%) and 1-decyne (0.42 g, 30%). The spectral data for the 2-t-butyl-1-decene are given later.

Carbocupration of less reactive 1-alkynes utilizing t-BuMgCl/$MgBr_2$/CuCl reagent system in THF:

To a suspension of Mg (80 mmol, 2.0 g) and t-BuCl (30 mmol, 2.76 g) in THF (80 ml) under nitrogen, 1,2-dibromoethane (30 mmol, 5.4 g) was added dropwise at room temperature and the resulting mixture was stirred for 4 h. CuCl (30 mmol, 3.0 g) was added at -24°C and the mixture was stirred for 2 h at -20°. 1-Decyne (10 mmol, 1.4 g) was injected to this black mixture. The contents were brought to room temperature during 2 h and stirred further for 15 h. The black reaction mixture was quenched with D_2O (2 ml) and stirred for 30 min. The mixture was poured into dil. HCl (50 ml, 3N) and saturated with solid sodium chloride. The organic layer was separated and the aqueous layer was extracted with ether (3x30 ml). The combined ether extract was successively washed with water (50 ml), brine solution (50 ml) and dried over anhydrous $MgSO_4$. The solvent was evaporated and the residue was chromatographed on a silica gel column using hexane as eluent to isolate 2-t-butyl-1-decene (1.2 g, 60%) and unreacted starting material 1-decyne (0.28 g, 20%).

Spectral data for 2-t-butyl-1-decene (H_2O work-up)

IR (neat): ν_{max}: 3100, 2950, 1640, 1470, 970, 890 cm^{-1}.

^1H NMR (100 MHz, $CDCl_3$): δ ppm 4.7 (br,-CH_2), 2.0 (m,CH_2), 1.4-1.3 (m, other CH_2 hydrogens), 1.2-1.0 (m,CH_3 hydrogen).

^{13}C NMR (25.0 MHz, $CDCl_3$): δ ppm 158.1, ($\underline{C}=CH_2$), 106.0 ($C=\underline{C}H_2$), 36.2, 32.1, 30.1, 29.9, 29.6, 29.4, 22.9, 14.2. 22.9, 14.2. **(spectrum No. 2A)**

Mass spectrum (m/e): 196 (M^+).

^{13}C NMR spectral data for 2-t-butyl-1-decene (D_2O work-up) (spectrum No. 2)

^{13}C NMR (25.0 MHz, $CDCl_3$): δ ppm 158.1 (C̲=CHD), 106.6, 105.7, 104.7 (C=C̲HD), 36.2, 32.1, 30.1, 29.9, 29.6, 29.4, 22.9, 14.2.

The procedure outlined in the previous experiment was followed for carbocupration of 1-octyne using t-BuMgCl/$MgBr_2$/CuCl reagent system and the reaction mixture was quenched with D_2O before work-up.

Spectral data for 2-t-butyl-1-octene

Yield: 60% (1.09). Recovered 1-octyne (0.27 g, 25%).

IR (neat): ν_{max}: 3100, 2950, 1640, 970, 890 cm^{-1}.

^{1}H NMR (100 MHz, $CDCl_3$): δ ppm 4.7 (br,=CHD), 2.05 (m,-CH_2), 1.5-1.3 (br, other CH_2 hydrogens), 1.2-0.9 (m,CH_3 hydrogens). **(spectrum No. 3)**

^{13}C NMR (25.0 MHz, $CDCl_3$): δ ppm 157.8 (C̲=CHD), 106.6, 105.9, 104.7 (C=C̲HD), 36.1, 32.1, 29.9, 29.7, 29.4, 22.8, 14.1. **(spectrum No. 3A)**

The ^{13}C NMR data are in agreement with the data reported for some 1,1-disubstituted model alkenes.[122]

Carbocupration of 1-decyne utilizing iso-PrMgBr/$MgBr_2$/CuCl reagent system in THF:

1,2-Dibromoethane (30 mmol, 5.4 g) was added dropwise during a period of 5 min at room temperature under nitrogen to a mixture of Mg (80 mmol, 2.0 g) and iso-propyl bromide (30 mmol, 3.6 g) in THF and stirred for 4 h. The Grignard reagent was cooled to -24°C (CCl_4 and liq.N_2 bath) and CuCl (30 mmol, 30 g) was added. The mixture was stirred for 2 h at -20°C. 1-Decyne (10 mmol, 1.4 g) was added. The black reaction mixture was stirred for 2 h at -20°C, brought to room temperature and stirred further for 15 h. The mixture was hydrolysed with dil.HCl (50 ml, 3N) 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 successively with water (50 ml), brine solution (50 ml) and dried over anhydrous $MgSO_4$. The solvent was evaporated and the remaining residue was chromatographed on a silica gel column using hexane as eluent to isolate 2-iso-propyl-1-decene (1.0 g, 60%) and unreacted 1-decyne (0.34 g, 25%).

Spectral data for 2-iso-propyl-2-decene

IR (neat): ν_{max}: 3050, 2950, 1640, 970, 900 cm^{-1}.

^{13}C NMR (25.0 MHz, $CDCl_3$): δ ppm 155.9 ($\underline{C}=CH_2$), 106.1 ($C=\underline{C}H_2$), 34.4, 31.9, 29.6, 29.3, 28.2, 22.7, 21.7, 13.9.

Mass spectrum (m/e): 182 (M^+).

Carbocupration of 1-decyne using t-AmylMgCl/$MgBr_2$/CuCl reagent system in THF:

To a mixture of Mg (80 mmol, 2.0 g) and t-amylchloride (30 mmol, 3.2 g) in THF (80 ml), 1,2-dibromoethane (30 mmol, 5.4 g) was slowly added at room temperature under nitrogen atmosphere and stirred for 4 h. The mixture was cooled to -24°C (CCl_4 and liq.N_2) and CuCl (30 mmol, 3.0 g) was added. The resulting black mixture was stirred for 2 h and 1-decyne (10 mmol, 1.4 g) was added. Stirring was continued for 2 h at -20° and brought to room temperature. The mixture was stirred further for 15 h. The reaction mixture was quenched with D_2O (2 ml) and after usual work-up, chromatography, 2-t-amyl-1-decene (40%) was isolated and 1-decyne (0.56 g, 40%) was recovered.

Spectral data for 2-t-amyl-1-decene (spectrum No. 4)

Yield: 40% (0.84 g).

IR (neat): ν_{max}: 2950, 1620, 1000, 920, 900 cm^{-1}.

^1H NMR (100 MHz, $CDCl_3$): δ ppm 4.9 (br,=CHD), 1.98 (m,-CH_2), 1.4-1.3 (m, other CH_2 hydrogens), 1.08-0.7 (m, CH_3 hydrogens).

Mass spectrum (m/e): 211 (M^+, 10%), 210 (M^+-1, 3.3%).

Spectral data for 2-t-amyl-1-octene (spectrum No. 4A)

Yield: 40% (0.72 g). Recovered 1-decyne (0.56 g, 40%).

IR (neat): ν_{max}: 2950, 1630, 1020, 920, 900 cm^{-1}.

^1H NMR (100 MHz, $CDCl_3$): δ ppm 4.8 (br,=CHD), 2.0 (m,-CH_2), 1.5-1.3 (m, other CH_2 hydrogens), 1.1-0.7 (m,CH_3 hydrogens).

Mass spectrum (m/e): 183 (M^+, 10%), 182 (M^+-1, 4%).

Examination of the effect of copper salt on the carbocupration of 1-alkynes: Utilization of CuBr.DMS complex instead of CuCl:

To a mixture of Mg (80 mmol, 2.0 g) and t-BuCl (30 mmol, 2.7 g) in THF (80 ml), 1,2-dibromoethane (30 mmol, 5.4 g) was added under nitrogen atmosphere and stirred for 4 h at room temperature. It was cooled to -24°C and CuBr.DMS complex (30 mmol, 6.4 g) dissolved in EE (25 ml) and DMS (25 ml) was added. Stirring was continued for 2 h at -20°C and 1-decyne (10 mmol, 1.4 g) was added. The resulting mixture was brought to room temperature during 2 h and stirred further for 15 h. The black reaction mixture was poured into saturated aqueous ammonium chloride solution (100 ml) and the organic layer was separated. The aqueous layer was extracted with ether (3x30 ml). The combined organic extract was washed with brine solution (50 ml) and dried over anhydrous $MgSO_4$. The solvent was evaporated and the residue was subjected to chromatography on a silica gel column using hexane as eluent. 1-Decyne was recovered essentially quantitatively.

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CHAPTER 2

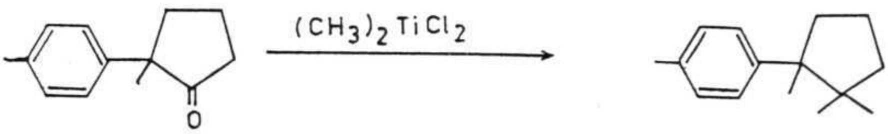
Studies on the Reactivities of Titanium Reagents Generated utilizing the Mg/$BrCH_2CH_2Br$ System and Cp_2TiCl_2 or $TiCl_4$

INTRODUCTION

As outlined in chapter 1, we have observed that the Cp_2TiCl_2/t-BuMgCl reagent isomerizes some 1-alkenes into 2-alkenes. A brief survey of the literature indicated that it may be fruitful to investigate this system further and we decided to do so. A brief review on the reagents produced by the treatment of $TiCl_4$ and Cp_2TiCl_2 species with RM (or R_2M), reducing agents such as alkalimetals, alkalimetal naphthalenides and magnesium-amalgam and the reactivities of the resulting reagents with various organic substrates will be helpful for the discussion.

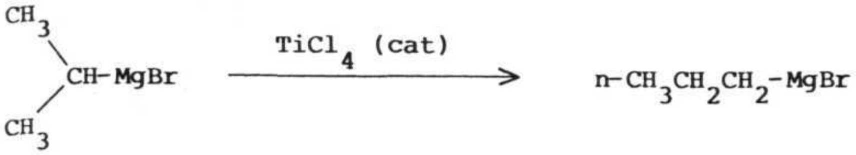
Reactivities of the $TiCl_4$, Cp_2TiCl_2/RM (or R_2M) systems:

The CH_3TiCl_3 and $(CH_3)_2TiCl_2$ reagents prepared utilizing $(CH_3)_2Zn$ have been proved to be useful reagents.[1] For example, gem dimethyl groups can be directly introduced even in difficult cases using the $(CH_3)_2TiCl_2$ reagent.[2]



Several such alkyl transfer reactions, including some involving asymmetric transformations have been developed and utilized extensively by Seebach and coworkers.[1]

The $TiCl_4$ (cat)/RMgX reagent system effects the following transformations.[4]



$$(CH_3)_2CH\text{-}MgBr \xrightarrow{TiCl_4\ (cat)} n\text{-}CH_3CH_2CH_2\text{-}MgBr$$

$$CH_2{=}CH\text{-}(CH_2)_5\text{-}CH_3 + CH_3\text{-}CH_2\text{-}CH_2\text{-}MgCl \xrightarrow{TiCl_4(cat)} CH_3\text{-}CH{=}CH_2 + CH_3\text{-}(CH_2)_6\text{-}CH_2MgCl$$

The reaction has been rationalized by the steps depicted in Scheme 1.[4]

Scheme 1

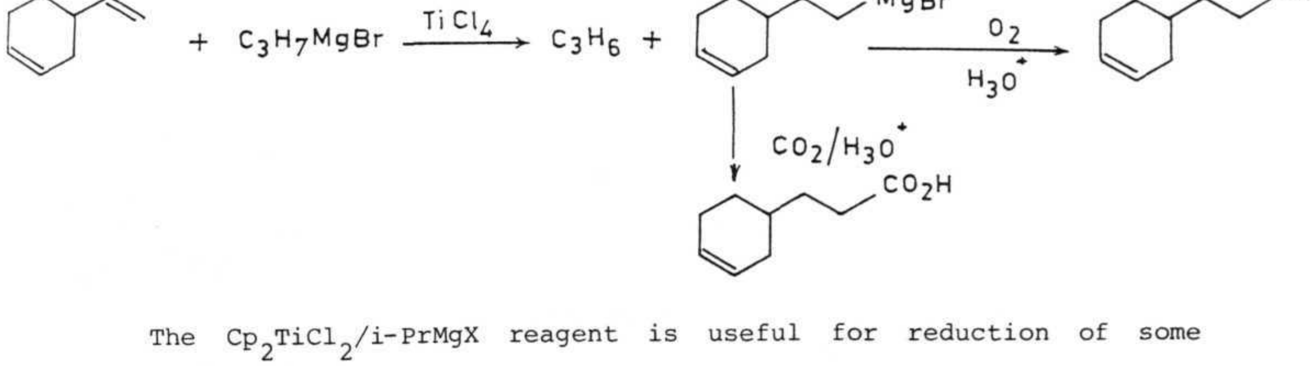
$$(CH_3)_2CH\text{-}MgBr + TiCl_4 \longrightarrow (CH_3)_2CH.TiCl_3 + MgBrCl$$

$$(CH_3)_2CH.TiCl_3 \longrightarrow TiHCl_3 + CH_3\text{-}CH{=}CH_2$$

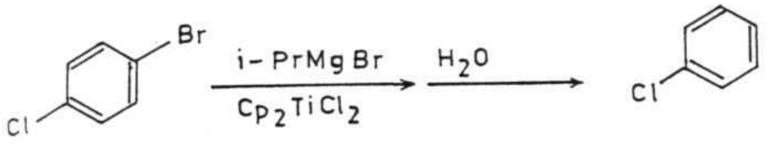
$$TiHCl_3 + CH_3\text{-}CH{=}CH_2 \rightleftarrows CH_3CH_2CH_2TiCl_3$$

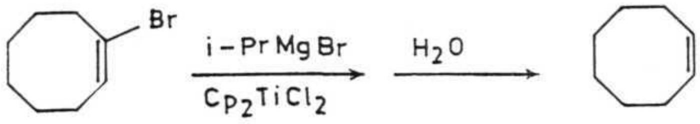
$$CH_3CH_2CH_2TiCl_3 + RMgBr \longrightarrow CH_3CH_2CH_2MgBr + RTiCl_3$$

This type of olefin exchange has been utilized for some selective transformations.[5]



The Cp_2TiCl_2/i-PrMgX reagent is useful for reduction of some substrates.[6]



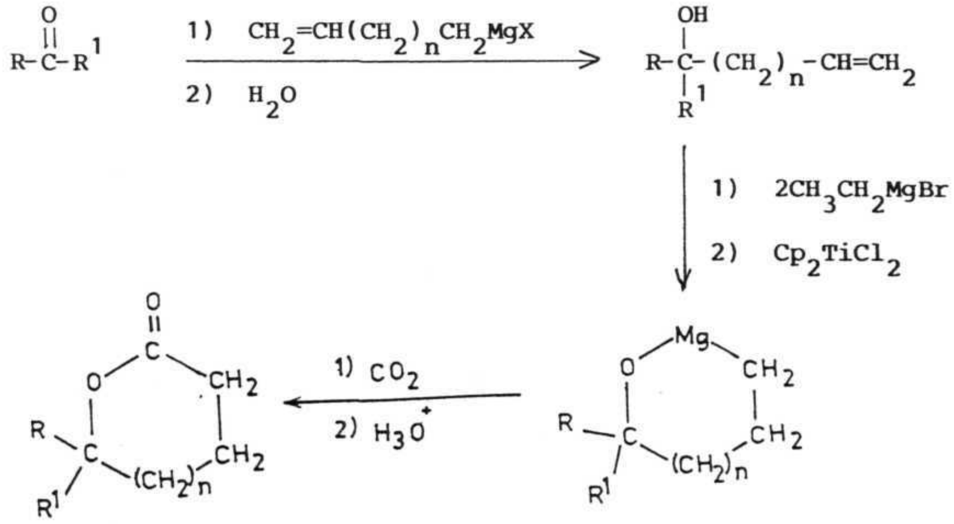


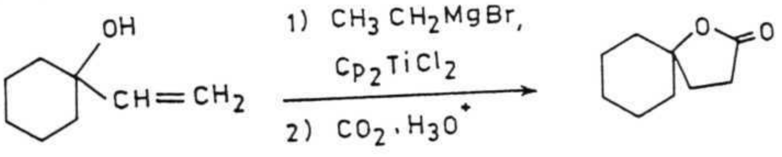
$$n\text{-}C_{12}H_{25}Br \xrightarrow[Cp_2TiCl_2]{i\text{-}PrMgBr} \xrightarrow{H_2O} \underset{74\%}{n\text{-}C_{12}H_{26}} + \underset{26\%}{n\text{-}C_9H_{19}\text{-}CH{=}CH\text{-}CH_3}$$

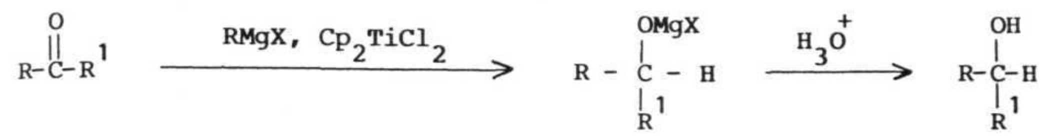
$$n\text{-}C_8H_{17}\text{-}CH{=}CH_2 \xrightarrow[Cp_2TiCl_2]{i\text{-}PrMgBr} \xrightarrow{H_2O} \underset{30\%}{n\text{-}C_{10}H_{22}} + \underset{50\%}{n\text{-}C_8H_{17}CH{=}CH_2} + \underset{20\%}{C_7H_{15}CH{=}CH\text{-}CH_3}$$

$$n\text{-}C_8H_{17}C\equiv CH \xrightarrow[Cp_2TiCl_2]{i\text{-}PrMgBr} \xrightarrow{H_2O} \underset{80\%}{n\text{-}C_7H_{15}C\equiv C\text{-}CH_3} + \underset{15\%}{CH_3\text{-}(CH_2)_8CH_3} + \underset{5\%}{n\text{-}C_8H_{17}\text{-}CH{=}CH_2}$$

These reactions have been shown to go through Cp_2TiX, Cp_2TiR and Cp_2TiH intermediates.[6] The Cp_2TiCl_2 catalyzed hydrometalation reactions have many applications.[7]

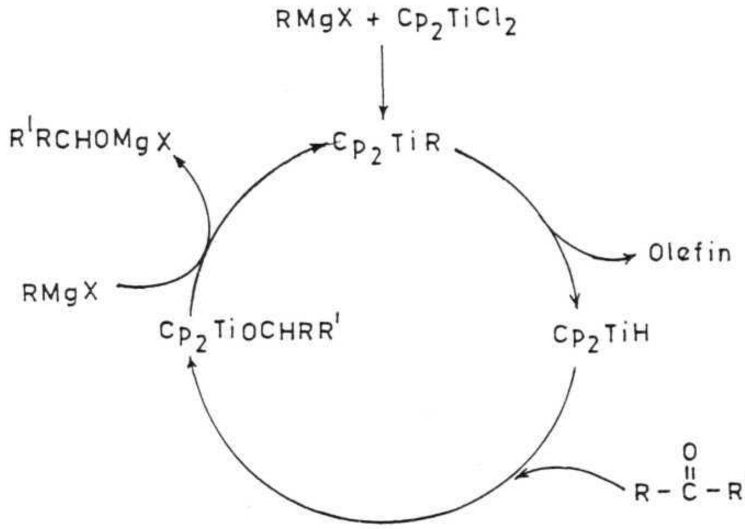






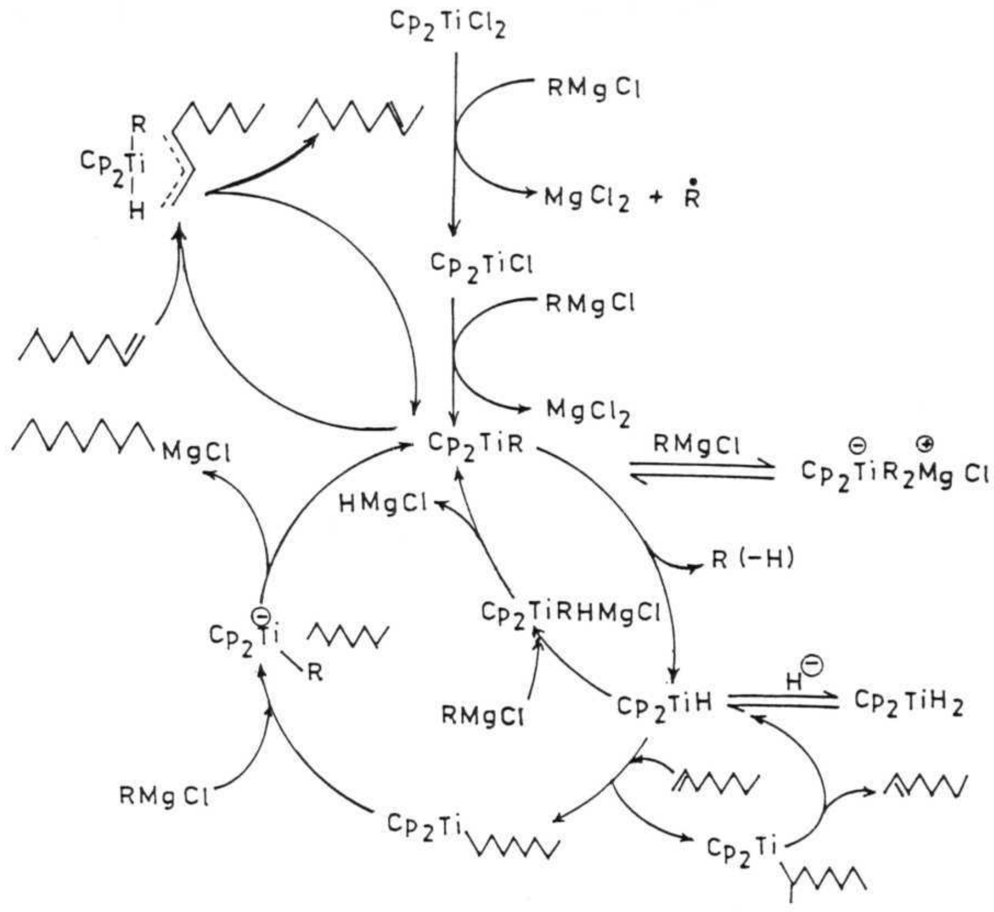
The ketone reduction has been rationalized by the mechanism shown in Scheme 2.[7]

Scheme 2



Ashby and coworkers extensively studied the hydrometalation of 1-octene by a series of Grignard reagents [EtMgCl, EtMgBr, n-PrMgCl, i-PrMgCl, n-BuMgCl, sec-BuMgCl, iso-BuMgCl, iso-BuMgBr and iso-BuMgI], dialkylmagnesium compounds [Me_2Mg, Et_2Mg, n-Pr_2Mg, i-Pr_2Mg, n-Bu_2Mg, sec-Bu_2Mg, iso-Bu_2Mg and t-Bu_2Mg] and magnesium hydrides [MgH_2, HMgCl and HMgBr] in the presence of 5 mol % of Cp_2TiCl_2 in THF under argon atmosphere.[8] The products were found to be a mixture of 2-octenes and octane in many cases. The catalytic cycle depicted in Scheme 3 has been suggested to be operative.[8]

Scheme 3



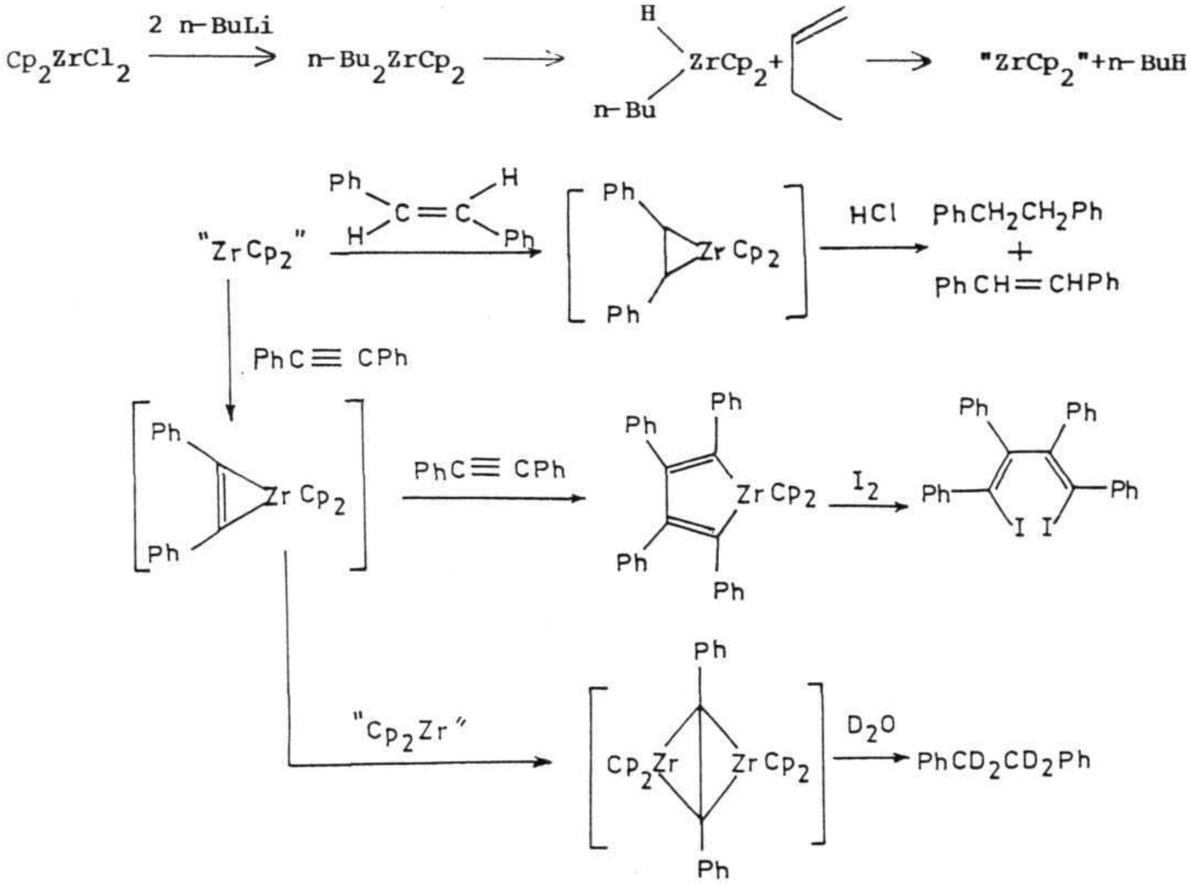
The Cp_2TiCl_2/i-PrMgCl reagent has been reported to give titanocene-nitrogen complexes under nitrogen atmosphere.[9]

$$\begin{tikzcd}
Cp_2TiCl_2 \text{ (or } Cp_2TiCl) \arrow[r, "RMgX"] & Cp_2TiR \arrow[r, "N_2"] & (Cp_2TiR)_2N_2 \arrow[r] \arrow[d, "H^+"] & {} \\
 & & N_2 &
\end{tikzcd}$$

$$\begin{tikzcd}
{[Cp_2Ti]_2N_2} \arrow[rr, "RMgX"] \arrow[d, "H^+"] & & {[Cp_2Ti]_2N_2MgX} \arrow[r, "RMgX"] \arrow[dl, "H^+"'] \arrow[d, "{LiPh,\ H^+}"] & Cp_2TiN(MgX)_2 \arrow[r, "H^+"] & NH_3 \\
N_2H_2 & N_2H_4 & NH_3 + PhNH_2 & &
\end{tikzcd}$$

It has been recently reported that the Cp_2ZrCl_2 reagent reacts with 2 equivalents of n-BuLi to give 'zirconocene', 'Cp_2Zr', which has been shown to give several interesting transformations (Scheme 4).[10]

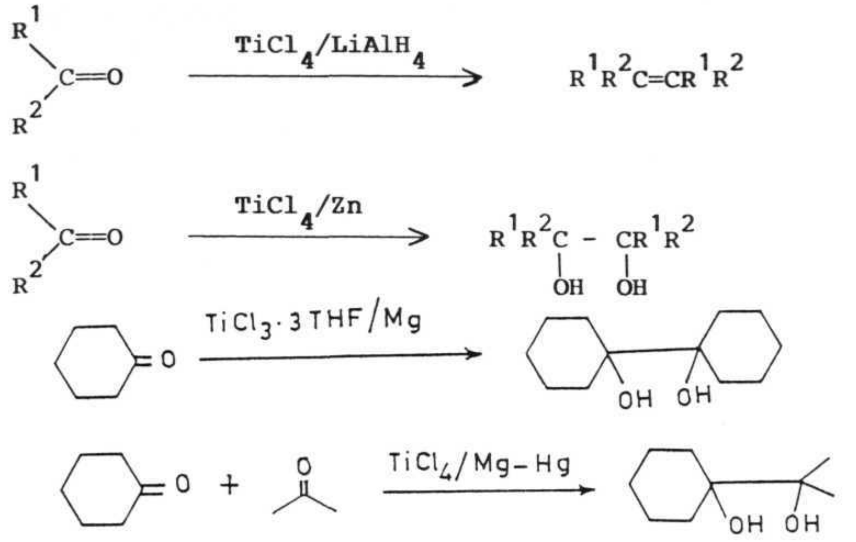
Scheme 4



The titanocene and zirconocene or their equivalents can be readily prepared by the reduction of Cp_2MCl_2 species with Na, sodium naphthalenide and Mg/Hg, etc. It is helpful to briefly review various methods of preparation and reactivities of the titanocene and zirconocene.

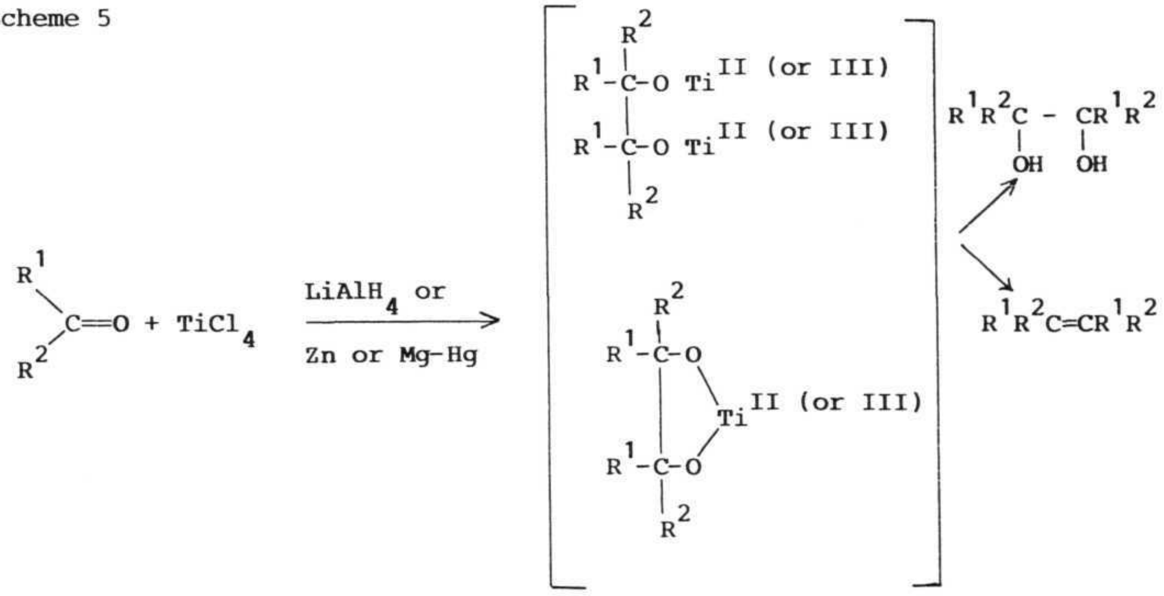
Reactivities of the M_TCl_4/M, $Cp_2M_TCl_2$/M systems [M_T=Ti, Zr and M=Na, Li or Na naphthalenide or Mg/Hg]:

Low valent titanium reagents obtained by the reduction of $TiCl_4$/$LiAlH_4$,[11] $TiCl_4$/Zn[12] or Mg-Hg[13] and $TiCl_3$/Mg[14] reacts with aldehydes and ketones to give the corresponding olefins or pinacols.

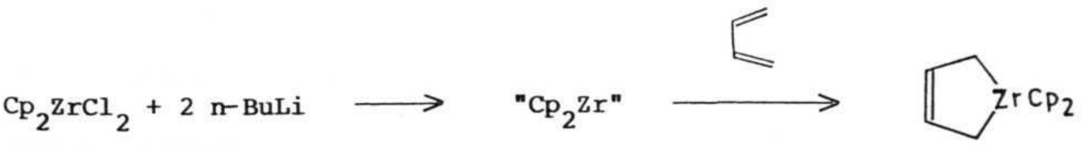


The mechanism involving low valent titanium species has been suggested to account for these results (Scheme 5).[12,13]

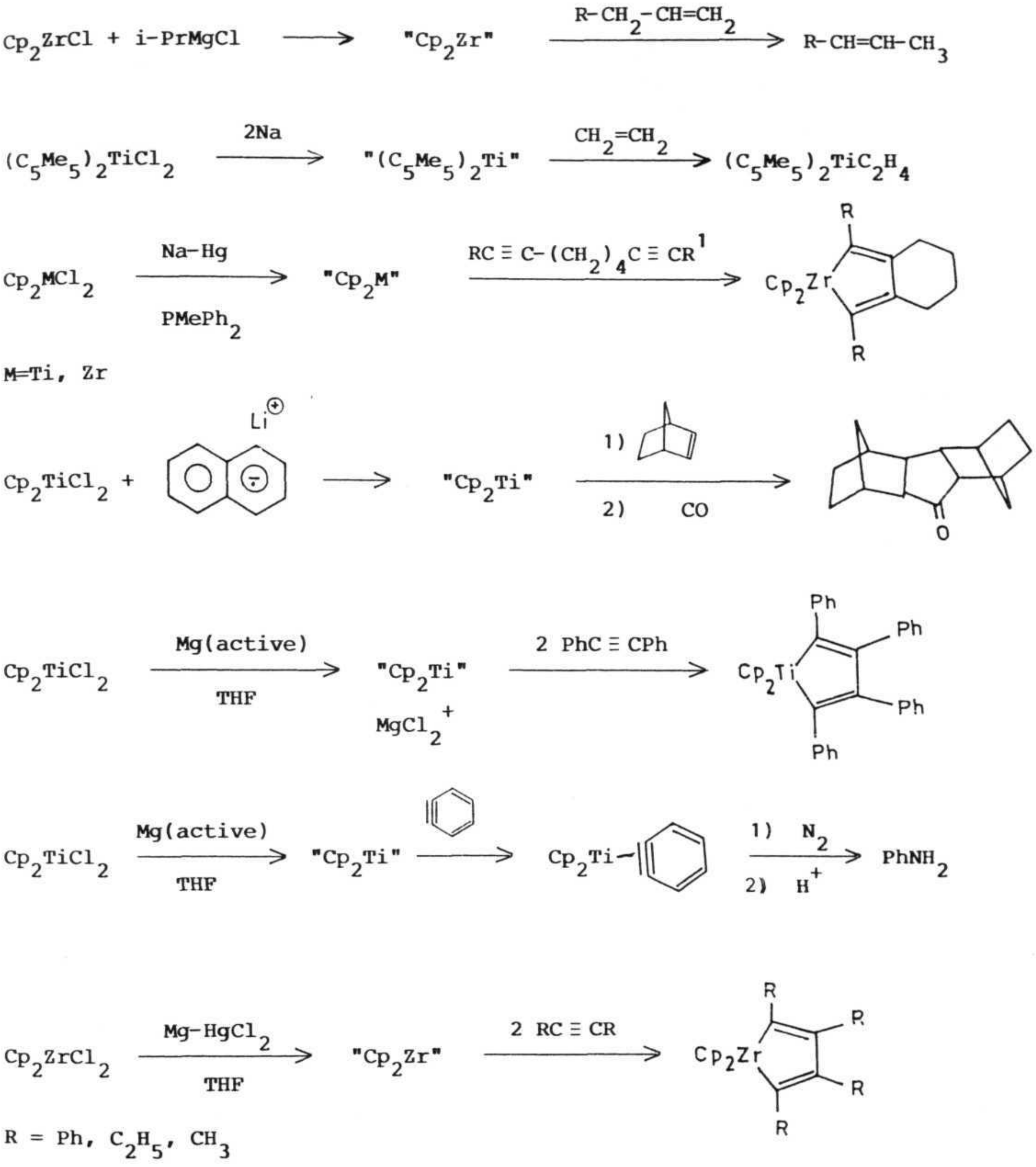
Scheme 5



The "Cp_2M" species, prepared by the reduction of the Cp_2MCl_2 (M=Ti, Zr) reagents have been trapped utilising appropriate reagents (i.e. ethylene, acetylene).[10,15-21]

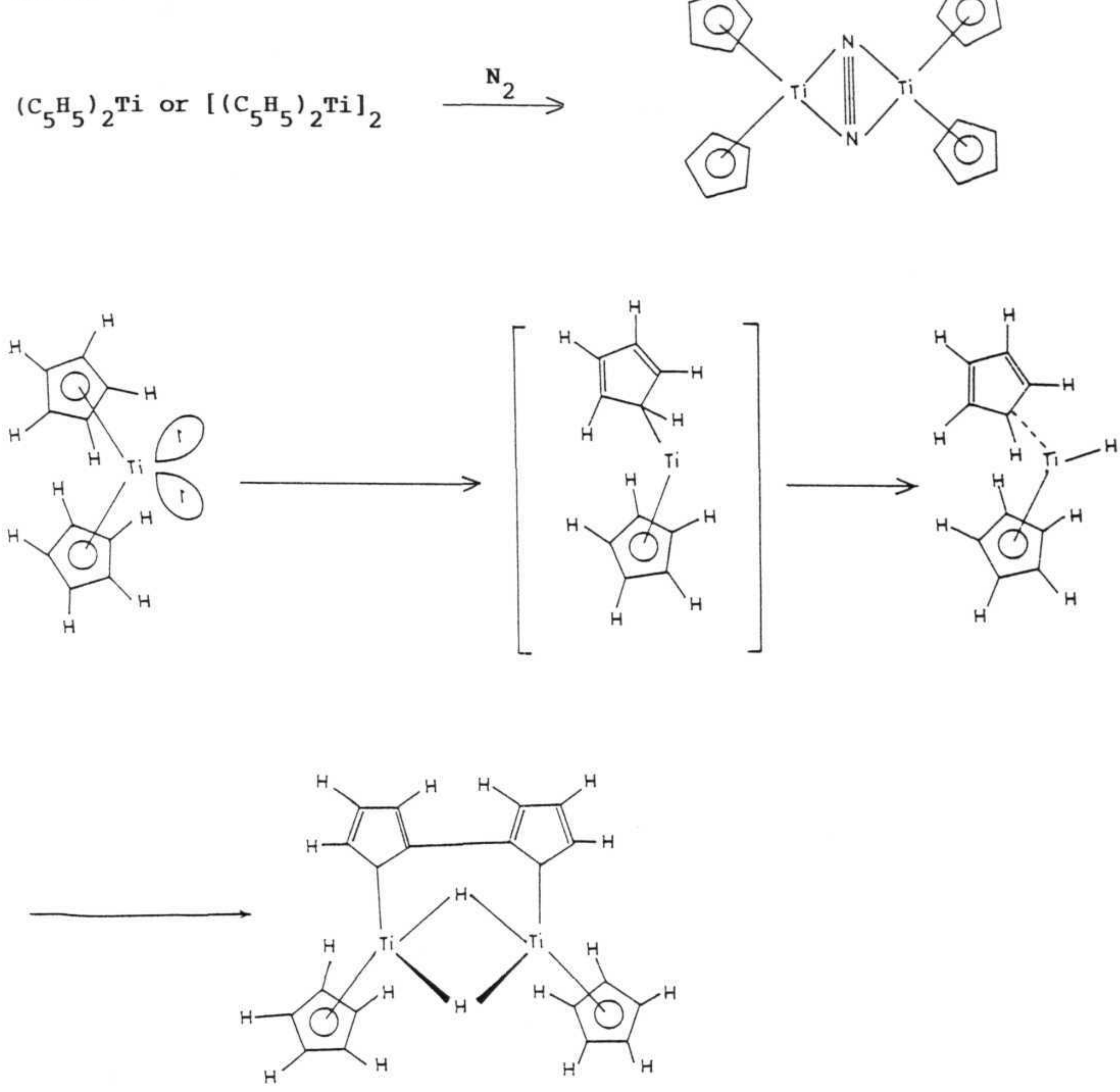


$$(C_5Me_5)_2TiCl_2 + i\text{-}PrMgCl \longrightarrow {}'(C_5Me_5)_2Ti' \xrightarrow{R-CH_2-CH=CH_2} R-CH=CH-CH_3$$



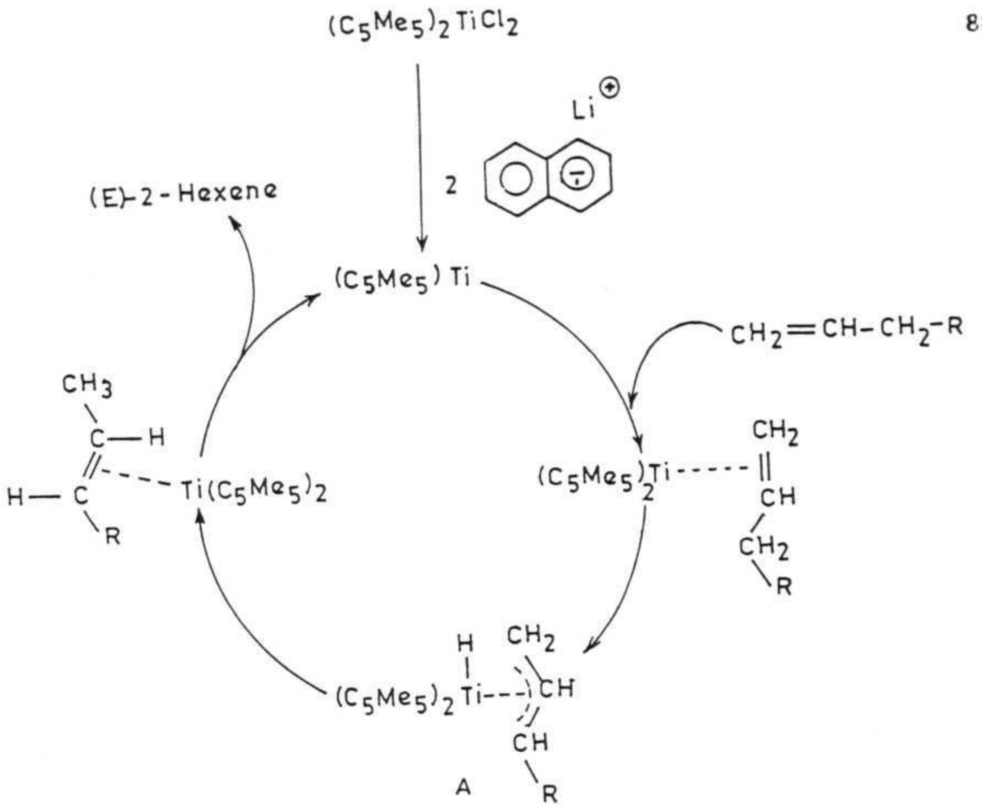
The titanocene, 'Cp_2Ti', itself has been found to be highly unstable and has never been isolated in pure form. It readily complexes with molecular nitrogen.[22] Also, it decomposes to give the corresponding hydride species which readily undergoes dimerization (Scheme 6).[23]

Scheme 6



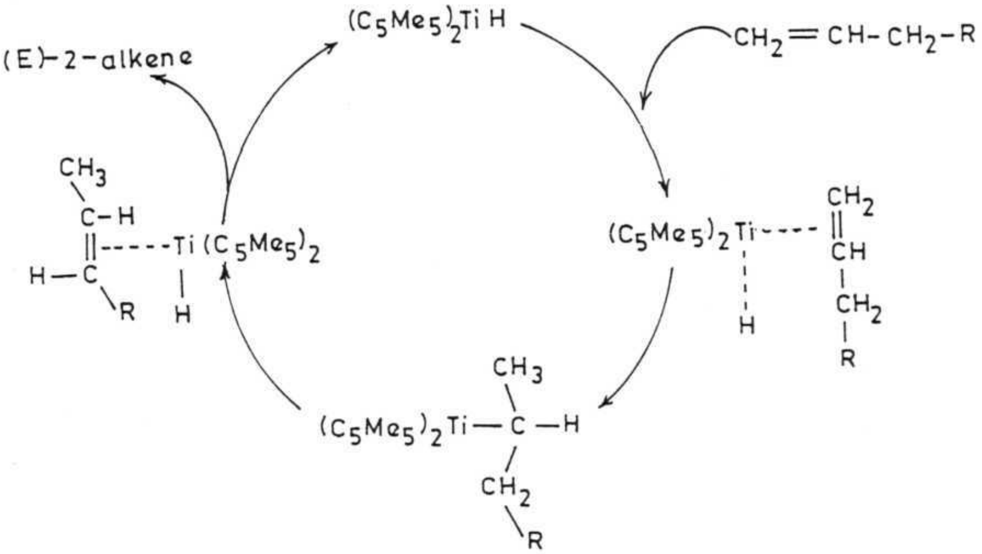
The $(C_5Me_5)_2TiCl_2/NaC_{10}H_7$ reagent has been found to isomerize 1-alkenes to trans-2-alkenes.[15] The reaction has been proposed to go through the mechanism outlined in Scheme 7 involving (π^3-allyl) TiH intermediate (Scheme 7).[15]

Scheme 7



A similar allyltitanium hydride(A) intermediate has been also proposed as an intermediate in olefin hydrogenation reactions.[24] However, since the $(C_5Me_2)_2Ti$ species readily decomposes into the $(C_5Me_5)[C_5(CH_3)_4CH_2]TiH$ species, the authors pointed out that the results can also be rationalized by the conventional addition-elimination pathway depicted in Scheme 8.[15]

Scheme 8

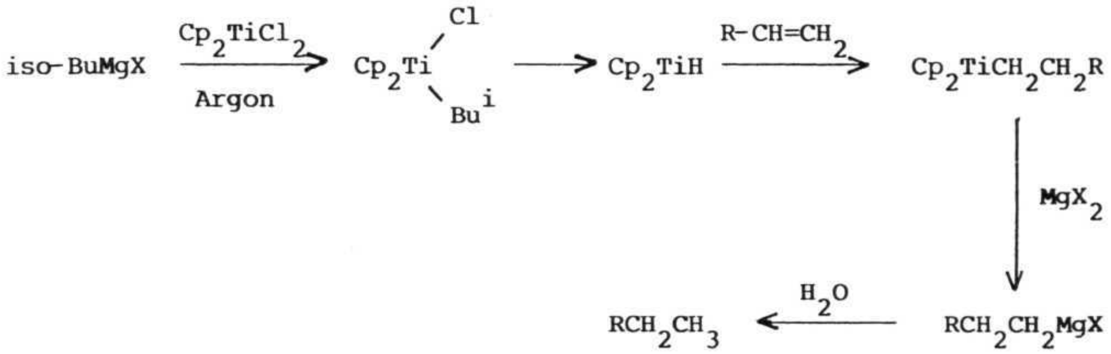


Our preliminary observations indicated that the $Cp_2TiCl_2/BrCH_2CH_2Br$ system is a promising simple system for the generation of titanocene or its equivalent and we decided to explore the reactivities of the reagent system further.

RESULTS AND DISCUSSION

Reactivities of the titanium and zirconium reagents generated utilizing Cp_2MCl_2(M=Ti,Zr)/Mg/$BrCH_2CH_2Br$ reagent systems with alkenes and alkynes:

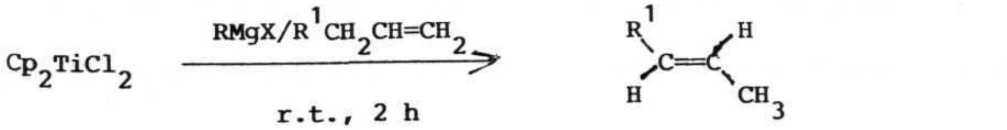
As outlined in the introduction, the Grignard reagents can be readily prepared from olefin by the exchange reaction.[3-5]



As discussed in the first chapter, we have attempted a similar transmetalation from the supposed intermediates (i.e. $Cp_2TiCH_2CH_2R$ or RCH_2CH_2MgX) to copper by carrying out a similar experiment in the presence of copper salts. However, it was found that when 1-decyne (10 mmol) was added to a mixture containing t-butyl chloride (15 mmol), Grignard grade magnesium (50 mmol), 1,2-dibromoethane (15 mmol), Cp_2TiCl_2 (2 mmol) and CuCl (15 mmol) in THF at -10°C (ice-salt bath) under nitrogen and the reaction mixture was stirred for 12 h, work-up gave only a yellow oily polymeric compound. The same polymeric compound was also obtained in the absence of CuCl.

Also, it was observed that when 1-decene (10 mmol) was added to the mixture containing isobutyl magnesium bromide (12 mmol) and Cp_2TiCl_2 (2 mmol) in (THF 80 ml) at room temperature under nitrogen and the reaction mixture was stirred for 2 h, after work-up, only a mixture of trans-2-decene and cis-2-decene (~ 85/15) in 75% yield was obtained, and no decane was formed. This observation is in contrast to the finding that the Cp_2TiCl_2/iso-BuMgX/1-octene under argon atmosphere gives 1-octylmagnesium halide.[8] However, as outlined previously, a literature report indicates that the Cp_2TiCl_2/iso-PrMgX system gives titanocene nitrogen complex, $[Cp_2Ti]_2N_2$.[9] Unfortunately, the reactivity of these species with 1-alkenes has not been reported. However, our observation clearly indicates that the Cp_2TiCl_2/iso-BuMgBr system under nitrogen atmosphere isomerizes 1-alkenes into 2-alkenes and does not give the Cp_2TiH species which is capable of catalyzing the hydrotitanation-transmetalation to give the corresponding organomagnesium compound.[3-5,8]

We have also observed that the t-BuMgCl reagent, prepared from t-BuCl (16 mmol), Mg (40 mmol) and 1,2-dibromoethane (15 mmol) reacts with Cp_2TiCl_2 (2 mmol) to give a reagent which also isomerizes 1-decene into trans-2-decene and cis-2-decene (~ 85/15) in 75% yield under nitrogen (Table 1). Previously, it has been reported that the Cp_2TiCl_2/t-BuMgCl reagent or Cp_2TiCl_2/t-Bu_2Mg reagent isomerizes 1-octene to trans-2-octene and cis-2-octene under argon atmosphere and evidence was presented for the presence of Cp_2Ti(t-Bu) species in the reaction mixture.[8]



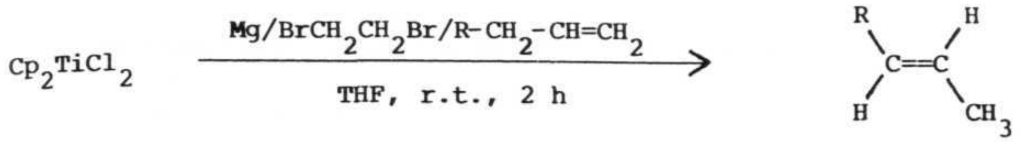
R = iso-butyl or t-butyl

(85% trans and 15% cis)

$R^1 = n\text{-}C_7H_{15}$

It has been reported that a solid material, considered to be a titanocene equivalent, prepared by the evaporation of the solvent from the reaction mixture of the Cp_2TiCl_2/i-PrMgBr in diethyl ether, isomerizes neat 1-hexene into a mixture of trans-2-hexene, cis-2-hexene and trans-3-hexene in the ratio of 51/29/20. Under our conditions, 1-decene does not give any 3-decene or 4-decene and so the new method gives a more selective transformation. The differences in the reactivities indicate that the active species and mechanism may also be different. These findings indicate that titanocene, "Cp_2Ti", and/or the $>$TiH species formed by the decomposition of the "Cp_2Ti" species isomerize some alkenes with selectivities depending on the source of the catalyst.

It was thought that it might be possible to achieve the isomerization of 1-alkenes even without utilizing the RMgX in the above experiments since it is known that active magnesium reduces Cp_2TiCl_2 into "Cp_2Ti".[19] In order to examine this possibility, we have carried out an experiment in the absence of RMgX as follows: 1,2-Dibromoethane (15 mmol) was added to a mixture of Grignard grade magnesium (20 mmol) in THF (80 ml) containing Cp_2TiCl_2(2 mmol) at room temperature under nitrogen atmosphere. The colour of the reaction mixture changed from orange to dark green during 30 min. 1-Decene (10 mmol) was added and stirred further for 2 h. After work-up and chromatography, a mixture of trans-2-decene and cis-2-decene (~ 85/15) were isolated in 75% yield. This clearly suggests that the Grignard grade magnesium and 1,2-dibromoethane system is capable of reducing Cp_2TiCl_2 to "titanocene" or $>$Ti-H species (Scheme 6) which may be responsible for the isomerization of 1-alkenes into 2-alkenes.



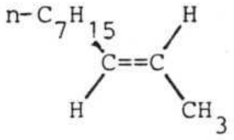
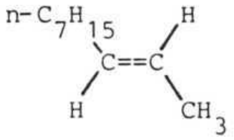
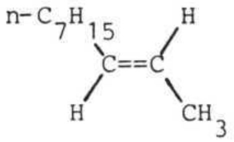
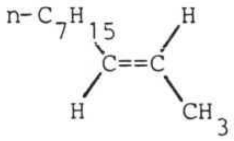
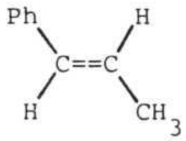
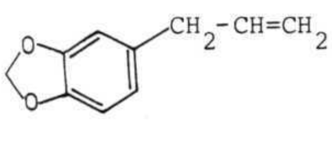
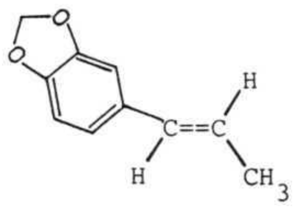
(85% trans and 15% cis)

Control experiments indicated that 50 mmol of 1-decene can be converted into a mixture of trans-2-decene and cis-2-decene (~ 85/15) in 12 h at room temperature (Table 1). The reaction was found to be a general one. Allylbenzene and safrole were converted into the corresponding trans-β-methylstyrenes in 77% and 80% yields, respectively (Table 1). Cis, cis-1,5-cyclooctadiene, which undergoes conjugation to give cis,cis-1,3-cyclooctadiene with several isomerization catalysts,[25] is not affected by the present reagent system and neither is limonene. These results indicate that the 'titanocene' reagent prepared using the $Mg/BrCH_2CH_2Br$ reagent shows promise for use in the selective isomerization of mono-substituted olefinic moiety in the presence of the disubstituted and trisubstituted olefinic groups. The inertness of disubstituted olefins towards the reagent is also indicated by the absence of 3-decenes and 4-decenes in the isomerization of 1-decene into 2-decenes.

Isomerization of 1-alkenes to 2-alkenes can also be achieved using Cp_2TiCl_2, prepared in situ by the reaction of $TiCl_4$ (2.5 mmol), t-BuMgCl (6 mmol) and freshly distilled cyclopentadiene (5 mmol) and Mg (20 mmol), 1,2-dibromoethane (15 mmol) in THF at room temperature.

As outlined previously, a number of reagents have been shown to reduce Cp_2TiCl_2 into "titanocene" or its equivalent.[18,19,21,22b,26-29] The reaction of titanocene species produced in these reductions with

Table 1: Isomerization of 1-alkenes to 2-alkenes.

1-alkene	Reagent system (Cp_2TiCl_2 and)	Reaction time	Product[f]	Yield[e]
n-$C_7H_{15}CH_2$-CH=CH_2	$CH_3CH(CH_3)CH_2MgX^{a}$	2		75^{f}
n-$C_7H_{15}CH_2$-CH=CH_2	$(CH_3)_3CMgX^{b}$	2		75^{f}
n-$C_7H_{15}CH_2$-CH=CH_2	$BrCH_2CH_2Br/Mg^{c}$	2		78^{f}
n-$C_7H_{15}CH_2$-CH=CH_2	$BrCH_2CH_2Br/Mg^{d}$	12		75^{f}
Ph-CH_2-CH=CH_2	$BrCH_2CH_2Br/Mg^{b,c}$	2		77^{g}
	$BrCH_2CH_2Br/Mg^{b,c}$	2		80^{g}

a) The reactions were carried out at room temperature under nitrogen by use of Cp_2TiCl_2 (2 mmol), the Grignard reagent prepared from Mg (25 mmol), isobutyl bromide (12 mmol) and 1-decene (10 mmol).

b) The reactions were carried out with Cp_2TiCl_2 (2 mmol), Mg (40 mmol), t-BuCl (15 mmol), 1,2-dibromoethane (15 mmol) and 1-decene (10 mmol). The same procedure was also applicable to isomerization of allylbenzene and safrole.

c) The reactions were carried out with Cp_2TiCl_2 (2 mmol), 1,2-dibromoethane (15 mmol), Mg (20 mmol) and 1-decene (10 mmol).

d) The reaction was carried out with 50 mmol of 1-decene.

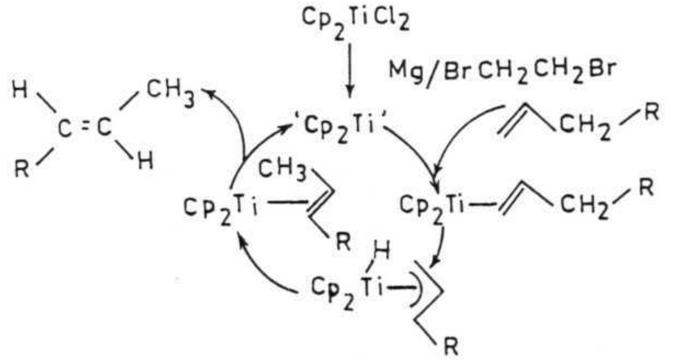
e) The products were isolated by column chromatography (silica gel with hexane as eluent) and identifned by their IR and ^{13}C NMR spectral data and comparision with literature data.

f) The trans/cis ratio ~ 85/15% (see experimental).

g) 100% trans product.

alkenes has not been studied in many cases. The ethylene complex, bis (pentamethylcyclopentadiene)titanocene, $[C_5Me_5]_2Ti(CH_2{=}CH_2)$, has been reported to catalyze isomerization of 1-hexene into trans-2-hexene.[16] It has been shown that the Cp_2TiCl_2 and Cp_2TiCl reagents do not isomerize 1-alkenes.[8] The complex, $(C_5H_5)_3(C_5H_4)Ti_2$, prepared by reducing Cp_2TiCl_2 with potassium naphthalenide in THF at -80°C, catalyzes rapid isomerization of 1-heptene to trans-2-heptene (~95%) and cis-2-heptene (~ 5%).[30] This reagent also catalyzes rapid isomerization of cis,cis-1,5-cyclooctadiene, in contrast to the present reagent system. The $[C_5Me_5]_2Ti(CH_2{=}CH_2)$ system has been reported to isomerize 1-hexene into primarily trans-2-hexene but in that system the $[C_5(CH_3)_5][C_5(CH_3)_4CH_2]TiH$ species was shown to be the catalyst.[16] Although the reactive species in the present reagent system may not be simply "Cp_2Ti", it was thought that the isomerization may be tentatively visualized in terms of the mechanism involving a 1,3-hydride shift assuming the intermediacy of Cp_2Ti and the formation of Cp_2Ti-olefin complexes (Scheme 9).

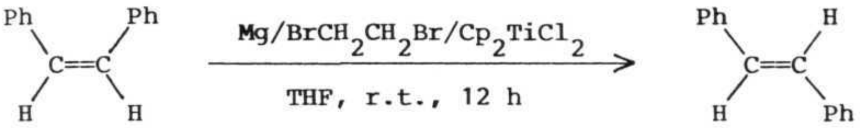
Scheme 9



As outlined in the introduction, a similar type of mechanism has been proposed in the highly stereoselective isomerization of monosubstituted 1-alkenes to 2-alkenes by the reaction of $(C_5Me_5)_2TiCl_2$

with two equivalents of sodium naphthalenide, i-PrMgBr, n-BuLi or $LiAlH_4$ in the presence of 1-alkene.[15] This mechanism has been strongly supported by the isolation of crystalline $(C_5H_5)_2$ Ti(syn-η^3-butenyl) and characterization of it by X-ray studies.[31]

We have observed that the $Cp_2TiCl_2/Mg/BrCH_2CH_2Br$ system also isomerizes cis-stilbene to trans-stilbene.

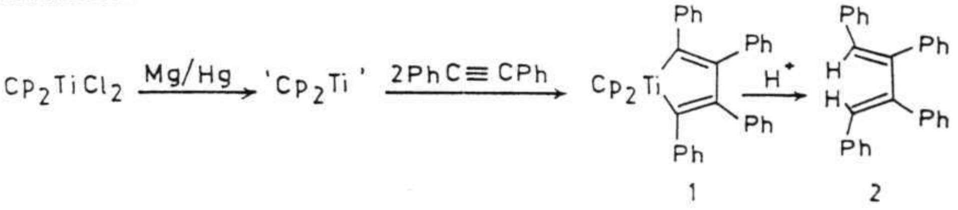


Since there is no question of allyl titanium species formed here, the isomerization here should result from the Ti-H species, most probably produced by decomposition of "Cp_2Ti" (Scheme 6). Consequently, the isomerization observed with the present reagent systems can be also visualized by the conventional addition-elimination mechanism involving Ti-H species.[32]

In order to examine the reactivity of the $Cp_2ZrCl_2/Mg/BrCH_2CH_2Br$ system with 1-decene, we carried out the following experiment. 1,2-Dibromoethane (30 mmol) was added to a mixture of Grignard grade magnesium (50 mmol) containing Cp_2ZrCl_2 (5 mmol) in THF (80 ml). The mixture turned to light yellow colour during 30 min. 1-Decene (10 mmol) was added and stirring was continued for 12 h at room temperature. After work-up and chromatography, 1-decene was isolated quantitatively.

Simple method for the preparation of $Cp_2M(CH_2{=}CH_2)$ complexes in solution:

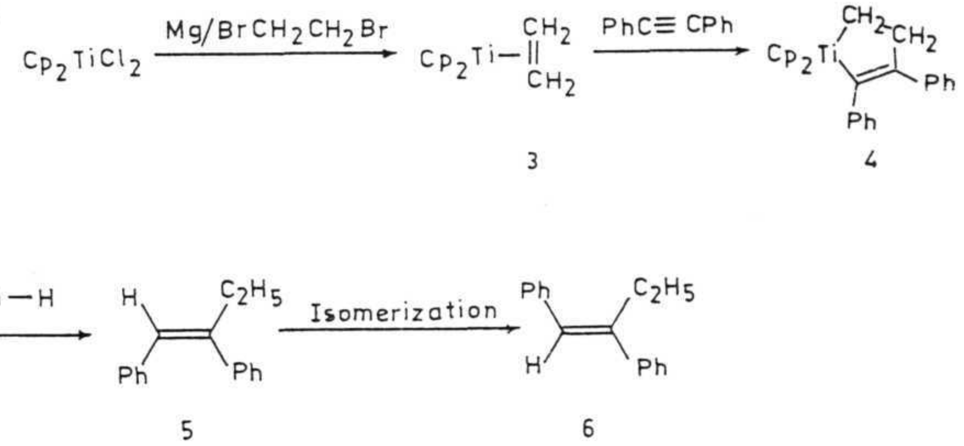
Titanocene, generated by the reduction of Cp_2TiCl_2 and Mg-Hg, gives the corresponding tetraphenyl titanacyclopentadiene **1** complex with diphenylacetylene which on hydrolysis yields 1,2,3,4-tetraphenyl-(E,E)-1,3-butadiene **2**.[19]



In order to compare the reactivity of the 'titanocene' generated using the $Cp_2TiCl_2/Mg/BrCH_2CH_2Br$ system with the reactivity of the Cp_2TiCl_2/Mg-Hg reagent, the following experiment was carried out. Diphenylacetylene (2 mmol) was added to the titanocene equivalent prepared from Cp_2TiCl_2 (2.5 mmol), Mg(25 mmol) and 1,2-dibromoethane (20 mmol) at room temperature and the mixture was stirred for 12 h under nitrogen atmosphere. After hydrolysis and work-up, in addition to the expected tetraphenyl butadiene (60%) another product, identified as 1,2-diphenyl-(E)-1-butene (30%) was also isolated. When the preparation of titanocene was carried out at 0°C, 1,2-diphenyl-(E)-1-butene (spectrum No. 5) was isolated in 80% yield.

It has been reported that the reactive titanocene, "Cp_2Ti" or its equivalent is formed in the reaction of Cp_2TiCl_2 and magnesium.[19] However, we have observed that when 1-decene (10 mmol) was added to Cp_2TiCl_2 (2 mmol) and Grignard grade magnesium (25 mmol) and the mixture was stirred for 2 h at room temperature, the 1-decene remained unchanged. Also, there is no indication of reduction of the orange coloured Cp_2TiCl_2 to the low valent titanium species. The original authors[19] did not specify whether they utilized Grignard grade magnesium or more reactive magnesium powder. 1,2-Dibromoethane is frequently utilized for activating magnesium in Grignard reactions.[33] It produces $MgBr_2$ and ethylene and continuously cleans the surface of the magnesium.[33] The resulting active magnesium might reduce Cp_2TiCl_2 to 'titanocene' in a more effecient manner. However, incorporation of the ethyl group derived from $BrCH_2CH_2Br$ in products obtained in the above experiments indicates that the role of 1,2-dibromoethane is much more than activating the Grignard grade magnesium. Presumably, the reactions take the course outlined in Scheme 10 resulting in the incorporation of ethyl group in the product.

Scheme 10



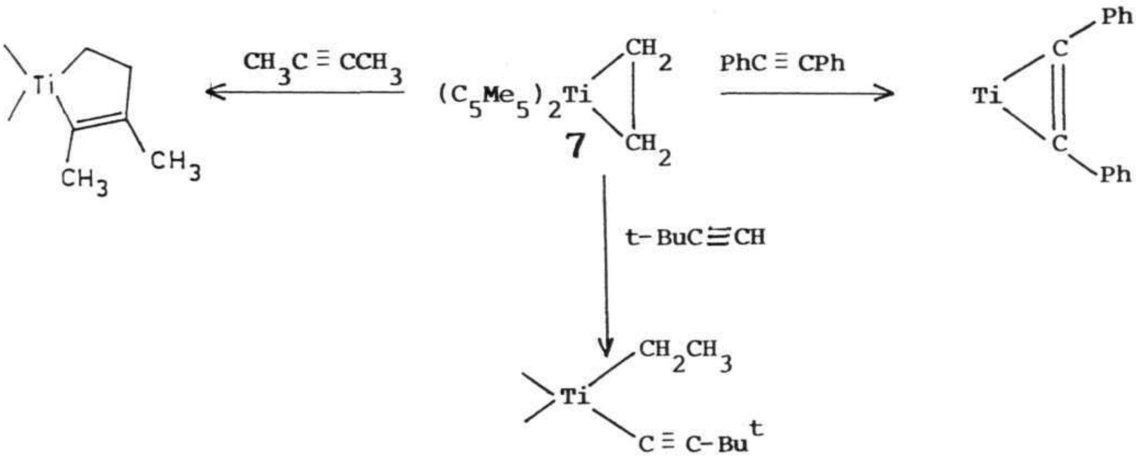
Initially, it was thought that the product would have the structure **5** since hydrolysis of the metallacycle **4** to **5** is a well-known reaction of such metallacycles. However, it has been reported that the compound **5** is a solid (mp.57°C)[34] whereas compound **6** is obtained as an oil. The compound obtained in the present case is a single compound and the oily product failed to crystallise. Accordingly, the compound was assigned the structure **6**. The isomerization of **5** to **6** can be rationalized by the hydrometalation-β-elimination sequence involving the titanocene hydride species (Scheme 6) formed by the decomposition of titanocene or its dimer. As discussed previously, cis-stilbene is isomerized to trans-stilbene under the present reaction conditions. This observation along with the isomerization of **5** to **6** indicates the presence of metal hydride species along with metallocenes and/or their equivalents. In addition, it is likely that the hydride species also cleaves the metallacycles (**4**) since quenching with D_2O before work-up did not give the deuterium containing product.

However, still another alternate possibility exists for the reduction. For example, it has been reported that in the reduction of N_2 into NH_3 by the Cp_2Ti species in THF at r.t. during several days, 10% of the hydrogen present in the product NH_3 comes from the THF.[35] Consequently, the possibility of THF serving as the hydrogen source cannot be ruled out and we do not have any data to confirm or rule out these possibilities. It may be of interest to note that the synthesis of stable metallocycle systems are usually carried out in hydrocarbon-solvents.[37-41] Unfortunately, the $Mg/BrCH_2CH_2Br$ system failed to reduce the Cp_2TiCl_2 in hydrocarbon solvents (toluene, benzene, etc.) and hence we have continued the utilization of THF for further studies.

The $Cp_2ZrCl_2/Mg/BrCH_2CH_2Br$ reagent system also gives 1,2-diphenyl-(E)-1-butene in 80% yield with diphenylacetylene under similar reaction conditions, indicating the formation of zirconocene-ethylene complex and the corresponding metallacycle as intermediates (Scheme 10).

The simple ethylene complexes of "Cp_2Ti" and "Cp_2Zr" have not been reported although the $(C_5Me_5)_2Ti(CH_2{=}CH_2)$ complex has been prepared and characterized.[16] It has been reported that the titanocene-ethylene **7** complex generated in this way is highly reactive towards alkynes. Internal alkynes whose π-acceptor property is less pronounced, are incorporated into the Ti-C bond to give the corresponding metallacyclo-2-pentene derivatives (Scheme 11). Alkynes which are good π-acceptor ligands exclusively undergo ligand exchange to give the corresponding π-complex. Terminal alkynes gave the alkynyl(ethyl)titanium compounds (Scheme 11).

Scheme 11

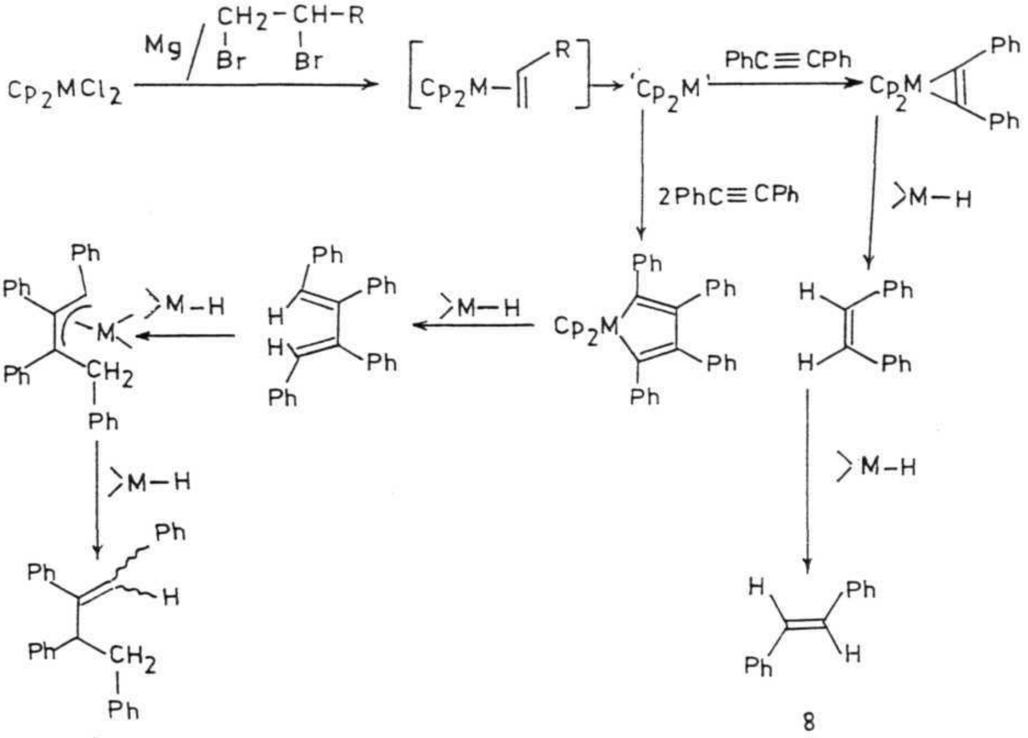


It has been reported that a similar zirconocene diphenyl-acetylene complex, prepared by the reaction of 'zirconocene' with 1 equivalent of diphenylacetylene, reacts with another equivalent of diphenylacetylene to produce tetraphenyl metallacyclopentadiene derivative which on hydrolysis gives 1,2,3,4-tetraphenyl-1,3-butadiene.[10] We have observed that when the experiment was carried out using 1-decyne with the $Cp_2TiCl_2/Mg/BrCH_2CH_2Br$ system, only polymerized product was isolated. The 1-decyne was unaffected by the zirconium system under the reaction conditions. It is of interest to note that the "Cp_2Ti" species prepared by the reaction of Cp_2TiCl_2 with Na/Hg in toluene under argon atmosphere catalyzes polymerization of 1-alkynes.[27]

The metallacycles similar to **4** have been prepared in hydrocarbon solvents and utilized extensively.[10,36] As discussed previously, the metallacycle **4**, generated under the present reaction conditions, undergoes reduction even before work-up as indicated by the absence of deuterium in the product when the reaction mixtures were treated with D_2O. The metallacycles such as **4** have been reported to give the corresponding cyclopentanone derivatives on carbonylation with carbon monoxide.[18,36] However, attempted carbonylation of the reaction mixtures obtained in runs with both Cp_2TiCl_2 and Cp_2ZrCl_2 did not furnish any other product other than the 1,2-diphenyl-(E)-1-butene **6**. Clearly, this product is formed before carbonylation.

In order to examine whether higher alkene complexes can be prepared utilizing the $Cp_2MCl_2/Mg/BrCH_2CH(R)Br$ (M=Ti or Zr) systems, we carried out the experiments replacing 1,2-dibromoethane with 1,2-dibromodecane or 1,2-dibromostyrene. 1,2-Dibromodecane (10 mmol) or styrene dibromide (10 mmol) was added to a mixture of Grignard grade magnesium (25 mmol) and zirconocene dichloride (2.5 mmol) in THF (80 ml) at 0°C under nitrogen atmosphere. After the reaction mixture became light yellow (25 min), diphenylacetylene was added and the reaction mixture was brought to r.t. and stirred further for 12 h. After work-up and chromatography, trans-stilbene **8** (35%) and 1,2,3,4-tetraphenyl-1-butenes **9** (50%) (spectrum No.6) were isolated besides 1-decene/2-decene or styrene. However, the corresponding alkylated stilbenes were not formed. The formation of these products can be rationalized tentatively as indicated in Scheme 12.

Scheme 12



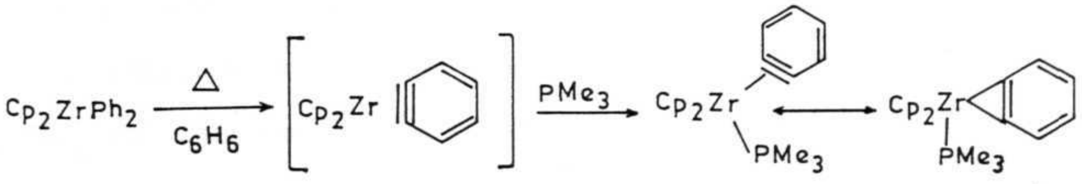
9

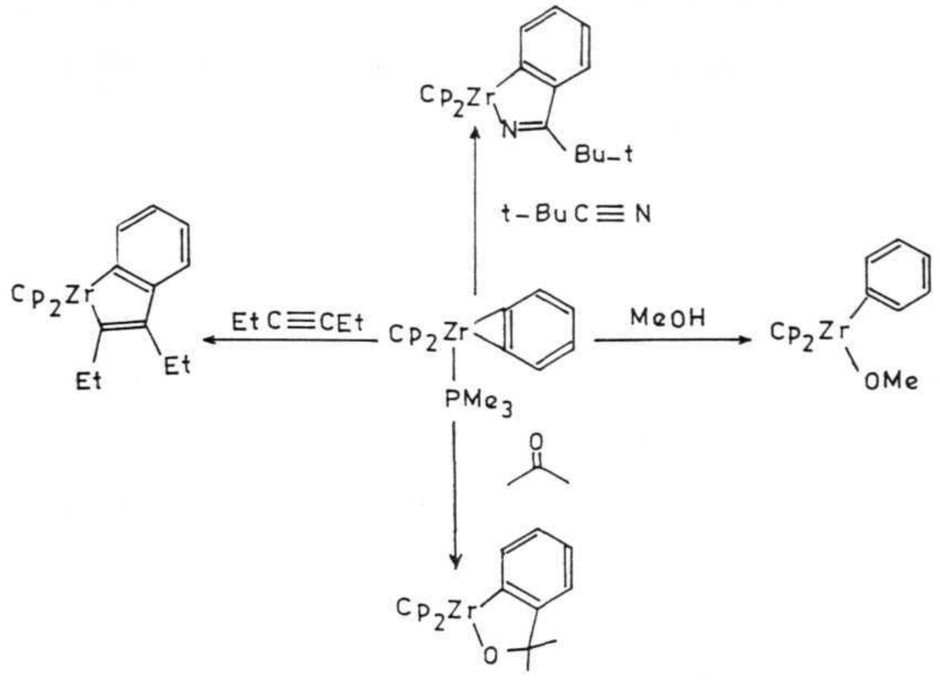
8

Surprisingly, these products (Scheme 12) were not obtained in runs utilizing 1,2-dibromoethane. Presumably, 'Cp_2M' species generated utilizing the 1,2-dibromodecane or 1,2-dibromostyrene are more reactive and give metal hydride species capable of reducing tetraphenyl butadiene and diphenylacetylene into trans-stilbene (Scheme 12).

In recent years, the zirconocene-alkyne and -benzyne complexes have received much attention (Scheme 13).[37-41]

Scheme 13

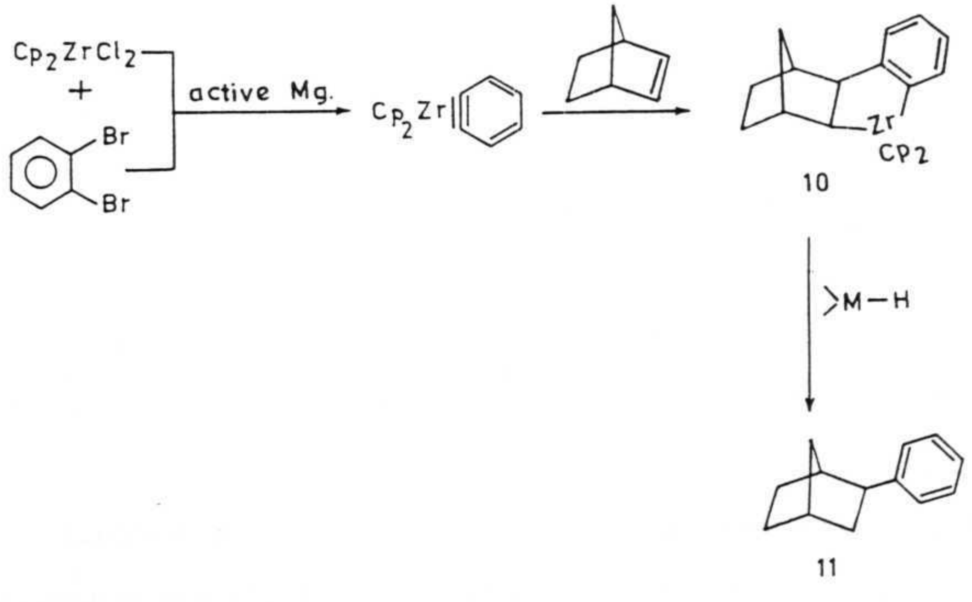




The titanocene- and zirconocene-benzyne complexes are generally prepared by the thermal decomposition of diphenylmetallocene.[42,43] Titanocene-benzyne complex has been also prepared in 15% yield by the reaction of Cp_2TiCl_2 with 1-bromo-2-fluorobenzene in the presence of magnesium in THF.[19] It was of interest to examine whether the titanocene- and zirconocene-benzyne complexes can be prepared in situ utilizing the Cp_2MCl_2 (M=Ti or Zr) and 1,2-dibromobenzene in the presence of magnesium for utilization in reactions with organic substrates.

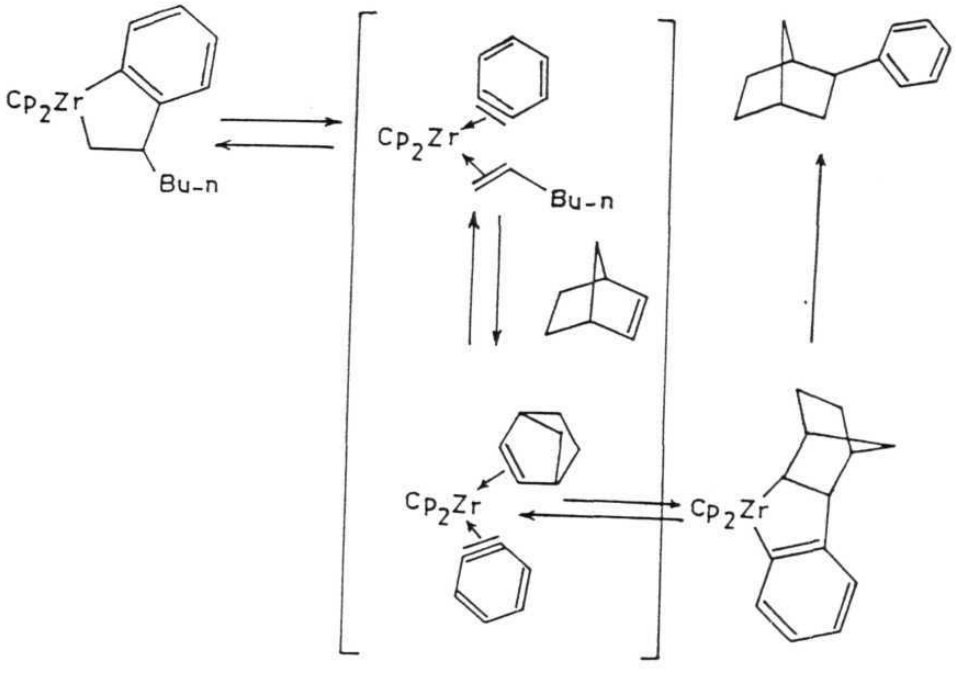
It was observed that the reaction of Grignard grade magnesium with Cp_2MCl_2 (M=Ti or Zr) and 1,2-dibromobenzene at room temperature in the presence of diphenylacetylene or norbornene gave only biphenyl as the reaction product. It appeared that if both the reduction of Cp_2MCl_2 and reaction of 1,2-dibromobenzene can be carried out at lower temperature, then it may be possible to prepare the corresponding benzyne complexes of Cp_2M. Grignard grade magnesium failed to react with 1,2-dibromobenzene at -24°C. However, the active magnesium, prepared in situ utilizing $MgBr_2$ and potassium metal,[44] reacts with 1,2-dibromobenzene (5 mmol) at -24°C in the presence of Cp_2ZrCl_2 (2.5 mmol). Norbornene (5 mmol) was added to this reagent system and the contents were stirred for 3 h at -24°C and at room temperature for 12 h. After work-up and chromatography, exo-2-phenylnorbornane **11** was isolated in 60% yield. The sample was identical (1:1 correspondence of the IR spectrum) to the sample obtained by the reaction of norbornene with benzene in Con.H_2SO_4.[45] It was also observed that when the above experiment was carried out without utilizing Cp_2ZrCl_2, only biphenyl (80%) was isolated. This indicates that zirconocene-benzyne complex is formed under the present reaction conditions. The result can be tentatively rationalized as outlined in scheme 14.

Scheme 14



It is of interest to note that the metallacycle product **10**, prepared by the exchange of olefin from 3-n-butylzirconaindane in the presence of excess norbornene (1.1-20 molar equivalent) without any solvent, has been found to be stable even at 100°C.[46] However, in solutions these metallacyclopentanes decompose and give only phenylalkanes (Scheme 15).[46]

Scheme 15



In runs utilizing Cp_2TiCl_2 in the place of Cp_2ZrCl_2 only biphenyl formation was observed. When the experiment was carried out replacing norbornene with diphenylacetylene only trans-stilbene was isolated (70%) in addition to biphenyl (70%). This is similar to the reactivities observed by the Cp_2M and $>$M-H species generated from $Cp_2MCl_2/Mg/BrCH_2CH(R)Br$ system which converts diphenylacetylene into trans-stilbene (Scheme 13).

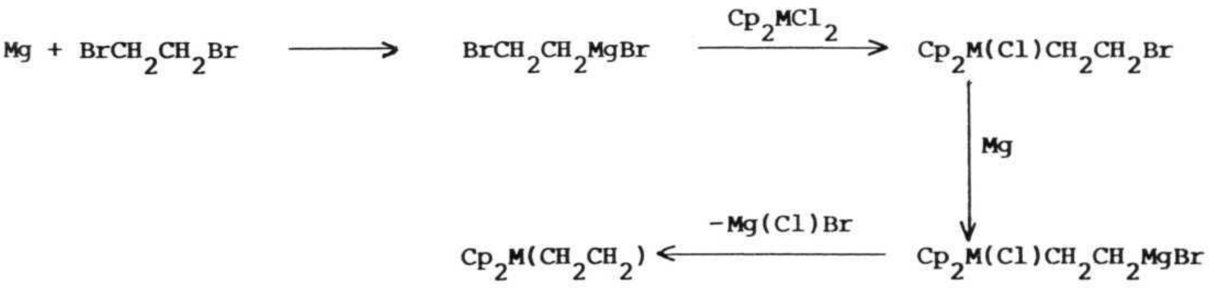
Although much to be desired regarding synthetic utilities, the 1,2-dibromoethane/Mg/Cp_2MCl_2 (M=Ti or Zr) and 1,2-dibromobenzene/Mg/Cp_2ZrCl_2

systems are promising as simple reagent systems for <u>in situ</u> preparation of the corresponding ethylene and benzyne complexes.

$TiCl_4/Mg/BrCH_2CH_2Br$ system: A 1,2-Diorganometallic equivalent:

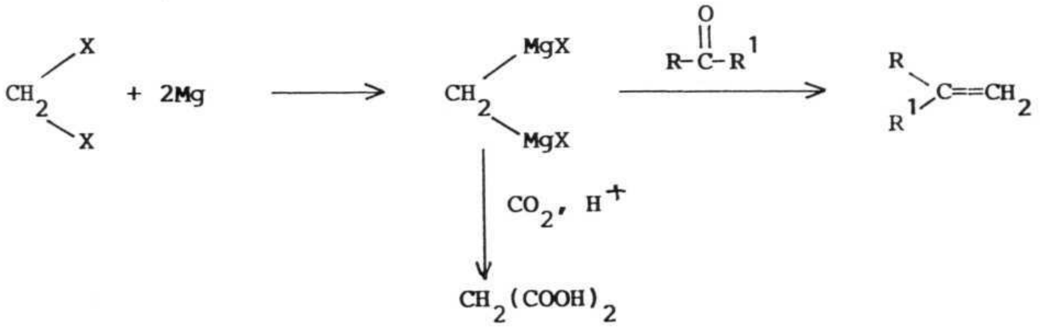
As discussed in the previous section, the Cp_2MCl_2 (M=Ti,Zr)/Mg/$BrCH_2CH_2Br$ reagent system reacts with diphenylacetylene to give ethylstilbene. This transformation was visualized as involving the $Cp_2Ti(CH_2=CH_2)$ species and a five membered metallacycle as intermediates (Scheme 10 and 11). The formation of $Cp_2M(CH_2=CH_2)$ can be tentatively rationalized as indicated by Scheme 16.

Scheme 16

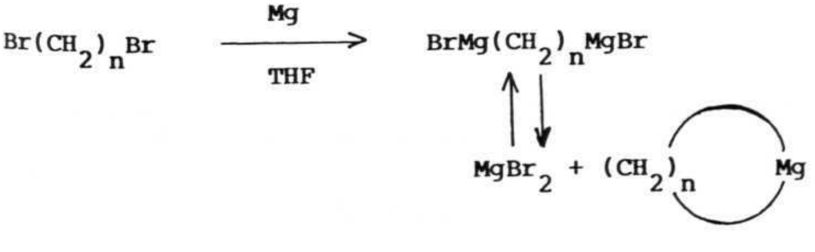


If the mechanism outlined in Scheme 16 is operative, it implies that the Cp_2MCl_2 reagent is able to trap the $BrCH_2CH_2MgBr$ intermediates. This is interesting since the $BrCH_2CH_2MgBr$ readily decomposes into $MgBr_2$ and ethylene.[33] However, the stability of the corresponding titanium reagent, $>Ti-CH_2CH_2Br$ is not entirely unexpected. It is known that whereas the o-fluorophenyl titanium derivatives are stable enough for reactions at temperatures upto 25°C,[1,47] the corresponding Li and Mg derivatives eliminate the metal fluoride above -50°C.[48-50] It is well-known that the organotitanium reagents, generated by the reaction of RMgX or RLi with $TiCl_4$, can readily transfer the alkyl groups to carbonyl groups.[1] Accordingly, we decided to examine the possibility of trapping the $BrCH_2CH_2MgBr$ species produced by the reaction of $BrCH_2CH_2MgBr$ with Cp_2TiCl_2 and/or $TiCl_4$ and also to examine the possibilities of transferring the $-CH_2CH_2-$ moiety to organic substrates. A brief survey on the synthesis of various diorganometallic derivatives will be helpful for the discussion.

The gem-dimagnesium compound can be readily obtained on treatment of methylene bromide or iodide with Mg turnings or with Mg/Hg at room temperature in ether-benzene solvent.[51,52] It reacts with aldehydes and ketones to give olefins, and malonic acid on carboxylation.



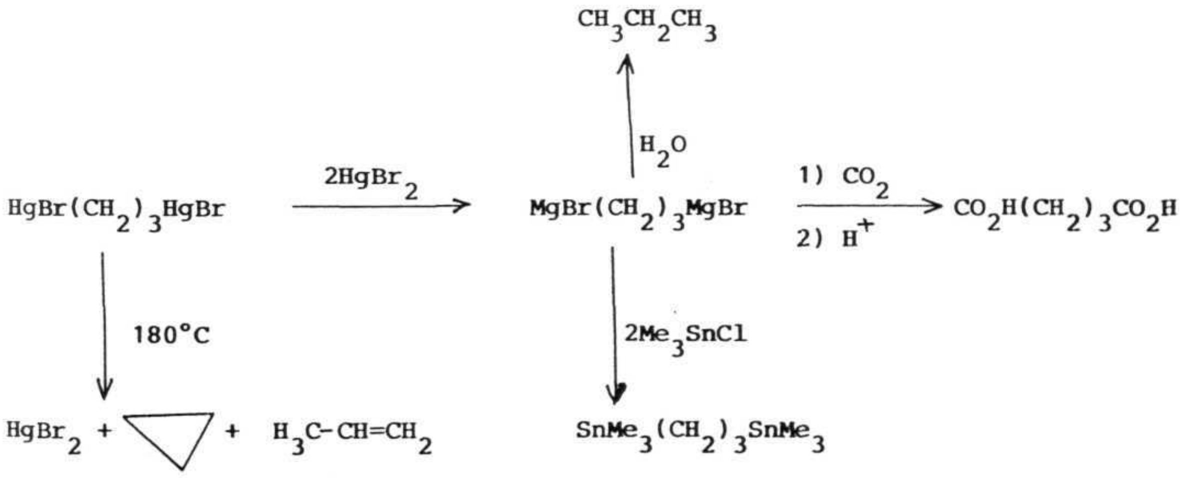
Several other applications have been reported.[52,53] Aliphatic α,ω-dimagnesium derivatives $XMg(CH_2)_nMgX$ are preparable by the reaction of $X(CH_2)_nX$ with magnesium when $n \geqslant 3$.[54-56]



The 1,3-dimagnesium bromide has been also prepared in 30% yield by careful addition of 1,3-dibromopropane to magnesium in ether for 24 h at room temperature.[57]

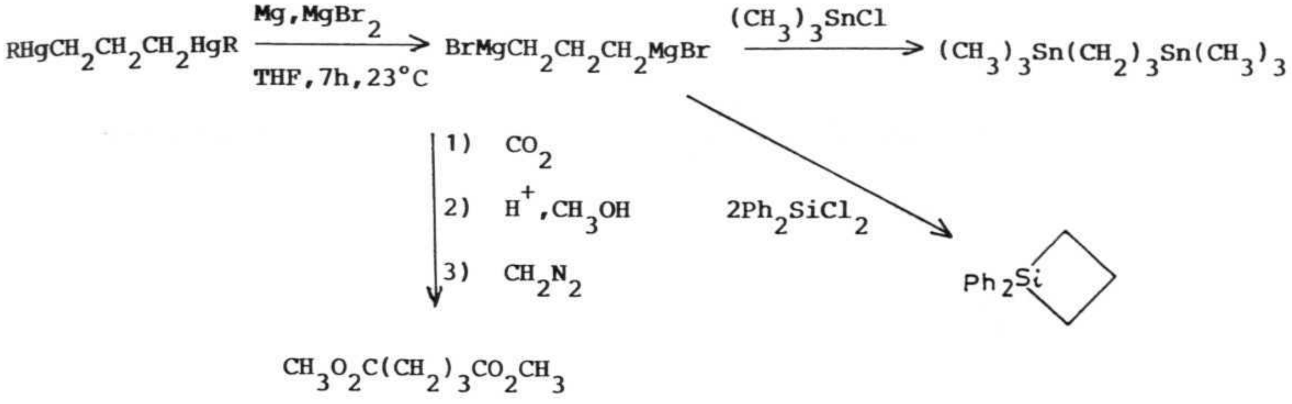
$$Br(CH_2)_3Br \xrightarrow[Et_2O]{Mg} MgBr(CH_2)_3MgBr + BrMg(CH_2)_6MgBr + BrMg\text{-}CH_2CH{=}CH_2$$

Its structure was confirmed by hydrolysis, carbonation, and transmetalation to mercury and cyclization to cyclopropane.



For the preparation of dimagnesium halide with n=3, a circutous route involving hydroboration of allene followed by mercuration with $Hg(OAc)_2$/NaCl and transmetalation with $Mg/MgBr_2$ is also available.[58]

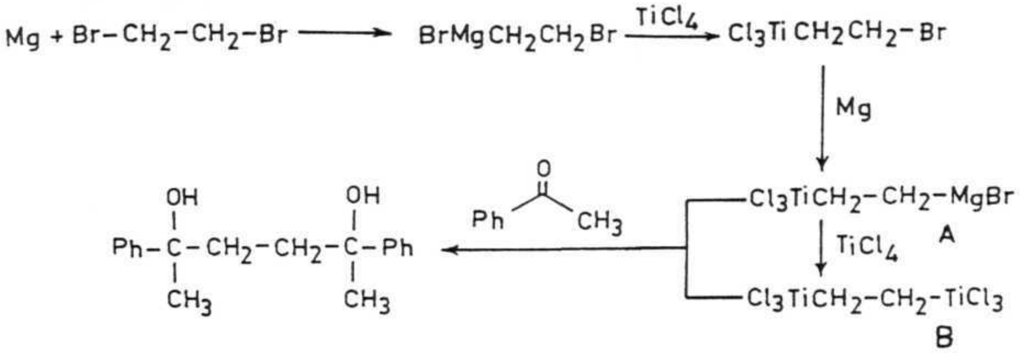
$$CH_2{=}C{=}CH_2 \xrightarrow[\substack{2)\ Hg(OAc)_2 \\ 3)\ NaCl}]{1)\ B_2H_6} ClHgCH_2CH_2CH_2HgCl \xrightarrow[THF,\,0°C]{2\ RLi}$$



However, the synthesis of the 1,2-dimagnesium derivatives, $BrMgCH_2CH_2MgBr$ is yet to be realized. Accordingly, it appeared desirable to examine the possibility of synthesising MCH_2CH_2M reagents which would react with organic substrates.

We have observed that the reagent prepared from Cp_2TiCl_2 (5 mmol)/Mg(25 mmol)/$BrCH_2CH_2Br$ (20 mmol) at 0°C failed to react with ketones (eg. acetophenone and cyclohexanone). We then carried out the experiment replacing Cp_2TiCl_2 with $TiCl_4$ as follows: 1,2-Dibromoethane (20 mmol) was added during a period of 5 min to a mixture of $TiCl_4$ (7 mmol) in benzene (15 ml) and Grignard grade magnesium (20 mmol) at 0°C (ice-bath) under nitrogen atmosphere. The contents were stirred for 30 min at 0°C and acetophenone (5 mmol) was added. The reaction mixture was warmed to 5-10°C and stirred further for 2 h. The black reaction mixture was quenched with saturated potassium carbonate solution (10 ml). After work-up and chromatography, 2,5-diphenylhexane-2,5-diol (spectrum No.7) was isolated in 50% yield. A likely mechanism for the transformation is shown in Scheme 17.

Scheme 17

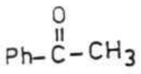
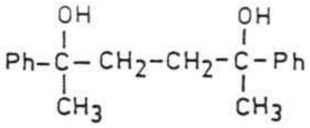
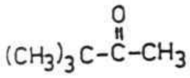
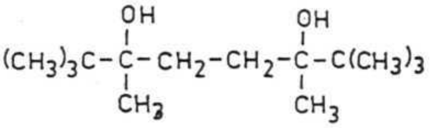
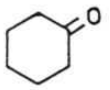
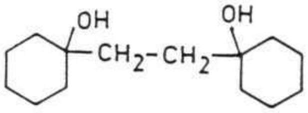
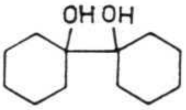
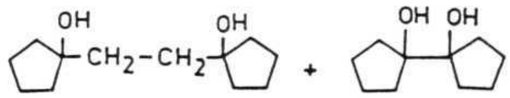
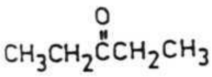
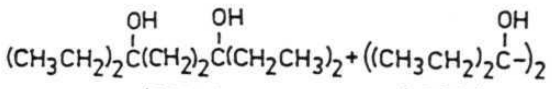
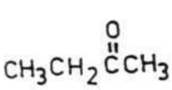
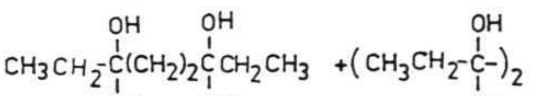


tert-Butyl methyl ketone (pinacolone) was converted into the corresponding 1,4-diol (spectrum No.8) in 55% yield. However, the reagent system gives both the 1,4- and 1,2- diols on reaction with cyclohexanone, cyclopentanone, 3-pentanone and ethyl methyl ketone. The results are summarized in Table 2.

It was found that the 1,2-diols are formed in low yields (~ 20%) when the reaction was carried out in the absence of $TiCl_4$. However, it is likely that in these cases the 1,2-diols are formed from the reaction of ketones with the low valent titanium species generated by the reduction of $TiCl_4$. As outlined in the introductory section, it has been reported that the $TiCl_4/Mg\text{-}Hg$[13], $TiCl_3/Mg$[14] and $TiCl_4/Zn$[12] systems give 1,2-diols as the only products with ketones.

The results indicate that there are two types of species present under the reaction conditions (Scheme 18). Presumably, in the case of acetophenone and pinacolone path A is very fast and path B is slow. In other cases, path B also interferes and the 1,2-diols are also formed.

Table 2: Conversion of ketones to 1,4-diols and 1,2-diols using $TiCl_4$/Mg/ $BrCH_2CH_2Br$ reagent system.

Substrate[a]	Product(s)	Yield(%)[b]	m.p.
 $Ph-\overset{O}{\overset{\Vert}{C}}-CH_3$	 $Ph-\overset{OH}{\underset{CH_3}{C}}-CH_2-CH_2-\overset{OH}{\underset{CH_3}{C}}-Ph$	50	121-122°C
 $(CH_3)_3C-\overset{O}{\overset{\Vert}{C}}-CH_3$	 $(CH_3)_3C-\overset{OH}{\underset{CH_3}{C}}-CH_2-CH_2-\overset{OH}{\underset{CH_3}{C}}-C(CH_3)_3$	55[c]	118-119°C
		35[d,e]	127-128°C
	+ 	35[d,f]	123-124°C
	 (50%) (50%)	60[g]	
 $CH_3CH_2\overset{O}{\overset{\Vert}{C}}CH_2CH_3$	 $(CH_3CH_2)_2\overset{OH}{C}(CH_2)_2\overset{OH}{C}(CH_2CH_3)_2 + ((CH_3CH_2)_2\overset{OH}{C}-)_2$ (50%) (50%)	60[g]	
 $CH_3CH_2\overset{O}{\overset{\Vert}{C}}CH_3$	 $CH_3CH_2-\overset{OH}{\underset{CH_3}{C}}(CH_2)_2\overset{OH}{\underset{CH_3}{C}}CH_2CH_3 + (CH_3CH_2-\overset{OH}{\underset{CH_3}{C}}-)_2$ (50%) (50%)	60[g]	

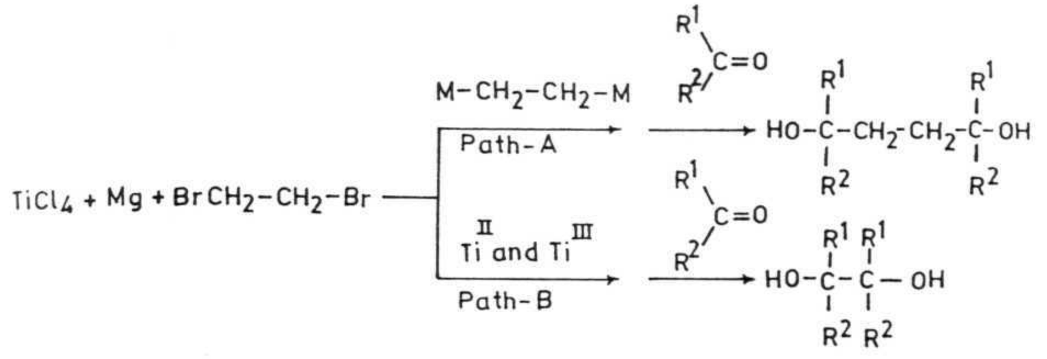
a) In all cases, the reactions were carried out in the same scale (see experimental section). Reaction time and temperature are also the same. All new compounds gave satisfactory analytical data (C±0.2% and H±0.2%).

b) Yields of the isolated products based on the starting ketone utilized.

c) Yield of products separated by chromatography on a silica gel column using hexane (80%) and ethylacetate (20%) as eluent.

d) Isolated as a mixture of 1,4- and 1,2- diols. The percentage compositions given in parentheses along with the structures were estimated by comparing the -C-OH carbon-13-NMR signal intensities and hence they can be only crude approximate estimates since these signals are also affected by NOE effects.

Scheme 18



The $TiCl_4/Mg/BrCH_2CH_2Br$ reagent does not affect benzophenone, n-octanal and pivalaldehyde, $(CH_3)_3CCHO$, gave the corresponding 1,2-diol. Also, electrophiles such as n-octyl bromide, n-octyl cyanide were not affected by the reagent system.

Attempts to prepare the 1,3-diorganometallic species using 1,3-dibromopropane instead of 1,2-dibromoethane and $Mg/TiCl_4$ in a run with cyclohexanone gave only the corresponding 1,2-diol (~ 20%) and the 1,5-diol was not formed.

It has been reported that the $ZrCl_4$ reagent does not readily get reduced to low valent zirconium species.[1] Accordingly, it was thought that the $ZrCl_4/BrCH_2CH_2Br/Mg$ reagent system will be more suitable for the preparation of the 1,4-diols. However, the reaction of cyclohexanone with $ZrCl_4/Mg/BrCH_2CH_2Br$ system gave only the 1,2-diol (~ 30%) which might have formed by the reaction of the ketone with magnesium.

In order to examine the possibility of preparation of substituted 1,2-diorganometallic reagents, an experiment utilizing 1,2-dibromohexane in the place of 1,2-dibromoethane was carried out under similar conditions. Unfortunately, only 1,2-diol was isolated in 40% yield and the substituted 1,4-diol was not formed.

SUMMARY

The reagent systems prepared <u>in situ</u> in tetrahydrofuran (THF) by the reaction of Cp_2TiCl_2 with iso-butyl or t-butylmagnesium halides or with Grignard grade magnesium and 1,2-dibromoethane provide simple reagents for the isomerization of some 1-alkenes into trans-2-alkenes under mild conditions. The 1,2-dibromoethane/Mg/Cp_2MCl_2 (M=Ti or Zr) and 1,2-dibromobenzene/Mg/Cp_2ZrCl_2 systems are promising as simple reagent systems for the <u>in situ</u> preparation of the corresponding ethylene and benzyne complexes as indicated by the incorporation of ethyl group into diphenylacetylene and incorporation of phenyl group into norbornene. A novel 1,2-diorganometallic species generated utilizing the $TiCl_4$/Mg/$BrCH_2CH_2Br$ reagent system reacts with some ketones to give the corresponding 1,4-diols. This reagent system is promising for introducing $-CH_2CH_2-$ group into appropriate organic substrates.

EXPERIMENTAL

Several items given in the experimental section of Chapter 1 are also applicable for the experiments outlined here.

The dichlorobis(cyclopentadiene)titanium (IV), Cp_2TiCl_2 and dichlorobis(cyclopentadiene)zirconium (IV), Cp_2ZrCl_2, supplied by Fluka, Switzerland were utilized. Titanium (IV) tetrachloride, $TiCl_4$, supplied by Riedel was utilized to make standard solution in benzene (50 mmol, 9.5 g of $TiCl_4$ in 100 ml of benzene). $ZrCl_4$ supplied by Fluka, Switzerland was used.

All alkenes utilized were commercial samples, supplied by Fluka, Switzerland. Diphenylacetylene was prepared following a reported procedure.[59] Acetophenone, cyclohexanone and cyclopentanone supplied by Ranbaxy, India were utilized. Pinacolone, 3-pentanone, 2-butanone, and pivalaldehyde utilized were supplied by Fluka, Switzerland. Benzophenone and n-octanal utilized were supplied by Sisco, India.

All 1,2-dibromo compounds, except 1,2-dibromoethane, utilized were prepared from alkenes by bromination in CCl_4.[60] 1,3-Dibromopropane and iso-butyl bromide were supplied by Fluka, Switzerland. t-Butyl chloride was prepared following a reported procedure.[61]

Reaction of 1-decene with the Cp_2TiCl_2/iso-butylmagnesium bromide reagent system in THF:

Iso-butylmagnesium bromide was prepared in THF (60 ml) using iso-butyl bromide (12 mmol, 1.64 g) and Grignard grade magnesium (20 mmol, 0.5 g) at room temperature under nitrogen atmosphere. A solution of dichlorobis(cyclopentadiene)titanium (IV) (2 mmol, 0.5 g) in THF (60 ml) was made in the reaction flask and the iso-butylmagnesium bromide solution was then transferred into it through a cannula under nitrogen atmosphere. After 30 min, 1-decene (10 mmol, 1.4 g) was injected and the mixture was stirred for 2 h at r.t. The mixture was treated with dil.HCl (50 ml, 2N) and saturated with solid sodium chloride. The organic layer was separated and the aqueous layer was extracted with ether (3x30 ml). The combined organic extract was washed successively with water (50 ml), brine solution (50 ml) and dried over anhydrous $MgSO_4$. The solvent was evaporated and the residue was chromatographed on a silica gel column using hexane as eluent to isolate a trans/cis mixture (~ 85:15) of 2-decenes (1.0 g, 75%).

B.P. 57-58°C/10 mm.

IR (neat): ν_{max}: 2960, 2850, 950 cm^{-1}.

^1H NMR (100 MHz, $CDCl_3$): δ ppm 6.4 (m,-CH), 2.3 (m,-CH_2), 1.9 (d,trans-CH_3), 1.8 (d,cis-CH_3), 1.3 (br,s, other CH_2 hydrogens), 0.9 (t,-CH_3).

^{13}C NMR (25.0 MHz, $CDCl_3$): δ ppm 131.6, 124.4, 32.6, 31.9, 29.7, 29.2, 22.6, 17.5, 13.8.

In addition small peaks at 130.7, 123.4, 26.8 and 12.7 ppm characteristic of cis-2-decene were also present. The ratios of trans/cis isomers of 2-decenes reported here can be only approximate as they are based on the relative intensities of the olefinic carbon signals which are also affected by different NOE factors. We previously reported (Ref.25) a trans/cis isomer ratio of 90/10 for the mixture of trans/cis-2-decenes obtained utilizing $CoCl_2/NaBH_4$ system, on the basis of relative intensities of the olefinic CH_3 proton signals (270 MHz spectrum). Comparison of the relative intensities of the olefinic carbon signals obtained in that case with those observed for the trans/cis isomers obtained in the present procedure indicates that the ratio is closer to 85/15.

Reaction of 1-decene with the Cp_2TiCl_2/t-BuMgCl reagent system in THF:

To a solution of Mg (40 mmol, 1.0 g) and t-BuCl (16 mmol, 1.5 g) in THF (80 l), 1,2-dibromoethane (15 mmol, 2.8 g) was added dropwise under nitrogen atmosphere at room temperature. To this Grignard reagent, Cp_2TiCl_2 (2 mmol, 0.5 g) was added followed by 1-decene (10 mmol, 1.4 g). The reaction mixture turned to black via green colour in 2 h. After work-up, the residue was subjected to chromatography on a silica gel column using hexane as eluent to isolate a trans/cis mixture (~ 85:15) of 2-decenes (1.0 g, 75%). The IR, ^1H NMR and ^{13}C NMR spectral data showed 1:1 correspondence to the spectra of the sample obtained in the previous experiment.

The above procedure utilizing Cp_2TiCl_2/t-BuMgCl system is also applicable for isomerization of allylbenzene and safrole (Table 1).

Isomerization of 1-decene using $Cp_2TiCl_2/Mg/BrCH_2CH_2Br$ reagent system in THF:

1,2-Dibromoethane (15 mmol, 2.8 g) was added at room temperature under nitrogen atmosphere during a period of 10 min to a THF (80 ml) solution of dichlorobis(cyclopentadiene)titanium (IV), Cp_2TiCl_2, (2 mmol, 0.5 g) in the presence of Grignard grade magnesium (20 mmol, 0.5 g). The mixture turned to dark green within 30 min. 1-Decene (10 mmol, 1.4 g) was added and the reaction mixture was stirred for 2 h at r.t. After work-up, the residue was chromatographed on a silica gel column using hexane as eluent to isolate a trans/cis mixture (~85:15) of 2-decenes (1.0 g, 78%). The IR, ^{1}H NMR and ^{13}C NMR spectral data showed 1:1 correspondence with those of the samples obtained previously.

The procedure outlined in the previous experiment utilizing the $Cp_2TiCl_2/Mg/BrCH_2CH_2Br$ reagent system in THF was followed for the isomerization of allylbenzene and safrole and the results obtained are presented below.

Yield: 77% (0.9 g).

B.P: 70°/12 mm, Lit.[62] b.p. 176-7°C/760 mm.

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

^{1}H NMR (100 MHz, $CDCl_3$): δ ppm 7.5 (m,$-C_6H_5$), 6.5 (m,-CH), 2.1 (d,$-CH_3$).

^{13}C NMR (25.0 MHz, $CDCl_3$): δ ppm 138.5, 131.9, 129.0, 127.3, 126.4, 125.7, 18.7.

Yield: 80% (1.2 g).

B.P: 120°C/10 mm, Lit.[63] b.p. 111°/6 mm.

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

^{13}C NMR (25.0 MHz, $CDCl_3$): δ ppm 148.3, 146.9, 132.7, 131.1, 123.6, 120.4, 108.3, 105.5, 101.1, 18.2.

Examination of the question whether the isomerization reaction using $Cp_2TiCl_2/Mg/BrCH_2CH_2Br$ reagent system is catalytic or not:

1,2-Dibromoethane (15 mmol, 2.8 g) was added dropwise to a THF (80 ml) solution containing dichlorobis(cyclopentadiene)titanium (IV), Cp_2TiCl_2, (2 mmol, 0.5 g) and Grignard grade magnesium (20 mmol, 0.5 g) under nitrogen atmosphere at room temperature. During 30 min, the colour changed from orange to black via green. 1-Decene (50 mmol, 7.0 g) was injected to this mixture and stirred further for 12 h at room temperature. After work-up, the residue was chromatographed on a silica gel column using hexane as eluent to isolate a trans/cis mixture (~85:15) of 2-decenes (5.25 g, 75%). The spectral data were again found to show 1:1 correspondence with the data of the samples obtained previously.

Isomerization of 1-decene using Cp_2TiCl_2 prepared in situ in THF:

t-Butylmagnesium chloride (6 mmol) in THF (80 ml) solution was prepared from magnesium (10 mmol, 0.25 g) and t-BuCl (6 mmol, 0.55 g) under nitrogen at r.t. during a period of 2 h. Freshly distilled cyclopentadiene (5 mmol, 0.33 g) was added to this mixture and stirred for 2 h at r.t. $TiCl_4$ (2.5 mmol, 12.5 ml in benzene, made by dissolving 10 mmol of $TiCl_4$ in 50 ml benzene) was added and stirred for further 1 h at r.t. to get a green coloured solution. Magnesium (20 mmol, 0.5 g) and 1,2-dibromoethane (15 mmol, 2.8 g) were added. After 30 min stirring, 1-decene (10 mmol, 1.4 g) was injected and the mixture was stirred for 24 h at room temperature. After work-up, the residue was subjected to chromatography on a silica gel column using hexane as eluent to isolate a trans/cis mixture (85:15) of 2-decenes (0.98 g, 70%).

Reaction of 1-decene using $Cp_2ZrCl_2/Mg/BrCH_2CH_2Br$ system in THF:

To a solution of dichlorobis(cyclopentadiene)zirconium (IV), Cp_2ZrCl_2, (5 mmol, 1.5 g) and magnesium (50 mmol, 1.25 g) in THF (80 ml), 1,2-dibromoethane (30 mmol, 5.4 g) was added dropwise during a period of 10 min under nitrogen at room temperature. The reaction mixture turned to light yellow within 30 min. 1-Decene (5 mmol, 0.7 g) was added and stirring was continued for 12 h at r.t. After work-up, unreacted 1-decene was recovered quantitatively.

Reaction of diphenylacetylene with $Cp_2TiCl_2/Mg/BrCH_2CH_2Br$ reagent system in THF at room temperature:

To a solution of dichlorobis(cyclopentadiene)titanium (IV), Cp_2TiCl_2, (2.5 mmol, 0.625 g) and Grignard grade magnesium (25 mmol, 0.625 g) in THF (80 ml), 1,2-dibromoethane (20 mmol, 3.7 g) was added under nitrogen at room temperature. During a period of 25 min, the colour of the solution turned from orange to black. Diphenylacetylene (2.1 mmol, 0.38 g) in THF (5 ml) was added and the contents were stirred for 12 h at r.t. After work-up, the residue was subjected to chromatography on a silica gel column using hexane as eluent. The expected 1,2,3,4-tetraphenyl-1,3-butadiene (0.21 g, 60%), m.p. 182-183°C, Lit.[21] mp.183°C and another product which was identified as 1,2-diphenyl-(E)-1-butene (0.12 g, 30%, spectral data given after the next experiment) were isolated.

Spectral data of 1,2,3,4-tetraphenyl-(E,E)-1,3-butadiene:

IR (KBr): ν_{max}: 3050, 1600, 760, 700 cm^{-1}.

^{1}H NMR (100 MHz, $CDCl_3$): δ ppm 7.36 (m,-8H), 7.0 (m,-8H), 6.75 (m,-4H), 6.3 (s,-2H).

^{13}C NMR (25.0 MHz, $CDCl_3$): δ ppm 144.3, 139.7, 137.1, 130.3, 129.4, 128.7, 128.1, 127.7, 127.3, 126.5.

Reaction with diphenylacetylene of the reagent system generated from $Cp_2TiCl_2/Mg/BrCH_2CH_2Br$ in THF:

1,2-Dibromoethane (20 mmol, 3.7 g) was added during 10 min to a THF solution (80 ml) of dichlorobis(cyclopentadiene)titanium (IV), Cp_2TiCl_2, (2.5 mmol, 0.625 g) in the presence of Grignard grade magnesium (25 mmol), 0.625 g) under nitrogen atmosphere at 0°C (ice-bath). The reaction mixture turned to dark greenish-black colour during 25 minutes. Diphenylacetylene (2.1 mmol, 0.38 g) in THF (5 ml) was added and the mixture was brought to room temperature during a period of 2 h and stirred further for 12 h. After work-up, the product mixture was chromatographed on a silica gel column using hexane as eluent to isolate 1,2-diphenyl-(E)-1-butene (0.35 g, 80%) b.p. 130-135°/2 mm, Lit.[34] b.p. 294-6°C (for 1,2-diphenyl(Z)butene, m.p. 57°[34]) and 1,2,3,4-tetraphenyl-(E,E)-1,3-butadiene (20 mg, 5%).

Spectral data of 1,2-diphenyl-(E)-1-butene

IR (neat): ν_{max}: 3050, 2950, 1610, 920, 760, 700 cm^{1}.

^{1}H NMR (100 MHz, $CDCl_3$): δ ppm 7.6-6.9 (m,-ph), 6.4 (s,-CH), 2.5 (q,-CH_2), 1.1 (t,-CH_3). **(Spectrum No. 5)**

^{13}C NMR (25.0 MHz, $CDCl_3$): δ ppm 145.4, 142.0, 139.1, 132.2, 129.6, 129.1, 128.9, 128.4, 127.4, 126.7, 125.8, 34.0 (t in OFR), 13.3 (q in OFR). **(Spectrum No. 5A)**

Mass spectral data (m/e): 208 (M^+, 50%), 193 (M^+-CH_3, 30%), 179 (M^+-CH_2CH_3, 100%), 115 (193-Ph, 30%).

Reaction with diphenylacetylene of the reagent system generated from the Cp_2ZrCl_2/Mg/$BrCH_2CH_2Br$ in THF:

To a solution of dichlorobis(cyclopentadiene)zirconium (IV), Cp_2ZrCl_2, (2.5 mmol, 0.73 g) and Grignard grade magnesium (25 mmol, 0.625 g) in THF (80 ml), 1,2-dibromoethane (20 mmol, 3.7 g) was added during 10 min at 0°C (ice-bath) under nitrogen atmosphere. The mixture turned to light yellow colour in 25 min. Diphenylacetylene (2.1 mmol, 0.38 g) in THF (5 ml) was injected and the contents were brought to room temperature within 2 h. The reaction mixture was stirred further for 12 h. After usual work-up the product mixture was chromatographed to isolate 1,2-diphenyl-(E)-1-butene (0.35 g, 80%) and 1,2,3,4-tetraphenyl-(E,E)-1,3-butadiene (20 mg, 5%). The spectral data (IR, ^{1}H NMR and ^{13}C NMR) showed 1:1 correspondence with the spectra of the samples obtained in the previous experiment.

Isomerization of cis-stilbene to trans-stilbene catalysed by the Cp_2ZrCl_2/Mg/$BrCH_2CH_2Br$ reagent system in THF:

To a solution of dichlorobis(cyclopentadiene)zirconium (IV), Cp_2ZrCl_2, (2.5 mmol, 0.73 g) and Grignard grade magnesium (25 mmol, 0.625 g) in THF (80 ml), 1,2-dibromoethane (20 mmol, 3.7 g) was added during 10 min at 0°C (ice-bath) under nitrogen atmosphere. cis-stilbene (2.1 mmol, 0.37 g) was injected after 25 min and the contents were brought to room temperature, stirred further for 12 h. The residue obtained after work-up was chromatographed on a silica gel column using hexane as eluent to isolate trans-stilbene (0.29 g, 80%).

M.P: 123-124°C, Lit.[64] m.p. 124°C.
^{13}C NMR (25.0 MHz, $CDCl_3$): δ ppm 137.5, 128.5, 127.7, 126.7.
Mass spectral data (m/e): 180 (M^+).

Reaction with diphenylacetylene of the reagent system generated from Cp_2ZrCl_2/Mg/1,2-dibromodecane in THF:

1,2-Dibromodecane (10 mmol, 3.0 g) was added dropwise during 10 min to a mixture of dichlorobis(cyclopentadiene)zirconium (IV),

Cp_2ZrCl_2, (2.5 mmol, 0.73 g) and Grignard grade magnesium (25 mmol, 0.625 g) in THF (80 ml) at 0°C under nitrogen. When the mixture became light yellow in colour (after ca.25 min), a solution of diphenylacetylene (2.1 mmol, 0.38 g) in THF (5 ml) was injected and it was allowed to warm to r.t. during 2 h. Stirring was continued for 12 h. Usual work-up gave 1-decene (contains 2-decenes to the extent of 5%), trans-silbene (15%) m.p. 123-124°C and 1,2,3,4-tetraphenyl-1-butene (0.23 g, 60%), m.p. 142-143°C.

Spectral data of 1,2,3,4-tetraphenyl-1-butene

IR (KBr): ν_{max}: 3050, 1610, 1080, 1040, 920, 760, 700 cm^{1}.

^{1}H NMR (100 MHz, $CDCl_3$): δ ppm 7.2-6.7 (m,Ph), 6.6 (s,-CH), 4.0 (t,-CH), 3.2 (t or overlap by doublets, $-CH_2-$ due to the presence of adjacent chiral centre). **(Spectrum No. 6)**

^{13}C NMR (25.0 MHz, $CDCl_3$): δ ppm 145.3, 141.2, 140.5, 137.4, 130.1, 129.3, 128.8, 128.0, 127.7, 127.1, 126.6, 124.1, 56.4 (d in OFR), 40.3 (t in OFR). **(Spectrum No. 6 A)**

Mass spectral data (m/e): 360 (M^+, 10%), 269 (M^+-CH_2Ph, 80%), 191 (269-Ph, 100%), 91 ($PhCH_2-$, 90%).

Analysis:	C%	H%
Calculated:	93.3,	6.66.
Found:	93.93,	6.79.

Reaction with diphenylacetylene of the reagent system generated from Cp_2ZrCl_2/Mg/styrenedibromide in THF:

Styrenedibromide (10 mmol, 2.64 g) was added under nitrogen atmosphere to a mixture of dichlorobis(cyclopentadiene)zirconium (IV), Cp_2ZrCl_2, (2.5 mmol, 0.73 g) and magnesium (25 mmol, 0.625 g) in THF (80 ml) at 0°C. After 30 min stirring, a solution of diphenylacetylene (2.1 mmol, 0.38 g) in THF (5 ml) was injected and the mixture was allowed to warm to room temperature during 1 h. Stirring was continued further for 12 h and after usual work-up styrene (0.6 g, 60%), trans-stilbene (0.12 g, 30%, m.p. 123-124°C, Lit.[64] m.p. 124°C) and 1,2,3,4-tetraphenyl-1-butene (0.15 g, 40%, m.p. 142-143°C) were isolated by chromatography. The spectral data (IR, ^1H NMR and ^{13}C NMR) showed 1:1 correspondence with the spectra of the sample obtained in the previous experiment.

Reaction with 1-decyne of the reagent system generated from Cp_2TiCl_2/Mg/ $BrCH_2CH_2Br$ in THF:

To a mixture of dichlorobis(cyclopentadiene)titanium (IV), Cp_2TiCl_2, (4.5 mmol, 1.1 g) and magnesium (30 mmol, 0.75 g) in THF (80 ml), 1,2-dibromoethane (15 mmol, 2.8 g) was added dropwise during 5 min under nitrogen at 0°C. After 25 min stirring, 1-decyne (4 mmol, 0.56 g) was injected and the mixture was brought to room temperature during 1 h. Stirring was continued for 12 h. After usual work-up and chromatography, a dark yellow oily compound was isolated. The compound did not distill upto 250°C at 0.1 mm Hg. It was concluded that it might be a oligomerization product. This product was not characterized further.

1-Decyne was unaffected when the Cp_2ZrCl_2 reagent was utilized instead of Cp_2TiCl_2 in the above experiment.

Reaction with norbornene of the reagent system generated from Cp_2ZrCl_2/Mg/1,2-dibromobenzene in THF:

The active form of magnesium was prepared by treating magnesium bromide, prepared from Grignard grade magnesium (20 mmol, 0.5 g). and 1,2-dibromoethane (20 mmol, 3.7 g) at room temperature, with potassium metal (30 mmol, 1.2 g) in refluxing THF (80 ml) for 3 h. 1,2-Dibromobenzene (5 mmol, 1.17 g) and dichlorobis(cyclopentadiene)zirconium (IV), Cp_2ZrCl_2, (2.5 mmol, 0.73 g) were then added at -24°C under nitrogen and after 20 min a THF (5 ml) solution of norbornene (5 mmol, 0.5 g) was injected. The mixture was stirred for 2 h at -24°C then allowed to warm to room temperature and stirred for a further 12 h. n-Butanol (5 ml) was then added (this operation was performed so as to avoid violent reaction (if any) due to the presence of excess potassium but it does not mean that excess potassium was present). Water (100 ml) was added and the mixture was saturated with solid sodium chloride. The two phases were separated and the aqueous phase was extracted with ether (3x30 ml). The combined organic extract was washed successively with water (50 ml), brine solution (50 ml) and dried over anhydrous $MgSO_4$. The filtrate was concentrated and the residue was subjected to chromatography on a silica gel column using hexane as eluent to isolate exo-2-phenylnorbornane (0.25 g, 60%, b.p. 84-86°C/1.8 mm Hg, Lit.[45] 76°C/0.8 mm Hg, yield based on the zirconocene dichloride used) and diphenyl (0.13 g, 70% yield based on the excess 1,2-dibromobenzene utilized), m.p. 70°C, Lit.[65] m.p. 71°C.

Spectral data for exo-2-phenylnorbornane:

IR (neat): ν_{max}: 3100, 3050, 2950, 1960, 1820, 1620, 1480, 1320, 1040, 820, 760, 700.

^{1}H NMR (100 MHz, $CDCl_3$): δ ppm 7.3-7.2 (m,-Ph), 2.8 (m,-CH), 2.4 (m,CH), 1.9-1.2 (m, remaining protons).

^{13}C NMR (25.0 MHz, $CDCl_3$): δ ppm 147.7, 128.3, 127.1, 125.4, 47.4, 42.9, 39.1, 36.8, 36.1, 30.6, 28.9.

The IR spectrum of the sample was identical to that of the sample obtained by the reaction of norbornene with benzene in concentrated H_2SO_4.[45] When the above procedure was repeated without using Cp_2ZrCl_2, only biphenyl (0.3 g, 80%) was isolated.

Reaction with diphenylacetylene of the reagent system generated from Cp_2ZrCl_2/Mg/1,2-dibromobenzene in THF:

The active form of magnesium was prepared in THF (80 ml), as outlined in the previous experiment. The contents were cooled to -24°C (liq.N_2 in CCl_4). 1,2-Dibromobenzene (5 mmol, 1.17 g) and dichlorobis-(cyclopentadiene)zirconium (IV), Cp_2ZrCl_2, (2.5 mmol, 0.73 g) were added. After 20 min stirring, a solution of diphenylacetylene (2.,1 mmol, 0.38 g) in THF (5 ml) was injected and the mixture was stirred for 2 h at -24°C. Then the mixture was brought to room temperature and stirred for 12 h. After work-up as outlined in the previous experiment, only trans-stilbene (0.3 g, 80%) m.p. 123-124°C, Lit.[64] 124°C and biphenyl (0.14 g, 80% based on the excess 1,2-dibromobenzene used m.p. 70°C, Lit.[65] m.p.71°C) were isolated.

Reaction of acetophenone with the 1,2-diorganometallic equivalent generated utilizing $TiCl_4/Mg/BrCH_2CH_2Br$ reagent system. A convenient method for the preparation of 1,4-diols from ketones:

To a mixture of $TiCl_4$ (7 mmol in 15 ml C_6H_6) and Grignard grade magnesium (20 mmol, 0.5 g) in THF (60 ml), 1,2-dibromoethane (20 mmol, 3.7 g) was added during a period of 5 min at 0°C (ice-bath) under nitrogen atmosphere. The contents were stirred for 30 min at 0°C and acetophenone (5 mmol, 0.6 g) was added. The reaction mixture was brought to 5-10°C and stirred further for 2 h. The black reaction mixture was quenched with saturated potassium carbonate solution (10 ml), poured into water (100 ml) and saturated with solid sodium chloride. The organic phase was separated and the aqueous phase was extracted with ether (3x30 ml). The combined organic extract was washed successively with water (50 ml), brine solution (50 ml) and dried over anhydrous $MgSO_4$. It was concentrated and the residue was subjected to chromatography on a silica gel column using 20% ethyl acetate in hexane as eluent to isolate the 2,5-diphenylhexan-2,5-diol (spectrum No.7). It was further purified by crystallization from ether-petroleum ether (1:4) mixture.

Yield: 50% (0.33 g).

M.P: 121-122°C.

IR (KBr): ν_{max}: 3450, 2950, 1280 cm^1.

^1H NMR (100 MHz, $CDCl_3$): δ ppm 73-7.2 (m,-Ph), 2.6-1.5 (br,OH), 1.6 (br,s,-CH_2), 1.5-1.4 (brs,-CH_3).
(spectrum No.7)

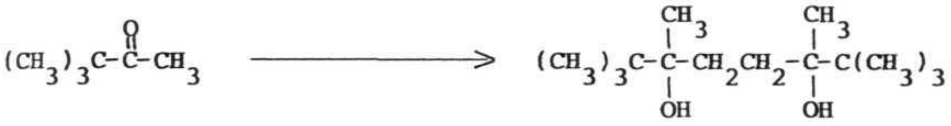
^{13}C NMR (25.0 MHz, $CDCl_3$): δ ppm 143.7, 127.5, 127.1, 79.0, 63.5 (t in OFR), 24.7 (q in OFR).
(spectrum No.7A)

Analysis: C% H%

Calculated: 80.0, 8.15.

Found: 80.15, 8.18.

The above procedure utilizing the $TiCl_4/Mg/BrCH_2CH_2Br$ reagent system in THF was followed for the conversion of pinacolone to the corresponding 1,4-diol (spectrum No.8) and other ketones such as cyclohexanone, cyclopentanone, 3-pentanone and 2-butanone into a mixture of 1,4- and 1,2- diols. The results are presented below.



$$(CH_3)_3C\text{-}\overset{O}{\overset{\|}{C}}\text{-}CH_3 \longrightarrow (CH_3)_3C\text{-}\underset{OH}{\overset{CH_3}{C}}\text{-}CH_2CH_2\text{-}\underset{OH}{\overset{CH_3}{C}}\text{-}C(CH_3)_3$$

Yield: 55% (0.31 g).

M.P: 118-119°C.

IR (KBr): ν_{max}: 3450, 2950, 1100 cm^{1}.

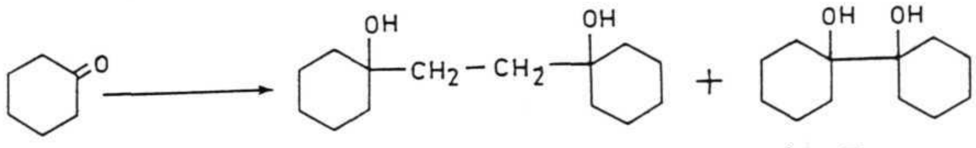
^1H NMR (100 MHz, $CDCl_3$): δ ppm 2.2-2.1 (br,s-OH), 1.1 (br,s,$-CH_2$), 1.0-0.9 (br,s,$-CH_3$). **(spectrum No.8)**

^{13}C NMR (25.0 MHz, $CDCl_3$): δ ppm 76.2, 38.3, 28.8, 25.3, 20.8. **(spectrum No.8A)**

Analysis: C% H%.

Calculated: 73.04, 13.04.

Found: 73.18, 13.10.



I (spectrum No. 10A) II

In this case, the products were separated by chromatography on a silica gel column using 20% ethyl acetate in hexane as eluent and the products were characterized by spectral analysis.

Spectral data for the 1,4-diol (I)

Yield: 35% (0.19 g).

M.P: 127-128°C.

IR (KBr): ν_{max}: 3400, 2950, 1460, 1280, 980 cm^{1}.

^{1}H NMR (100 MHz, $CDCl_3$): δ ppm 2.3 (br,s,-OH), 1.8-1.4 (m,-CH_2).**(Spectrum No. 9)**

^{13}C NMR (25.0 MHz, $CDCl_3$): δ ppm 71.0, 37.4, 34.5, 25.7, 22.1. **(Spectrum No. 9A)**

Analysis:	C%	H%.
Calculated:	74.3,	11.5.
Found:	75.6,	11.5.

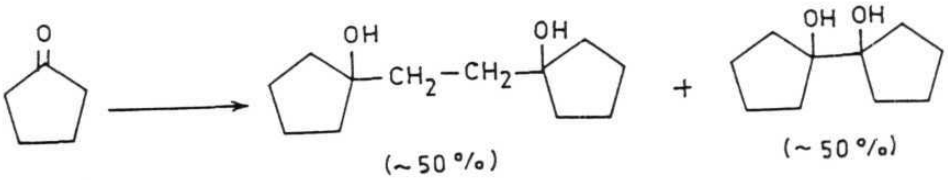
Spectral data for the 1,2-diol (II):

Yield: 35% (0.17 g).

M.P: 123-124°C, Lit.[66] 124.5-125.5°C.

IR (KBr): ν_{max}: 3400, 2950, 1460, 1360.

^{13}C NMR (25.0 MHz, $CDCl_3$): δ ppm 75.5, 30.5, 25.7, 21.5.

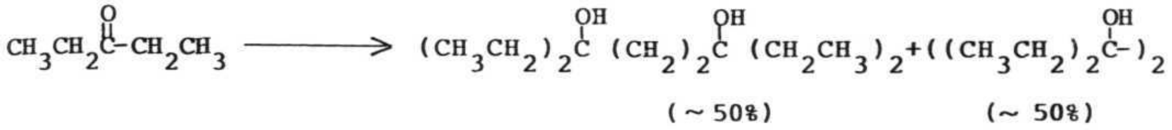


Yield (mixture): 0.25 g (spectrum No. 10).

IR (KBr): ν_{max}: 3400, 2950, 1180 cm^{1}.

^{13}C NMR (25.0 MHz, $CDCl_3$): δ ppm 87.2, 82.2, 39.6, 36.2, 24.7, 23.7.

The 1,4-and 1,2-diols obtained in this case and also in the following experiments were not separable by chromatography or crystallization. The ratios of the 1,4- and 1,2- diols were calculated by comparison of the intensities of the tertiary carbon ($\underline{C}$-OH) signals in the ^{13}C NMR spectra. So, these ratios can be only crude approximate values since the ^{13}C signals are also affected by NOE factors.

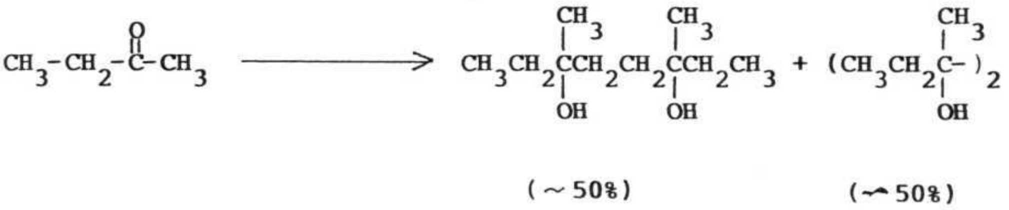


$$CH_3CH_2\overset{O}{\overset{\|}{C}}-CH_2CH_3 \longrightarrow \underset{(\sim 50\%)}{(CH_3CH_2)_2\overset{OH}{C}(CH_2)_2\overset{OH}{C}(CH_2CH_3)_2} + \underset{(\sim 50\%)}{((CH_3CH_2)_2\overset{OH}{C}-)_2}$$

Yield (mixture): 0.25 g.

IR (neat): ν_{max}: 3400, 2950, 1150-1000 cm^{1}.

^{13}C NMR (25.0 MHz, $CDCl_3$): δ ppm 78.8, 74.3, 31.1, 30.7, 27.0, 8.8, 7.7.



$$CH_3-CH_2-\overset{O}{\overset{\|}{C}}-CH_3 \longrightarrow \underset{(\sim 50\%)}{CH_3CH_2\underset{OH}{\overset{CH_3}{C}}CH_2CH_2\underset{OH}{\overset{CH_3}{C}}CH_2CH_3} + \underset{(\sim 50\%)}{(CH_3CH_2\underset{OH}{\overset{CH_3}{C}}-)_2}$$

Yield: (mixture) 0.19 g.

IR (neat): ν_{max}: 3400, 2960, 1380, 1150, 1000, 900 cm^{1}.

^{13}C NMR (25.0 MHz, $CDCl_3$): δ ppm 77.1, 72.5, 34.3, 28.2, 27.9, 25.9, 20.1, 19.6, 8.0.

Control experiment without using $TiCl_4$:

To a mixture of Grignard grade magnesium (20 mmol, 0.5 g) in THF (60 ml), 1,2-dibromoethane (20 mmol, 3.7 g) was added during 5 min at 0°C (ice-bath) under nitrogen atmosphere. After 30 min stirring, cyclohexanone (5 mmol, 0.49 g) was added and the mixture was allowed to warm to 10-15°C. Stirring was continued further for 2 h and quenched with saturated potassium carbonate solution (5 ml). After usual work-up the crude product mixture containing the starting ketone and an alcoholic product was crystallized from ether-petroleum ether (1:4) to isolate the corresponding coupled 1,2-diol (II) (0.09 g, 20%), m.p. 123-124°C, Lit.[66] 124-125°C.

Reaction of cyclohexanone with $TiCl_4$/Mg/1,2-dibromohexane system in THF:

1,2-Dibromohexane (10 mmol, 2.44 g) was added at 0°C (ice-bath) to a mixture of $TiCl_4$ (7 mmol in 15 ml C_6H_6) and magnesium (15 mmol, 0.37 g) in THF (60 ml) under nitrogen. The mixture became a brick-red colour during 40 min, cyclohexanone (5 mmol, 0.49 g) was added. The reaction mixture was brought to room temperature and stirred further for 2 h. It was quenched with saturated potassium carbonate solution (5 ml). After usual work-up, the 1,2-diol (II) was isolated by crystallization from ether-petroleum ether (1:4) in 40% (0.19 g) yield, m.p. 123-124°C, Lit.[66] m.p. 124-126°C.

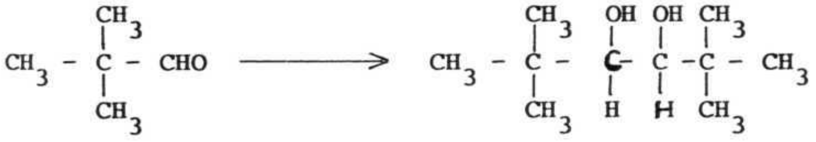
Reaction of cyclohexanone with $TiCl_4$/Mg/$BrCH_2CH_2CH_2Br$ system in THF:

To a mixture of $TiCl_4$ (7 mmol, in 15 ml C_6H_6) and Grignard grade magnesium (20 mmol, 0.5 g) in THF (60 l), 1,3-dibromopropane was added at 0°C (ice-bath) under nitrogen atmosphere. The mixture became black within 30 min, cyclohexanone (5 mmol, 0.49 g) was added. The temperature was raised to 10°C and stirring was continued further for 2 h. The reaction mixture was quenched with saturated potassium carbonate solution (5 ml). After usual work-up, the 1,2-diol (II) was isolated by crystallization from ether-petroleum ether (1:4) yield: (0.19 g, 40%), m.p. 123-4°C, Lit.[66] m.p. 124-126°C.

Reaction of cyclohexanone with $ZrCl_4/Mg/BrCH_2CH_2Br$ system in THF:

To a mixture of $ZrCl_4$ (5 mmol, 1.17 g) and Grignard grade magnesium (20 mmol, 0.5 g) in THF (60 ml), 1,2-dibromoethane (20 mmol, 3.7 g) was added during a period of 10 min at 0°C under nitrogen atmosphere. After 30 min stirring, cyclohexanone (5 mmol, 0.49 g) was added. The contents were brought to r.t. and stirred further for 2 h. The reaction mixture was quenched with saturated potassium carbonate solution (5 ml). After usual work-up, only the 1,2-diol (II) (0.09 g, 20%) was isolated.

In runs with $TiCl_4$, benzophenone and 1-octanal were unaffected and the starting ketones were recovered back quantitatively. However, pivalaldehyde (5 mmol) gave the corresponding 1,2-diol.



$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-CHO \longrightarrow CH_3-\underset{CH_3}{\overset{CH_3}{C}}-\underset{H}{\overset{OH}{C}}-\underset{H}{\overset{OH}{C}}-\underset{CH_3}{\overset{CH_3}{C}}-CH_3$$

Yield: 40% (0.17 g).

IR (KBr): ν_{max}: 3400, 2950, 1280, 1100-1000 cm^{1}.

^{13}C NMR (25.0 MHz, $CDCl_3$): δ ppm 74.5, 35.0, 25.7.

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CHAPTER 3

Studies on the Reactivities of Transition Metal Reagents Generated utilizing Transition metal complexes and Magnesium Hydride

INTRODUCTION

The transition metal hydrides are generally stable only when the metal is bonded to other supporting ligands such as CO, tertiary phosphines, cyclopentadiene, cyanide and nitrogen bases.[1] Without the support of such ligands most of these hydrides decompose into the metal and hydrogen even at low temperatures.[2,3] As it was discussed in chapter 1, we have observed that the "CuH" species, prepared using the $NaH/MgBr_2/CuCl$ reagent system hydrodimerizes, 1-alkynes into the corresponding dienes. We decided to explore the reactions of other $MX_n/NaH/MgBr_2$ systems with alkenes and alkynes in order to have a broad view about the reactivities of these systems. Reaction of sodium borohydride with many first row transition metal halides (eg. Fe, Co, Ni) gives the corresponding metal borides. The use of such metal borides for organic synthesis has been reviewed[4] and it is not discussed here. It was decided to review briefly only the reactivities of the reagents prepared from the $MX_n/LiAlH_4$, $MX_n/NaH/NaOR$ and MX_n/MgH_2 systems in order to facilitate the discussion.

Reactivities of the transition metal hydrides prepared from transition metal halides and Lithium aluminium hydride:

Titanium hydride species, generated by the reaction of titanium tetrachloride with lithium aluminium hydride, has been utilized for the reduction of alkynes and monosubstituted alkenes.[5]

$$CH_3\text{-}(CH_2)_5\text{-}CH{=}CH_2 \xrightarrow{TiCl_4\text{-}LiAlH_4} CH_3(CH_2)_6CH_3$$

Disubstituted alkenes are reduced with excess reagent. Terminal alkynes are readily reduced to alkanes but the reaction can be stopped at the alkene stage using equimolar amounts of $LiAlH_4$ and $TiCl_4$.[5]

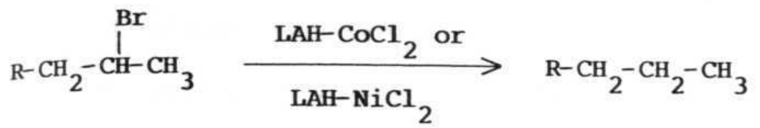
The combinations of several first row transition metal halides with lithium aluminium hydride were found to be effective reducing reagents for alkenes, alkynes and alkyl halides.[6] However, VCl_3, $MnCl_2$ and $CuI\text{-}LiAlH_4$ systems were found to be ineffective.[6] The reductions using $TiCl_3$, $NiCl_2$ and $CoCl_2$ are also catalytic but the reduction of internal alkenes and alkynes requires stoichiometric amounts of transition metal halides.[6]

$$R\text{-}CH_2\text{-}CH{=}CH_2 \xrightarrow{MX_n\text{-}LiAlH_4} RCH_2CH_2CH_3$$

$$R\text{-}C \equiv CH \xrightarrow{MX_n\text{-}LiAlH_4} R\text{-}CH{=}CH_2$$

$$R\text{-}X \xrightarrow{MX_n\text{-}LiAlH_4} R\text{-}H$$

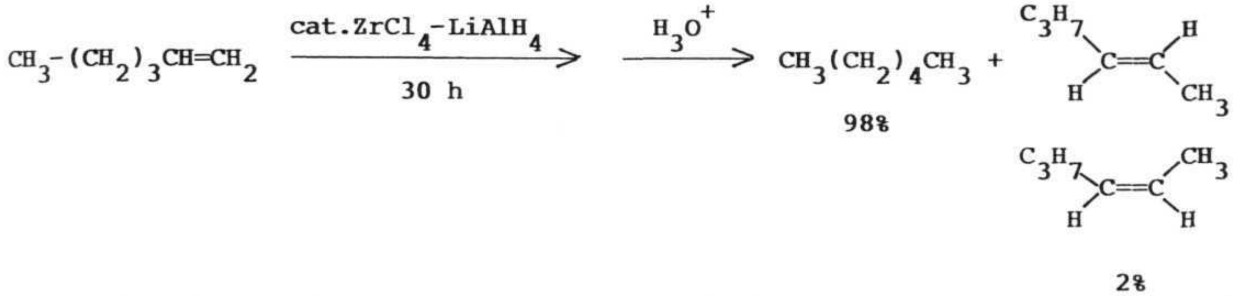
High functional selectivities have been observed in the reduction of terminal alkynes to alkenes using $LiAlH_4\text{-}NiCl_2$ system and 100% stereoselectivity was observed with internal alkynes. It was found that the $LiAlH_4\text{-}NiCl_2$ system is more selective than the $LiAlH_4\text{-}CoCl_2$ system.[6] The $LAH\text{-}CoCl_2$ and $LAH\text{-}NiCl_2$ reagent systems were found to be excellent reagents for the reduction of organic halides. Secondary, tertiary, alicyclic and aryl bromides which are normally more difficult to reduce, can be quantitatively reduced utilising these reagents.[6]



$$R{-}CH_2{-}\overset{\displaystyle Br}{\overset{|}{C}H}{-}CH_3 \xrightarrow[LAH{-}NiCl_2]{LAH{-}CoCl_2\ or} R{-}CH_2{-}CH_2{-}CH_3$$

$$Ph{-}Br \xrightarrow[LAH{-}NiCl_2]{LAH{-}CoCl_2\ or} Ph{-}H$$

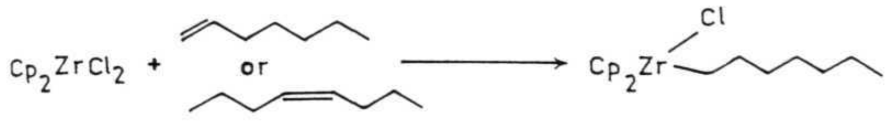
The combination of catalytic amount of zirconium tetrachloride and $LiAlH_4$ provides a convenient method for the hydrogenation of olefins. The reaction proceeds via hydrozirconation.[7]

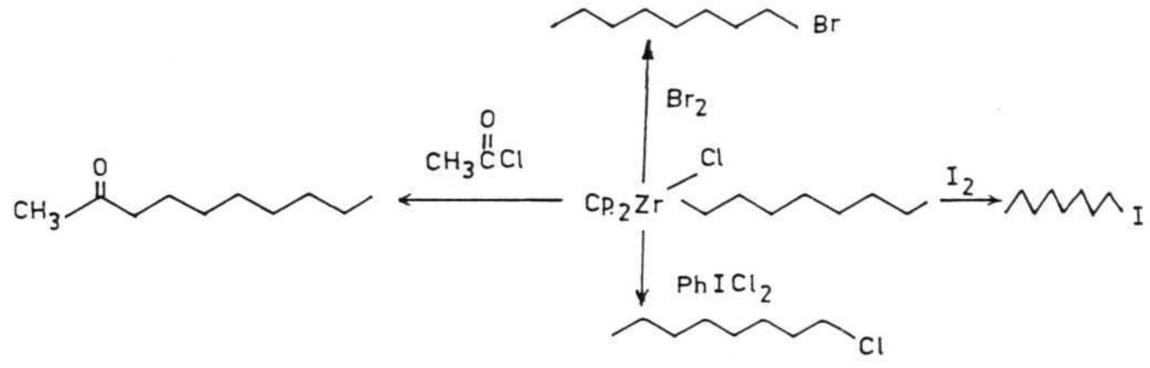


Stoichiometric mixtures of $ZrCl_4$ and $LiAlH_4$ catalyse isomerization of 1-alkenes into 2-alkenes in 4 days at r.t.[7] Quantitative yields of 1-bromoalkanes were obtained when the reaction mixture was treated with Br_2 before work-up.[7]

A stable bis(cyclopentadienyl)zirconium(IV) hydridochloride has been prepared by the addition of $LiAlH_4$ (o.25 eq) in THF to Cp_2ZrCl_2 (1 eq).[8] This complex was obtained in a purer form when $LiAl(OBu^t)_3H$ (1 eq) was used instead of $LiAlH_4$.[8] A stable Cp_2ZrH_2 was obtained by the addition of $LiAlH_4$ (1 eq) in THF to $Cp_2Zr(Cl)OZr(Cl)Cp_2$ in THF.[8] The dihydride has been also prepared by treating $Cp_2Zr(BH_4)_2$ with excess of trimethylamine.[9]

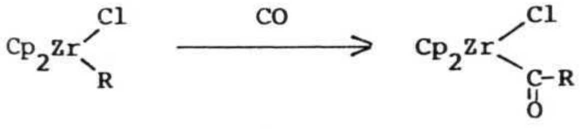
The reagent $Cp_2Zr(H)Cl$, prepared from $LiAlH_4$ or $LiAl(OCH_3)_3H$ and Cp_2ZrCl_2, has been utilized for hydrozirconation of alkenes to give a stable organometallic complex which can be further converted into a variety of organic derivatives by treating with various electrophiles.[10-13]

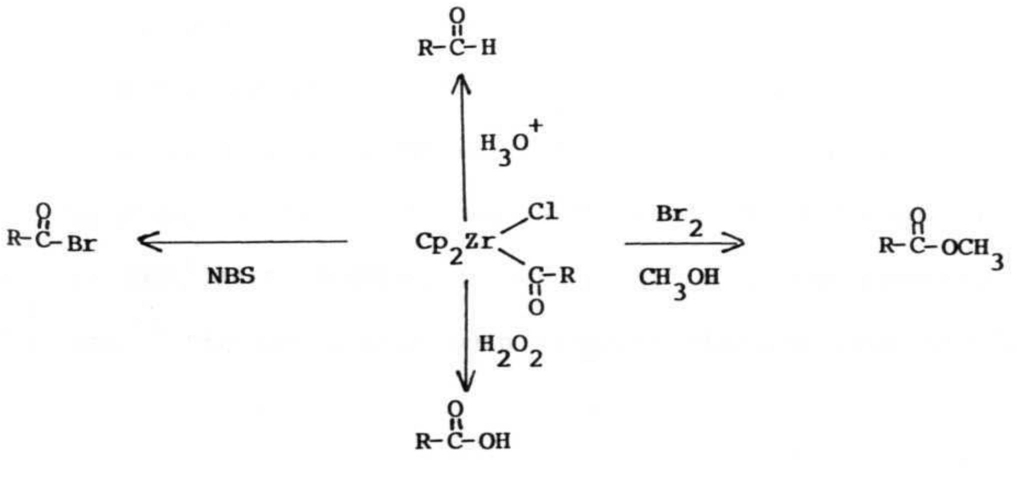




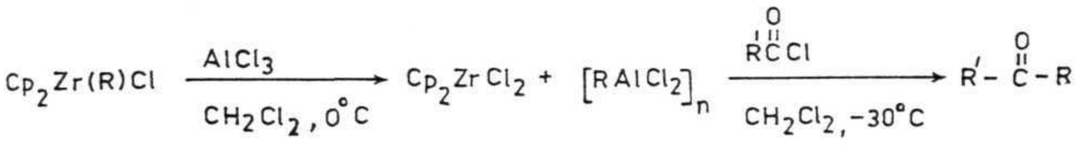
Formation of n-alkylzirconium(IV) species from internal alkenes involves the regiospecific addition of Zr-H to the internal olefin followed by rapid rearrangement via Zr-H elimination and readdition to place the metal in the less hindered position of the alkyl chain.[10]

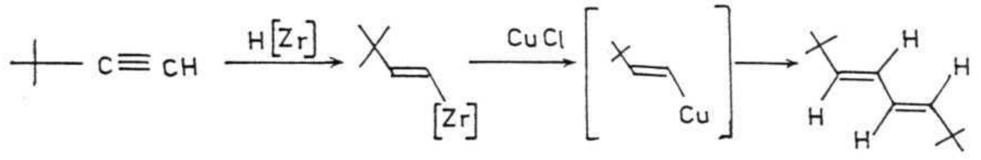
The alkylzirconium compounds can be readily carbonylated with CO under atmospheric pressure.[11]

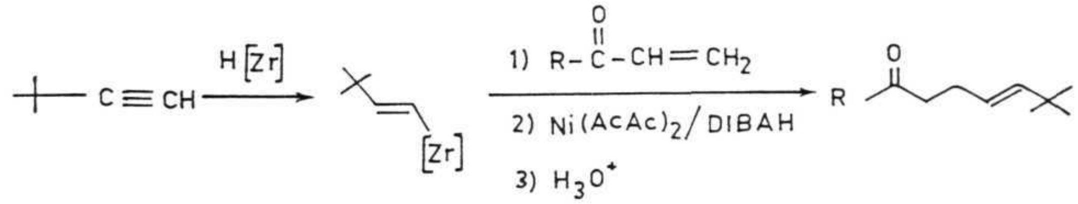




Transmetalation is an important reaction of the organozirconium intermediates. The alkyl group in Cp_2ZrRCl can be readily transferred to other metals.[14-16]



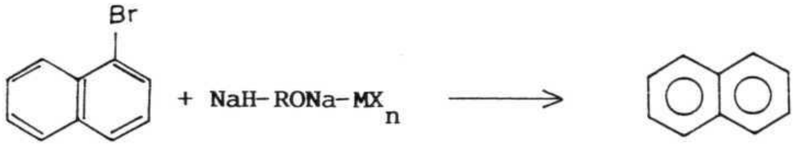




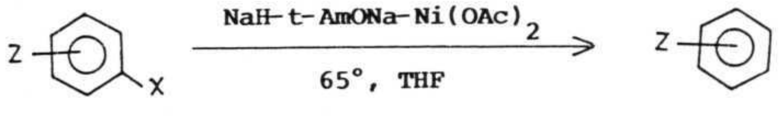
Reactivities of the transition metal halides/NaH/RONa systems-complex reducing agents (CRA):

Generally NaH is used as a base for proton abstraction in organic synthesis.[17] Its basic or reducing ability can be increased by the addition of RONa and the resulting NaH-RONa reagent has properties remarkably different from those of individual components.[18] A detailed study has been made concerning the utilities of NaH-RONa-transition metal salts, generally known as complex reducing agents [CRA].[18] The CRA's can be readily prepared by the addition of anhydrous metal salts to NaH-RONa, or by adding the alcohol to the suspension of NaH and MX_n in DME. After warming to 60-63°C in 2 h, the reagents are ready for use.[19] The CRA's have been prepared starting from the halides or acetates of Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Cd, Zr, Mo, Pd and W and several useful organic transformations have been realised.[18]

The CRA's prepared from Co or Ni salts have been utilized in the selective reduction of alkyl halides.[20] The CRA's obtained from NaH-RONa and Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Cd, Zr, Mo, Pd and W have been found to be effective reducing reagents for reduction of aryl halides.[19]

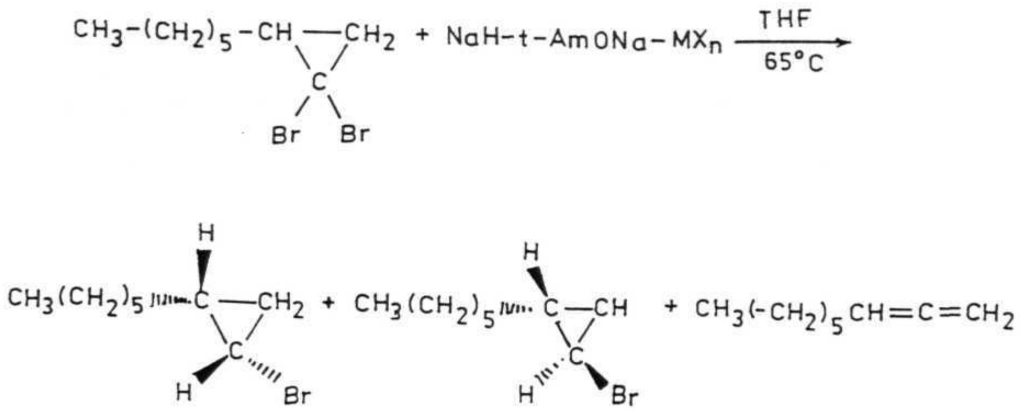


The coupling products, biaryls, were also formed along with the reduction products when $(PPh_3)_2NiCl_2$ or $ZrCl_4$ was utilized along with NaH/RONa.[20] The coupling products are the major products when the reaction was carried out in the presence of bipyridyl and $Ni(OAc)_2$.[20] The NiCRA has been found to be more selective reducing agent. It was observed that other functional groups in the aromatic molecule are not affected by this reagent.[21]

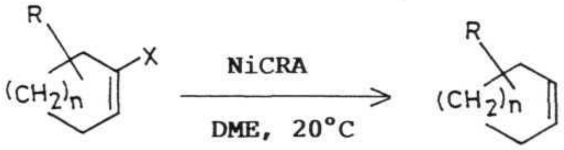


Z = CH_3, OCH_3, COOH, X = Br, Cl, F.

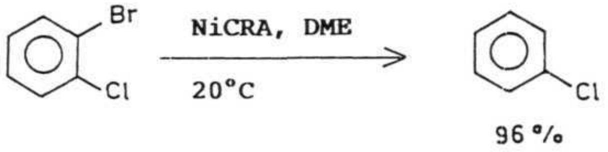
The CRA's, prepared from Ni, Co and Cu salts, have been utilized for the reduction of gem-dihalogenocyclopropanes into the corresponding monohalogeno derivatives.[22]

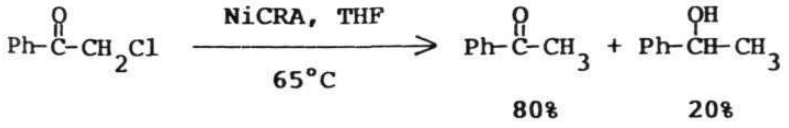


The NiCRA is effective under mild condition for the reduction of vinyl and alkyl halides.[20]



$$CH_3-(CH_2)_6-CH_2Br + CH_3(CH_2)_6CH_2Cl \xrightarrow[65^\circ C]{NiCRA,\ DME} \underset{100\%}{CH_3-(CH_2)_6-CH_3} + \underset{100\%}{CH_3(CH_2)_6CH_2Cl}$$



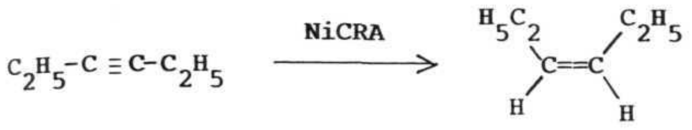


$$Ph-\overset{O}{\overset{\|}{C}}-CH_2Cl \xrightarrow[65^\circ C]{NiCRA,\ THF} \underset{80\%}{Ph-\overset{O}{\overset{\|}{C}}-CH_3} + \underset{20\%}{Ph-\overset{OH}{\overset{|}{C}H}-CH_3}$$

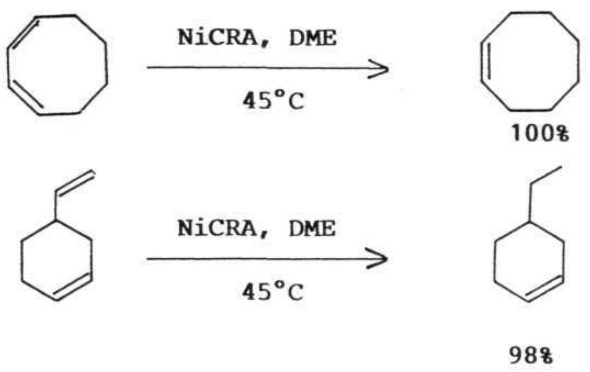
$$BrCH_2-(CH_2)_2-CO_2Et \xrightarrow[DME,\ 65^\circ]{NiCRA-WCl_6} CH_3-(CH_2)_2CO_2Et$$

The CRA's obtained from $FeCl_3$ and $NiCl_2$ have been found to be active and specific catalysts for heterogeneous hydrogenations of alkenes (eg. octene) and alkynes (eg. octyne).[23,24] Small amounts of isomerized

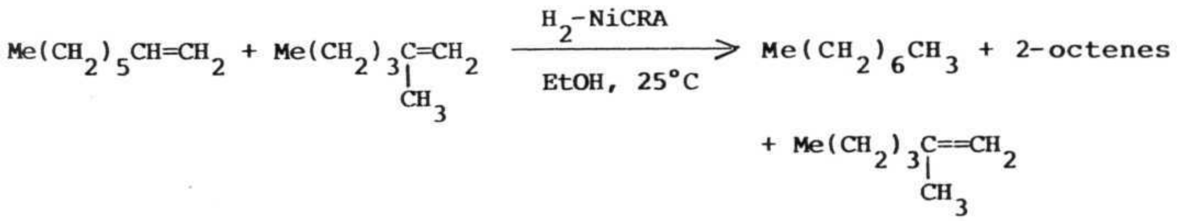
2-alkenes were also obtained. The formation of 2-alkenes clearly suggests the presence of nickel hydride species.[25] The cis-alkenes are obtained from disubstituted acetylenes via syn-addition with NiCRA.



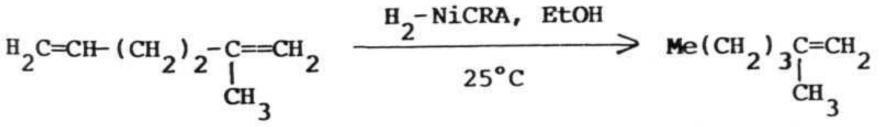
Some dienes were selectively reduced into alkenes using NiCRA.[25]



Selective hydrogenations were observed using NiCRA/H_2.[26,27]

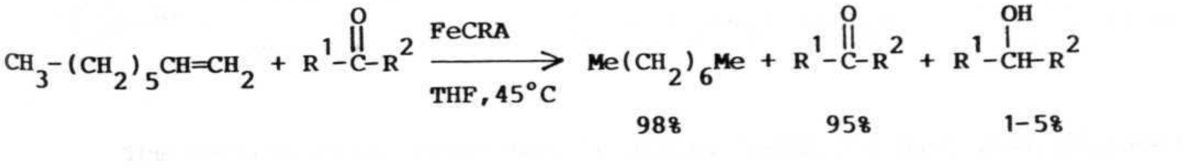


$$\mathrm{Me(CH_2)_5CH{=}CH_2 + Me(CH_2)_3\underset{CH_3}{C}{=}CH_2 \xrightarrow[EtOH,\ 25^\circ C]{H_2\text{-}NiCRA} Me(CH_2)_6CH_3 + 2\text{-}octenes + Me(CH_2)_3\underset{CH_3}{C}{=}CH_2}$$



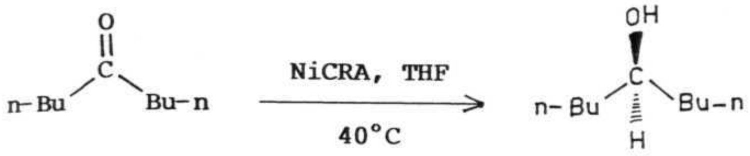
$$\mathrm{H_2C{=}CH\text{-}(CH_2)_2\text{-}\underset{CH_3}{C}{=}CH_2 \xrightarrow[25^\circ C]{H_2\text{-}NiCRA,\ EtOH} Me(CH_2)_3\underset{CH_3}{C}{=}CH_2}$$

Selective reduction of olefins were observed in the presence of a keto group using FeCRA.[28]



$$\mathrm{CH_3\text{-}(CH_2)_5CH{=}CH_2 + R^1\text{-}\overset{O}{\overset{\|}{C}}\text{-}R^2 \xrightarrow[THF,\ 45^\circ C]{FeCRA} \underset{98\%}{Me(CH_2)_6Me} + \underset{95\%}{R^1\text{-}\overset{O}{\overset{\|}{C}}\text{-}R^2} + \underset{1\text{-}5\%}{R^1\text{-}\overset{OH}{\overset{|}{C}}H\text{-}R^2}}$$

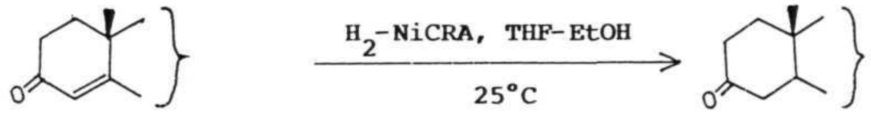
Enolizable ketones and aldehydes can be reduced by NaH-t-AmONa-$Ni(OAc)_2$ in good yields to alcohols.[23] The yields can be improved by the addition of lithium salts.



$$R\text{-}CHO \xrightarrow[40°C]{NiCRA,\ THF} R\text{-}CH_2OH$$

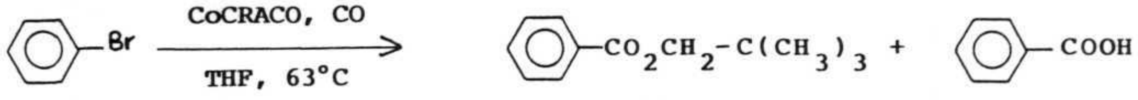
The reduction of carbonyl compounds using NiCRA was found to be catalytic with respect to NiX_2, t-AmONa and $MgBr_2$ when the CRA was prepared in the presence of $MgBr_2$.[29]

Highly regio-selective reduction of α,β-unsaturated ketones were demonstrated using NiCRA.[30]



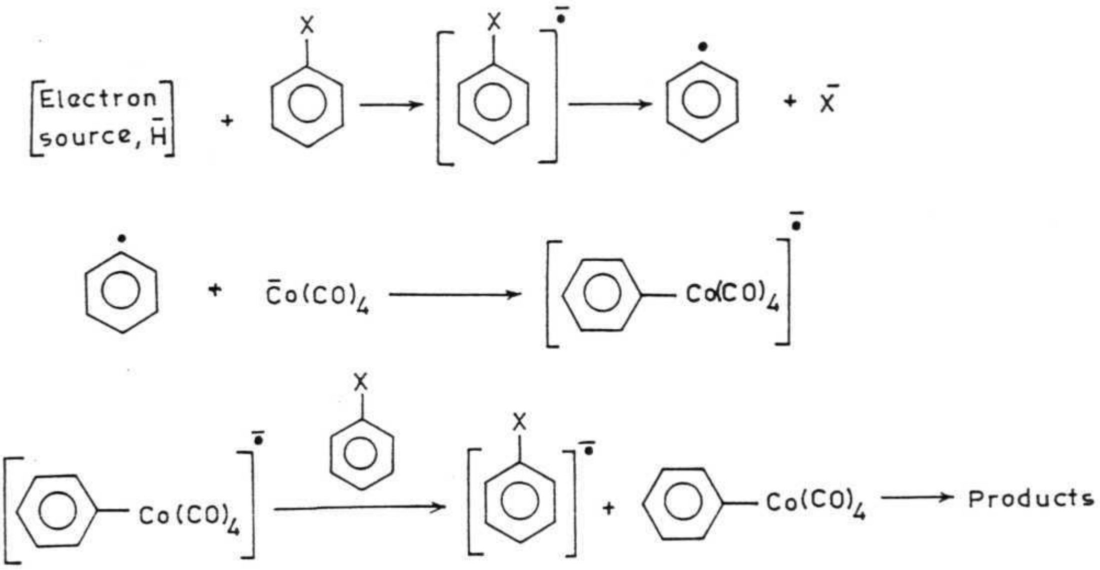
4-Cholesten-3-one

The CoCRA, prepared using $CoCl_2$/NaH/t-AmONa, reacts with CO at atmospheric pressure to give cobalt-carbonyl species containing $Co(CO)_4$. Carbonylation of aryl halides has been achieved using this reagent (ie. CoCRACO).[31,32]



The carbonylation reactions involving CoCRACO's have been proposed to go through a radical chain transfer mechanism as outlined in Scheme 1.

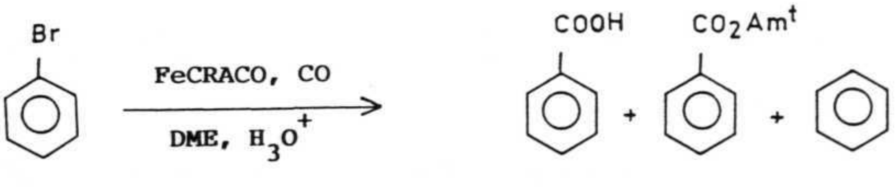
Scheme 1



In the same way FeCRACO has been prepared from t-AmONa/$FeCl_3$/NaH using CO at atmospheric pressure. The soluble fraction contains mainly $Na_2Fe(CO)_4$ and some $Na_2Fe_2(CO)_8$.[33] The $Na_2Fe(CO)_4$ produced in this way was found to exhibit different reactivities compared to the pure $Na_2Fe(CO)_4$.[34] Primary, secondary and even tertiary bromides and chlorides were carbonylated using FeCRACO. Bromobenzene underwent carbonylation to give benzoic acid and tert-amylbenzoate in 40% yield (Scheme 2).

Scheme 2

$$\mathrm{RX} \xrightarrow[\mathrm{DME,\ H_3O^+}]{\mathrm{FeCRACO,\ CO}} \mathrm{RCOOH} + \mathrm{RCO_2t\text{-}Am} + \mathrm{RCHO}$$



Again, radical chain mechanism has been considered but the nature of the reactive species responsible for the reactivity of the system is not clearly understood.[33]

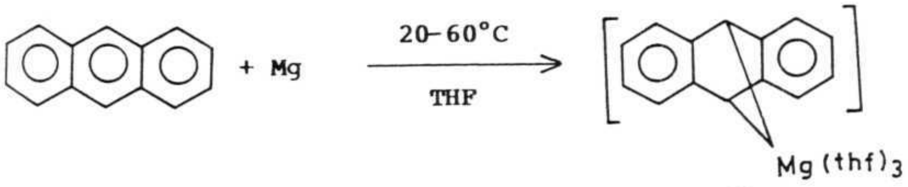
Reactivities of Transition metal salts/magnesium hydride systems:

Synthetic applications of this reagent system have not been explored in detail. The magnesium hydride can be prepared by the hydrogenation of magnesium but requires drastic conditions and long reaction times.[35] The rate of hydrogenation of magnesium can be increased in the presence of anthracene/transition metal halide catalyst.[36] The anthracene first reacts with magnesium in THF to give "magnesium-anthracene." This reacts with the halides of Cr, Ti or Fe in THF to produce the hydrogenation catalyst, active under mild conditions.[36]

$$\mathrm{Mg} + \mathrm{H_2}\ (1\text{-}80\ \mathrm{bar}) \xrightarrow[\text{20-65°C}]{\text{Mg-anthracene/MX}_n\text{/THF}} \mathrm{MgH_2}$$

The sequences shown in Scheme 3 have been suggested for this transformation.[37]

Scheme 3



I

$$\mathrm{I} + \mathrm{CrCl_3}\ (\mathrm{TiCl_4}) \xrightarrow[\text{THF}]{\text{20-30°C}} \text{Cr(Ti)-cat} + \text{anthracene}$$

$$\mathrm{I} + \mathrm{H_2} \xrightarrow[\text{THF}]{\text{Cr(Ti)-cat.}} \mathrm{MgH_2} + \text{anthracene}$$

The magnesium hydride can also be prepared by the reaction of diorganomagnesium compounds[38] or Grignard reagents with $LiAlH_4$.[39]

$$Et_2Mg + LiAlH_4 \longrightarrow MgH_2$$

$$EtMgX + LiAlH_4 \longrightarrow MgH_2$$

It was found that the MgH_2 obtained in this way is more reactive than the reagent prepared following the anthracene-catalyst method.[36]

A more convenient method for the preparation of MgH_2 involves the reaction between alkalimetal hydrides and magnesium halides in ether solvents at room temperature.[40]

$$2NaH + MgBr_2 \xrightarrow[\text{r.t. 2 days}]{\text{THF}} MgH_2 + 2NaBr$$

$$2NaH + MgI_2 \xrightarrow[\text{reflux, 36 h}]{\text{Ether}} MgH_2 + 2NaI$$

$$2LiH + MgBr_2 \xrightarrow[\text{reflux, 2 days}]{\text{THF}} MgH_2 + 2LiBr$$

$$2KH + MgI_2 \xrightarrow[\text{reflux, 1 day}]{\text{Ether}} MgH_2 + 2KI$$

It has been found that the direct reaction of 1-alkenes with MgH_2 affords very low yields of dialkylmagnesium compounds.[41] The presence of catalytic amount of Cp_2TiCl_2 allows the addition of "active" magnesium hydride, prepared using Et_2Mg and $LiAlH_4$ in diethyl ether, to 1-alkenes and alkynes to afford the reduced products after hydrolysis.[42a]

$$CH_3-(CH_2)_3-CH{=}CH_2 \xrightarrow[\text{THF, 1 h}]{\text{cat.}Cp_2TiCl_2/MgH_2} \xrightarrow{H_2O} CH_3(CH_2)_4CH_3$$

$$CH_3-CH{=}CH-(CH_2)_2-CH_3 \xrightarrow[\text{THF, 68 h}]{\text{cat.}Cp_2TiCl_2/MgH_2} \xrightarrow{H_2O} CH_3(CH_2)_4CH_3$$

$$HC{\equiv}C-(CH_2)_5CH_3 \xrightarrow[\text{THF, 1 h}]{\text{cat.}Cp_2TiCl_2/MgH_2} \xrightarrow{H_2O} \underset{60}{CH_2{=}CH-(CH_2)_5CH_3} + \underset{40}{HC{\equiv}C-(CH_2)_5CH_3}$$

60 : 40

$$C_3H_7C{\equiv}CC_3H_7 \xrightarrow[\text{THF, 1 h}]{\text{cat.}Cp_2TiCl_2/MgH_2} \xrightarrow{H_2O} C_3H_7HC{=}CH-C_3H_7$$

The formation of cis-olefin from 4-octyne clearly suggests that the addition of M-H takes place in a syn manner. In the case of terminal alkynes deprotonation is a competitive side reaction.

The combinations of $TiCl_3$ or $ZrCl_4$ with MgH_2 were not found to be effective in the reduction of alkenes and alkynes.[42a] However, active magnesium hydride prepared using anthracene and $TiCl_4$ catalyst adds to alkenes to afford dialkylmagnesium.[36]

As outlined in the first chapter that the "CuH" species, prepared utilizing $CuCl/MgH_2$ system, hydrodimerizes some 1-alkynes. It was of interest to examine the reactivities of other transition metal hydrides, prepared using magnesium hydride and the corresponding transition metal halides, towards alkenes and alkynes.

RESULTS AND DISCUSSION

Reactivities of the transition metal halide/NaH/$MgBr_2$ systems with alkenes and alkynes:

In the first chapter we described the utilization of copper(I) hydride reagent, generated by the decomposition of $CuBH_4$, for hydrocupration of 1-alkynes in the presence of NEt_3 and $MgBr_2$. The hydrocupration was also achieved using NaH and $MgBr_2$ or MgH_2, prepared by the reaction of NaH and $MgBr_2$ in THF for 36 h, in place of $NaBH_4$. An obvious extension would be to study the reactivities of the reagent system generated by the reaction of MgH_2 and first row transition metal halides towards alkenes and alkynes.

As outlined in the introductory section, the MX_n/NaH/RONa reagent systems, known as complex reducing agents, (CRA) have been studied in detail.[18] However, reactivities of the MgH_2/MX_n reagents, which can be readily prepared using the NaH/$MgBr_2$ reagent, has not been studied in detail. We decided to examine the reactivities of the MX_n/MgH_2 reagents with alkenes and alkynes.

The $TiCl_4$ is commercially available and hence we selected this reagent for our studies and carried out the following experiment: 1-Decene (10 mmol) was added to the reaction mixture containing MgH_2 (~ 15 mmol) and $TiCl_4$ (10 mmol) in THF (60 ml) under nitrogen at 0°C. The resulting yellow colour solution was brought to r.t. during 3 h and stirred further for 12 h. After work-up and distillation, unreacted 1-decene was recovered back quantitatively. It is of interest to note that the combination of $TiCl_4$ with $LiAlH_4$ reduces mono- and disubstituted alkenes.[5]

It has been reported that the MgH_2 reagent, prepared by the reaction of $LiAlH_4$ and $MgEt_2$ in diethyl ether,[38] adds readily to carbon-carbon multiple bonds in the presence of Cp_2TiCl_2 catalyst to give the reduced product after hydrolysis.[42] In order to compare the reactivity of the MgH_2, produced in this way with the reagent prepared by the reaction of NaH with $MgBr_2$, we have carried out the following experiment. 1-Decene (10 mmol) was added to a slurry of MgH_2 (~15 mmol) and Cp_2TiCl_2 (5 mmol) in THF (60 ml) at 0°C. The contents were brought to r.t. and stirred further for 12 h. After work-up and chromatography, decane was isolated in 80% yield.

$$CH_3-(CH_2)_7CH{=}CH_2 \xrightarrow[\text{THF}]{MgH_2-Cp_2TiCl_2} CH_3-(CH_2)_8-CH_3$$

The reagent system also converts 1-decyne (10 mmol) into 1-decene in 80% yield. The results indicate that the reagent system MgH_2/Cp_2TiCl_2 is able to hydrometalate 1-alkenes and 1-alkynes to give the corresponding alkane and 1-alkene. It has been reported that the MgH_2 reagent prepared using $MgEt_2/LiAlH_4$ reacts with 1-octene at room temperature in the presence of catalytic amount of Cp_2TiCl_2 under argon atmosphere to give the corresponding Grignard reagent which reacts with D_2O to produce $n\text{-}C_7H_{15}CH_2D$ (~95% D). However, when the reaction mixture was treated with D_2O, in the present case in a run with 1-decene, the product obtained did not contain any deuterium (this aspect will be discussed later).

$$CH_3-(CH_2)_7C\equiv CH \xrightarrow[\text{THF}]{MgH_2-Cp_2TiCl_2} CH_3-(CH_2)_7-CH{=}CH_2$$

The reduction of olefins was also achieved by the reaction with $LiAlH_4$ in the presence of $ZrCl_4$.[7] However, it has been reported that the MgH_2 and $ZrCl_4$ system was not effective in the reduction of olefins.[42] We have also observed the same when we carried out the reaction using MgH_2 (~15 mmol), $ZrCl_4$ (15 mmol) and 1-decene (10 mmol) in THF for 12 h.

As outlined in the introductory section, the Cp_2ZrH_2 or $Cp_2Zr(H)Cl$ reagent can be readily prepared using $LiAlH_4$ and $Cp_2Zr(Cl)OZr(Cl)Cp_2$ or $LiAlH_4$ or $LiAlH(OBu^t)$ and Cp_2ZrCl_2.[8] These reagents were extensively utilized. In order to examine the reactivity of the Cp_2ZrCl_2/MgH_2 reagent, we carried out the following experiment. 1-Decene (10 mmol) was added at -10°C (ice-salt) to a suspension of MgH_2 (~ 15 mmol) and Cp_2ZrCl_2 (5 mmol) in THF under nitrogen. The mixture turned to brick-red colour when it was brought to room temperature. It was stirred further for 12 h. After work-up and chromatography decane was isolated.

$$CH_3(CH_2)_7-CH{=}CH_2 \xrightarrow[\text{THF, } -10^\circ\text{C to r.t., 12 h}]{MgH_2-Cp_2ZrCl_2\text{(cat)}} CH_3(CH_2)_8CH_3$$

1-Decyne underwent reduction to give 1-decene (85%). This indicates that the 1-decyne undergoes reduction in a fast manner and further reduction does not take place because of the reactivity difference between 1-decene and 1-decyne.

$$CH_3-(CH_2)_7C\equiv CH \xrightarrow[\text{THF, } -10^\circ\text{C to r.t., 5 h}]{MgH_2-Cp_2ZrCl_2} CH_3-(CH_2)_7CH{=}CH_2$$

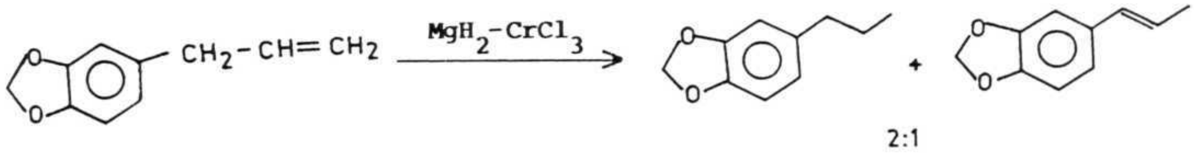
When the reaction mixtures obtained in the runs using Cp_2ZrCl_2/MgH_2 and 1-decene (or 1-decyne) were quenched with D_2O before work-up, the isolated products did not contain any deuterium. As described previously, the Cp_2TiCl_2/MgH_2 also gave same results. This is somewhat unexpected since it has been reported that the Cp_2TiCl_2 and MgH_2, prepared utilizing Et_2Mg and $LiAlH_4$, reacts with 1-octene to give n-$C_8H_{17}MgX$ which on D_2O treatment gives n-$C_8H_{17}D$ (95%).[42] A notable difference is that whereas the reported work utilizing MgH_2, prepared from $LiAlH_4/Et_2Mg$, has been carried out under argon atmosphere, the present work was carried out under nitrogen atmosphere. Although it may be difficult to understand that such reactivity differences can be caused because of N_2, it is well known that the reduced 'Ti' species reacts with molecular nitrogen in which the ether solvents serve as hydrogen sources.[42b]

When the Cp_2ZrCl_2 and MgH_2 reagents were utilized in 2:1 molar ratio with 1-decene (1 eq), the decane was isolated in 90% and small amount (~10%) of 1-decene remained unreacted. Here, also D_2O treatment of the reaction mixture did not give decane containing deuterium. Clearly, the Cp_2MCl_2/MgH_2 gives new type of reactivities different from the Ashby's reagent Cp_2TiCl_2/MgH_2 and Schwartz reagent $Cp_2Zr(H)Cl$. Presumably, in the present case a new type of species is formed in which the cyclopentadienyl hydrogens and/or the THF hydrogens act as a hydrogen source. Similar observations were also made with the titanocene and zirconocene systems (chapter 2). However, at present we do not have any data in order to examine these observations further.

We then turned our attention to examine the reactivities of the $CrCl_3/MgH_2$ reagent system towards 1-alkenes and 1-alkynes. Anhydrous $CrCl_3$ (12 mmol) was added to a magnetically stirred suspension of MgH_2 (~ 15 mmol) (gas evolution, H_2) in THF (60 ml) at 0°C under nitrogen. 1-Decene (10 mmol) was added and the contents were brought to r.t. during 1 h and stirred further for 12 h. During this period the mixture turned to black. After work-up, decane was isolated in 80% yield. When the reaction mixture was treated with D_2O, the decane isolated did not contain any deuterium. This indicates that the intermediate formed after hydrometalation undergoes reductive cleavage or reductive elemination before D_2O treatment.

$$CH_3-(CH_2)_7CH{=}CH_2 \xrightarrow[THF]{MgH_2-CrCl_3} CH_3-(CH_2)_8-CH_3$$

Under the same conditions, safrole was converted into a mixture of products containing the reduction and isomerization products. NMR spectral analysis indicate that these products are present in 2:1 ratio.



In the case of methyl-10-undecenoate, the $CrCl_3/MgH_2$ system cleaves the ester group. The corresponding unsaturated acid was isolated.

$$CH_2{=}CH-(CH_2)_8CO_2Me \xrightarrow[THF]{MgH_2-CrCl_3} CH_2{=}CH-(CH_2)_8COOH$$

The $CuCl/MgH_2$ system also behaves in a similar way with esters (chapter 1).

The MgH_2 (~ 15 mmol) and $CrCl_3$ (12 mmol) reagent system converted 1-decyne into a yellow coloured compound (1.1 g). However, we have found that the product is polymeric in nature. The product was not characterized further. The results obtained with the $MgH_2/CrCl_3$ system indicate that the system most probably gives a highly reactive chromium hydride species which has the capability of reducing 1-decene to decane and polymerize 1-alkynes.

In order to examine the reactivity of the $MnCl_2/MgH_2$ system, we carried out the following experiment. 1-Decene (10 mmol) was added to a slurry of MgH_2 (~ 15 mmol) and anhydrous $MnCl_2$ (15 mmol) in THF (60 ml) under nitrogen at 0°C. The reaction mixture was brought to r.t. during 1 h and stirred further for 12 h. The original pink colour did not change at all. 1-Decene was recovered quantitatively after work-up. Also, it appears that the $MnCl_2$ does not react with MgH_2.

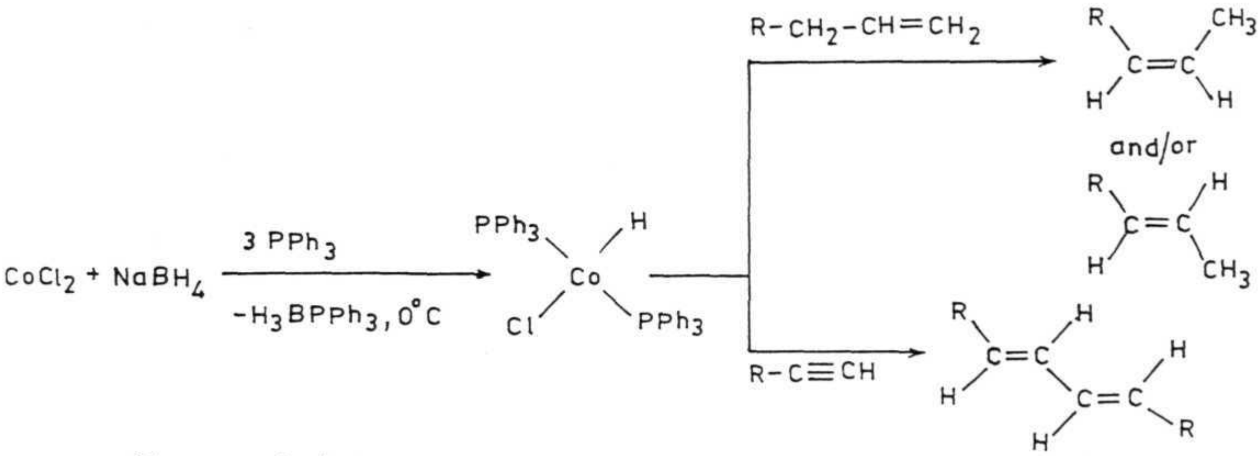
It was observed that the $FeCl_3/MgH_2$ (~ 15 mmol) system also effects the reduction of 1-decene into decane but converts 1-decyne into a product of polymeric in nature. It may be of interest to note that the FeCRA, $FeCl_3$/t-AmONa/NaH, reagent effects reduction of 1-alkenes and 1-alkynes to the alkanes and 1-alkenes respectively.[23,24]

$$CH_2{=}CH{-}(CH_2)_7{-}CH_3 \xrightarrow[THF]{MgH_2{-}FeCl_3} CH_3{-}(CH_2)_8CH_3$$

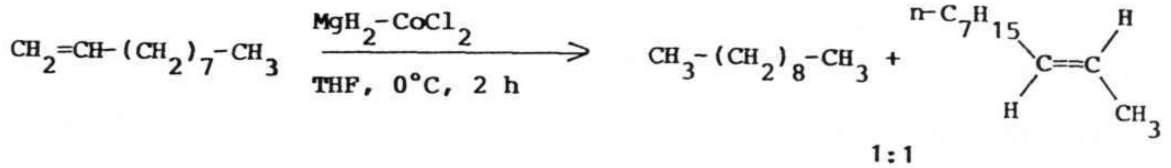
The $CoCl_2/NaBH_4$ reagent system was studied extensively in our laboratory.[4]

$$CoCl_2 + NaBH_4 \xrightarrow{THF} \xrightarrow{RCH=CH_2} R-CH_2-CH_2-B< \xrightarrow{H_2O_2/\bar{O}H} RCH_2CH_2OH$$

$$CoCl_2 + NaBH_4 \xrightarrow{THF/MeOH} \xrightarrow{RCH_2=CH_2} R-CH_2CH_3$$



It was of interest to examine the reactivity of the $CoCl_2/MgH_2$ system in THF with alkenes and alkynes. The $CoCl_2$ (15 mmol) was added to a magnetically stirred suspension of MgH_2 (~15 mmol) in THF (60 ml) at 0°C under nitrogen. The blue coloured contents turned black after $CoCl_2$ addition. Gas evolution (H_2) ceased in 5 minutes. 1-Decene (15 mmol) was added and the mixture was stirred for 2 h at 0°C. After work-up, a mixture (1.9 g) containing both reduced product decane and isomerized 2-decenes was obtained. GC analysis of the mixture showed that they are in 1:1 ratio.



1:1

All our efforts to standardise conditions to get exclusively decane or isomerized 2-decenes were unsuccessful. The black colour formation and gas evolution indicate that a cobalt hydride is formed and decomposes into Co metal and H_2 to some extent. It is known that cobalt hydrides are not stable in the absence of ligands such as CO or PPh_3.[43]

When methyl-10-undecenoate (10 mmol) was utilized in the place of 1-decene in the above experiment, only the reduction product methyl undecanoate was obtained. The spectral data indicate that the isomerized 2-alkyl group is not present in the product.

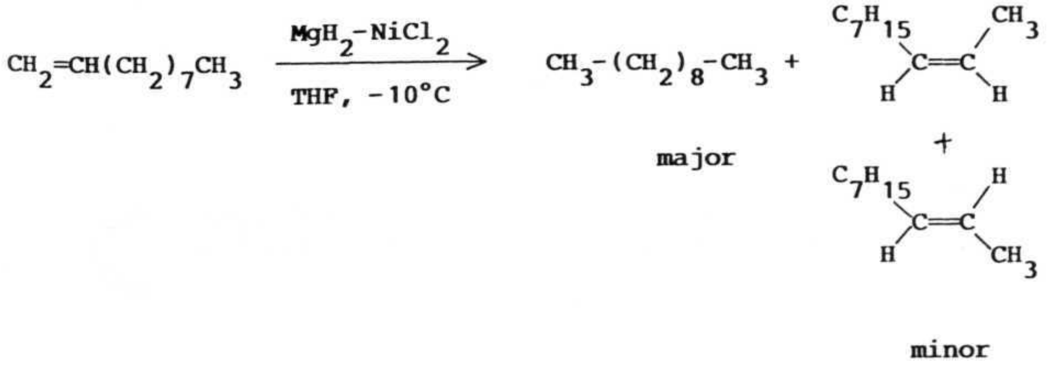
$$\mathrm{CH_2{=}CH{-}(CH_2)_8CO_2Me} \xrightarrow[\mathrm{THF,\ 0^{\circ}C}]{\mathrm{MgH_2{-}CoCl_2}} \mathrm{CH_3(CH_2)_9CO_2Me}$$

Also, this observation indicates that the ester group is not cleaved by the $CoCl_2/MgH_2$ system in contrast to the behaviour of the $CrCl_3/MgH_2$ and $CuCl/MgH_2$ systems (chapter 1).

The MgH_2-$CoCl_2$ system converts allylbenzene and safrole into the corresponding n-propyl benzenes and β-methyl styrenes in approximately 60:40 ratio. In the case of 1-decyne, only a polymeric product was obtained. Polymerization could not be prevented when the experiment was carried out using $(PPh_3)_2CoCl_2$ in the place of $CoCl_2$ at -24°C to -10°C.

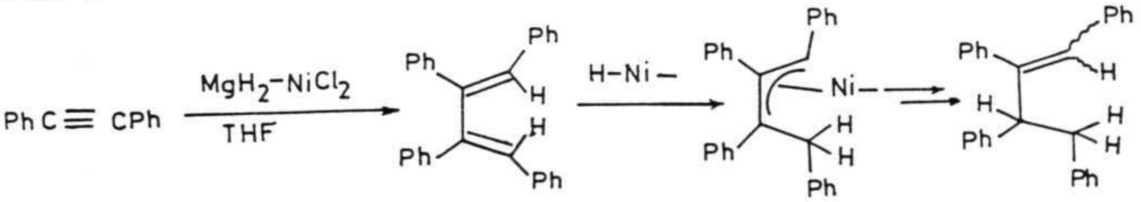
It has been reported that the $(Ph_3P)_2Co(H)Cl$ reagent, prepared utilizing $(Ph_3P)_2CoCl_2$ (1 eq), Ph_3P (3 eq) and $NaBH_4$ (1 eq), converts 1-alkynes into the corresponding 1,4-dialkyl-1,3-dienes.[44] However, the $(Ph_3P)_2CoCl_2$ (2 eq)/MgH_2 (1 eq) gives polymerization even at -24°C. Obviously, the species present in both cases may not be the same. It is likely that the $(Ph_3P)_2CoCl_2$ (2 eq)/MgH_2 may give $(Ph_3P)_2CoH$ via $(Ph_3P)_2CoH_2$ which may have different reactivities. In addition, presence of soluble MgX_2 may also alter the reactivities of the Co-H species as it does with the CuH species (chapter 1).

We then turned our attention to examining the reactivities of the $NiCl_2/MgH_2$ system towards alkenes, alkynes and alkyl halides. The following experiment was carried out in the run with 1-decene. Anhydrous $NiCl_2$ (15 mmol) was added to a magnetically stirred suspension of MgH_2 ($\sim$15 mmol) in THF (80 ml) at -10°C (ice-salt) under nitrogen. Within 15 min the colour turned to black (gas evolution). 1-Decene (15 mmol) was added and the contents were stirred further for 3 h at 0°C. After work-up and distillation a mixture containing decane and cis/trans-2-decenes were isolated. The intensities of ^{13}C NMR signals at 134.3, 130.5, 124.1, 123.1, 32.1 and 17.3 due to trans-2-decene and cis-2-decene are relatively small compared to those present in pure cis-2-decene or trans-2-decene which indicate that the reduction product decane is the major product in this experiment. The formation of 2-alkenes clearly demonstrate the presence of nickel hydride species. Similar species (Ni-H) was suggested in the reaction of 1-alkenes with NiCRA, prepared by the reaction of $NiCl_2$ with NaH and t-AmONa.[25]

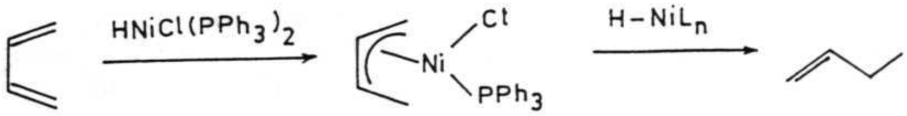


Use of 1-decyne in the above experiment gave yellow coloured polymeric compound. It was not characterized further. It may be of interest to note that the NiCRA, $NiCl_2$/NaH/t-AmONa reduces 1-alkynes into 1-alkenes along with small amount of 2-alkenes arising from the isomerization of 1-alkenes.[25] The experiment was carried out using diphenylacetylene in the place of 1-decyne under the above conditions and the resulting mixture was stirred for 12 h at r.t. After work-up, both starting diphenylacetylene (50%) and 1,2,3,4-tetraphenyl-1-butene (20%) were isolated. The spectral data (IR, ^{1}H- and ^{13}C NMR) of the latter compound was found to be identical to the spectra of the sample obtained previously in the reaction of diphenylacetylene with the Cp_2TiCl_2/Mg/1,2-dibromodecane or styrene dibromide reagent systems (chapter 2). Formation of this product may be rationalized by hydrodimerization reductive cleavage of diphenylacetylene followed by the reduction of butadiene to butene through the corresponding allyl nickel species as shown in Scheme 4.

Scheme 4



It may be of interest to note that the $(PPh_3)_2Ni(H)Cl$ reagent reduces butadiene to butene through the corresponding allyl nickel species.[45]



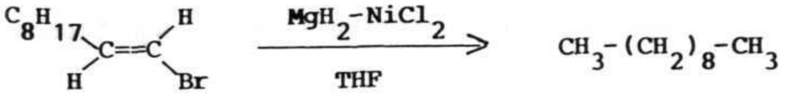
Although the reaction conditions are very much different, a similar mechanistic sequence may also operate in the present case.

It has been reported that the zerovalent nickel species obtained from Ni(COD)[46] or NiL_n and Zn,[47] is an effective reagent for the coupling reactions of alkyl halides and alkenyl halides.

$$2\ RX + L_nNi(0) + Zn \longrightarrow R\text{-}R + L_nNiX_m$$

$$L_nNiX_m + Zn \longrightarrow L_nNi(0) + ZnX_2$$

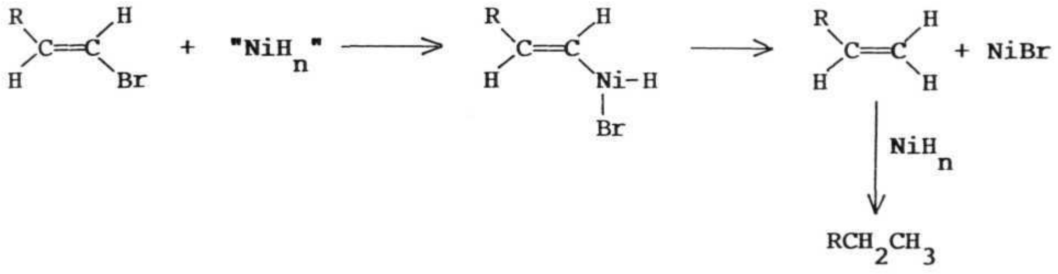
In order to examine whether the MgH_2-$NiCl_2$ reagent system gives Ni(0) species in addition to nickel hydride species, we carried out the following experiment. 1-Bromooctane (15 mmol) was added to a magnetically stirred black suspension of MgH_2 ($\sim$15 mmol) and $NiCl_2$ (15 mmol) in THF (80 ml) at -10°C (ice-salt) under nitrogen. The contents were brought to room temperature during 1 h and stirred further for 12 h. After work-up, 1-bromooctane was recovered quantitatively. When the experiment was carried out using 1-bromo-1-decene in the place of 1-bromooctane under the above conditions, decane was isolated and the diene was not formed.



This observation may be tentatively rationalized as shown in Scheme 5.

Scheme 5

$MgH_2 + NiCl_2 \longrightarrow$ "NiH_n"



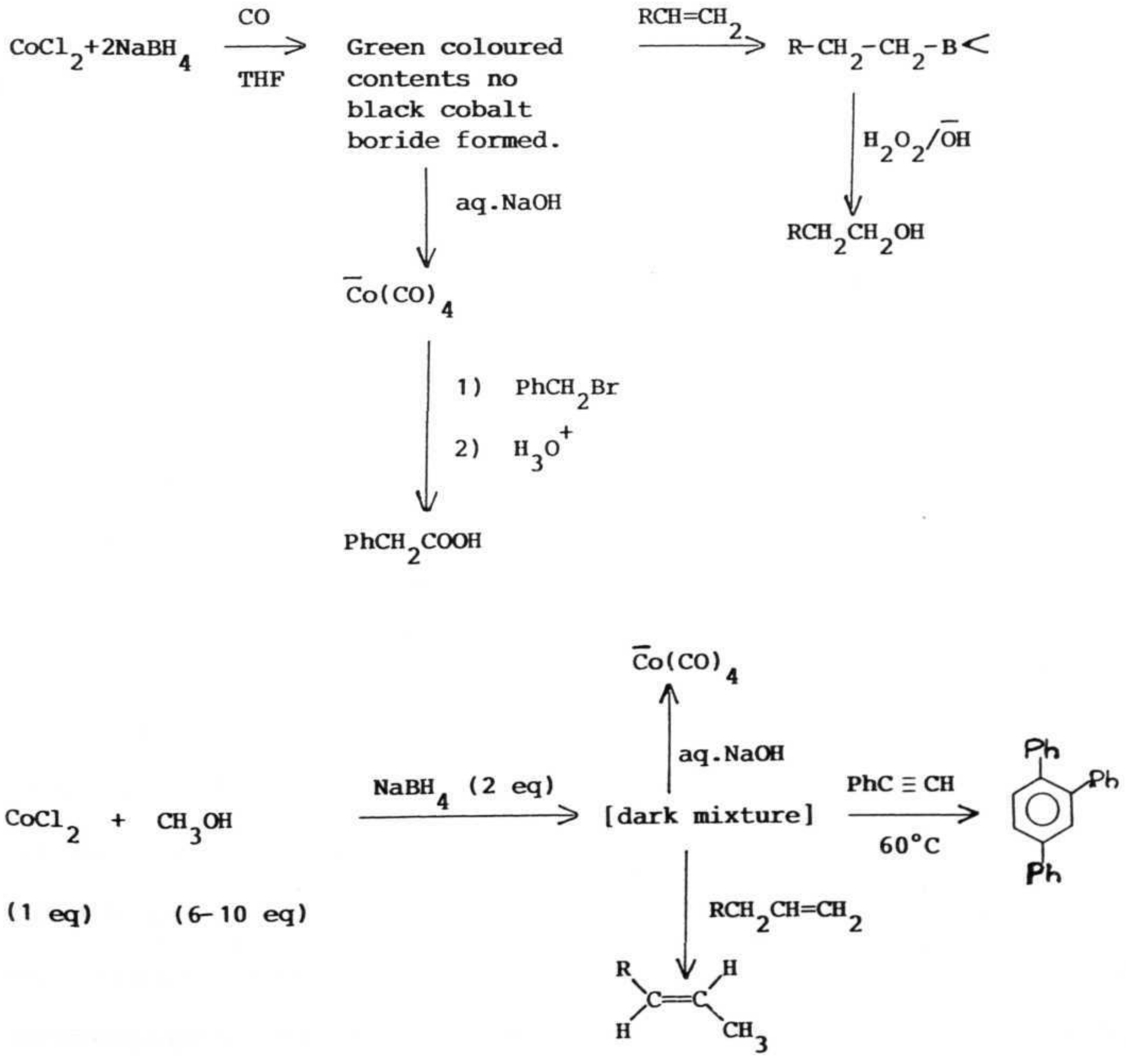
It should be pointed out here that the isomerized 2-decenes which are minor products in runs with 1-decene itself, were not formed in this case, although the mechanism envisioned in Scheme 5 implies the intermediacy of 1-decene. It is likely that the 'NiH_n' species may be present in a polymeric form and the 1-decene is not released from the complex before it is completely reduced into decane.

As outlined in the above discussion, the explorative study of the reactivities of the MX_n/MgH_2 system in THF reveals interesting synthetic possibilities. There are some reactivity differences which seem to be dependent on the nature of the metal atom. Further work towards standardization of conditions to get optimum results and utilization of the organometallic intermediates produced in these transformations should open up more synthetic possibilities.

Reactivities of the metal carbonyl reagents generated utilizing $MgH_2/CoCl_2$ in the presence of CO:

Recently, it has been observed in our laboratory that the reagent prepared from $CoCl_2/NaBH_4/CO$ system exhibits reactivities different from the reactivities of $CoCl_2/NaBH_4$ and the $CoCl_2/NaBH_4/Ph_3P$ reagent systems (Chart 1).[4]

Chart 1

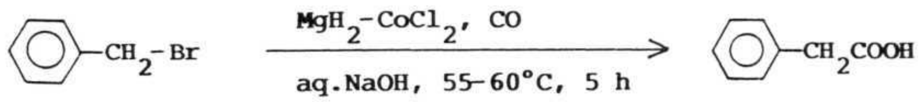


The results revealed that the $CoCl_2/NaBH_4/CO$ system can be made to undergo a variety of reactions characteristic of $>$B-H species, $\bar{C}o(CO)_4$ and $HCo(CO)_n$ species. As outlined in the introductory section, the "CoCRACO" reagent[31,32] and "FeCRACO" reagent,[33] prepared utilizing the CoX_2/NaH/t-AmONa/CO and $FeCl_3$/NaH/t-AmONa/CO reagents respectively, give a variety of interesting reactions. As described previously in this chapter, the transition metal halide/NaH/$MgBr_2$ reagent systems seem to give the corresponding metal hydride species which decompose to give metal and H_2 in many cases. The results obtained with the $CoCl_2/NaBH_4/CO$ system (Chart 1) and MX_n(M=Co or Fe)/NaH/t-AmONa/CO systems (Scheme 1 and 2) and the observations in the literature that several metal carbonyl derivatives can be readily prepared by the reduction of transition metal salts [eg.MX_n(M=Cr, Fe, CO, Ni)] under carbon monoxide[48] indicate the possibilities of utilizing the $MX_n/MgH_2/CO$ reagemt systems for the in situ preparation and utilization of metal carbonyl derivatives. We have decided to examine the reactivities of the MX_n($CoCl_2$, $FeCl_3$ and $CrCl_3$)/MgH_2 reagent systems in the presence of carbon monoxide.

We first examined the $CoCl_2/MgH_2/CO$ reagent system in order to compare its reactivities with the $CoCl_2/NaBH_4/CH_3OH/CO$ system.[4] The MgH_2 ($\sim$15 mmol) slurry in THF (60 ml) was added during 20 min to a suspension of $CoCl_2$ (15 mmol) in THF (60 ml) at 0°C while bubbling carbon monoxide. The colour of the contents changed from blue to black through green while adding MgH_2 slurry. The contents were stirred further for 1 h under CO at r.t. 1-Decene (15 mmol) was added and the contents were stirred further for 6 h under CO atmosphere. After work-up and chromatography, the 1-decene was recovered quantitatively. However, the i.r. spectrum of the reaction mixture in THF exhibits strong absorptions at 2050(s), 1940(sh), 1910(vs) and 1820(s) indicating the presence of a metal carbonyl derivative. Clearly, a metal carbonyl derivative which does not react with 1-decene is present in the reaction mixture. As described previously, the $CoCl_2/MgH_2$ reagent reduces and isomerizes 1-decene. The results indicate that the $CoCl_2/MgH_2$ reagent loses this reactivity when the $CoCl_2$ and MgH_2 reagents are mixed under carbon monoxide.

It was thought that the $CoCl_2/MgH_2$ reagent system might give the $HCo(Co)_4$ species in the presence of CO. However, it is known that the $HCo(CO)_4$ reagent is highly acidic (i.e. the H-Co bond polarises as $\overset{\delta+}{H}$ — $\overset{\delta-}{Co}$). Accordingly, it was thought that even if the $HCo(CO)_4$ species are formed in the reduction of $CoCl_2$ with MgH_2 under CO, it is likely to give the anionic species $\overset{-}{Co}(CO)_4$ through further reaction with MgH_2. As outlined previously, it is known that $\overset{-}{Co}(CO)_4$ reagent reacts with benzyl halides to give acylcobalt species.[31,32,49] In order to examine the possibility of $\overset{-}{Co}(CO)_4$ formation, we carried out the following experiment. The MgH_2 (~ 15 mmol) slurry in THF (60 ml) was added during 20 min from a pressure equiliser to a suspension of $CoCl_2$ (15 mmol) in THF (60 ml) at 0°C while bubbling carbon monoxide. The contents were stirred at 0°C for further 1 h under CO and benzyl bromide (15 mmol) in THF (5 ml) was added. The temperature was raised to 55-60°C and the contents were stirred for 5 h. After work-up, the residue was found to be only benzyl bromide and no carbonylated product was formed.

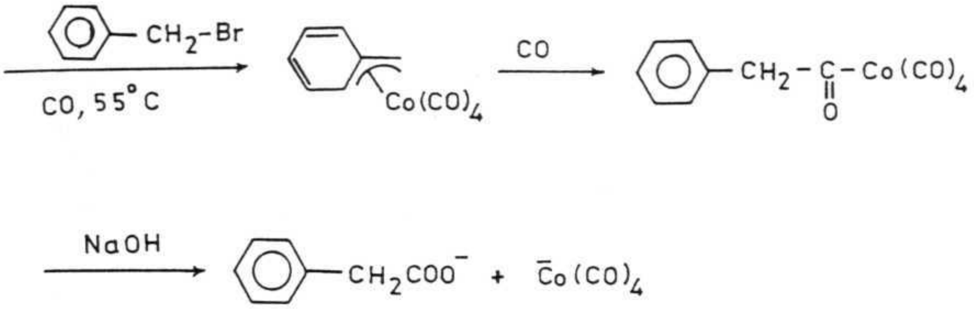
It has been reported that the $CoCl_2/NaH/t\text{-}AmONa/CO$ reagent system gives $NaCo(CO)_4$ in 10% yield and the system has been utilized for carbonylation of benzyl halides.[31,32] It is also known that the $NaCo(CO)_4$ reagent is generally prepared by the reaction of $Co_2(CO)_8$ with aqueous NaOH.[49] In order to examine whether $Co_2(CO)_8$ is formed in the present case, we carried out the following experiment. The metal carbonyl species was generated by the addition of MgH_2 (~ 15 mmol) slurry in THF (60 ml) from a pressure equiliser to a suspension of $CoCl_2$ (15 mmol) in THF (60 ml) at 0°C and the contents were stirred for 1 h at r.t. under CO. Aqueous NaOH (5N, 15 ml) was carefully added (vigorous reaction and gas evolution). Benzyl bromide (15 mmol) in THF (10 ml) was added to the black reaction mixture and the temperature was raised to 55-60°C. The contents were stirred further for 5 h at this temperature under carbon monoxide. After work-up (see experimental section) phenylacetic acid was isolated in 80% yield.



This observation clearly indicates the presence of $\overline{C}o(CO)_4$ species after aqueous NaOH treatment. Presumably, the major portion of the metal carbonyl species formed in the reaction of $MgH_2/CoCl_2/CO$ system might be the $Co_2(CO)_8$ species. The carbonylation of benzyl bromide into phenyhlacetic acid can be tentatively rationalized as mentioned in Scheme 6.

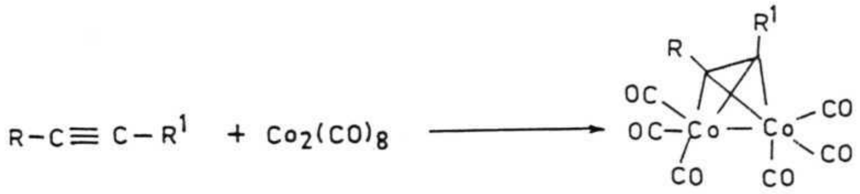
Scheme 6

$$CoCl_2 + MgH_2 \xrightarrow[1h,\ r.t.]{CO} Co_2(CO)_8 \xrightarrow{aq.\,NaOH} \overline{C}o(CO)_4$$



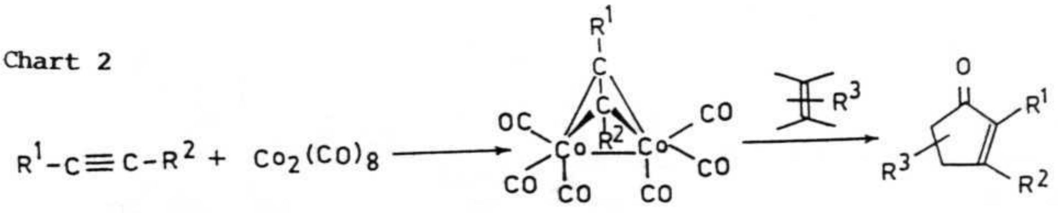
It was also observed that the carbonylation of benzyl bromide using solid powdered NaOH (125 mmol) and PTC (0.1 g) (benzyl triethyl ammonium bromide) in the place of aqueous NaOH gave only a small amount of phenylacetic acid (50 mg) besides the starting benzyl bromide. This observation indicates that only after aqueous NaOH treatment, the $Co_2(CO)_8$ gives sufficient amount of the reactive $\bar{C}o(CO)_4$. The $\bar{C}o(CO)_4$ species has been proved to be a useful reagent in organic synthesis[50-55] and the present in situ preparation of the $\bar{C}o(CO)_4$ reagent should be a good addition to the existing pool of reagents.

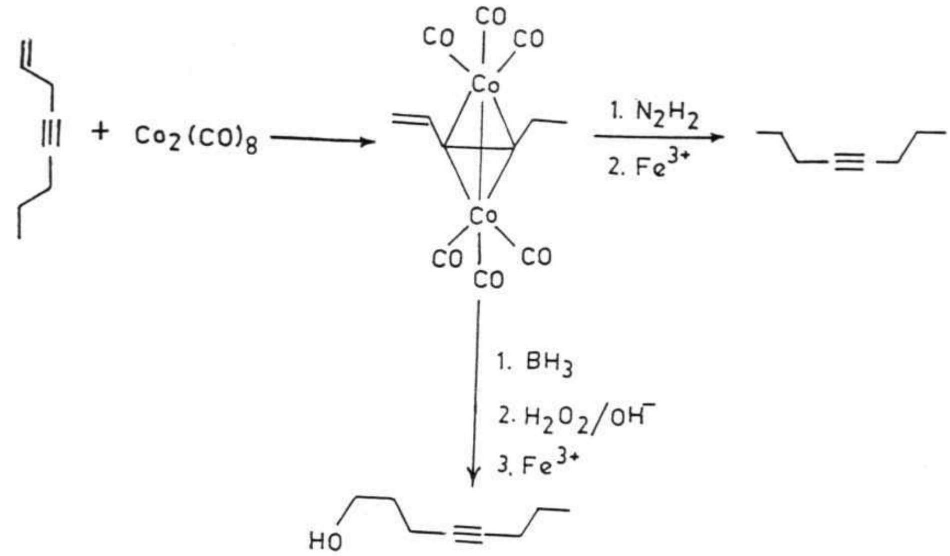
Dicobalt octacarbonyl, $Co_2(CO)_8$, has a very rich chemistry.[48] The chemical reactions of $Co_2(CO)_8$ have been reviewed.[56] It readily forms bridged complexes with alkynes.[57]

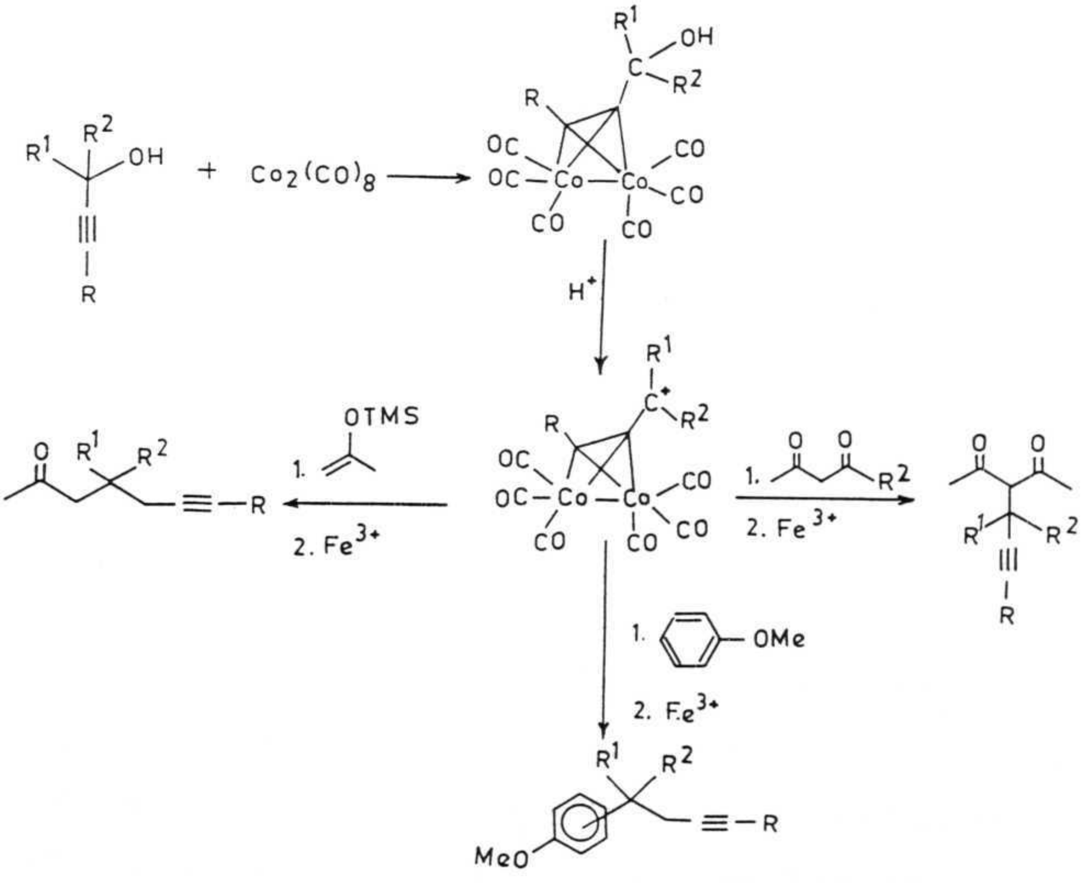


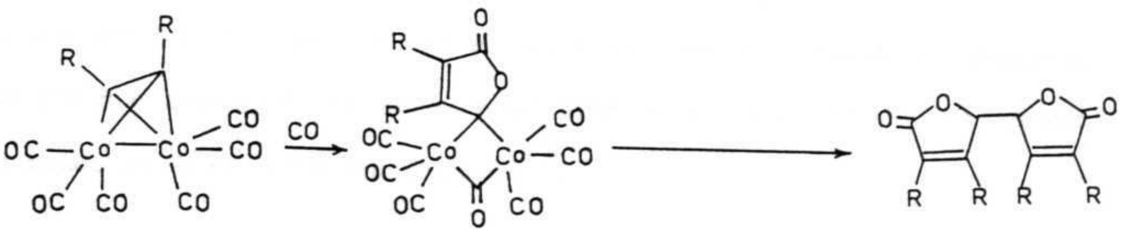
Such acetylene complexes have a very rich organic chemistry. Representative examples are shown in Chart 2.[58-63]

Chart 2

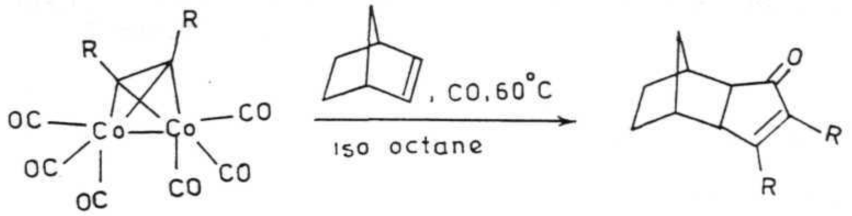



+ $Co_2(CO)_8$
CO
Co
1. N_2H_2
2. Fe^{3+}
1. BH_3
2. H_2O_2/OH^-
3. Fe^{3+}
HO

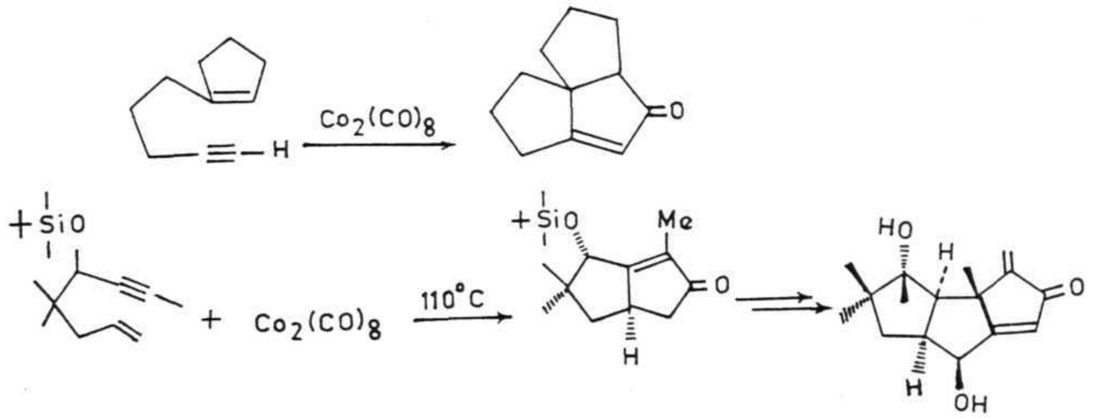

R^1
R^2
OH
R
+ $Co_2(CO)_8$
OC
CO
Co
H^+
C+
OTMS
1.
2. Fe^{3+}
OMe
MeO


R
OC
CO
Co
O

The alkyne complexes readily undergo the Pauson-Khand cyclization reaction with strained olefins.[64,65]



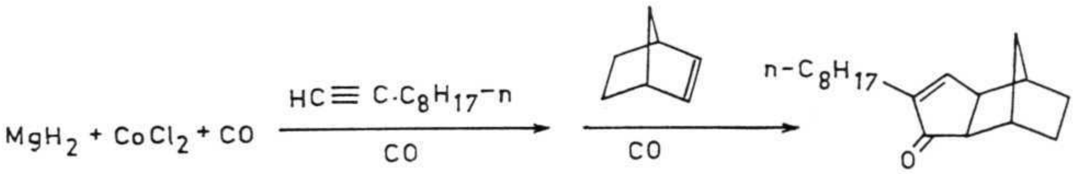
Simple olefins (eg. cyclopentene and propene) require more drastic conditions and give poor yields of the cyclic products. When the alkene and alkyne moieties are present in one molecule intramolecular cyclization readily occurs.[66-70]



It was of interest to examine whether the metal carbonyl derivative, prepared utilizing $CoCl_2/MgH_2/CO$ system, complexes with alkynes and also to examine whether the resulting complex undergoes the Pauson-Khand cyclization with norbornene. It was observed that 1-decyne readily reacts with the metal carbonyl generated using $CoCl_2/MgH_2/CO$ system. The metal carbonyl was generated by slow addition of MgH_2 (~ 15 mmol) slurry in THF (60 ml) to a blue suspension of $CoCl_2$ (15 mmol) in THF (60 ml) at 0°C while bubbling carbon monoxide. The mixture was stirred further for 2 h at r.t. 1-Decyne (10 mmol) was added and the stirring was continued for 5 h at r.t. After work-up, the i.r. spectral analysis of the residue revealed the absence of acetylenic absorptions but showed strong bands at 2090, 2050 and 2025 cm^{-1}.

$$MgH_2 + CoCl_2 \xrightarrow[\text{THF},0^{\circ}\text{-r.t.}]{CO} \xrightarrow{2h} \xrightarrow{HC{\equiv}C\text{-}(CH_3)_7\text{-}CH_3} (HC{\equiv}C(CH_2)_7CH_3)Co_2(CO)_6$$

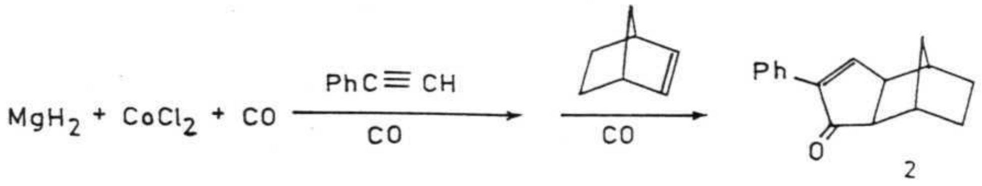
This observation indicates that the metal carbonyl generated utilizing the $CoCl_2/MgH_2/CO$ system complexes with 1-decyne. In order to examine whether the 1-decyne complex prepared utilizing the $CoCl_2/MgH_2/CO$ system could undergo the Pauson-Khand reaction, we carried out the following experiment. To the 1-decyne complex, prepared as above in THF, norbornene (20 mmol) was added. The reaction mixture heated to 70-80°C and stirred further for 6 h under CO atmosphere. After work-up and chromatography of the coloured material, a coloured metal carbonyl derivative (200 mg) was isolated by eluting with hexane and the Pauson-Khand product **1** was isolated by eluting with 5% ethyl acetate in hexane.



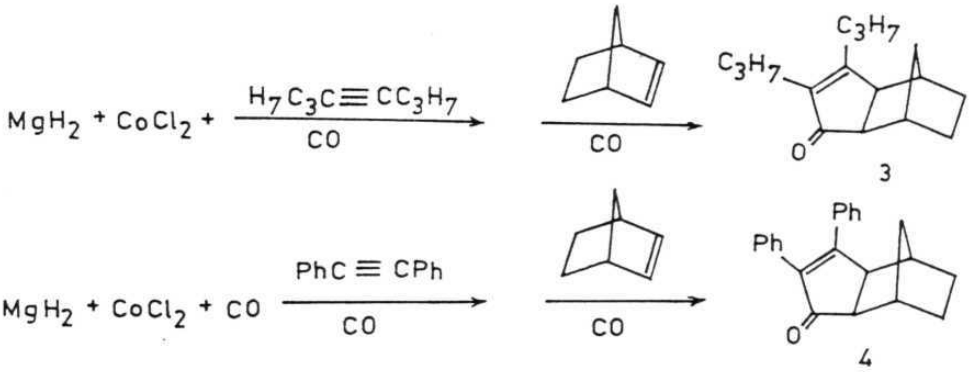
1

The ketone **1** was identified by comparison of the ^1H NMR spectrum with the spectrum reported in the literature and analysis of the ^{13}C NMR and mass spectral data. Only one regio isomer was obtained. It has been reported that in the Pauson-Khand reaction with norbornene, substituted acetylenes prefer the orientation which always places the bulky substituent in the α-position of the resulting cyclopentenone.[65]

Under similar conditions, the phenylacetylene-norbornene combination gave the desired Pauson-Khand ketone **2** in 40% yield, m.p. 92-94°C, Lit.[65] m.p. 93-95°C.

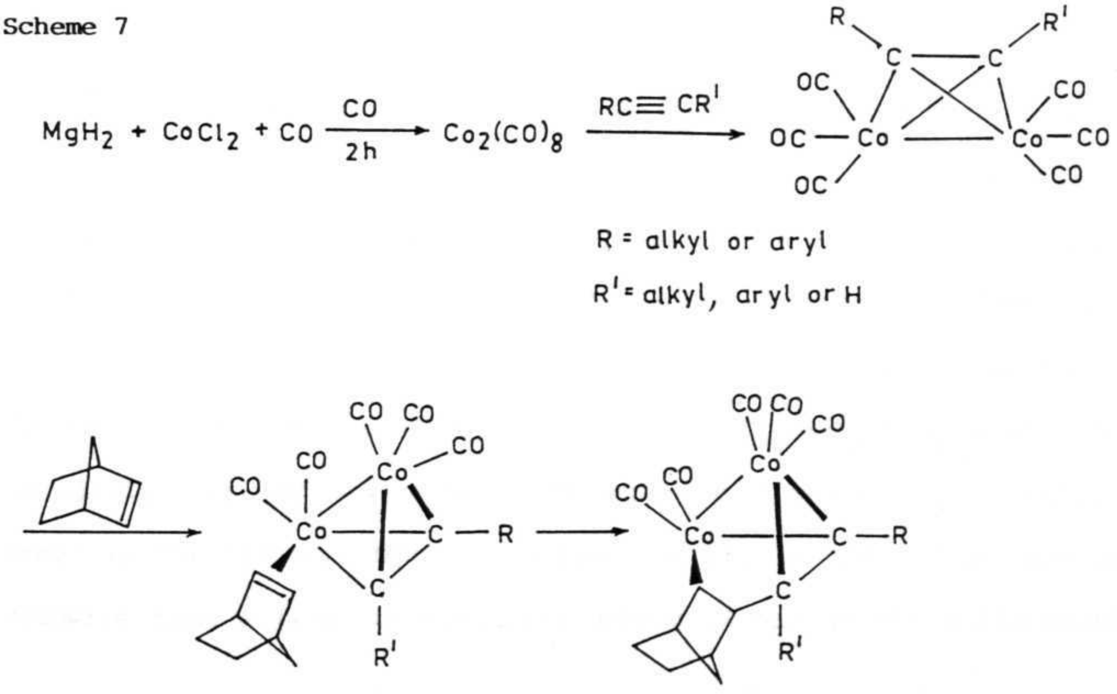


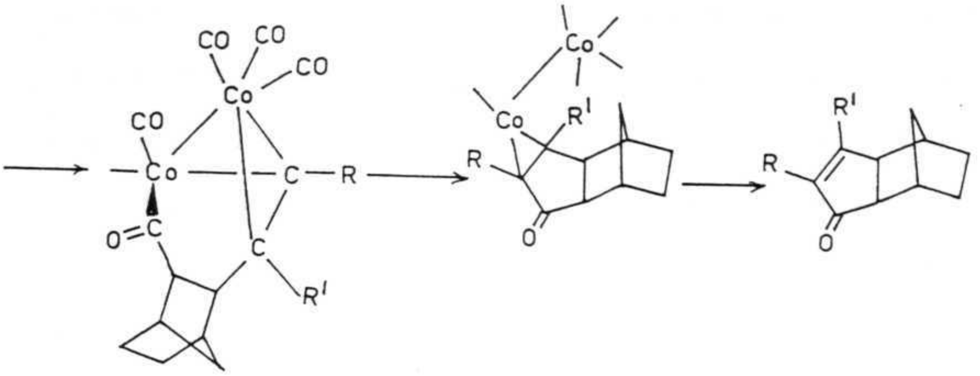
The internal alkynes, 4-octyne and diphenylacetylene form a stable alkyne cobalt carbonyl complexes which further react with norbornene to give the ketones **3** and **4** in 20% and 30% yield respectively. These substrates also give poor results in reactions under Pauson-Khand conditions.[65]



Recently, there is much interest in the mechanism of the Pauson-Khand reaction,[71] and the following mechanism has been proposed (Scheme 7).

Scheme 7





As described previously, the Pauson-Khand reaction has been utilized in crucial steps in the synthesis of some complex cyclopentanoid natural products.[66-70] Although dicobalt octacarbonyl is commercially available, the present in situ method of synthesis of the metal carbonyl complexes would make the procedure attractive for synthetic applications since it alleviates the need for purchasing and storing a metal carbonyl reagent.

Attempted preparation of iron and chromium carbnonyl complexes using $FeCl_3$ or $CrCl_3/MgH_2$ under CO pressure:

As outlined previously, the $FeCl_3/MgH_2$ reagent system reduced 1-alkenes to alkanes. It was of interest to study the reactivities of this reagent system prepared under CO. It is known that the hydrido ironcarbonyls (i.e. $H_2Fe(CO)_4$ and $NaHFe(CO)_4$) hydrocarbonylate olefins to give the corresponding aldehyde after carbon monoxide insertion.[72] In order to examine the reactivities of the $FeCl_3/MgH_2/CO$ reagent system, we carried out the following experiment. To a suspension of $FeCl_3$ (15 mmol) in THF (60 ml), MgH_2 (~ 15 mmol) slurry in THF (60 ml) was added dropwise from a pressure equilizer during 20 min at 0°C while bubbling carbon monoxide. The reaction mixture turned to yellow colour during 2 h under CO. 1-Decene (10 mmol) was added and the temperature of the reaction mixture was raised to 60-70°C and stirred for 6 h under CO atmosphere. The contents were brought to r.t. and poured into water (50 ml). After work-up, the infrared spectrum of the crude residue showed the presence of metal carbonyl absorption at 2100(w), 2040(vs) and 1980(s) along with the 1-decene absorptions at 3100 and 1640 cm^{-1}. The results indicate that the 1-decene does not react with the metal carbonyl derivative produced in the $FeCl_3/MgH_2/CO$ reagent system. 1-Decyne was also unaffected by the reagent. However, as outlined briefly in General Introduction, iron carbonyl derivatives have a very rich chemistry[73] and hence further systematic investigations on the utilization of these derivatives should be fruitful.

Under similar conditions the $CrCl_3/MgH_2/CO$ system also did not react with 1-decene and 1-decyne. The infrared spectrum of the crude reaction product after aqueous work-up in a run with 1-decene indicated the presence of a very strong metal carbonyl absorption at 2000 cm^{-1} along with unreacted 1-decene absorptions. As outlined previously, the $CrCl_3/MgH_2$ system did react with 1-decene and 1-decyne. This indicates that the reagent generated under the carbon monoxide atmosphere does not retain the original reactivity. Again, the carbonyl derivatives of chromium also have a very rich chemistry[74] and further systematic investigations should be fruitful.

SUMMARY

The reactivities of the $MX_n/MgH_2/THF$ and $MX_n/MgH_2/CO/THF$ reagent systems have been explored in the work described in this chapter. It was observed that the $Cp_2MCl_2(M=Ti,Zr)/MgH_2$ reagent systems reduce 1-alkenes and 1-alkynes to the corresponding alkanes and 1-alkenes respectively. The combination of MgH_2 and transition metal salts (eg. $CrCl_3$, $FeCl_3$, $CoCl_2$ and $NiCl_2$) are able to reduce 1-alkenes to alkanes along with small amount of isomerized products in some cases. 1-Decyne underwent oligomerization or polymerization with these systems. The $MX_n(M=Co, Fe, Cr)/MgH_2/CO/THF$ reagent systems gave the corresponding metal carbonyl derivatives. Metal carbonyl derivative obtained utilizing the $CoCl_2/MgH_2/CO$ reagent system on treatment with aq.NaOH gives $\overline{Co}(CO)_4$ reagent which converts benzyl bromide to phenyl acetic acid. The metal carbonyl derivative prepared using the $CoCl_2/MgH_2/CO$ system readily complexes with alkynes. These complexes undergo Pauson-Khand cyclization with norbornene. This constitutes a convenient single pot, *in situ* procedure for Pauson-Khand cyclizations.

The studies described in this chapter are purely exploratory in nature. Further investigations on the optimization/generalization of the conditions and efforts to utilize the organometallic intermediates generated in this way for other types of transformations should be fruitful.

EXPERIMENTAL

Several items given in the experimental section of chapter 1 and 2 are also applicable for the experiments outlined here. Anhydrous $CrCl_3$, $CoCl_2$ and $NiCl_2$ were prepared from their hydrated metal salts, supplied by Fluka, Switzerland, LOBA-CHEMIE, India and E.Merck, India. The hydrated metal salts were kept in the air oven at 150°C for 5-6 h and further dried at 150°C for 4 h under vacuum, and were kept under nitrogen in a dessicator. In some cases, the anhydrous salts were also prepared by refluxing with 2,2-dimethoxypropane. Anhydrous $FeCl_3$ supplied by Ranbaxy, India was dried at 150°C for 3 h under vacuum before use. Anhydrous $MnCl_2$ supplied by Fluka, Switzerland was utilized. Benzyl bromide supplied by Fluka, Switzerland, was utilized.

Reactions of the first row transition metal salts-MgH_2 reagent systems:

General method for the preparation of MgH_2 slurry in THF:

The $MgBr_2$ (20 mmol) solution in THF (60 ml) was prepared by the reaction of Mg (20 mmol, 0.5 g) with 1,2-dibromoethane (20 mmol, 3.7 g) under nitrogen atmosphere at room temperature during 3 h. NaH (30 mmol, 1.5 g in oil) was taken in a three-necked 250 ml RB flask under nitrogen atmosphere following glove bag techniques. The oil was removed by washing with dry THF (2x15 ml) under nitrogen. The $MgBr_2$ (20 mmol) solution in THF (60 ml) was transferred to the NaH flask under nitrogen using a double ended needle. The resulting suspension was stirred for 36 h at room temperature. This slurry was utilized in reactions with transition metal salts.

Reaction of the reagent prepared from MgH_2 slurry and $TiCl_4$ with 1-decene:

$TiCl_4$ (10 mmol in C_6H_6, 20 ml) was added to a magnetically stirred suspension of MgH_2 (~ 15 mmol) in THF (60 ml) under nitrogen atmosphere at 0°C (ice-bath). 1-Decene (10 mmol, 1.4 g) was added to the resulting yellow colour solution and stirred for 2 h at 0°C. It was brought to room temperature during 1 h and stirred further for 12 h. The mixture was poured into dil.HCl (50 ml, 2N) and saturated with solid sodium chloride. The layers were separated and the aqueous layer was extracted with ether (3x30 ml). The combined organic extract was washed successively with water (50 ml), brine solution (50 ml) and dried over anhydrous $MgSO_4$. The ether solvent was evaporated and the residue was distilled to isolate unreacted 1-decene (90%, 1.26 g). The IR spectrum was superimposable with the spectrum of starting 1-decene.

Reduction of 1-decene to decane utilizing the MgH_2/Cp_2TiCl_2 reagent in THF:

Cp_2TiCl_2 (5 mmol, 1.2 g) was added to the slurry of MgH_2 (~ 15 mmol) in THF (60 ml) under nitrogen atmosphere at 0°C (ice-bath). 1-Decene (10 mmol, 1.4 g) was injected to the resulting orange colour solution. The contents were brought to room temperature during 1 h and stirred further for 12 h. The black reaction mixture was treated with dil.HCl (50 ml, 2N) and saturated with solid sodium chloride. The organic layer was separated and the aqueous layer was extracted with ether (3x30 ml). The organic extract was washed with water (50 ml), brine solution (50 ml) and dried over anhydrous $MgSO_4$. The solvent was evaporated and the residue was chromatographed on a silica gel column using hexane as eluent to isolate n-decane.

Yield: 80% (1.1 g).

B.P: 56-57°C/10 mm, Lit.[75] b.p. 63°/15 mm.

IR (neat): ν_{max}: 2950, 1470, 1390.

^{1}H NMR (100 MHz, $CDCl_3$): δ ppm 1.1 (m, for all CH_2 protons), 0.9 (br,t, $-CH_3$).

^{13}C NMR (25.0 MHz, $CDCl_3$): δ ppm 32.0, 29.7, 29.4, 22.7, 13.8.

Reaction of the reagent prepared from MgH_2 and Cp_2TiCl_2 with 1-decyne in THF:

The MgH_2 (~15 mmol) slurry was prepared in THF (60 ml) in the usual way. Cp_2TiCl_2 (5 mmol, 1.2 g) was added under nitrogen atmosphere at 0°C followed by 1-decyne (10 mmol, 1.4 g). The resulting mixture was stirred for 12 h at room temperature. After work-up, the crude product was subjected to chromatography on a silica gel column using hexane as eluent to isolate 1-decene (80%, 1.12 g).

IR (neat): ν_{max}: 3100, 2950, 1640, 1000, 910 cm^{-1}.

^{1}H NMR (100 MHz, $CDCl_3$): δ ppm 6.0-5.5 (m, olefinic CH), 5.2-4.8 (m, olefinic CH_2), 2.0 (m,CH_2 attached to olefinic double bond), 1.3 (m all other CH_2 hydrogens), 0.9 (br,t,$-CH_3$).

^{13}C NMR (25.0 MHz, $CDCl_3$): δ ppm 139.3 (CH olefinic carbon), 114.1 (CH_2 olefinic carbon), 33.8, 32.0, 29.7, 29.4, 29.2, 22.7, 14.0.

The spectral data were identical with the data obtained for the authentic sample.

Reaction of the reagent generated from MgH_2 and $ZrCl_4$ with 1-decene in THF:

Anhydrous $ZrCl_4$ (15 mmol, 3.5 g) was added to a magnetically stirred suspension of MgH_2 (~15 mmol) in THF (80 ml) at -10°C (ice-salt bath) under nitrogen atmosphere. 1-Decene (10 mmol, 1.4 g) was injected and the contents were brought to room temperature during 1 h and stirred further for 12 h. After usual work-up, the residue was distilled to isolate unreacted 1-decene essentially quantitatively.

Reaction of 1-decene with MgH_2/Cp_2ZrCl_2 reagent in THF:

To a suspension of MgH_2 (~15 mmol) in THF (80 ml), Cp_2ZrCl_2, (5 mmol, 1.5 g) was added at -10°C (ice-salt bath) under nitrogen atmosphere. 1-Decene (10 mmol, 1.4 g) was added and the reaction mixture was brought to room temperature. It turned to brick-red colour. It was stirred further for 12 h. After work-up, the product was subjected to chromatography on a silica gel column using hexane as eluent to isolate decane (90%, 1.2 g). The spectral data (IR, ^1H NMR and ^{13}C NMR) were found to be identical with the data of the sample obtained previously.

Reduction of 1-decyne utilizing MgH_2/Cp_2ZrCl_2 reagent in THF:

To a suspension of MgH_2 (~15 mmol) in THF (80 ml), Cp_2ZrCl_2, (5 mmol, 1.5 g) was added at -10°C (ice-salt bath) under nitrogen atmosphere followed by 1-decyne (10 mmol, 1.4 g). The colour of the contents changed from light yellow to orange while bringing to room temperature. The mixture was stirred further for 5 h. After work-up, as outlined in the previous experiments, 1-decene was isolated (85%, 1.15 g), b.p. 57-58°C/10 mm. The spectral data (IR, ^1H NMR and ^{13}C NMR) were identical to the data of the authentic sample.

Reaction of the $MgH_2/CrCl_3$ reagent with 1-decene in THF:

Anhydrous $CrCl_3$ (12 mmol, 1.9 g) was added to a magnetically stirred suspension of MgH_2 (~15 mmol) in THF (80 ml) under nitrogen atmosphere at 0°C (ice-bath). After 10 min stirring, 1-decene (10 mmol, 1.4 g) was added and the contents were brought to room temperature during 1 h and stirred further for 12 h. After work-up, the residue was chromatographed on a silica gel column using hexane as eluent to isolate decane (80%, 1.1 g). The spectral data (IR, ^1H NMR and ^{13}C NMR) were identical to the data of the authentic sample. When the reaction mixture was quenched with D_2O before work-up, the isolated decane did not contain any deuterium.

The above procedure was followed for the reaction with safrole. In this case, NMR analysis showed that the product (1.2 g) is a mixture of the corresponding n-propyl and trans-1-propenyl derivatives.

In the case of methyl-10-undecenoate, the ester group was cleaved and the corresponding unsaturated acid was isolated (70%, 1.3 g). The IR spectrum showed 1:1 correspondence with the authentic sample.[76]

Reaction of the reagent prepared from MgH_2 and $CrCl_3$ with 1-decyne in THF:

To a slurry of MgH_2 (~15 mmol) in THF (80 ml), anhydrous $CrCl_3$ (12 mmol, 1.9 g) was added under nitrogen atmosphere at 0°C (ice-bath). 1-Decyne (10 mmol, 1.4 g) was added and the contents were brought to room temperature during 1 h and stirred further for 12 h. After work-up, a yellow coloured compound (1.1 g) was isolated. The product did not distill out even at 300°C/1.5 mm Hg. The product was not characterized further.

Reaction of the reagent generated from MgH_2 and $MnCl_2$ with 1-decene in THF:

The MgH_2 (~ 15 mmol) slurry in THF (80 ml), prepared in the usual way, was cooled to 0°C (ice-bath) and $MnCl_2$ (15 mmol, 1.87 g) was added under nitrogen atmosphere followed by 1-decene (10 mmol, 1.4 g). The reaction mixture was brought to room temperature during a period of 1 h and stirred further for 12 h. After usual work-up, the residue was distilled to isolate unreacted 1-decene (90%, 1.25 g) at 56-58°C/10 mm.

Reaction of the reagent system prepared from MgH_2 and $FeCl_3$ with 1-decene in THF:

Anhydrous $FeCl_3$ (15 mmol, 2.4 g) was added to a magnetically stirred suspension of MgH_2 (~ 15 mmol) in THF (80 ml) under nitrogen at 0°C. Immediately the colour turned to black with gas evolution (H_2). 1-Decene (10 mmol, 1.4 g) was added. The resulting mixture was brought to room temperature during 1 h and stirred further for 48 h. After usual work-up, the residue was distilled to isolate decane (80%, 1.1 g). The IR spectrum showed 1:1 correspondence with the spectrum of the authentic sample.[76]

Reaction of the reagent system prepared from MgH_2 and $FeCl_3$ with 1-decyne in THF:

To a slurry of MgH_2 (~ 15 mmol) in THF (80 ml), anhydrous $FeCl_3$ (15 mmol, 2.4 g) was added under nitrogen at 0°C (ice-bath). 1-Decyne (10 mmol, 1.4 g) was injected and the mixture was brought to room temperature during 1 h, stirred further for 12 h. After work-up a yellow oily compound (1.1 g) was isolated. However, the compound is of polymeric in nature and it was not characterised further.

Reaction of the reagent system generated from MgH_2 and $CoCl_2$ with 1-decene in THF:

Anhydrous $CoCl_2$ (15 mmol, 2.0 g) was added to a magnetically stirred suspension of MgH_2 (~ 15 mmol) in THF (80 ml) at -10°C (ice-salt bath) under nitrogen atmosphere. The mixture immediately turned to black colour with evolution of a gas (H_2). 1-Decene (15 mmol, 2.1 g) was added. The resulting black reaction mixture was stirred for 2 h at 0°C.After work-up, the residue was chromatographed on a silica gel column using hexane as eluent to isolate a mixture (1.9 g) containing both reduced decane and isomerized 2-decenes. GC analysis showed that they are in 1:1 ratio.

When methyl-10-undecenate (10 mmol) was used instead of 1-decene in the above experiment, only the reduction product was obtained. However, allylbenzene and safrole gave the corresponding n-propyl and 1-propenyl derivatives in 60:40 ratio.

$$CH_2{=}CH{-}(CH_2)_8CO_2Me \longrightarrow CH_3(CH_2)_9CO_2Me$$

Yield: 80% (1.6 g).

IR (neat): ν_{max}: 2950, 1740, 1200 cm^{-1}.

^1H NMR (100 MHz, $CDCl_3$): δ ppm 3.7 (s,$-OC\underline{H}_3$), 2.3 (t,$-C\underline{H}_2\overset{O}{\overset{\|}{C}}$), 1.8-0.8 (m,$-CH_2$ remaining protons, also terminal CH_3 protons).

^{13}C NMR (25.0 MHz, $CDCl_3$): δ ppm 173.9($\overset{O}{\overset{\|}{\underline{C}}}$-OMe), 51.1 ($-O\underline{C}H_3$), 34.1 ($\underline{C}H_2-\overset{O}{\overset{\|}{C}}-$), 31.9, 29.5, 29.3, 25.0, 22.6, 13.9.

Utilization of 1-decyne in the above experiment gave only a polymeric product. Reaction of 1-decyne with the reagent system generated utilizing MgH_2 and $(Ph_3P)_2CoCl_2$ system also gave only the polymeric product. The oligomerization or polymerization took place even when the experiments were carried out at -24°C using liq.N_2 and CCl_4 as cooling bath.

Reaction of the reagent prepared from MgH_2 and $NiCl_2$ with 1-decene in THF:

Anhydrous $NiCl_2$ (15 mmol, 0.2 g) was added to a magnetically stirred suspension of MgH_2 (~ 15 mmol) in THF (80 ml) at -10°C (ice-salt bath) under nitrogen atmosphere. Within 15 min the colour turned to black with evolution of a gas (H_2). 1-Decene (15 mmol, 2.1 g) was added and stirred further for 3 h at 0-5°C. After work-up, the residue was distilled out at 58°C/10 mm Hg to isolate a mixture (1.9 g) containing decane and cis/trans-2-decenes. The intensities of ^{13}C NMR signals at 134.3, 130.5, 124.1, 123.1, 32.1 and 17.3 due to trans-2-decene and cis-2-decene are relatively small compared to the spectra of pure sample of 2-decenes. This indicates that the reduction product is the major product in the above experiment. The use of 1-decyne in the place of 1-decene in the above experiment gave only a polymeric material which was not characterized further.

Examination of the question whether the reagent system will give Ni(O) species: Reaction with 1-bromo octane:

1-Bromooctane (15 mmol, 2.8 g) was added to a magnetically stirred black suspension of MgH_2 (~ 15 mmol) and $NiCl_2$ (15 mmol, 0.2 g) in THF (80 ml) at -10°C (ice-salt bath) under nitrogen atmosphere. The contents were brought to room temperature during a period of 1 h and stirred for 12 h. After usual work-up, unreacted 1-bromooctane was recovered back quantitatively.

Reaction of 1-bromo-1-decene with low valent nickel reagent generated using $NiCl_2/MgH_2$:

The MgH_2 (~ 15 mmol) slurry was made in the usual way. Anhydrous $NiCl_2$ (15 mmol, 0.2 g) was added to this slurry under nitrogen atmosphere at -10°C (ice-salt bath) followed by 1-bromo-1-decene (15 mmol, 3.3 g). It was brought to room temperature during 1 h, stirred further for 12 h. The reaction mixture was treated with dil-HCl (50 ml, 2N). After work-up, the residue was distilled to isolate decane 80% (1.9 g) at 56-57°C/10 mm, Lit.[75] b.p. 63°C/15 mm. The spectral data (IR, ^1H NMR and ^{13}C NMR) were identical to the data of the authentic sample.[76]

Reaction of the reagent system generated from MgH_2 and $NiCl_2$ with diphenylacetylene in THF:

Anhydrous $NiCl_2$ (15 mmol, 0.2 g) was added to a magnetically stirred suspension of MgH_2 (~ 15 mmol) in THF (80 ml) under nitrogen atmosphere at 0°C (ice-salt bath). After 10 min diphenylacetylene (3.5 mmol, 0.6 g) was added and the contents were brought to room temperature during a period of 2 h. The mixture was stirred further for 12 h at r.t. After usual work-up, diphenylacetylene (0.31 g) and 1,2,3,4-tetraphenyl-1-butene 20% (0.13 g) were isolated. The spectral data (IR, ^1H NMR and ^{13}C NMR) of the latter were identical to the data of the sample obtained previously (chapter 2).

M.P: 142-143°C.

IR (KBr): ν_{max}: 3050, 1610, 1080, 1040, 920, 760, 700 cm^{-1}.

^1H NMR (100 MHz, $CDCl_3$): δ ppm 7.2-6.7 (m,-Ph), 6.6 (s, olefinic CH), 4.0 (t,-CH), 3.2 (t or overlap by doublets, CH_2 due to the presence of adjacent chiral center).

^{13}C NMR (25.0 MHz, $CDCl_3$): δ ppm 145.3, 141.2, 140.5, 137.4, 130.1, 129.3, 128.8, 128.0, 127.7, 127.1, 126.6, 124.1, 56.4 (d in OFR), 40.3 (t in OFR).

METAL CARBONYLS PREPARATION BY DECOMPOSITION OF TRANSITION METAL HYDRIDES UNDER CARBON MONOXIDE:

Attempted carbonylation of 1-decene utilizing the $MgH_2/CoCl_2$ reagent system under carbon monoxide:

A slurry of MgH_2 (~15 mmol) was prepared in the usual way. Anhydrous $CoCl_2$ (15 mmol, 2.0 g) was taken in THF (60 ml) in a 3-necked RB flask and a pressure equiliser was mounted at one neck under nitrogen. The freshly prepared MgH_2 (~15 mmol) slurry was transferred to the pressure equiliser under nitrogen using a double ended needle. This slurry was added dropwise during 20 min to the $CoCl_2$ suspension at 0°C (ice-bath) while bubbling carbon monoxide. The colour changed from blue to black through green while adding MgH_2 slurry. The black mixture was stirred for 1 h under CO at room temperature and 1-decene (10 mmol, 1.4 g) was added. The contents were stirred further for 6 h at r.t. under carbon monoxide atmosphere. The black reaction mixture was poured into dil.HCl (50 ml, 2N) and saturated with solid sodium chloride.

The organic layer was separated and the aqueous layer was extracted with ether (3x30 ml). The combined organic extract was washed successively with water (50 ml), brine solution (50 ml) and dried over anhydrous $MgSO_4$. The filtrate was concentrated and the residue was chromatographed on a silica gel column using hexane as eluent to isolate unreacted 1-decene quantitatively.

Carbonylation of benzyl bromide utilizing $MgH_2/CoCl_2/CO/NaOH$ system:

The MgH_2 ($\sim$15 mmol) slurry in THF (60 ml) was added during 20 min to a magnetically stirred suspension of $CoCl_2$ (15 mmol, 2.0 g) in THF (60 ml) at 0°C while bubbling carbon monoxide. The contents were brought to room temperature during 1 h and aqueous NaOH (15 ml, 5 N) was carefully added (gas evolution was observed). Benzyl bromide (15 mmol, 2.56 g) in THF (10 ml) was added. The mixture was heated to 55-60°C and stirred further for 5 h at this temperature under carbon monoxide. The bubbling of carbon monoxide was stopped and the gas present above the surface of the mixture was flushed away by a stream of nitrogen. The contents were brought to room temperature and poured into water (100 ml). The precipitate was filtered off and the two layers were separated. The aqueous phase neutralised with conc.HCl and extracted with ether (3x30 ml). The ether layer was washed with water (50 ml), brine solution (50 ml) and dried over anhydrous $MgSO_4$. The solvent was evaporated and the residue was recrystallized from water to isolate phenylacetic acid (80%, 1.68 g).

M.P: 76°C, Lit.[77] m.p. 76-76.5°C.

IR (KBr): ν_{max}: 3500-3000, 1710, 750, 700 cm^{-1}.

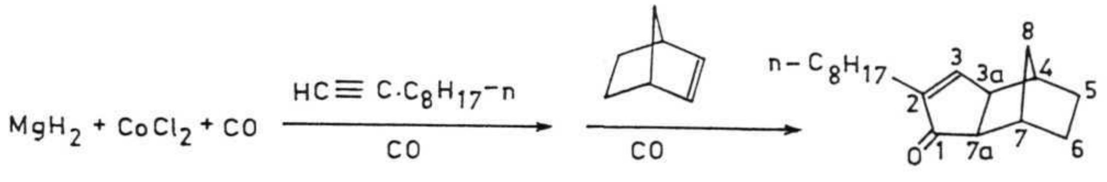
^{13}C NMR (25.0 MHz, $CDCl_3$): δ ppm 178.8, 133.6, 129.7, 129.0, 127.6, 41.2.

Preparation of (1-decyne) hexacarbonyl dicobalt complex, $(R^1C_2R^2)Co_2(CO)_6$, by the reaction of $MgH_2/CoCl_2/CO$ reagent with 1-decyne:

The MgH_2 (~15 mmol) slurry in THF (60 ml) was added during 20 min from the pressure equiliser to a suspension of $CoCl_2$ (15 mmol, 2.0 g) in THF (60 ml) at 0°C (ice-bath) while bubbling carbon monoxide. The black reaction mixture was brought to room temperature during 30 min and stirred further for 2 at r.t. 1-Decyne (10 mmol, 1.4 g) was added and stirred further for 5 h. The black reaction mixture was poured into water (50 ml). The precipitate was filtered off and the two layers were separated. The aqueous phase was extracted with ether (3x30 ml). The combined organic extract was washed successively with water (50 ml), brine solution (50 ml) and dried over anhydrous $MgSO_4$. The solvent was evaporated to isolate a dark coloured residue. IR spectrum of this product indicated the absence of acetylenic absorptions but exhibited strong absorption bands at 2150, 2050 and 2020 cm^{-1} characteristic of a metal carbonyl derivative most probably the 1-decyne-cobalt hexacarbonyl complex.[57]

Preparation of decyne hexacarbonyl dicobalt complex and its reaction with norbornene: Pauson-Khand reaction: Evidence for the formation of $Co_2(CO)_8$ species:

To a magnetically stirred suspension of $CoCl_2$ (15 mmol, 2.0 g) in THF (60 ml), MgH_2 (~15 mmol) slurry in THF (60 ml) was added during 20 min at 0°C (ice-bath) while bubbling carbon monoxide and stirred further for 2 h. 1-Decyne (10 mmol, 1.4 g) was added followed by norbornene (20 mmol, 2.0 g). The reaction mixture was heated to 70-80°C and stirred further for 6 h under carbon monoxide. It was brought to r.t. and poured into water (100 ml). The precipitate was filtered off and the two phases were separated. The aqueous phase was extracted with ether (3x30 ml). The combined organic extract was washed successively with water (50 ml), brine solution (50 ml) and dried over anhydrous $MgSO_4$. The solvent was evaporated and the dark coloured residue was subjected to chromatography on a silica gel column. Hexane eluted the coloured metal carbonyl derivative and 5% ethyl acetate in hexane eluted the Pauson-Khand reaction product **1** (spectrum No.11).



1

Yield: 50% (1.3 g).

IR (neat): ν_{max}: 2950, 1700, 1150-1000 (broad) cm^{-1}

^1H NMR (100 MHz, $CDCl_3$): δ ppm 7.0 (br,3H), 2.5 (br), 2.3 (br), 2.1 (br) (3aH,4H,7H,7aH),(1.6-1.1 (m,5H,6H,8H) and alkyl protons), 0.8 (br,t,$-CH_3$).

(spectrum No.11)

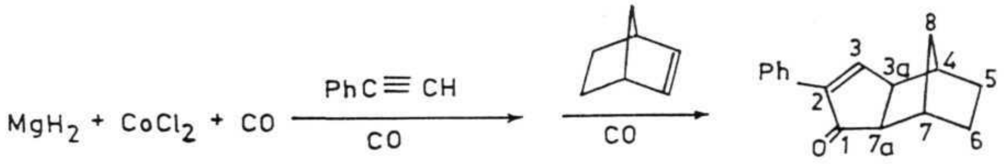
^{13}C NMR (25.0 MHz, $CDCl_3$): δ ppm 209.3 (C_1), 157.2 (C_3), 148.8 (C_2), 52.9, 47.2, 38.1, 37.3, 31.1, 30.1, 28.5, 27.6, 27.1, 23.9, 21.8, 13.3.

(spectrum No.11A)

Mass spectral data (m/e): 260 (M^+, 50%), 232 (10%), 163 (100%), 162 (40%).

Preparation of $(PhC\equiv CH)Co_2(CO)_6$ using $MgH_2/CoCl_2/CO/PhC\equiv CH$ system and its reaction with norbornene:

The freshly prepared MgH_2 (~15 mmol) slurry in THF (60 ml) was added dropwise during 20 min to a suspension of $CoCl_2$ (15 mmol, 2.0 g) in THF (60 ml) under carbon monoxide bubbling at 0°C. The mixture was stirred for 2 h at room temperature and phenylacetylene (10 mmol, 1.2 g) was added followed by norbornene (20 mmol, 2.0 g). The black reaction mixture was heated to 70-80°C and stirred further for 7 h under carbon monoxide atmosphere. After work-up and chromatography, as outlined in the previous experiment, the dark metal carbonyl complex was eluted first with hexane and the desired Pauson-Khand ketone **2** was eluted with 5% ethyl acetate in hexane. The ketone was recrystallized from pentane (spectrum No.12).



2

Yield: 40% (0.89 g).

M.P: 92-94°, Lit.[65] m.p. 93-95°C.

IR (KBr): ν_{max}: 3010, 2950, 1700, 1610 cm^{-1}.

^1H NMR (100 MHz, $CDCl_3$): δ ppm 7.7-7.5 (m,3H and some phenyl protons), 7.4-7.1 (m, remaining phenyl protons), 2.6 (br,t,3aH), 2.5-2.1 (m,4H,7H and 7aH), 1.7-1.1 (m,5H and 6H), 1.1-0.9 (m,8H).

(spectrum No.12)

^{13}C NMR (25.0 MHz, $CDCl_3$): δ ppm 208.8 (C_1), 160.0 (C_3), 144.7 (C_2), 131.3, 128.5, 128.1, 127.3, 126.7, 54.5, 47.2, 39.0, 37.9, 30.8, 28.7, 28.0.

(spectrum No.12A)

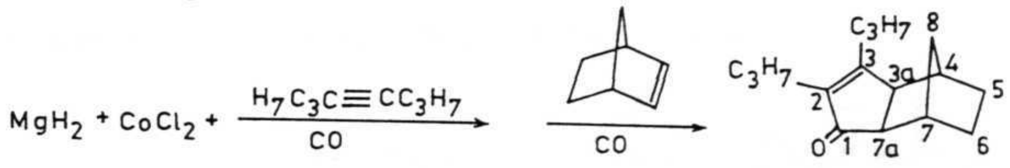
Mass spectral data (m/e): 224 (M^+, 100%), 196 (10%), 158 (75%), 156 (60%).

Analysis:	C%	H%
Calculated:	85.6,	7.14.
Found:	85.43,	7.17.

The ^{1}H NMR spectral data showed 1:1 correspondence with the reported data.[65]

Preparation of $(C_3H_7C\equiv CC_3H_7)Co_2(CO)_6$ species using $MgH_2/CoCl_2/CO/C_3H_7C\equiv CC_3H_7$ system and its reaction with norbornene:

The MgH_2 (~15 mmol) slurry in THF (60 ml) was added during 20 min to a magnetically stirred blue suspension of $CoCl_2$ (15 mmol, 2.0 g) in THF (60 ml) at 0°C while bubbling carbon monoxide and stirred further for 2 h at room temperature. 4-Octyne (10 mmol, 1.1 g) was added followed by norbornene (20 mmol, 2.0 g). The contents were stirred for 7 h at 70-80°C. After work-up and chromatography, the metal carbonyl compound was isolated by eluting with hexane (IR spectrum of this compound exhibits strong metal carbonyl absorptions at 2110 and 2050 cm^{-1}). The desired cyclopentenone **3** derivative was eluted with 2% ethyl acetate in hexane (spectrum No.13).



3

Yield: 20% (0.46 g).

IR (neat): ν_{max}: 1700, 1640, 1350, 1100 cm^{1}.

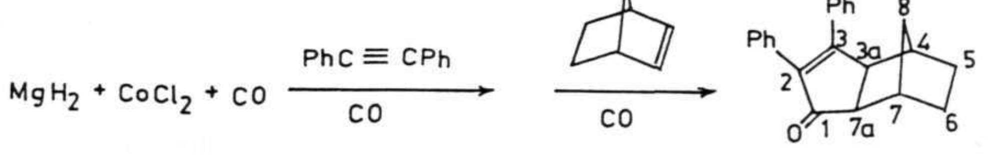
^1H NMR (100 MHz, $CDCl_3$): δ ppm 2.5-1.9 (m, 3aH, 4H, 7H and 7aH), 1.6-1.1 (m, 5H, 6H and 8H), 1.0-0.7 (m, alkyl protons).
(spectrum No.13)

^{13}C NMR (25.0 MHz, $CDCl_3$): ppm 210.8 (C_1), 174.4 (C_3), 143.7 (C_2), 53.3, 50.0, 38.6, 37.1, 31.3, 31.0, 29.0, 28.5, 25.0, 21.7, 20.8, 14.1, 14.0.
(spectrum No.13A)

Mass spectral data (m/e): 232 (M^+, 40%), 217 (100%), 204 (10%), 189 (30%).

Preparation of $(PhC\equiv CPh)Co_2(CO)_6$ complex using $MgH_2/CoCl_2/CO/PhC\equiv CPh$ system and its reaction with norbornene:

To a magnetically stirred suspension of $CoCl_2$ (15 mmol, 2.0 g) in THF (60 ml), the MgH_2 (~15 mmol) slurry in THF (60 ml) was added dropwise during 20 min at 0°C while bubbling carbon monoxide. The reaction mixture turned to black via green colour. After 2 h stirring at room temperature, diphenylacetylene (10 mmol, 1.98 g) was added followed by norbornene (20 mmol, 2.0 g). The temperature was raised to 70-80°C and stirred further for 7 h at this temperature under carbon monoxide. After work-up, the dark coloured metal carbonyl derivative was eluted with hexane and the desired ketone **4** was eluted with 2% ethyl acetate in hexane. The ketone was recrystallized from pentane.



4

Yield: 30% (0.9 g).

M.P. 129-130°, Lit.[65] m.p. 130-131°C.

IR (KBr): ν_{max}: 3050, 2950, 1700, 1600, 1500, 1450, 1360-1160, 1080-1020, 760, 700 cm^{1}.

^{1}H NMR (100 MHz, $CDCl_3$): δ ppm 7.3-7.0 (m, phenyl protons), 3.1 (br), 2.5-2.3 (m), 2.0 (br), (3aH,4H,7H and 7aH), 1.6-0.8 (m,5H,6H and 8H).

^{13}C NMR (25.0 MHz, $CDCl_3$): δ ppm 209.1, 171.1, 134.9, 132.4, 129.6, 129.5, 128.7, 128.5, 127.9, 53.8, 50.5, 39.2, 38.0, 31.3, 29.6, 29.0.

The ^{1}H NMR spectral data showed 1:1 correspondence with the reported data.[65]

IR spectral study of the metal carbonyl reagent system generated utilizing $MgH_2/CoCl_2$ under carbon monoxide:

To a suspension of $CoCl_2$ (15 mmol, 2.0 g) in THF (60 ml), MgH_2 (~15 mmol) slurry in THF (60 ml) was added dropwise during 20 min from pressure equiliser at 0°C while bubbling carbon monoxide. The black reaction mixture was stirred further for 2 h at room temperature. The IR spectrum of the reaction mixture in THF showed the presence of metal carbonyl absorptions at 2050 (s), 1940 (sh), 1910 (vs) and 1820 (s).

Attempted reaction of 1-decene with the $MgH_2/FeCl_3$ system under carbon monoxide:

The MgH_2 (~15 mmol) slurry in THF (60 ml) was added dropwise during 20 min to a magnetically stirred suspension of $FeCl_3$ (15 mmol, 2.4 g) in THF (60 ml) at 0°C while bubbling carbon monoxide. The mixture turned to yellow colour during 2 h under CO bubbling. 1-Decene (10 mmol, 1.4 g) was added and the temperature was raised to 70°C and stirred for 6 h. The reaction mixture was brought to room temperature and poured into water (100 ml) and saturated with solid sodium chloride. The two layers were separated and the aqueous phase was extracted with ether (3x30 ml). The combined organic extract was washed with brine solution (50 1) and dried over anhydrous $MgSO_4$. After evaporation of the solvent, the crude residue exhibited metal carbonyl absorptions at 2100 (w), 2040 (vs) and 1980 (s) along with 1-decene absorptions at 3100 and 1640 cm^{-1} in the IR spectrum (spectrum No.14).

Attempted reaction of 1-decene with the $MgH_2/CrCl_3$ system under carbon monoxide:

To a suspension of $CrCl_3$ (15 mmol, 2.7 g) in THF (60 ml), MgH_2 ($\sim$15 mmol) slurry in THF (60 ml) was added dropwise during 20 min at 0°C while bubbling carbon monoxide. The contents were brought to room temperature and stirred for 2 h. 1-Decene (10 mmol, 1.4 g) was added and the reaction mixture was heated to 70°C. The mixture was stirred further for 6 h under carbon monoxide. After work-up, the IR spectrum of the crude residue showed very strong metal carbonyl absorption at 2000 cm^{-1} along with 1-decene absorptions (spectrum No.14**A**).

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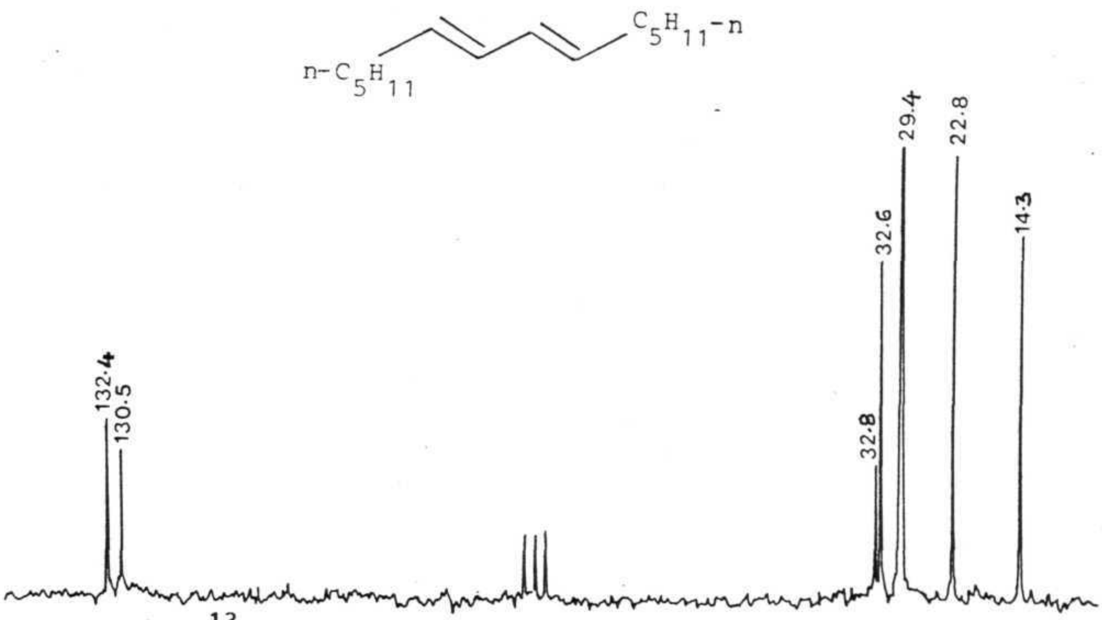
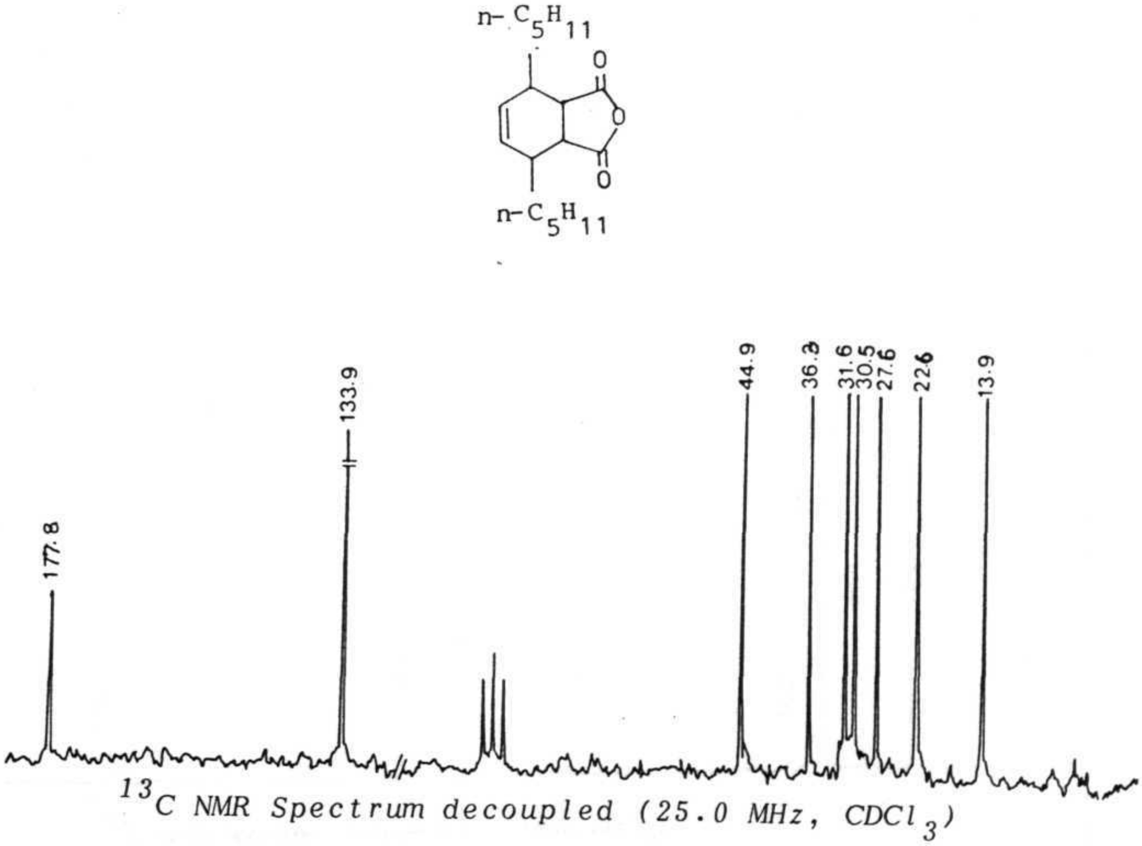
Spectrum Number 1



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

Spectrum Number 1 A



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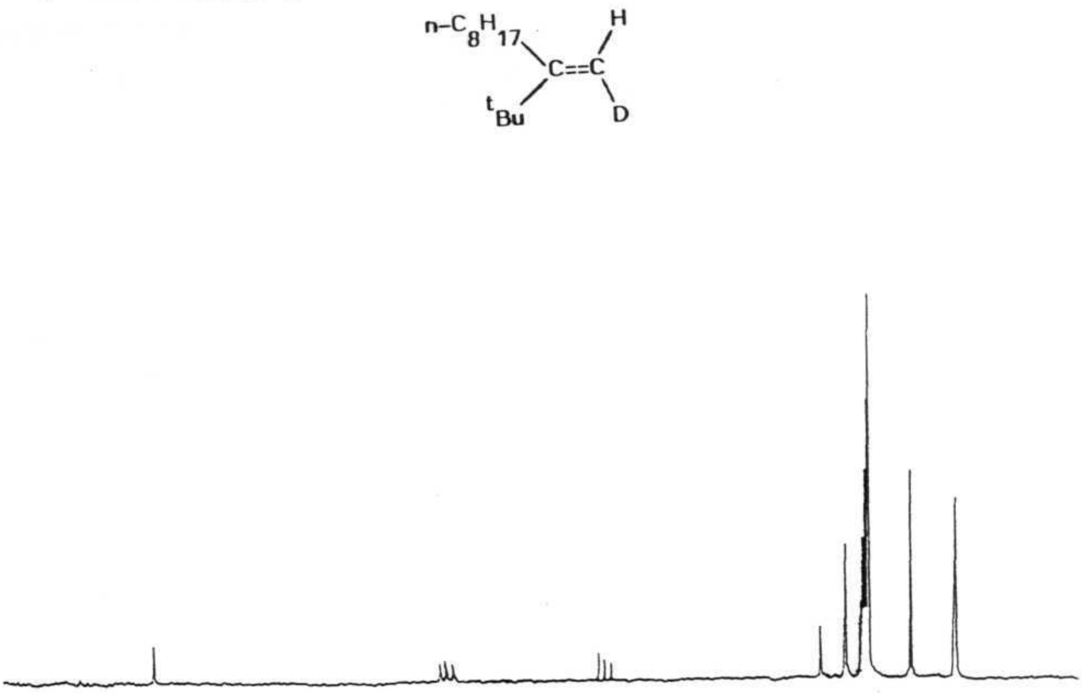

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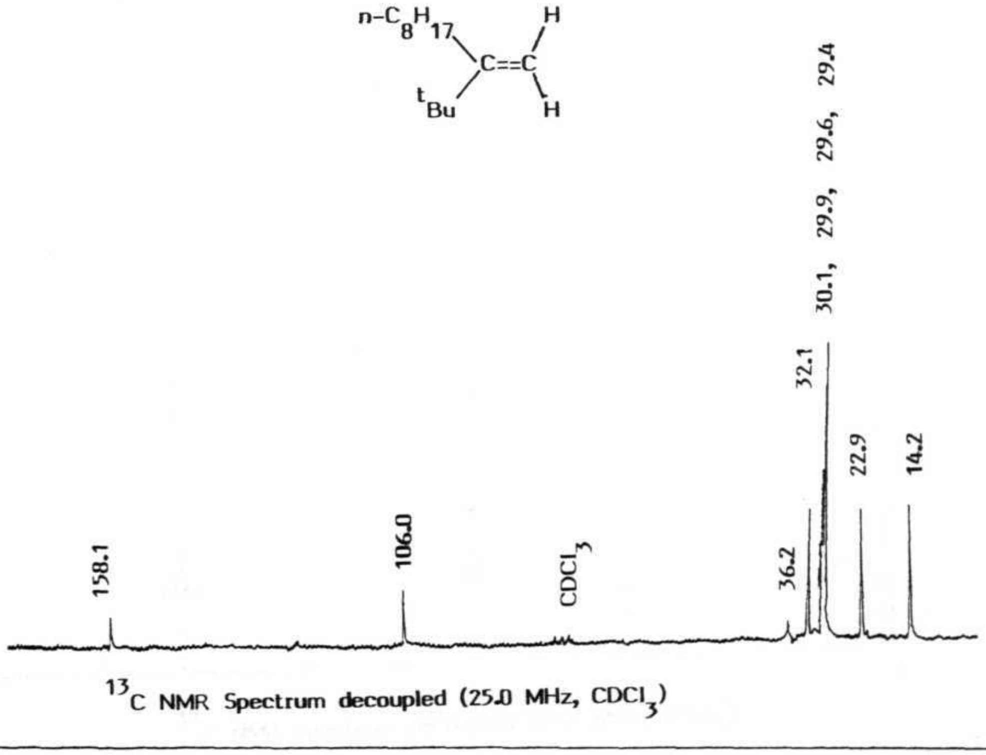

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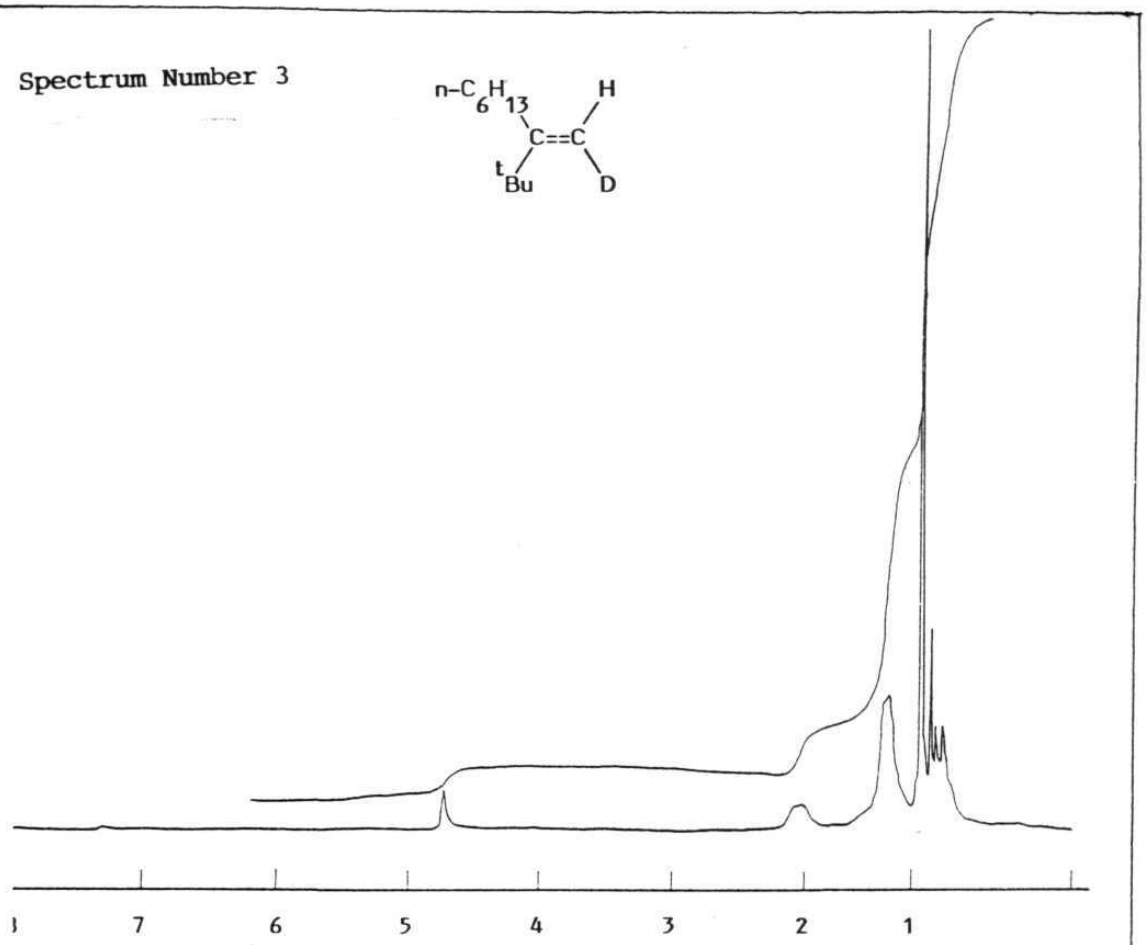

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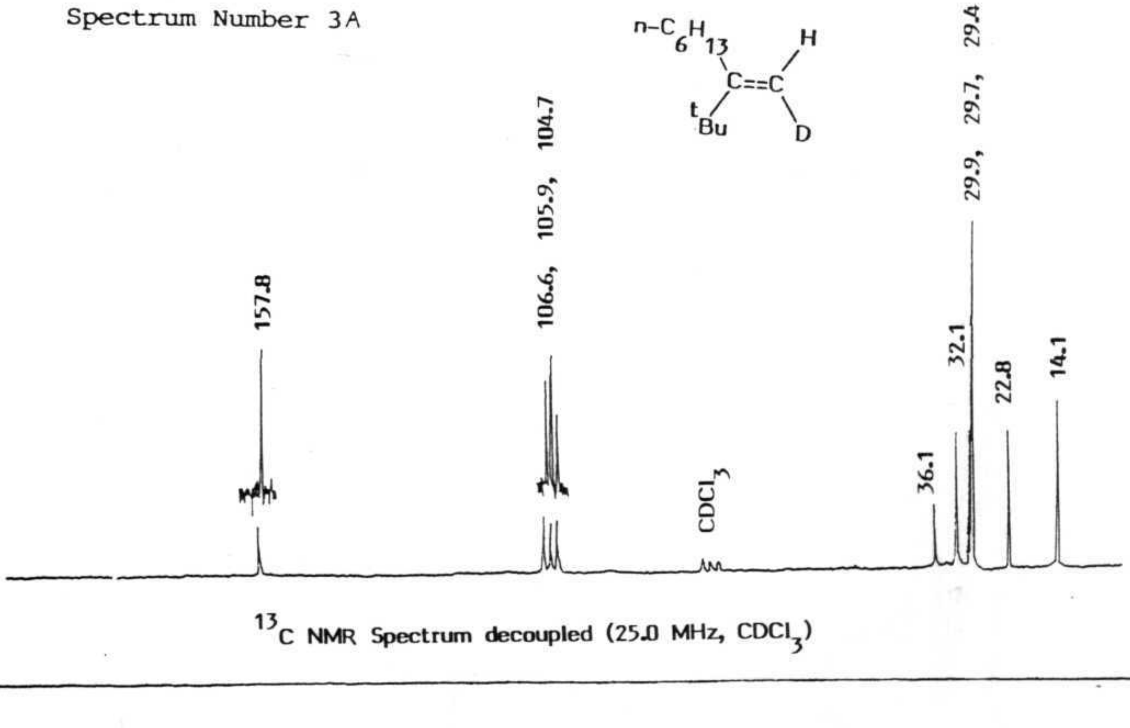

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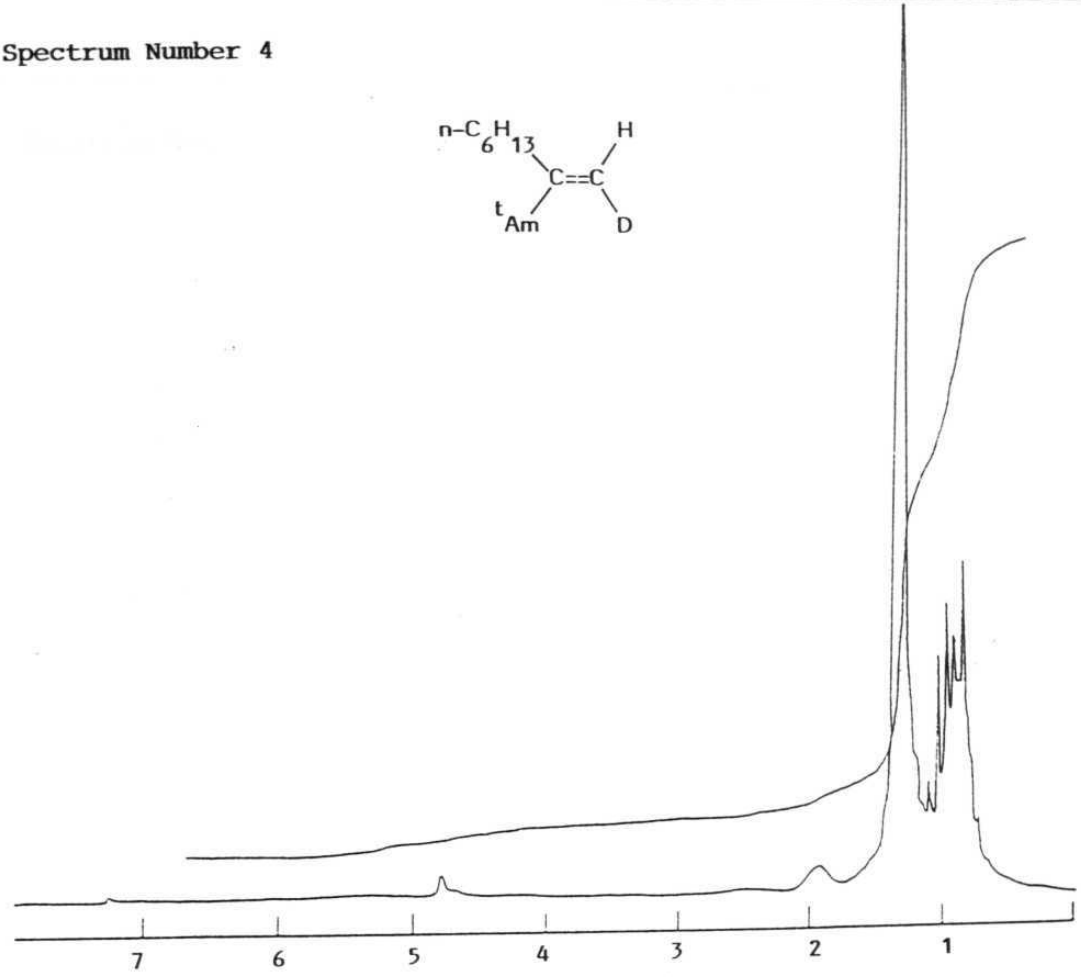

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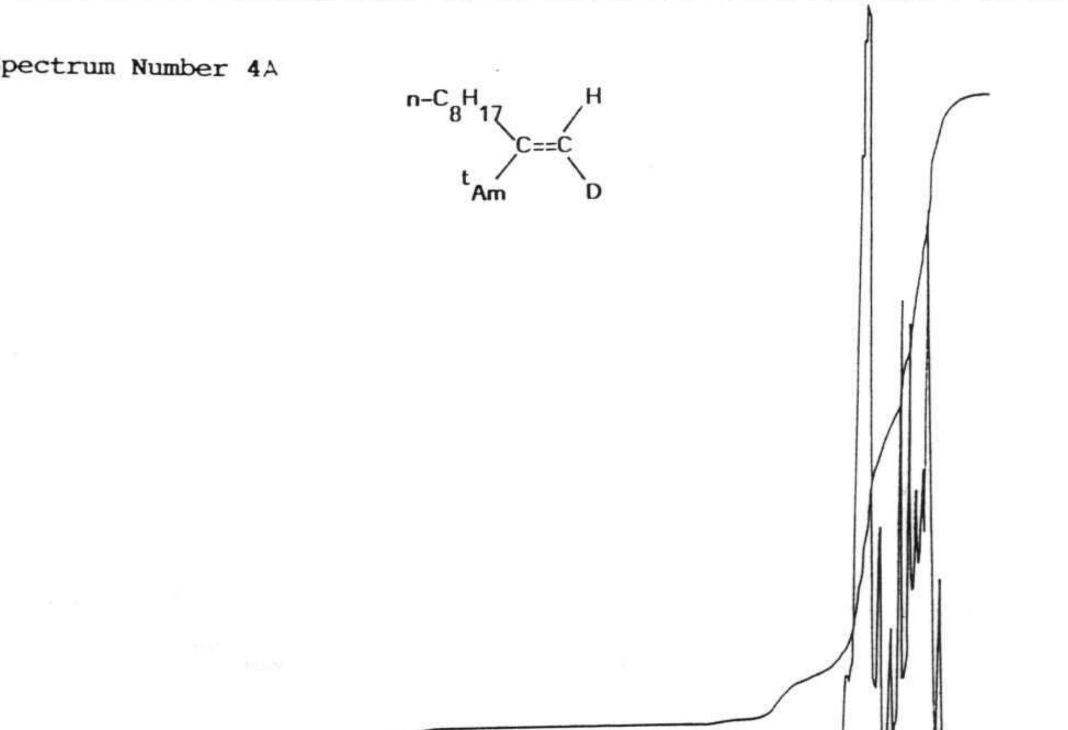

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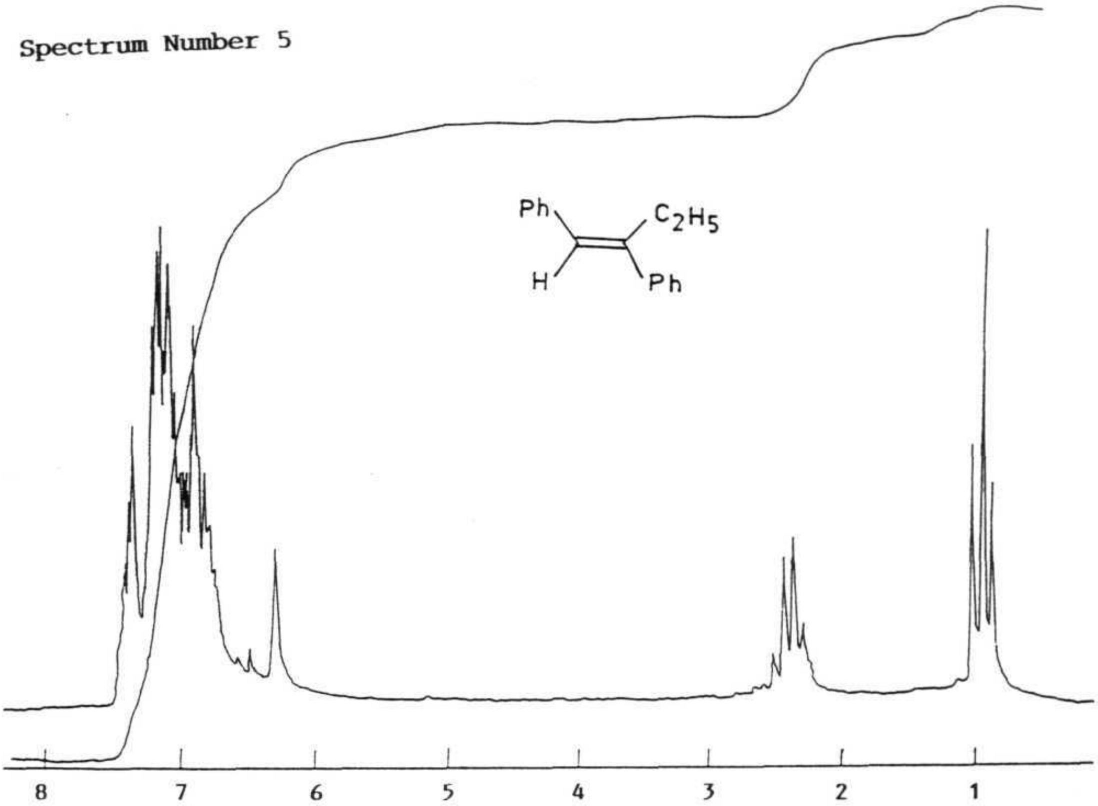

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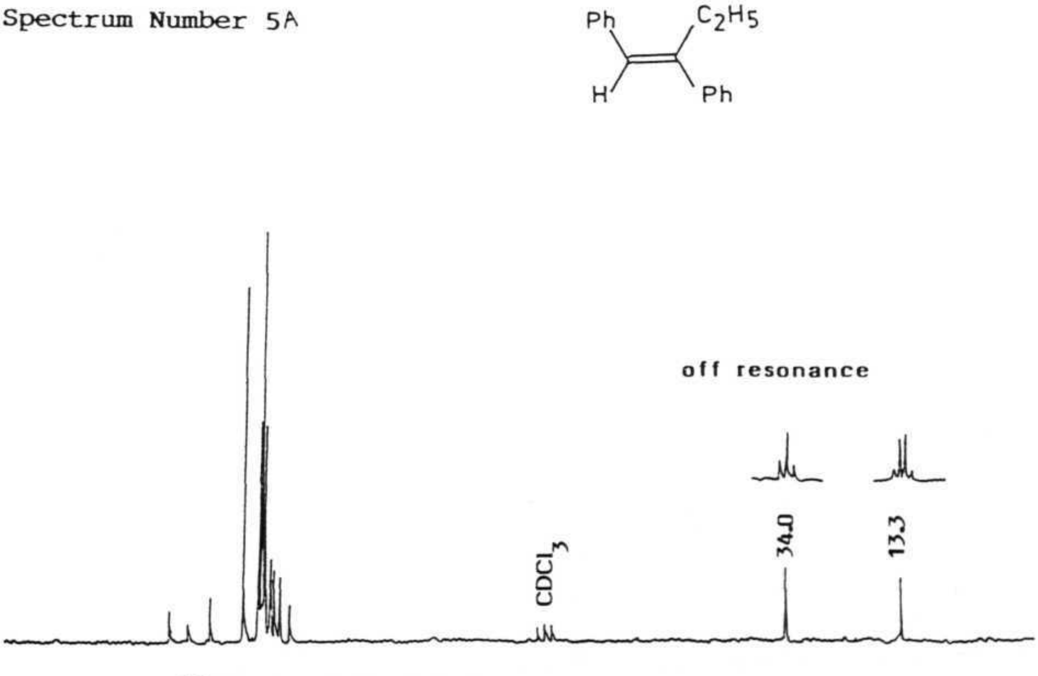

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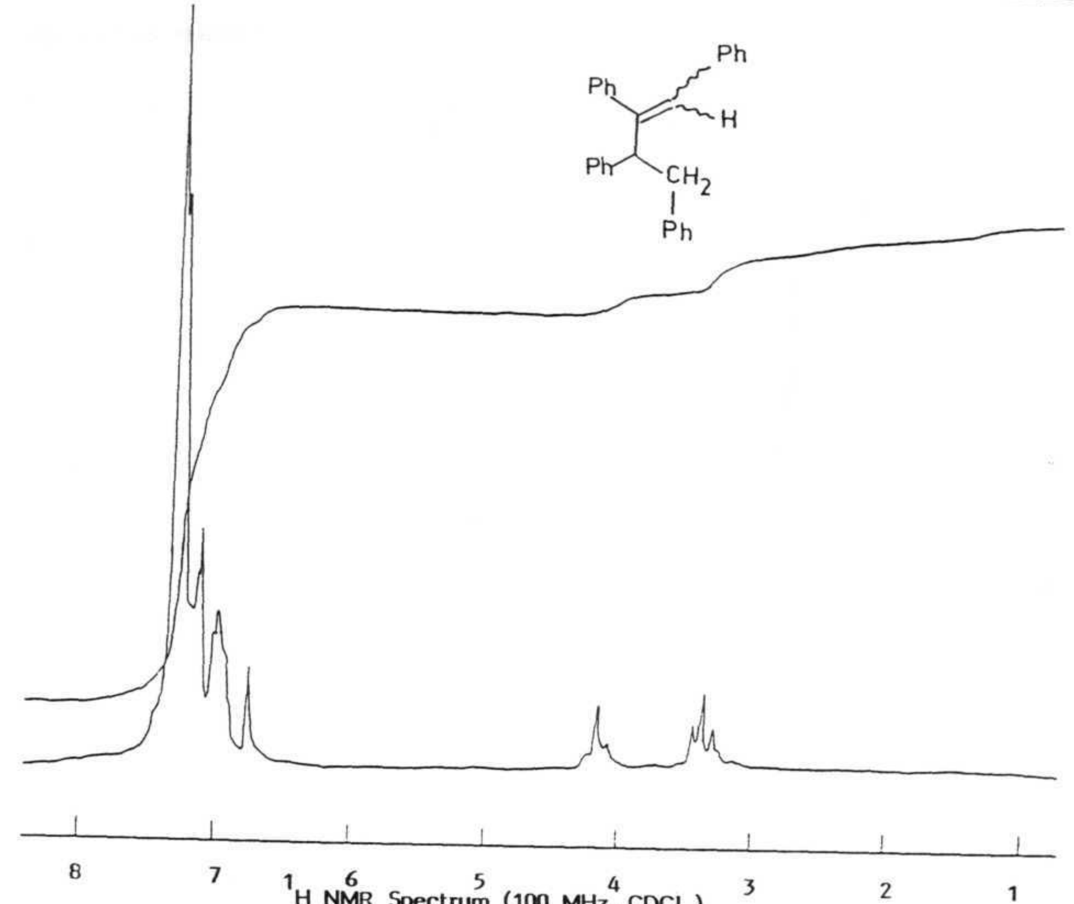

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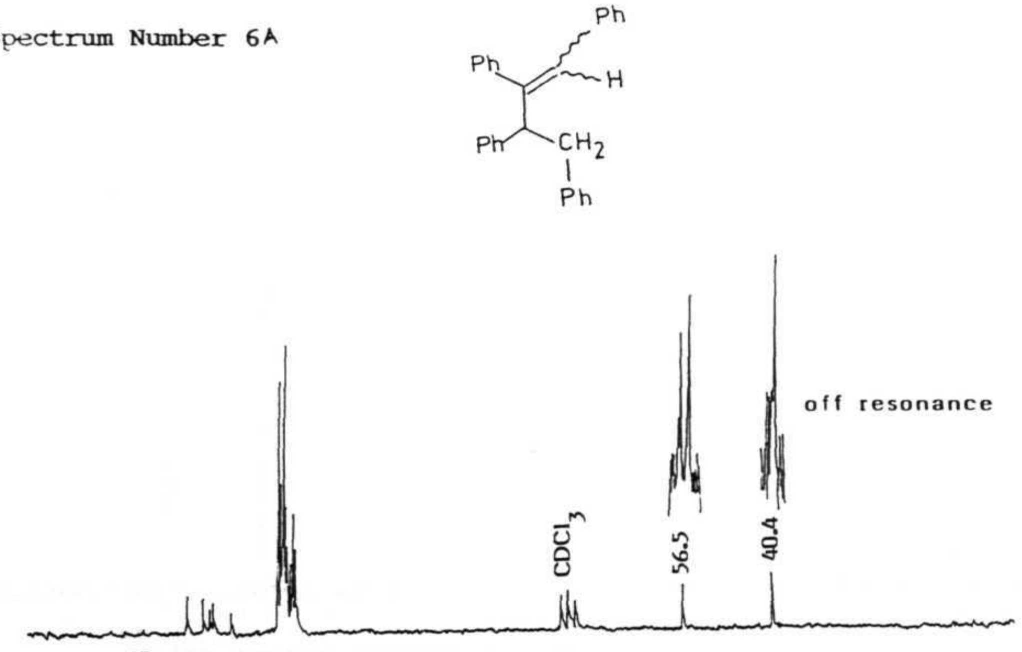

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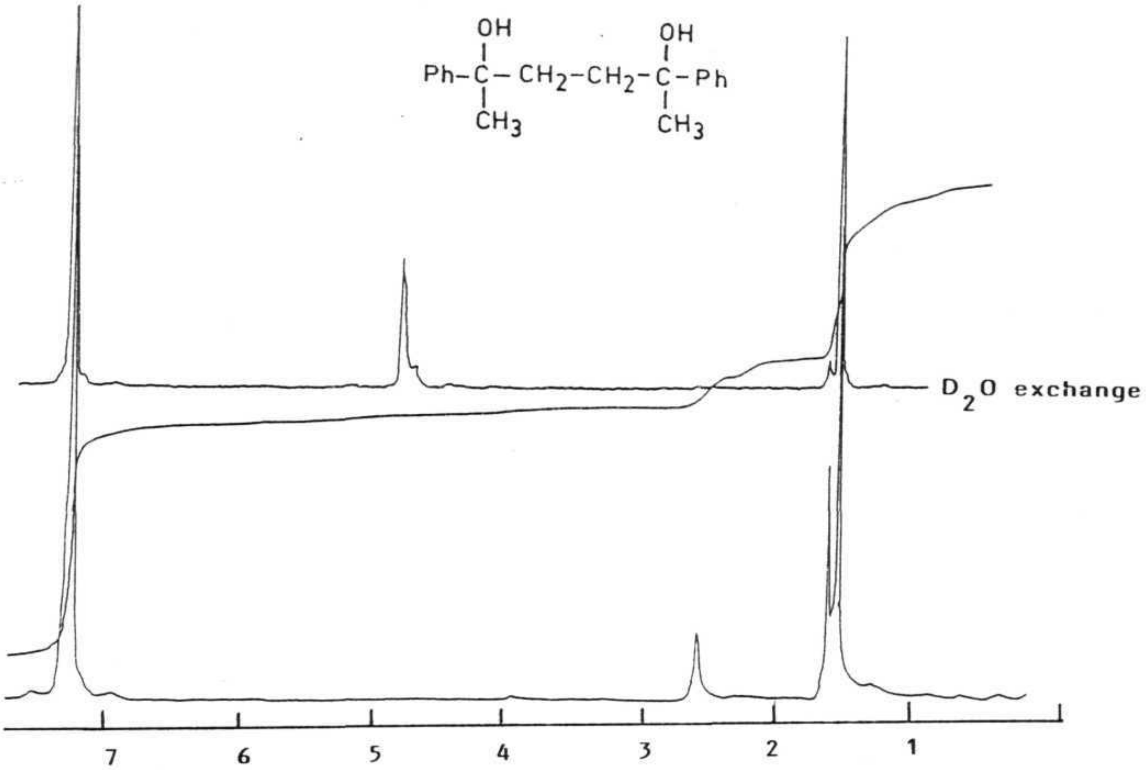

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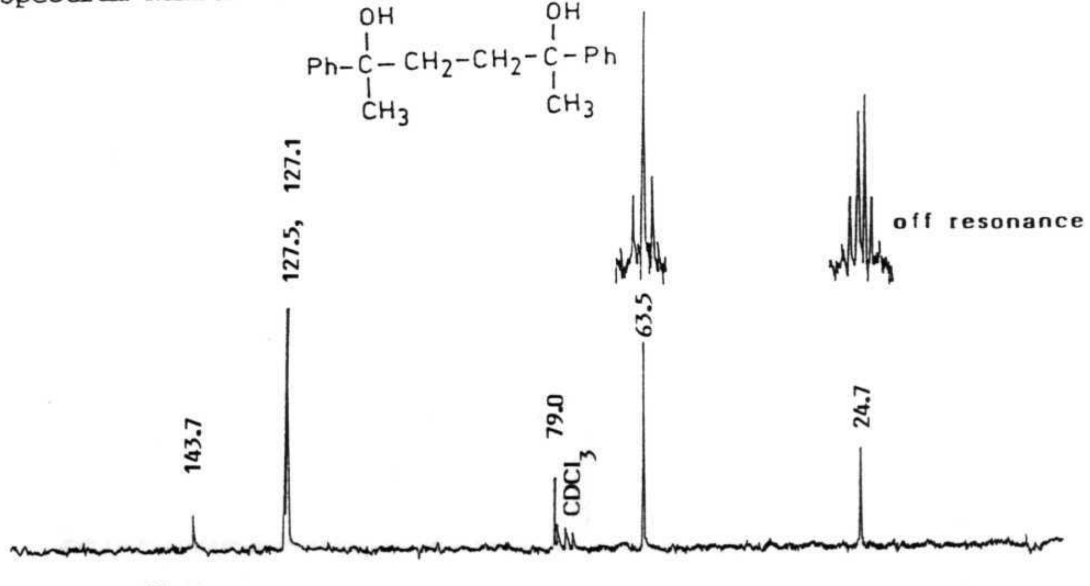

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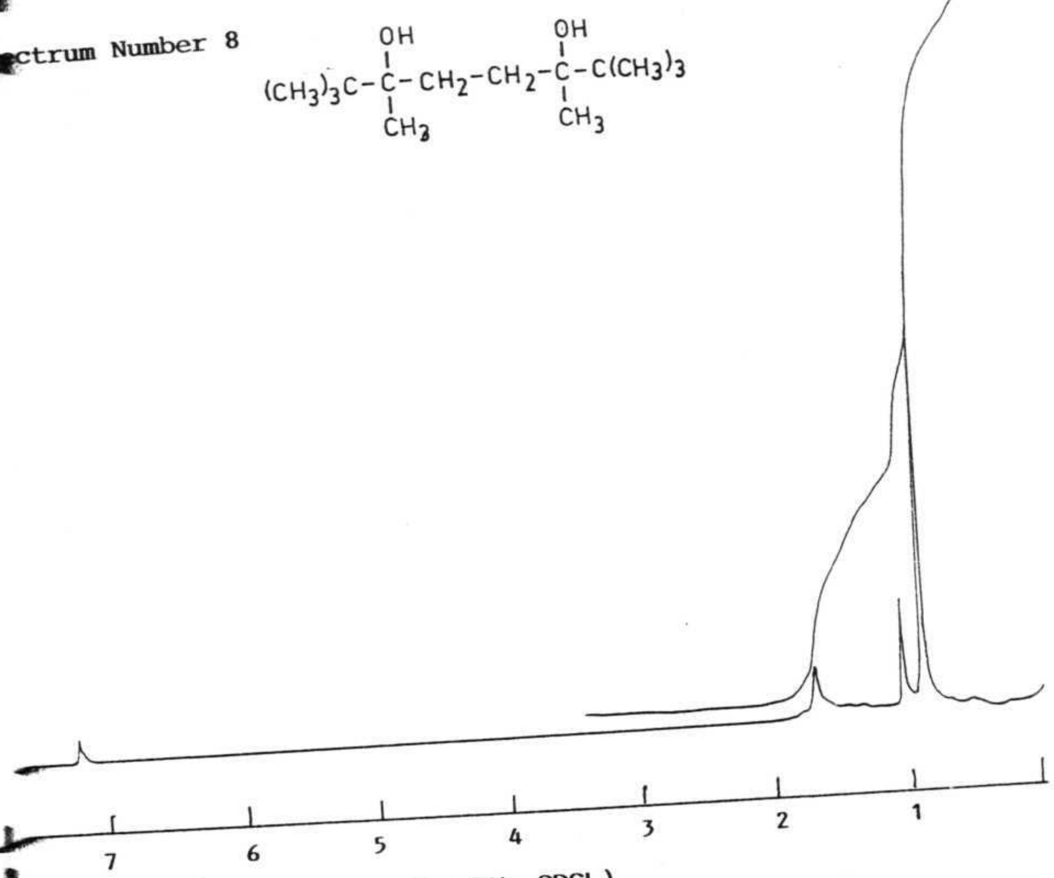
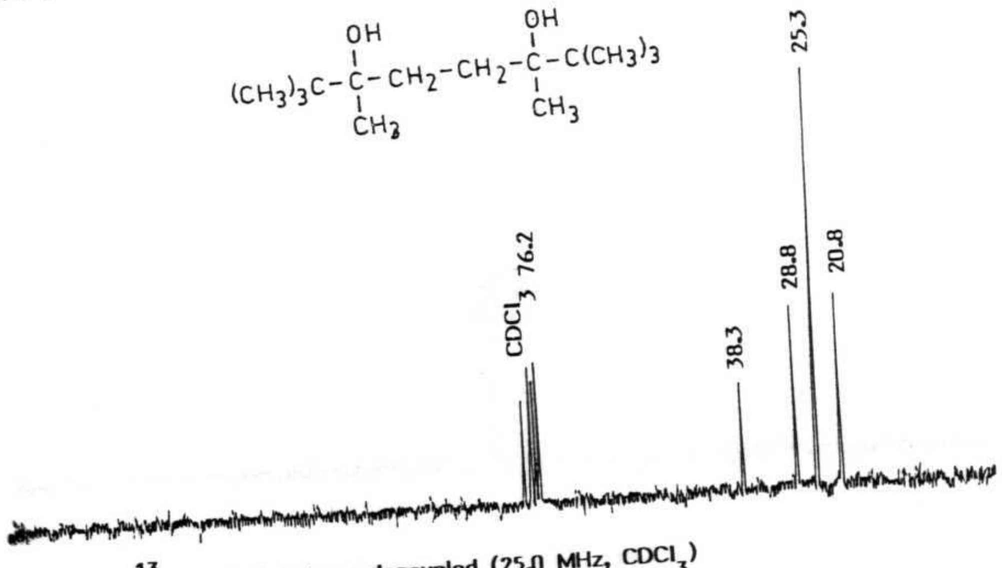
ctrum Number 8



$$(CH_3)_3C-\underset{CH_3}{\overset{OH}{C}}-CH_2-CH_2-\underset{CH_3}{\overset{OH}{C}}-C(CH_3)_3$$

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

trum Number 8A



$$(CH_3)_3C-\underset{CH_3}{\overset{OH}{C}}-CH_2-CH_2-\underset{CH_3}{\overset{OH}{C}}-C(CH_3)_3$$

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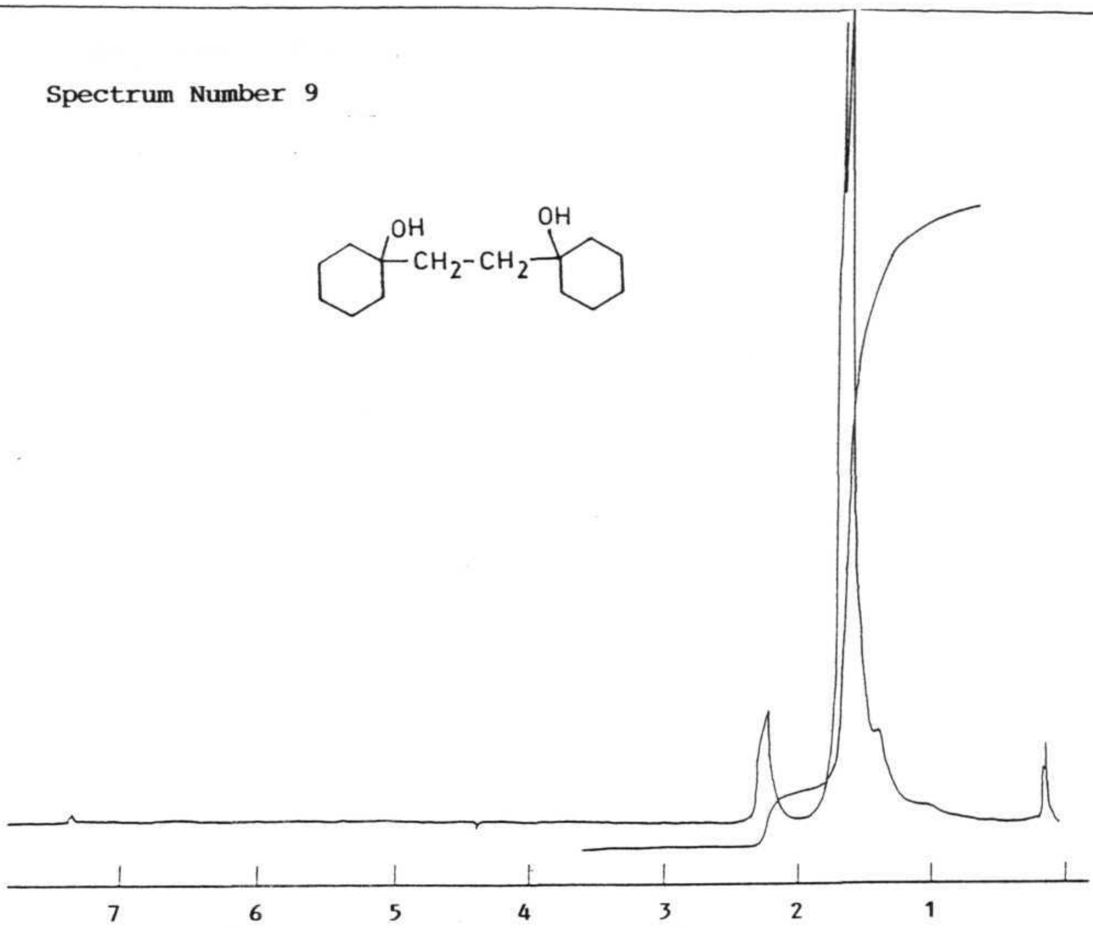
Spectrum Number 9



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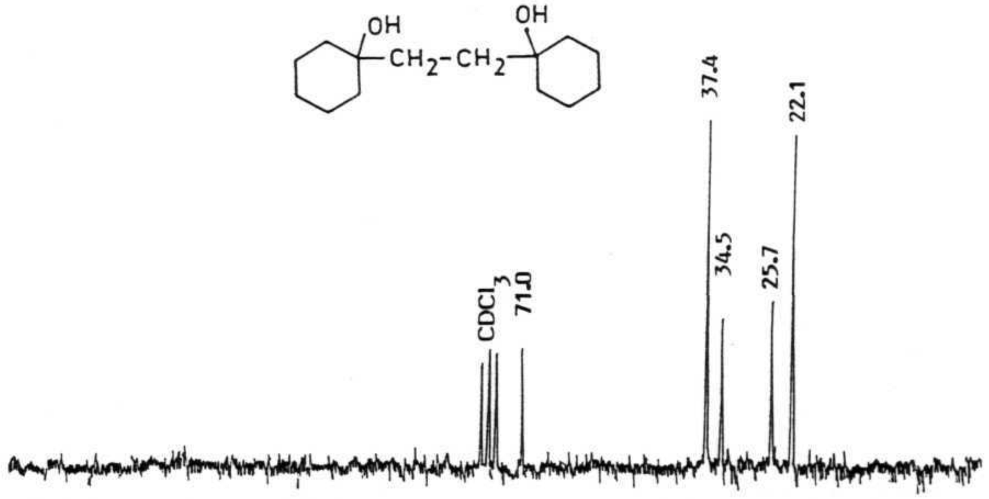
Spectrum Number 9A



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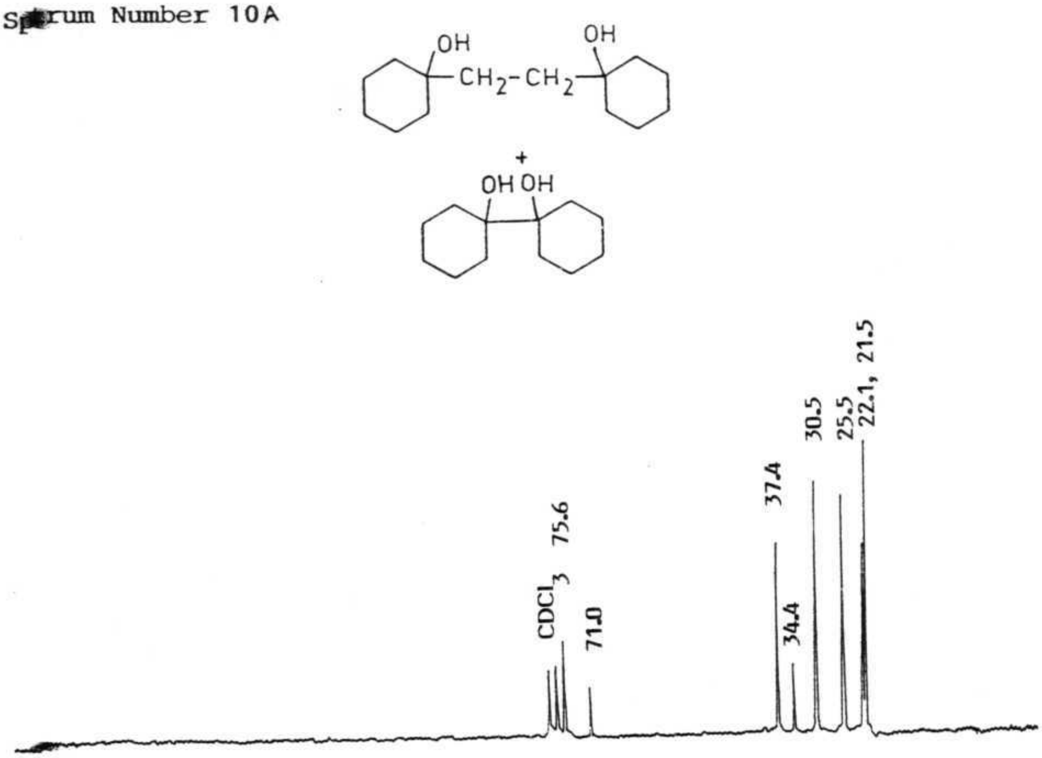

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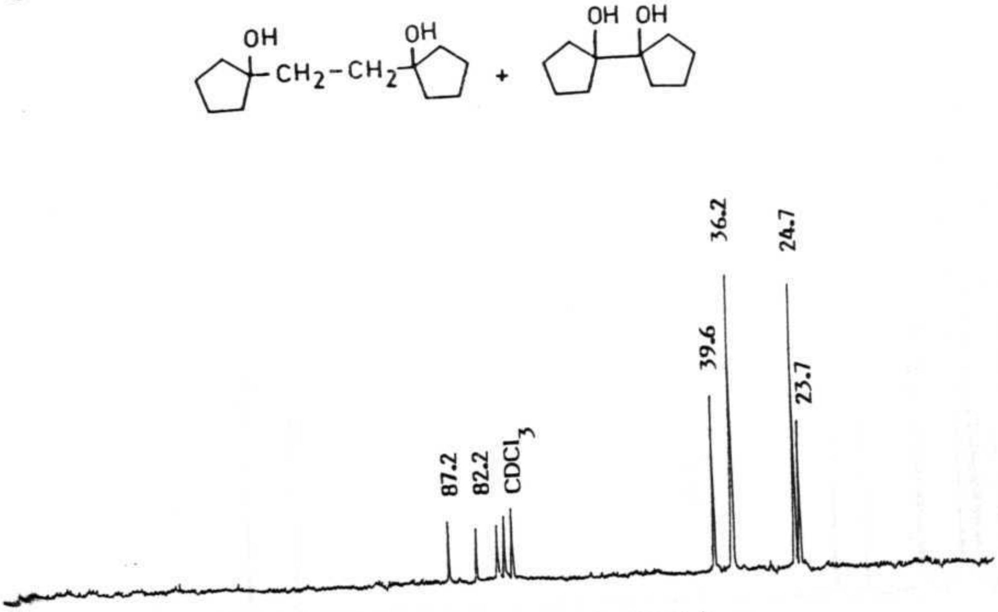

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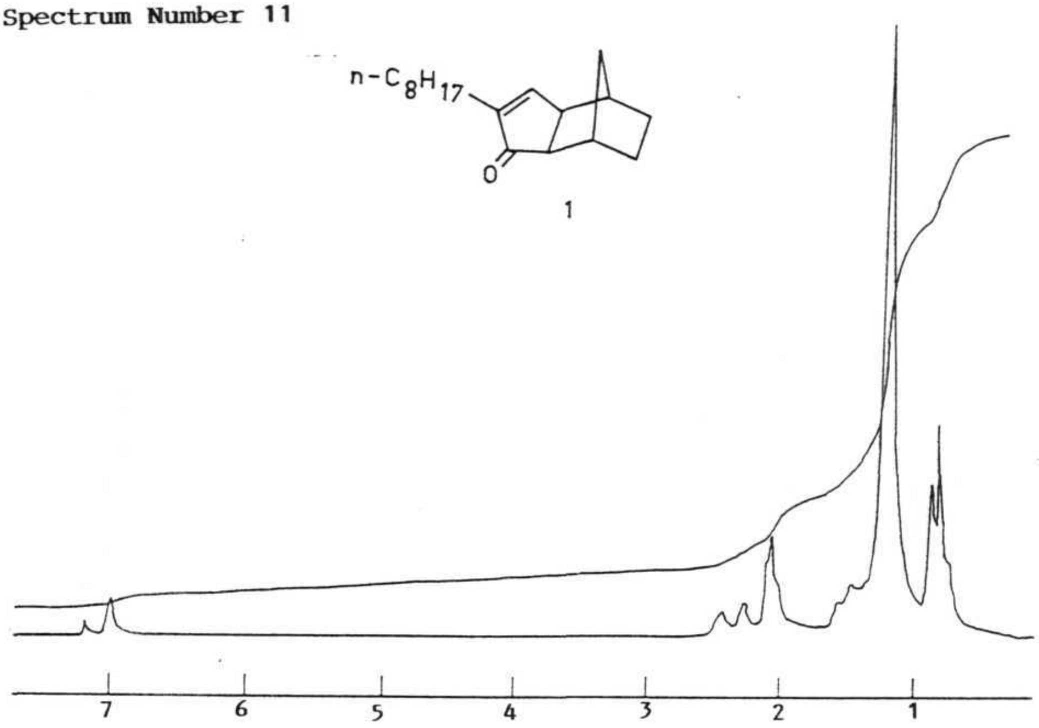

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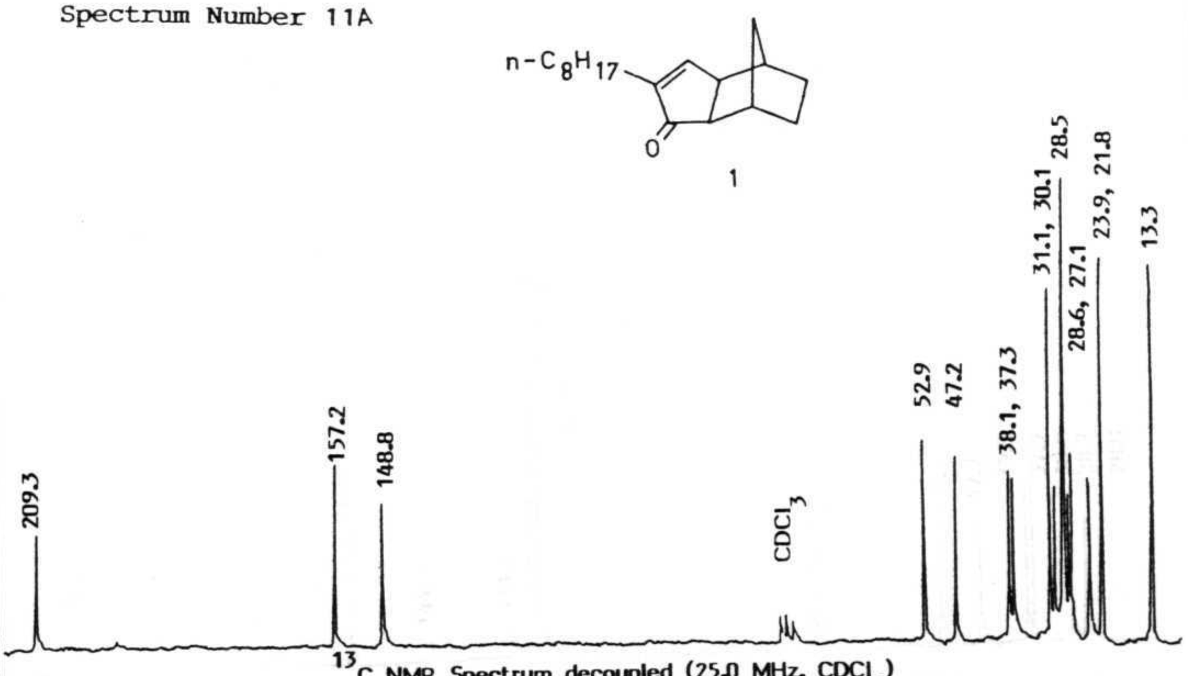

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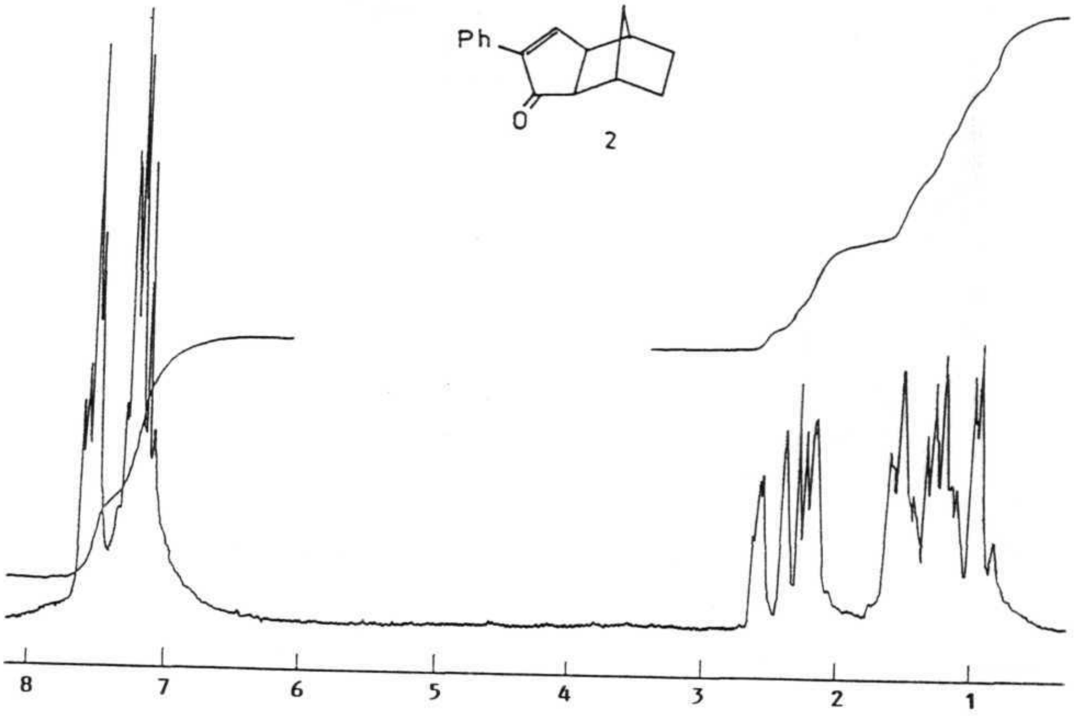

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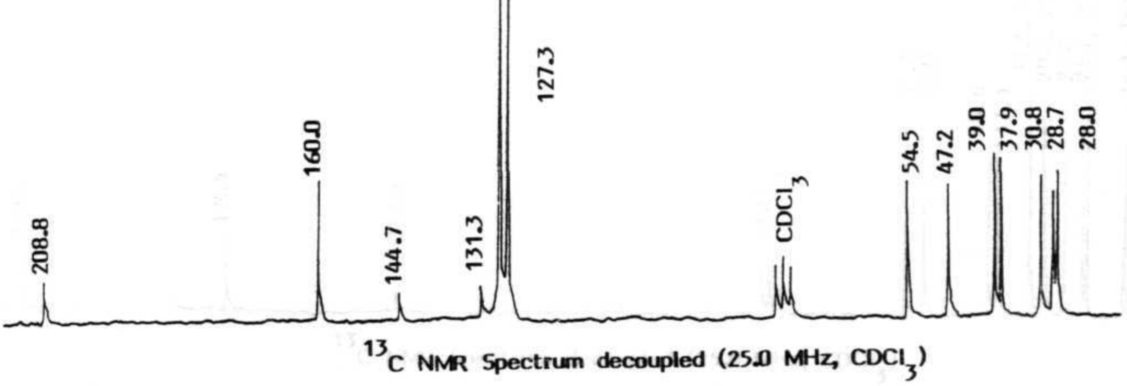

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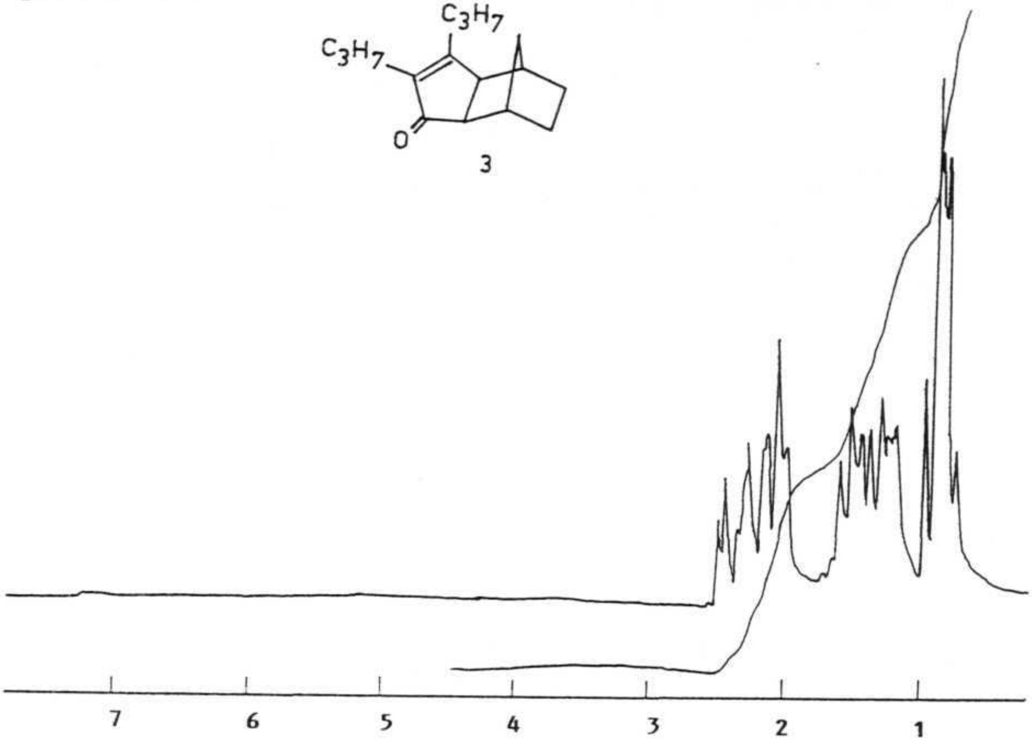
Spectrum Number 13

3



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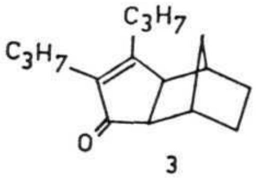
Spectrum Number 13A



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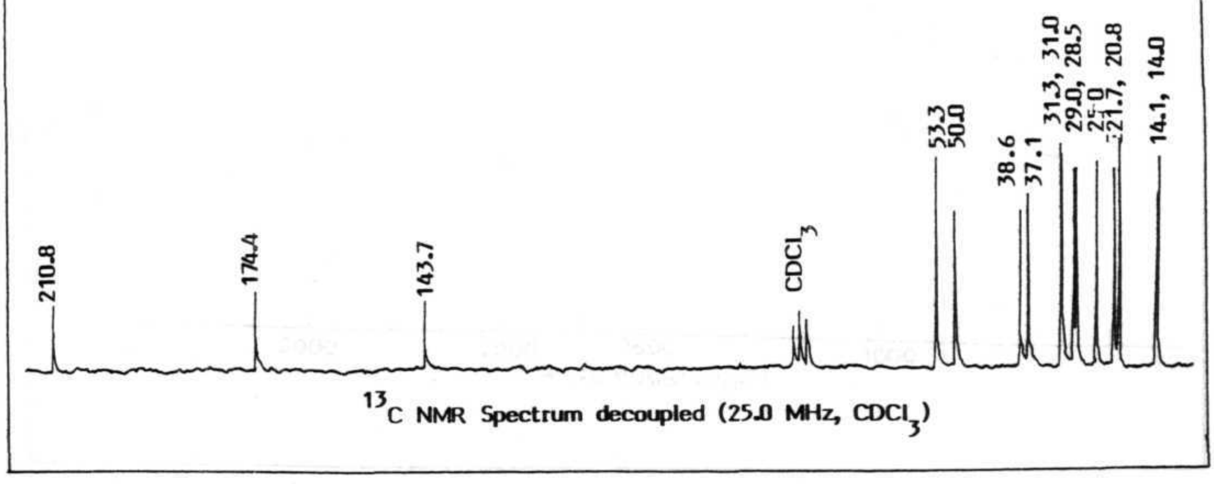

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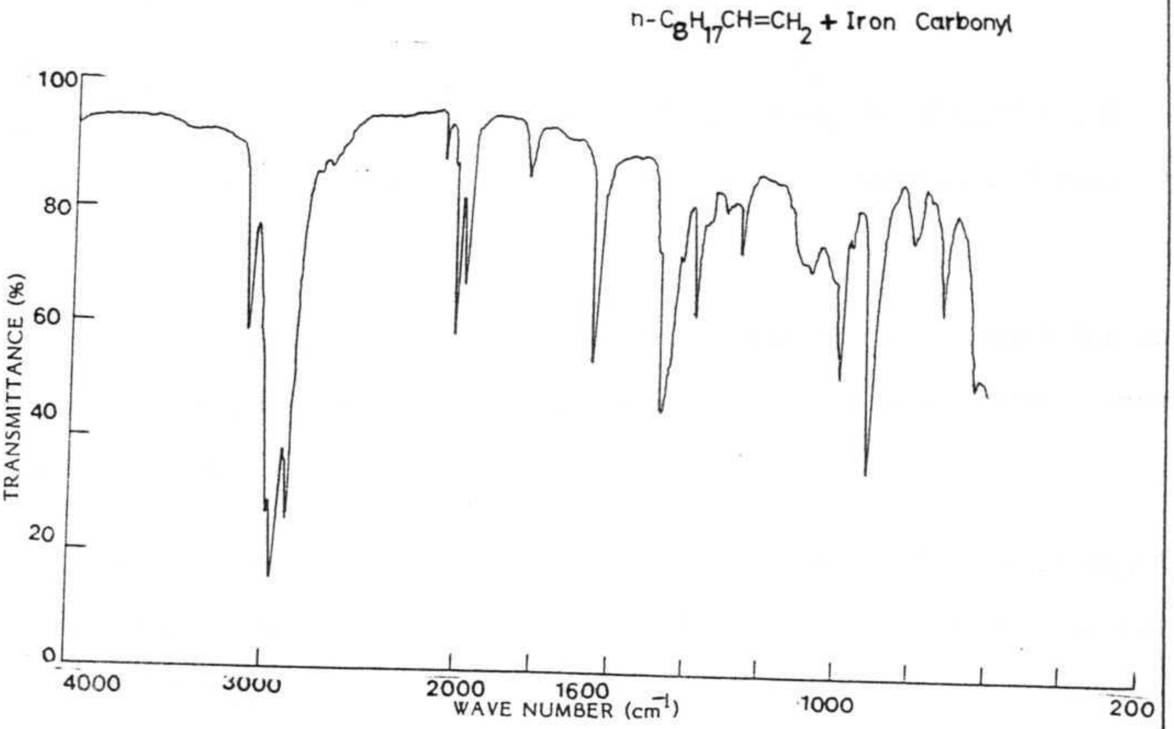

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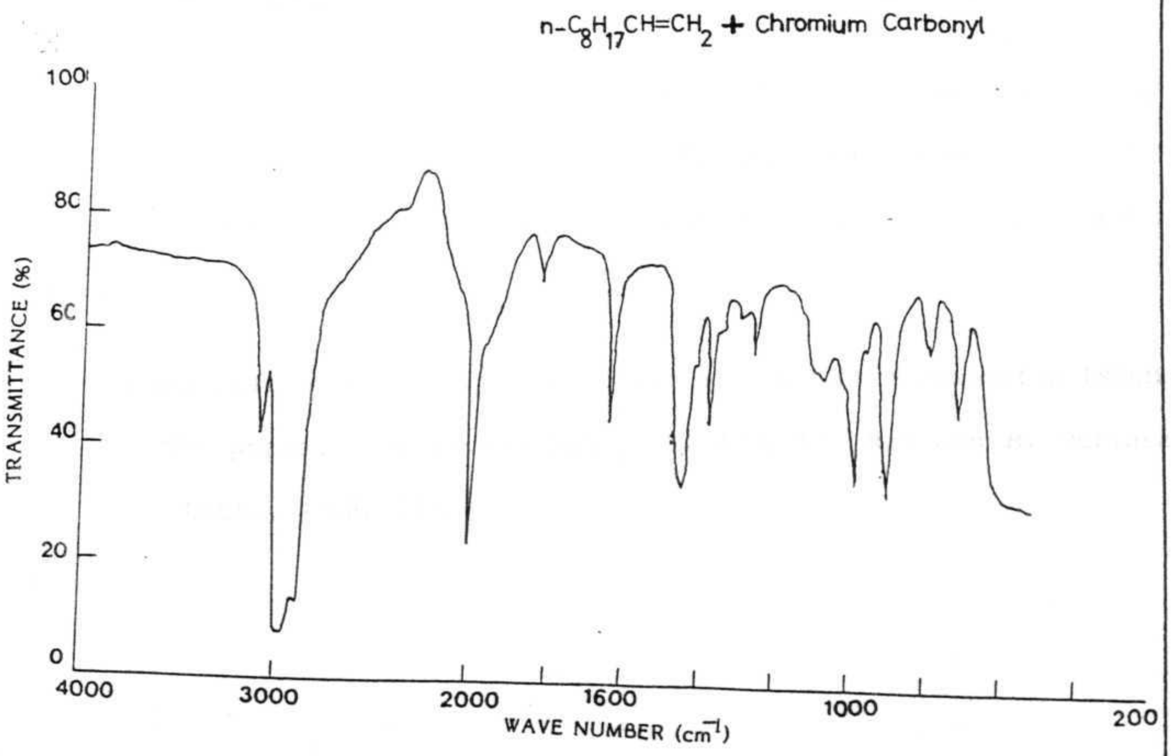

PUBLICATIONS

1. Copper(I) alkylborohydrides from alkenes using the CuCl/$NaBH_4$ reagent system. S. Achyutha Rao and M. Periasamy, J. Organomet. Chem., 1986, **309**, C39.

2. Hydrocupration of Alkynes: A Simple Synthesis of (E,E)-1,3-Dienes. S. Achyutha Rao and M. Periasamy, J. Chem. Soc., Chem. Commun., 1987, 495.

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