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To my son

NIMESH

ACKNOWLEDGEMENTS

Prof. H. Alper while supervising this research rendered expert guidance and great encouragement. I record my highest esteem and deep gratitude.

Acknowledgements are also made to the Government of Canada for a Commonwealth Scholarship. I also wish to thank the staff of the Department of Chemistry, University of Ottawa for their assistance. Special thanks go to Dr. J. Kraus and Mr. R. Capoor for recording the mass, ^{13}C and 100 MHz NMR spectra.

I am very grateful to my husband Wimal for his understanding and encouragement throughout this period, and to my parents and my aunt for all their help and support. I also wish to thank Miss Vinitha Aryaratne for typing this dissertation.

Ottawa, Canada — Shiyamalie Amaratunga

December, 1982

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ABBREVIATIONS

IR	-	Infrared
NMR	-	Nuclear Magnetic Resonance
Mp.	-	Melting point
Bp.	-	Boiling point
RT.	-	Room temperature
PTC	-	Phase transfer catalysis
SET	-	Single electron transfer
Aliquat 333	-	Tricaprylmethylammonium chloride
dipy	-	Dipyridyl
$AsPh_3$	-	Triphenylarsine

ABSTRACT

The considerable potential of phase transfer catalysis in stoichiometric and catalytic organometallic chemistry is described. Phase transfer catalyzed reactions of diene-iron tricarbonyl, triruthenium dodecacarbonyl and dicobalt octacarbonyl are reviewed followed by the description of the work carried out under homogeneous conditions.

Various reagents employed for carrying out different reactions are presented in three sections.

Complexation of the diene unit as a diene-iron tricarbonyl protects it from the addition of the phase transfer generated dibromocarbene. This enables the carbene to insert into a saturated carbon-hydrogen bond of the complex to give the dibromomethyl diene-iron tricarbonyl complex in reasonable yield. The latter is of importance as an intermediate in organic synthesis.

Phase transfer catalysis was also used to reduce nitro compounds to amines by a stoichiometric amount of triiron dodecacarbonyl. Substituting the iron complex by triruthenium dodecacarbonyl showed that only a catalytic amount of the metal catalyst was needed to give excellent yields of the amino compound in benzene and aqueous hydroxide with benzyltriethylammonium chloride as the phase transfer catalyst under an atmosphere of carbon monoxide. These conditions are significantly milder than those using water gas shift reaction conditions. Formamides were obtained when this reaction was carried out under homogeneous conditions using sodium methoxide instead of aqueous sodium

hydroxide in tetrahydrofuran under carbon monoxide.

The study of the phase transfer catalyzed reaction of acylcobalt tetracarbonyl on a carbon nitrogen double bond system proved to be interesting as it gave regioselective reductive acylation. Neither the carbonyl group (α-ketoimines) nor the carbon-carbon double bond was affected in these reactions. When the reaction was carried out under homogeneous conditions using sodium triethylborohydride to generate the cobalt tetrcarbonyl anion, the anticipated methyl amide was obtained as the major product but some ethyl amide was also present as a minor product. This indicated the unprecedented participation of the triethylborane which is a by-product in the generation of the cobalt tetracarbonyl anion. It was subsequently found that the presence of a catalytic amount of dicobalt octacarbonyl results in the reductive carbonylation and alkylation of Schiff bases by trialkyl and triarylboranes and carbon monoxide to give amides. This is the first example of an organoborane reaction catalyzed by metal carbonyl complexes.

C H A P T E R I

1. INTRODUCTION

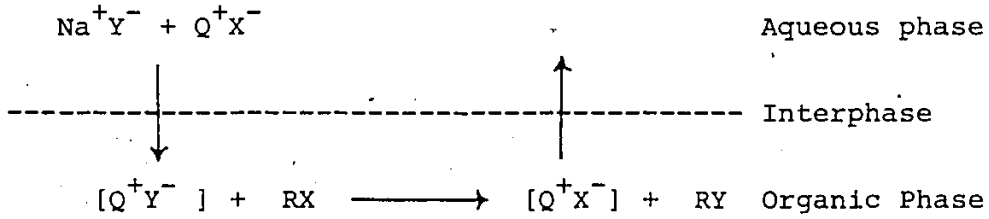
One of the fastest developing preparative methods in organic chemistry is phase transfer catalysis. During the past seventeen years it has become a widely used and versatile method for organic synthesis. In these reactions substances located partly in the aqueous and partly in the organic phase are made to react with the help of phase transfer catalysts such as ammonium or phosphonium salts or crown ethers.

An attractive feature of phase transfer catalysis is the ability to carry out reactions at low temperature, low pressure and with short reaction times. This method also saves on expensive anhydrous aprotic solvents and the much cheaper and easy to handle aqueous sodium hydroxide is used instead of alkali metal alkoxides.

The workup of these reactions is much simpler and the selectivity as well as the product ratio can be modified. Yields are also improved with the suppression of side reactions.

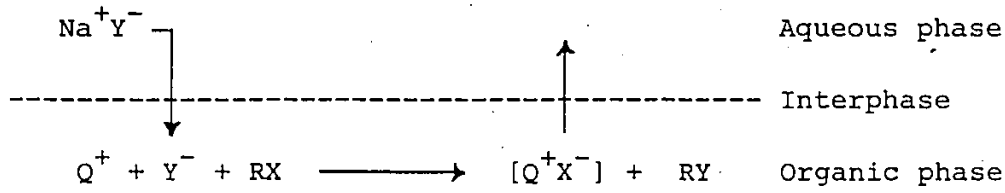
Reactions have also been discovered in phase transfer mediated processes which do not otherwise occur.

Consider the nucleophilic displacement reaction depicted in Scheme 1. Q^+ is an ammonium or phosphonium salt cation and Y^- is assumed to be more lipophilic than X^-. The catalyst cation Q^+ migrates with the anion Y^- from the aqueous phase into the organic phase where the weakly solvated ion pair undergoes rapid subsequent reaction, after which Q^+ returns to the aqueous phase with the anion X^{-1}.



Scheme 1

When highly lipophilic catalyst cations are used, this scheme has to be modified in order to account for the fact that the cation will remain in the organic phase whereas the anion can exist in both phases, as shown in Scheme 2[2].



Scheme 2

The principle function of crown ethers in liquid-solid phase transfer catalysis is to bind the cation of a salt thereby solubilizing the salt in the liquid phase and enhancing the nucleophilicity of the anion. Mechanistically in Scheme 1, Q^+ could be considered as an alkali metal cation complexed with a crown ether.[3]

1.2. Phase transfer catalyzed organic reactions.

1.2.1. Simple displacement reactions.

Anions such as cyanides, halides, alkoxides, thiophenoxides, carboxylates, azides and thiocyanates function well under both liquid-liquid and liquid-solid phase transfer conditions. These anions are transported to the organic phase by common phase transfer agents and once there, behave as potent nucleophilic species in a wide variety of displacement reactions. Simple displacement by this technique generally follows the behaviour expected for S_N2 reactions. Relative displacement reactivity of alkyl halides follows the usual order of primary > α-branched primary > secondary > tertiary, cyclohexyl. The relative order of $R\text{-}OSO_2CH_3$ > R-Br > R-Cl is also followed in these phase transfer catalyzed substitution reactions.[4]

1.2.2. Alkylation and condensation reactions.

Phase transfer catalyzed and related techniques allow much experimental simplification for a variety of alkylation, arylation and condensation reactions as compared to classical methods for these reactions. This technique, first demonstrated by Jarrouse[5] and extensively developed by Makosza[6], is useful for most types of alkylation except those with simple esters or other easily hydrolyzed functional groups. In the absence of an aqueous phase as in solid-liquid phase transfer conditions hydrolysis could be completely eliminated. A typical reaction is shown below.[6a]

$$C_6H_5CH_2CN + CH_3CH_2Cl + NaOH \xrightarrow[\text{or crown either}]{PhCH_2(C_2H_5)_3N^+Cl^-} C_6H_5-\underset{\displaystyle CH_2CH_3}{\overset{\displaystyle |}{CH}}-CN + NaCl$$

The second technique, known as ion pair extraction is useful for all types of alkylation reactions including esters. It involves several steps and requires a full molar quantity of quaternary ammonium bisulfate rather than a catalytic amount. The reactions are shown below.

$$(C_4H_9)_4N^+HSO_4^- + NaOH \longrightarrow (C_4H_9)_4N^+OH^- + NaHSO_4$$

aq. org/aq. aq.

$$(C_4H_9)_4N^+OH^- + CH_2(COOEt)_2 \longrightarrow (C_4H_9)_4N^+CH^-(COOEt)_2 + H_2O$$

aq/org. CH_2Cl_2, Sol. org.

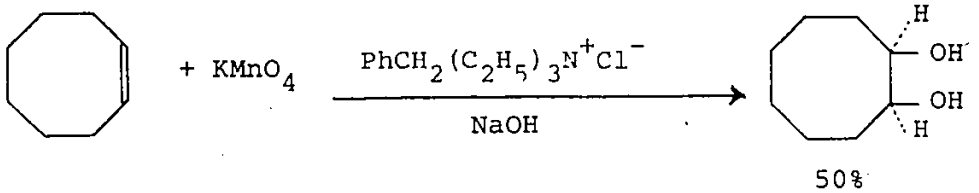
$$(C_4H_9)_4N^+CH^-(COOEt)_2 + RX \longrightarrow RCH(COOEt)_2 + (C_4H_9)_4N^+X^-$$

org. org. org. aq.

Chiral phase transfer catalysis can be used to produce optically active alkylation products as demonstrated by Fiaud in the alkylation of β - keto esters.[8]

1.2.3. Oxidation and reduction reactions.

Conventional oxidation techniques for many organic compounds with permanganate salts are experimentally difficult. Results obtained by phase transfer catalyzed permanganate oxidations are usually superior to those obtained using classical methods. This technique is also useful for analytical purposes, e.g. the titration of reducible substances. Under alkaline conditions Weber and Shepherd[9] obtained good yields of cis 1,2-cyclooctane diol from cyclooctene.



50%

Only 7% yield is obtained by the classical method.[10]

Chromate has also been tested under phase transfer methods.[11-18] It has been shown that $HCrO_4^-$ and $HCr_2O_7^-$ are readily phase transferred so long as the aqueous phase is acidic; but almost no transfer occurs from alkaline aqueous solutions. Lee and Freedman[19] have demonstrated that hypochlorite anions can be transferred into organic solutions by quaternary cations.

Quaternary ammonium salts or trialkyl amines function very effectively as phase transfer catalysts for heterogeneous osmium catalyzed olefin oxidations with periodic acids.[20]

Other metal complexes such as potassium ferricyanide can also be used as oxidants in phase transfer catalyzed reactions.[21] Air oxidation of carbanions also takes place in the presence of quaternary ammonium or phosphonium salts.[22]

Colonna and Fornasier have found that quaternary ammonium salts containing a hydroxyl group on the β-carbon are superior catalysts for borohydride reduction.[23] Asymmetric induction during phase transfer catalyzed reduction of ketones, using catalysts based on ephedrine, was reported almost simultaneously by Balcelle, Colonna and Fornasier[24] and by Masse and Povayre.[25]

1.2.4 Ylid mediated reaction.

Markl and Merz[26] demonstrated that alkyltriphenyl phosphonium salts react with aqueous sodium hydroxide to generate ylids, which are then capable of combining with aldehydes in the organic phase to produce olefins.

$$(C_6H_5)_3P^+-CH_2C_6H_5\ Cl^- + NaOH\ aq \xrightarrow{CH_2Cl_2}$$

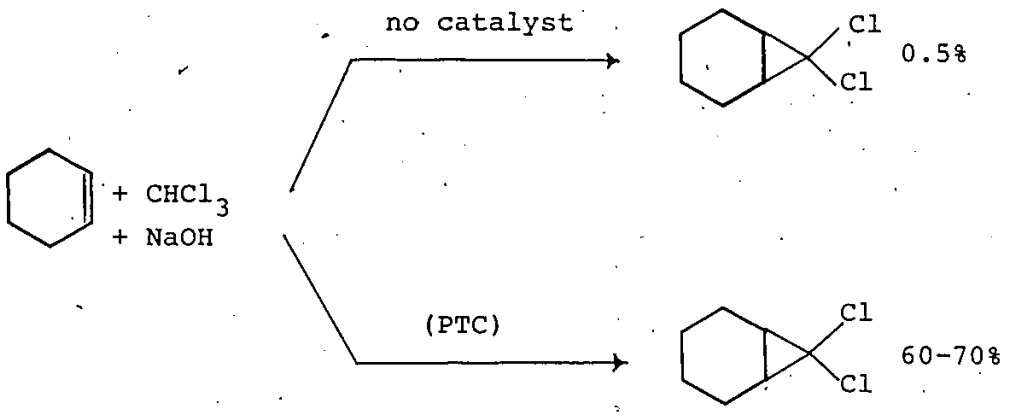
$$[(C_6H_5)_3P=CH\,C_6H_5 \xrightarrow{RCHO} RCH=CHC_6H_5 + (C_6H_5)_3\,PO$$

This two phase Wittig reaction with sodium hydroxide is limited to aldehydes. No olefin was obtained from acetophenone, and only traces were detected from reactions with cyclohexanone and 2-hexanone.[27] In spite of this limitation this method is exceptionally convenient and useful for the preparation of a variety of olefins having the RCH=CHR structure.

1.2.5. Generation and reactions of dihalocarbenes and other carbenes.

The formation of dihalocarbene is one of the most useful phase transfer processes developed in organic chemistry. Addition of chloroform to a mixture of cyclohexene and aqueous 25% sodium hydroxide gives less than 0.5% yield of the addition product.[28] However, by use of a phase

transfer catalyst such as tridecylmethylammonium chloride[29,30] or benzyltriethylammonium chloride[31] the addition product is obtained in 60-70% yields.

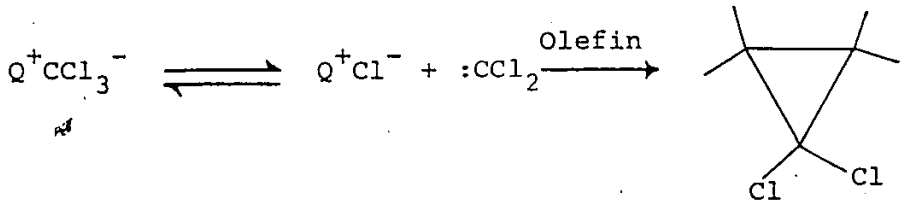


In the absence of quaternary salts the CCl_3^- anion intermediate is generated in the aqueous phase or at the interphase where its reaction with water is faster than that with cyclohexene.

Makoza and Wawrzyniewicz[31] formulated the mechanism as the reaction of $CHCl_3$ with OH^- at the interphase by the quaternary cation.

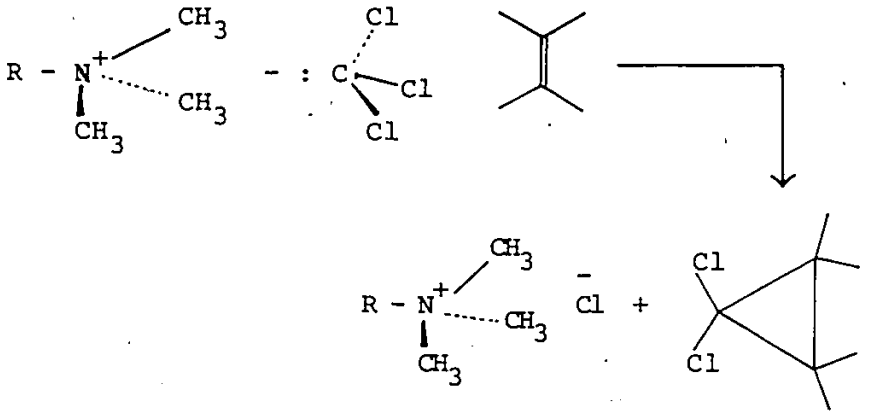
$$HCCl_3 + OH^- \longrightarrow CCl_3^- + H_2O \xrightarrow{Q^+} Q^+CCl_3^- \longrightarrow \text{Org.phase}$$

Association with Q^+ allows CCl_3^- to be distributed in the organic phase before it decomposes to dichlorocarbene.

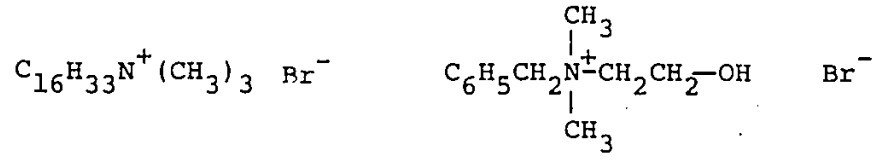


Of particular interest in phase transfer catalyzed dicholorocarbene reactions are the effects of the catalyst structure. Catalysts such as $Et_4N^+Br^-$ and $C_{16}H_{33}N^+(CH_3)_3Br^-$ which are very poor catalysts for displacement reactions are among the best for $:CCl_2$ reactions.[32] Trialkyl sulfonium salts have also been found to be exceptionally good catalysts for dichlorocyclopropanation[33]; but are poor catalysts for displacement reactions. These facts suggest that the formation of tight ion pairs $Q^+CCl_3^-$ is desirable in $:CCl_2$ reactions where an intramolecular decomposition is a critical step. This is in contrast to displacement reactions where large interion distances, $Q^+ \longleftrightarrow X^-$ favour lower activation energies for the intermolecular reaction. Steric factors may also be important since cations such as $R\text{-}N^+(CH_3)_3$ present minimum resistance to approach by the CCl_3^- anion; a

factor of multiple importance if the olefin must also be accommodated in the transition state; as shown below.

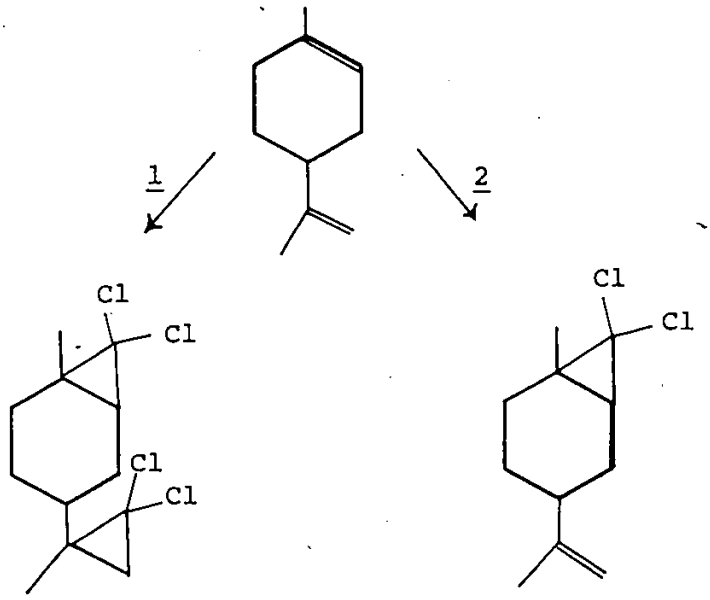


The foregoing facts do not explain the high reactivity and selectivity observed with β-hydroxyethyl substituted quaternary salts as catalysts for dichlorocyclopropanation. Hyama and coworkers[34,35,36] compared the activity of catalyst 1 and 2.



(1) (2)

They found that 2 is markedly more selective than 1.

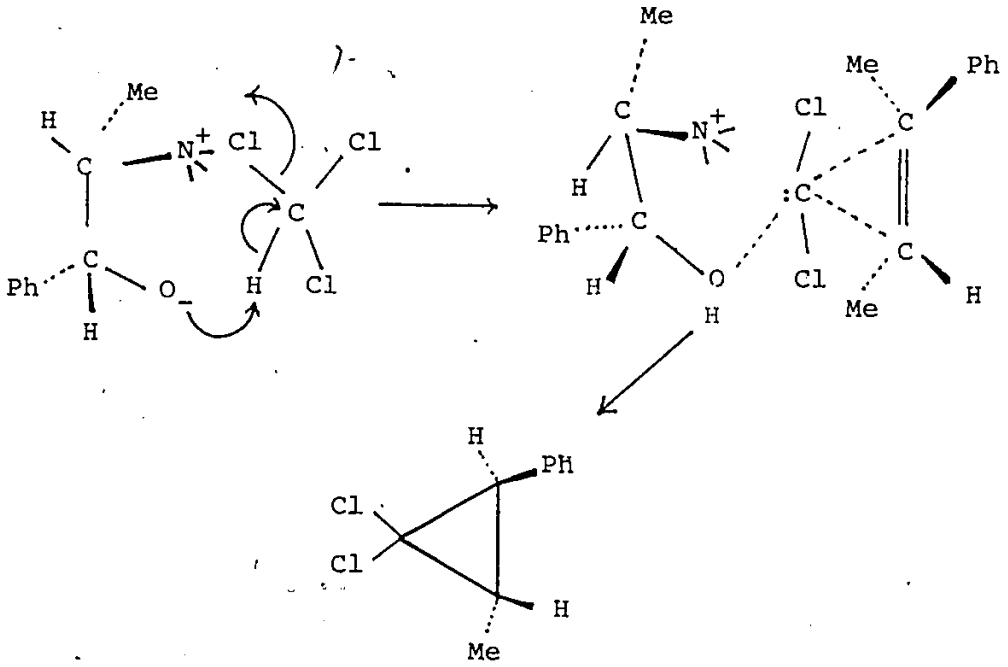


The high effectiveness of the β-hydroxyethyl substituted catalyst is thought to be due to its conversion, at the interphase or in the aqueous phase to a zwitterion[36] which is then transferred to the organic phase with ease.

$$R_3N^+CH_2CH_2OH\ X^- + NaOH \rightleftharpoons R_3N^+CH_2CH_2O^- + NaX$$

Proton abstraction from haloform and loss of Cl^-, taking place entirely within the organic phase, are thought to produce a dihalocarbene which is loosely associated with

the hydroxyl group of the catalyst, and which attacks the C=C double bonds slowly but with increased selectivity.

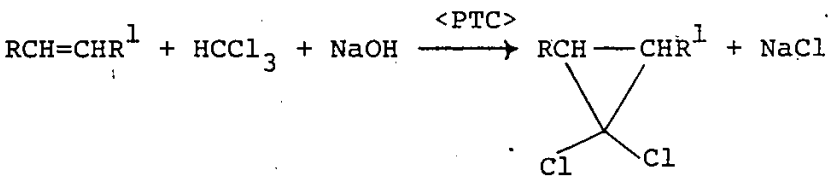


It is not only quaternary salts thathave been shown to be strong phase transfer catalysts for the generation of synthetically useful dichlorocarbene, but also trialkylamines[37] and crown ethers[38-41] have been demonstrated to be equally good.

Utilization of the phase transfer catalyzed generation of dichlorocarbene has been tested for a variety of synthetic purposes. These include addition of $:CCl_2$ to C=C and C=N bonds, insertion into CH and NH bonds, reaction with primary amines to yield isocyanides, and reaction with alcohols. The Seyferth reagent for generation of dichlorocarbene, $C_6H_5HgCCl_3$ may be easily generated by a

phase transfer catalyzed reaction described by Fedorynski and Makosza.[42]

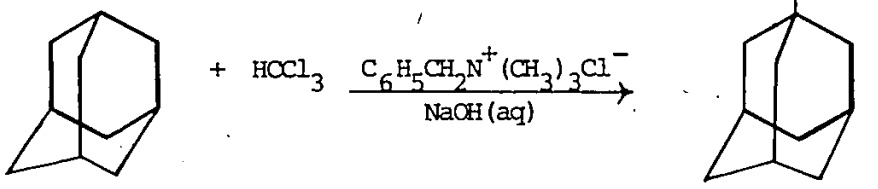
Compared to conventional procedures[43] for the generation of dihalocarbenes, the phase transfer catalyzed method for preparation of 1,1-dihalocyclopropanes is extremely simple.



$$RCH{=}CHR^1 + HCCl_3 + NaOH \xrightarrow{\langle PTC \rangle} RCH\text{—}CHR^1 + NaCl$$

(Cl, Cl)

It has also been shown that $:CBr_2$ is more electrophilic and reactive than $:CCl_2$.[60] Dihalocarbenes generated by the phase transfer catalysis technique undergo insertion reactions into C-H bonds with a limited number of compounds.[44-49] Adamantane and ethers are the most active substrates.

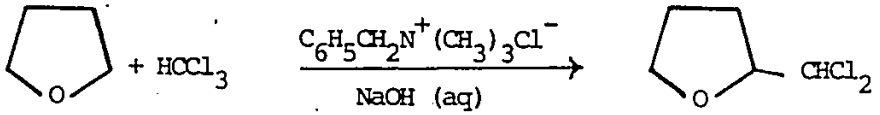


$$+ HCCl_3 \xrightarrow[NaOH(aq)]{C_6H_5CH_2N^+(CH_3)_3Cl^-}$$

$CHCl_2$

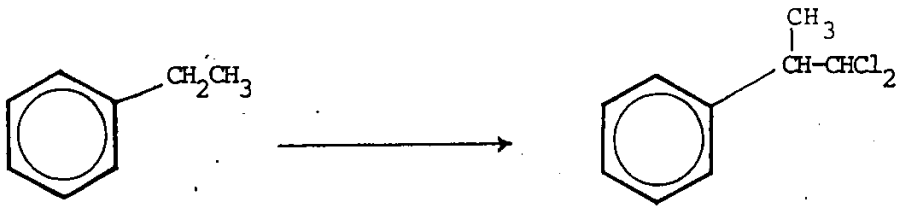
ref.

54 & 47



ref. 18 & 38, 45

Other reactions that give fairly good yields are,



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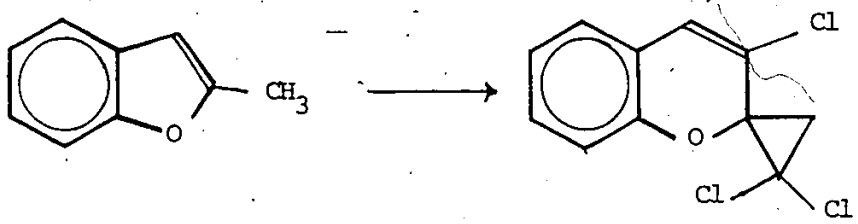
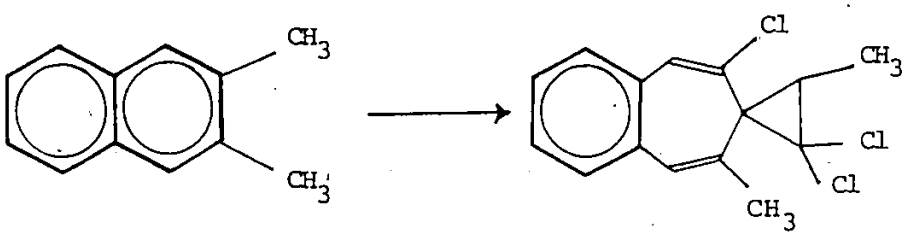


38 & 46



49 & 46

Compared to the cyclopropanation of olefins the carbene insertion into CH bonds gives very low yields in phase transfer catalyzed reactions, as well as by the classical techniques.

In order to find a convenient method for the synthesis of dichloromethylsilanes Larson[50] and coworkers tried to insert dichlorocarbene into the silicon hydrogen bond.

$$R_3SiH + :CCl_2 \longrightarrow R_2SiCHCl_2$$

When the phase transfer approach of Makosza[51] was employed it resulted in the hydrolysis of the silane.[52]

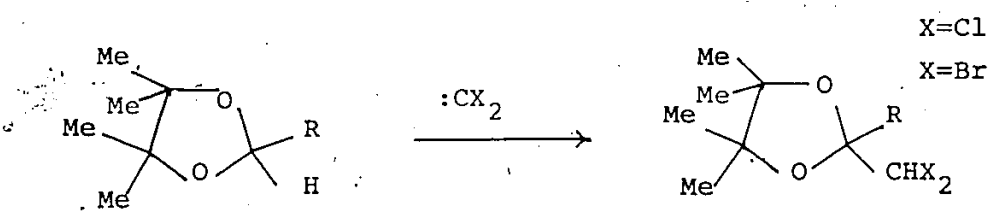
$$Et_3SiH + CHCl_3 \xrightarrow[Q^+X^-]{NaOH} Et_3SiOSiEt_3$$

Based on some early work of Seyferth[53] and some recent results of Dehmlow[54] and Idimori[55], Larson found that the phase transfer catalyzed decomposition of sodium-trichloroacetate in the presence of organosilanes is a useful route to dichloromethylsilanes.

$$Et_3SiH + 3Cl_3C\text{-}CO_2Na \xrightarrow[\text{toluene/ reflux}]{\text{18-crown-6}} Et_3SiCHCl_2$$

Interestingly the reaction did not proceed using potassium trichloroacetate as the dichlorocarbene source and crown ether catalysts other than 18-crown-6 were also ineffective. For example one molar equivalent of polyethylene glycol (PEG) 200 worked almost as well, although PEG 400 was useless. It is of interest to note that (+)- α - naphthylphenylmethylsilane was converted to (+) - (dichloromethyl)- α - naphthylphenylmethylsilane in 70% yield and 100% optical purity with retention of configuration at silicon.[50]

Dihalocarbene generated by phase transfer catalysis[56] undergoes insertion into the C(2)-H bond of 1,3-dioxolanes with high regio and stereospecificity.[57,58] This reaction provides a route to isomerically pure cyclic acetals of dihalogenomethyl ketones. The 4,4,5,5 - tetramethyl-1,3-dioxolanes with simple alkyl or aryl substituents in position 2 were converted into the corresponding 2-dichloromethyl derivative in yields of 88-95%. The analogous 2-bromomethyl compound was formed in 60-90% yield.[59]



It is shown that alkyl groups in position 4 and 5 increase the reactivity of the C(2)-H bond. It is conceivable that the carbene attacks the C-H bond from above the dioxolane ring, probably with some loose intermediate complex formation with the oxygen atom.[57]

Although hundreds of examples of the application of phase transfer catalysis to organic chemistry have appeared in the literature, there were prior to 1976 no such examples in organometallic chemistry. Investigations during the past five years have demonstrated that phase transfer catalysis is of considerable importance to metal catalyzed reactions as well as to the synthesis of certain organometallic compounds such as π-allyl and cluster complexes. Organometallic phase transfer catalyzed reactions can be classified into three groups: organometallic synthesis, stoichiometric organic reactions and catalytic organic reactions. An account of these reactions is given below.[61]

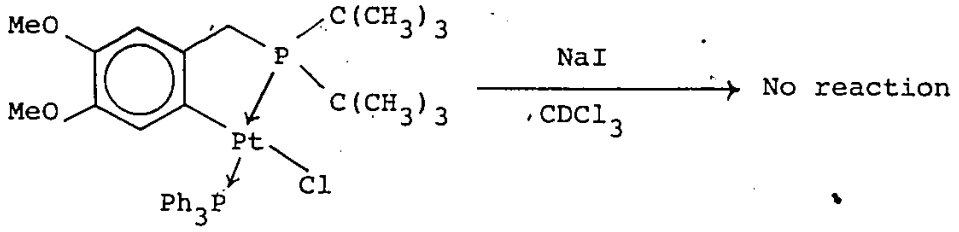
1.3 Phase transfer catalyzed organometallic synthesis. Ligand Substitution.

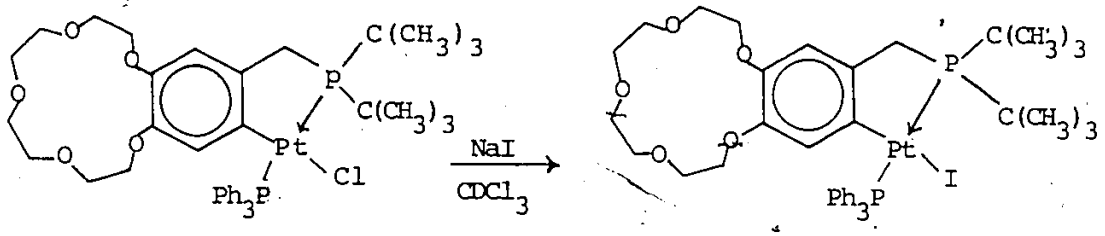
Phase transfer catalysis can effect the substitution of group VI metal carbonyls by nitrogen, phosphorus and arsenic ligands. Reaction of $M(CO)_6$ [M=Cr,Mo,W] with a group V ligand and tetra-n-butylammonium iodide in benzene and

sodium hydroxide (50%) at 25-80°C resulted in the formation of ligand substituted products in 51-94% yield.[62] Some examples of ligands used include dipy (dipyridyl), $AsPh_3$ (triphenylarsine)[62], t-butylisonitrile and p-tolylisonitrile.[63]

The synthesis of bridging hydroxo complexes of platinum has been reported by Fakely and Pidcock.[64] Treatment of bridging chloro complexes with aqueous KOH, benzene and a crown ether catalyst affords the corresponding hydroxo complexes. Cyanide ion can similarly displace a neutral ligand of mononuclear platinum complexes. Platinum complexes containing Pt-C bonds have been synthesized by Almedia and Pidcock.[65] Complexes PtR_2L_2 , and $PtR(Cl)L_2$, containing phosphines (L) and the σ-carbyl ligands R, (R = CH_2NO_2, C≡C-Ph, CH_2CN, CH_2COPh, $CH_2COC_6H_4$-NO_2-4, $CH_2COC_6H_4OMe$-2, CH_2COMe) have been prepared from $[PtCl_2L_2]$, RH and KOH in the presence of 18-crown-6.

A crown ether moiety functioning as its own phase transfer agent in a ligand substitution reaction has been demonstrated by Hyde, Shaw and Shepherd.[66]

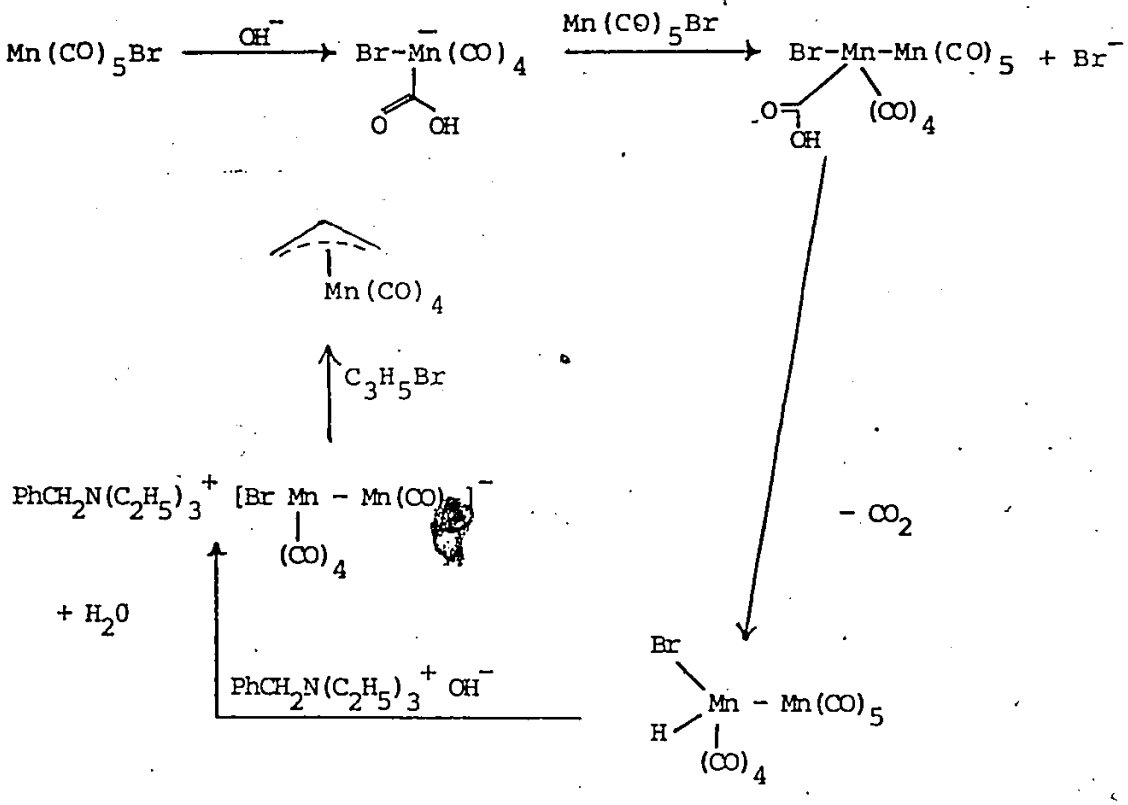




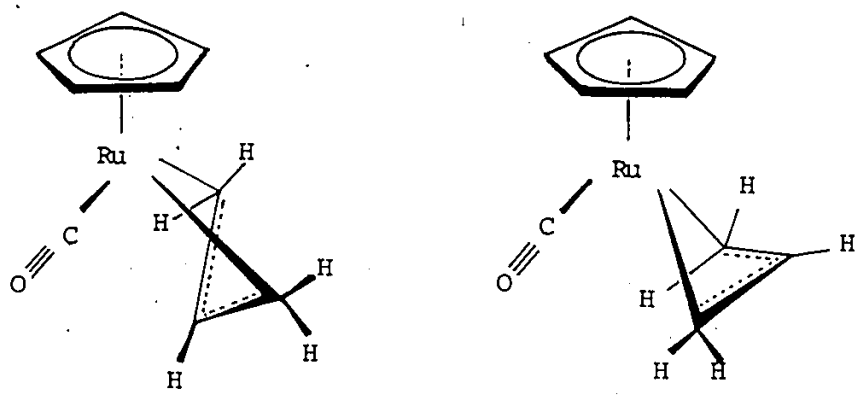
σ-and π-allyl complexes

π-allyl cobalt carbonyl complexes can be readily prepared from dicobalt octacarbonyl by phase transfer catalysis (discussed later). However, the use of other metal carbonyls gives poor results, e.g. $Mn_2(CO)_{10}$ gave 20-30% yield of (π-allyl)$Mn(CO)_4$ By using metal carbonyl halides and allyl halides Gibson and coworkers[67-69] developed a useful approach to the synthesis of π-and σ-allyl manganese, iron, molybdenum and ruthenium complexes. The usual reaction products are the π-allyl complexes but in some cases σ-allyl compounds were also isolated. This phase transfer reaction is very efficient and gives

good yields. A possible mechanism is given below.[68,61]



Phase transfer catalysis provides a high yield synthetic route to endo and exo η^5-cyclopentadienyl η^3-allyl ruthenium carbonyl and the corresponding η^3-2-methyl derivatives. In both cases the endo isomer thermally isomerizes to the more stable exo isomer. Prolonged photolysis of the η^3-allyl or 2-methallyl complexes leads to photostationary states in which the exo isomer is predominant.[70]

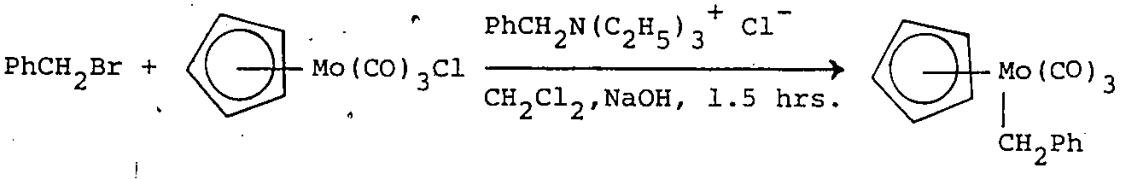


endo- exo-

η^5- C_5H_5- η^3- C_3H_5RuCO

σ-Benzyl complexes

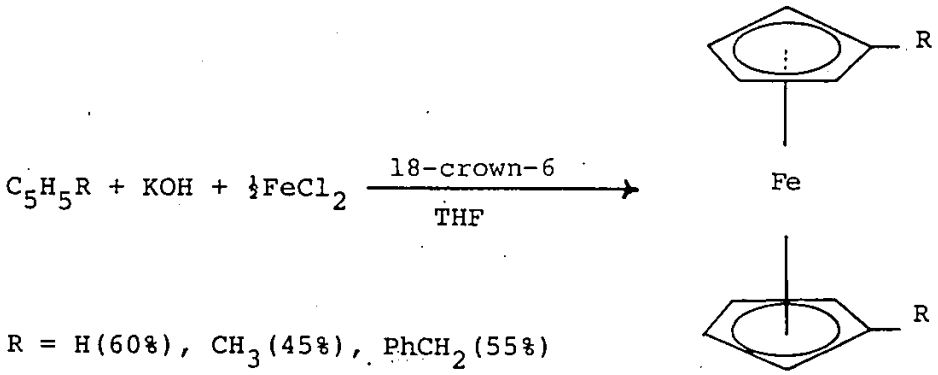
It was shown by Gibson and coworkers[71] that phase transfer catalysis is a good method for the synthesis of σ-benzyl complexes. When benzyl bromide was reacted with cyclopentadienylmolybdenum tricarbonyl chloride under phase transfer conditions the σ-benzyl complex was obtained in 89% yield.



When benzyl chloride was used the reaction was very slow, (26% yield in 4.5 hrs). The σ-benzyl complex was first synthesized by King and Fronzaglia in 67% yield in 16 hrs. using very dry conditions.[72]

Ferrocenes

Solid -liquid phase transfer catalysis is a mild way of synthesizing metallocenes.[73] 1,1'-Disubstituted ferrocenes are prepared by this method in less than one. hour.



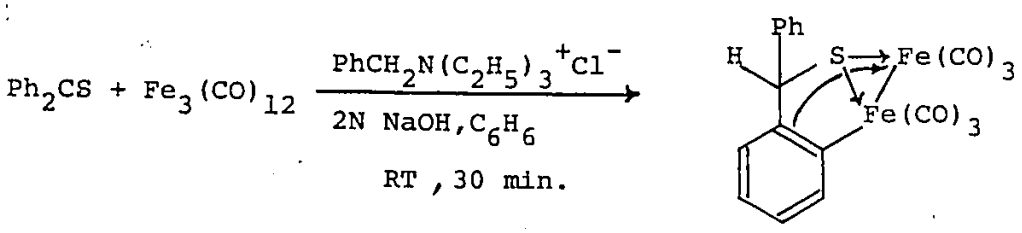
$C_5H_5R + KOH + \frac{1}{2}FeCl_2 \xrightarrow[THF]{18\text{-crown-6}}$

R = H(60%), CH_3(45%), $PhCH_2$(55%)
n-C_3H_7(40%), cyclohexyl (65%)

Arene Complexes

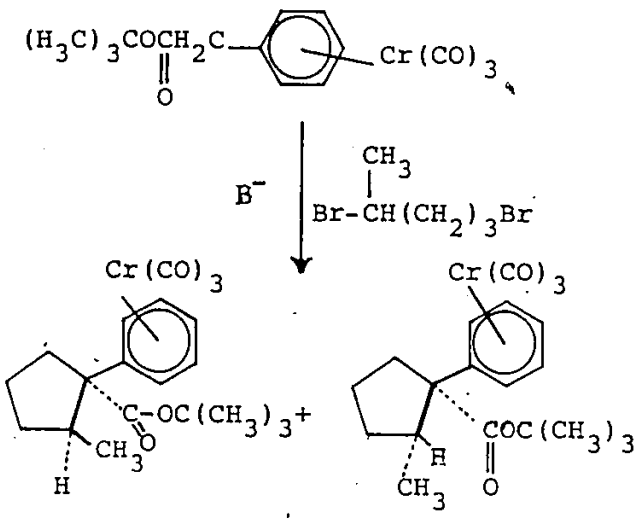
Sulfur-donor ligand ortho-metalated complexes are important in the synthesis of certain organic compounds which are either difficult to prepare or cannot be prepared by other methods.[74,75] They are also of structural interest

The synthesis of these ortho-metalated compounds required long reaction times, but the facile synthesis of these complexes can now be achieved by phase transfer catalysis. The reaction workup is easy as well.[76]



70 %

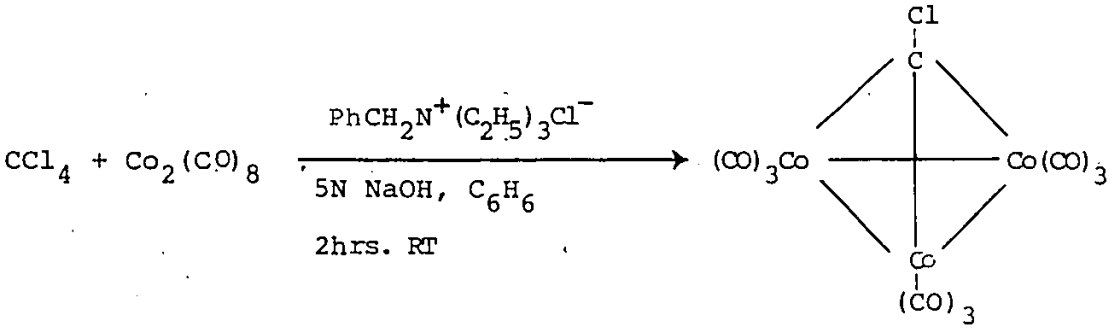
By using phase transfer catalysis or sodium hydride in N,N-dimethyl formamide, chromium tricarbonyl complexes of aryl acetic esters can be alkylated. Both these methods give similar stereochemical results.[77]



B^- = 50%NaOH, C_6H_6, $C_{16}H_{33}N(CH_3)_3Br$	72	:	28 (45%)
B^- = NaH / DMF	74	:	26 (100%)

Clusters

An interesting class of clusters are alkylidene-tricobalt nonacarbonyl complexes[78] which can be synthesized by the reaction of tri- or tetrahaloalkanes with dicobalt octacarbonyl under phase transfer conditions.[79]



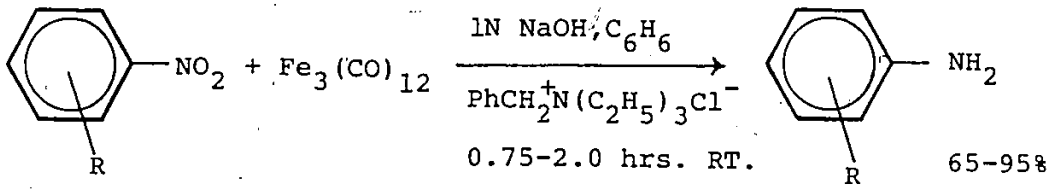
Partially or completely halogenated by-products are often isolated from these reactions.

1.4 Phase transfer catalyzed stoichiometric organometallic reactions.

Nitro Compounds

The first experiments on phase transfer catalysis in organometallic chemistry were done on the reduction of nitrobenzene to aniline by triiron dodecacarbonyl.[80] This

conversion had been effected before in benzene with methanol, and refluxing for 10 to 17 hours, with the hydridoundecacarbonyltriferrate anion as the likely key intermediate.[81] When sodium hydroxide is used as the aqueous phase, benzene as the organic phase and benzyltriethylammonium chloride as the phase transfer catalyst the reaction is complete in two hours or less. It occurs at room temperature and requires less metal carbonyl than when the reaction was done in a conventional manner.



Crown ether catalysis of the reduction is also useful with KOH used as the base and 18-crown-6 as the catalyst.[82]

The mechanistic details of the conversion of nitroarene to anilines by $HFe_3(CO)_{11}^-$ would be difficult to establish, but the generation of $HFe_3(CO)_{11}^-$ by phase transfer catalysis could proceed via one of the two pathways. (Scheme 3 and 4).

Aqueous $PhCH_2N(C_2H_5)_3^+ \ Cl^- + OH^- \longrightarrow PhCH_2N^+(C_2H_5)_3OH^- + Cl^-$

Organic $PhCH_2N(C_2H_5)_3^+OH^- + Fe_3(CO)_{12} \longrightarrow$

$PhCH_2N(C_2H_5)_3^+Fe_3(CO)_{11}COOH^-$

$\downarrow -CO_2$

$PhCH_2N(C_2H_5)_3^+HFe_3(CO)_{11}^-$

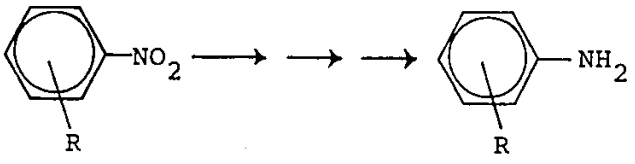
Scheme 3

Aqueous $PhCH_2N(C_2H_5)_3^+Cl^- + NaOH \longrightarrow PhCH_2N(C_2H_5)_3^+OH^- + NaCl$

Organic $4PhCH_2N(C_2H_5)_3^+OH^- + Fe_3(CO)_{12} \longrightarrow [PhCH_2N(C_2H_5)_3^+]_2$

$[Fe_3(CO)_{11}^{2-}] + 2H_2O + [PhCH_2N(C_2H_5)_3^+]_2 \ [CO_3^{2-}]$

Aqueous $Fe_3(CO)_{11}^{2-} + H_2O \longrightarrow HFe_3(CO)_{11}^- + OH^-$

$HFe_3(CO)_{11}^- +$ 

Scheme 4

In both pathways the initial step would be the conversion of the quaternary ammonium halide to the corresponding hydroxide ion in the aqueous phase. The ion pair after being transported to the organic phase can rapidly convert $Fe_3(CO)_{12}$ to the dianion $Fe_3(CO)_{11}^{2-}$ or it can attack a carbonyl carbon of $Fe_3(CO)_{12}$ to give the hydroxycarbonyl species, thus giving two possible pathways for the formation of $HFe_3(CO)_{11}^-$.

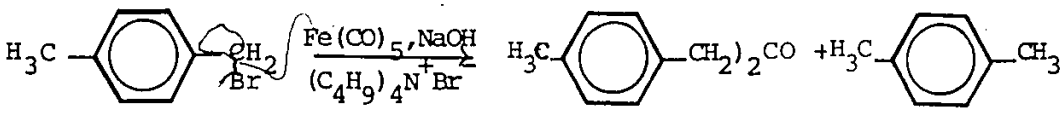
When the phase transfer process was repeated using a carbon monoxide atmosphere instead of N_2 atmosphere the yield of amine was significantly reduced. The organometallic complexes $(RN)_2Fe_3(CO)_9$ and $(RN)_2Fe_2(CO)_6$ were also isolated in low yields. This shows that CO either retards ligand dissociation of an intermediate, adds to the intermediate,or adds to the dissociated species reducing the rate of any subsequent reaction.[83]

The simpler iron carbonyls $Fe(CO)_5$ and $Fe_2(CO)_9$ can also effect reduction, however a phase transfer catalyst is unnecessary and its presence reduces the yields of amines. The nitro compound must be present to induce attack of hydroxide ion on $Fe(CO)_5$ to give $HFe(CO)_4$ [and possibly $HFe_2(CO)_8^-$][80]. This point was also noted by Pettit and coworkers in their work on the use of water gas shift reaction conditions for the $Fe(CO)_5$

catalyzed dioxygenation of nitrobenzene.

Halides

Halides react with $Fe(CO)_5$, base and tetrabutylammonium bromide to give ketones and hydrocarbon. When the concentration of the base was low the major product was the hydrocarbon and when the concentration of the base was high, the principal product was the ketone.[85]



	Product Distribution %	
% NaOH	Ketone	Hydrocarbon
2.0	33	67
3.8	50	50
16.6	85	15
33.0	95	5

The tetracarbonylferrate (II) species $Fe(CO)_4^{2-}$ is the supposed reagent at high concentrations while $HFe(CO)_4^-$ is assumed to be the active reagent at low base concentrations. The phase transfer catalyst is required for formation of the ketone but it is not clear if it is necessary for the

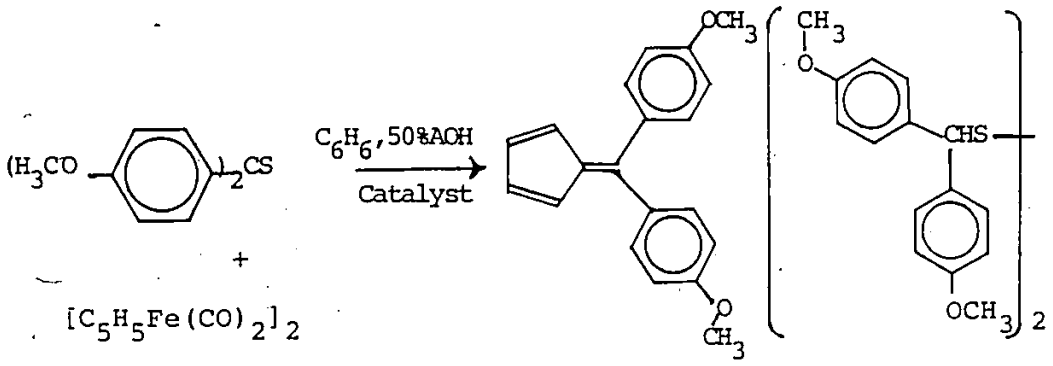
production of the hydrocarbon.[86]

α, β - Unsaturated ketones

Using 18-crown-6 or dicyclohexyl-18-crown-6 as the phase transfer catalyst the double bond of the unsaturated ketone, benzylidene acetone can be reduced. Either of the following reaction systems can be employed: $Fe(CO)_5$/KOH/crown ether/benzene or $Fe(CO)_5/RNH_2/H_2O$/crown ether/benzene.[87]

Thiobenzophenones

The in situ generated cyclopentadienyl metal carbonyl anions [η^5- $C_5H_5M(CO)_n^-$, M=Mo,W, n=3; M=Fe, n=2] couple with thiobenzophenones to give fulvenes in low to moderate yields with disulfides formed as byproducts. The highest yields were obtained when crown ethers were used as catalysts. Even if the product yields were lower when quaternary ammonium salts were used, they were still higher than those obtained by generation of the metal carbonyl anion by the reaction of the dimer with sodium-potassium alloy in tetrahydrofuran, under rigorously dry conditions.[88]



A = K , Cat = 18-crown-6 46 % 28 %

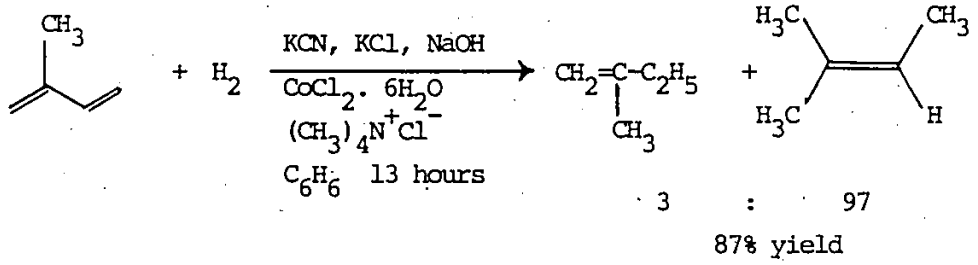
A = Na , Cat = $C_{16}H_{33}N(CH_3)_3^+Br^-$ 33 % 16 %

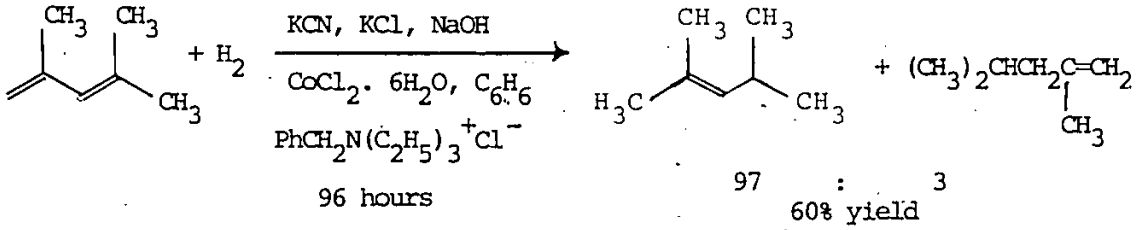
1.5 Phase transfer catalyzed catalytic organometallic reactions.

Hydrogenation

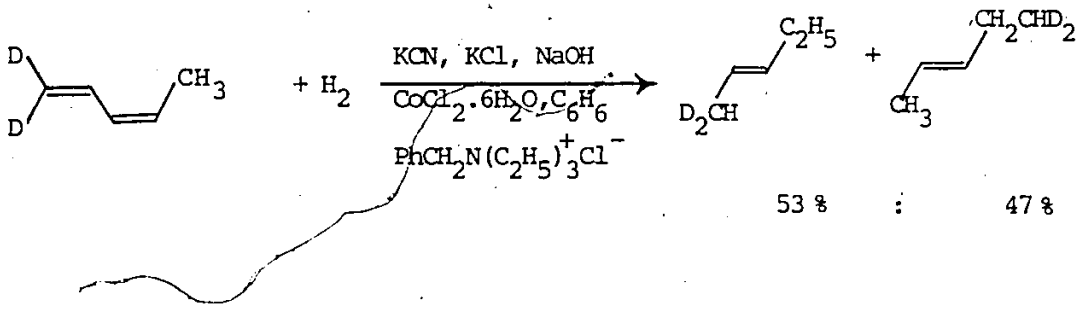
Water soluble rhodium complexes having sulfonated triphenyl phosphine ligands can catalyze the phase transfer reaction of cyclohexene with hydrogen. Wilkinson's catalyst can also be used for the hydrogenation of water soluble olefins in an aqueous-benzene solvent system.[89]

Conjugated dienes can be reduced to monoolefins by treating with hydrogen, hydrated cobalt chloride, potassium cyanide, potassium chloride, sodium hydroxide, and tetramethylammonium chloride or benzyltriethyl-ammonium chloride as the phase transfer catalyst. The probable metal catalyst is the hydridopentacyanocobaltate anion $HCo(CN)_5^{-3}$.[90-92] This reduction has also been done under micellular conditions.[90-93]

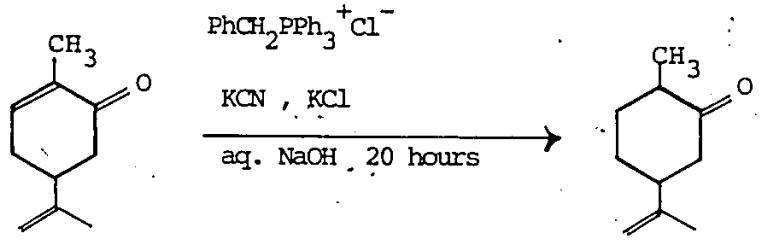




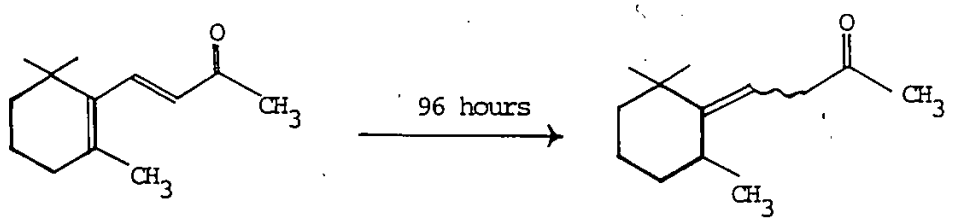
The phase transfer reagent prevents the decomposition of catalyst and accelerates the hydrogenation reaction. The reaction occurs by both 1,2-and 1,4-addition.



α,β-Unsaturated ketones can be hydrogenated at the double bond using $HCo(CN)_5^{3-}$ as the hydrogenation catalyst and benzyltriphenylphosphonium chloride as the phase transfer catalyst. Substitution α to the carbonyl group increases the rate of reaction and β substitution retards or completely inhibits the reaction.[92]

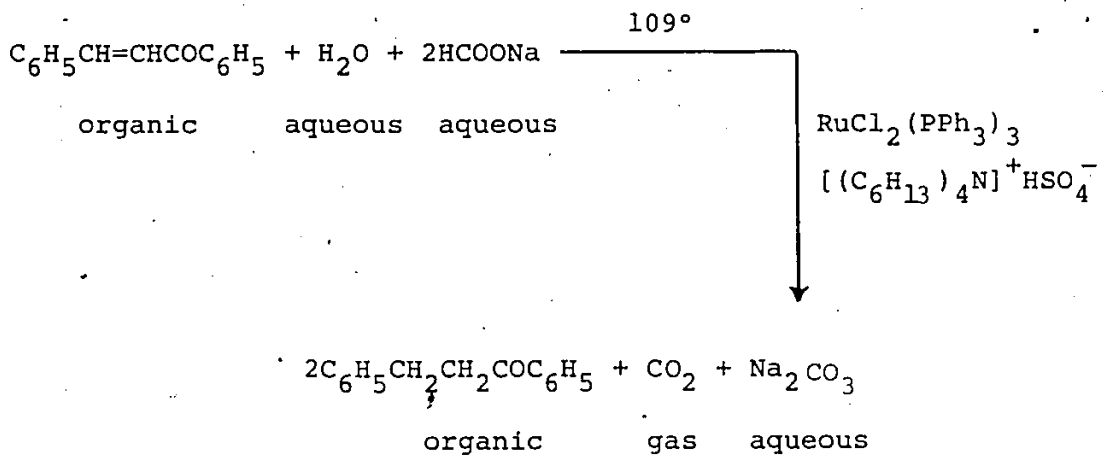


93 %



75 %

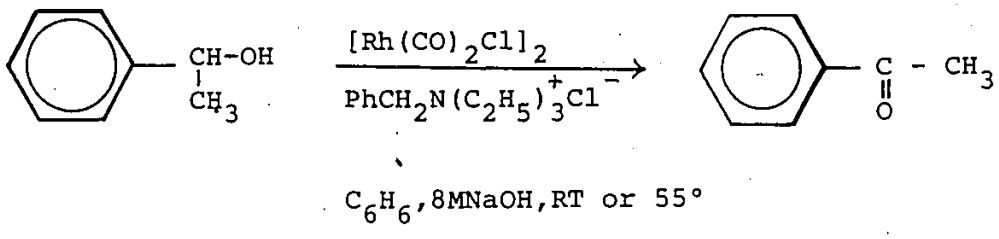
Recently it has been demonstrated that formate ion can be extracted from the aqueous to the organic phase by means of lipophilic quaternary ammonium or phosphonium salts.[94] This allows the application of aqueous solutions of sodium formate for the reduction of substrates in the organic phase in the presence of catalytic amounts of quaternary salts. This method is demonstrated by the selective formate reduction of 1,3-diphenyl-1-propen-3-one (chalcone) to 1,3-diphenylpropan-3-one in the presence of $RuCl_2(PPh_3)_3$ and quaternary salts.



Other metals complexes have also been used e.g. $RhCl(PPh_3)_3$, $PdCl_2(PPh_3)_2$, $Pd(PPh_3)_4$.[94]

Dehydrogenation

A catalytic amount of a rhodium (I) complex under phase transfer conditions dehydrogenates alcohols to carbonyl compounds. This reaction is particularly useful for benzyl alcohols such as 1-phenyl ethanol which gave acetophenone in 78% yield. This was done by using chlorodicarbonylrhodium (I) dimer as the metal catalyst and benzyltriethylammonium chloride or Aliquat 336 as the phase transfer catalyst.[95]



This reaction will also take place in the absence of the phase transfer catalyst but the yield is reduced.

Isomerization

When the rhodium catalyzed dehydrogenation reaction was tried using allylic alcohols, instead of getting the allylic ketones, the isomerized carbonyl compounds were obtained in high yield. This remarkably mild reaction can be done in the absence of the phase transfer catalyst, with nearly as good results.[96] The reaction intermediates are probably hydroxy π-allyl rhodium complexes. Allyl aromatics as well as allyl amines and sulfones undergo isomerization under these conditions.[98] For the allyl sulfones the rhodium (I) complex was not needed.

The same type of isomerization was reported using μ_3-oxotriruthenium acetate as the metal catalyst and heptane as the organic phase. The conversions are average and require high temperature.[97]

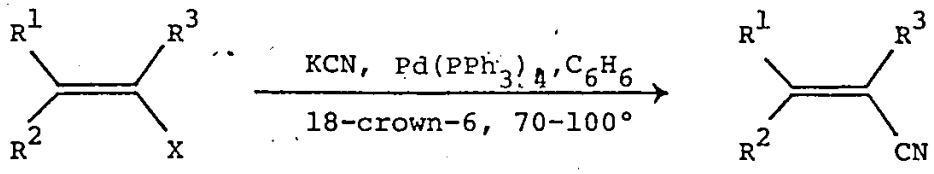
$$CH_3(CH_2)_6\underset{OH}{CHCH=CH_2} \xrightarrow[n\text{-}C_{16}H_{33}N(CH_3)_3{}^+Br^-,\ H_2O,\ C_7H_{16},\ 120^\circ]{[Ru_3O(OAc)_6(H_2O)_3][OAc]} CH_3(CH_2)_6\underset{O}{\overset{\|}{C}}\text{-}CH_2CH_3 \quad 53.5\%$$

Sasson and coworkers have described a liquid-liquid phase transfer method in which hydrated halides of group VIII metals are used for isomerization of water insoluble allylic compounds. With the aid of quaternary ammonium or phosphonium salts, the metal catalyst is extracted into the reagent containing phase and returned to the aqueous layer by lipophilic anions when the reaction is complete. The catalytic isomerization of allyl alcohols and allylarenes by some platinum metal chlorides has been demonstrated.[99]

$$CH_3(CH_2)_2CH(OH)\text{-}CH=CH_2 \xrightarrow[Aliquat\ 336,\ C_6H_6,\ 1\text{-bromohexane},\ 80^\circ]{RhCl_3.3H_2O/H_2O} CH_3(CH_2)_2\text{-}\overset{O}{\overset{\|}{C}}\text{-}CH_2CH_3$$

Cyanation

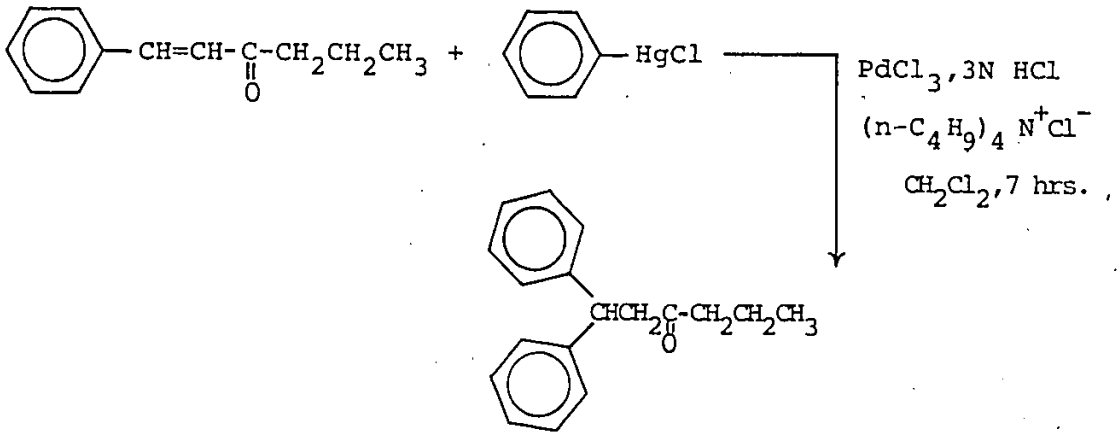
The palladium(0) catalyzed cyanation of vinyl halides in the presence of crown ether was described by Yamamura and Murahashi in 1977.[100] Unsaturated nitriles were isolated in excellent yields when 18-crown-6 was used as the catalyst.



When tetrakis(triphenylphospine)nickel(0) was employed as the catalyst this reaction could be carried out on aromatic halides.

Phenylation

α,β-Unsaturated ketones, when treated with phenyl mercuric chloride and a catalytic acidic solution of palladium chloride and tetrabutylammonium chloride gives the phenylated product.[102] This reaction is limited to substrates containing a disubstituted double bond.



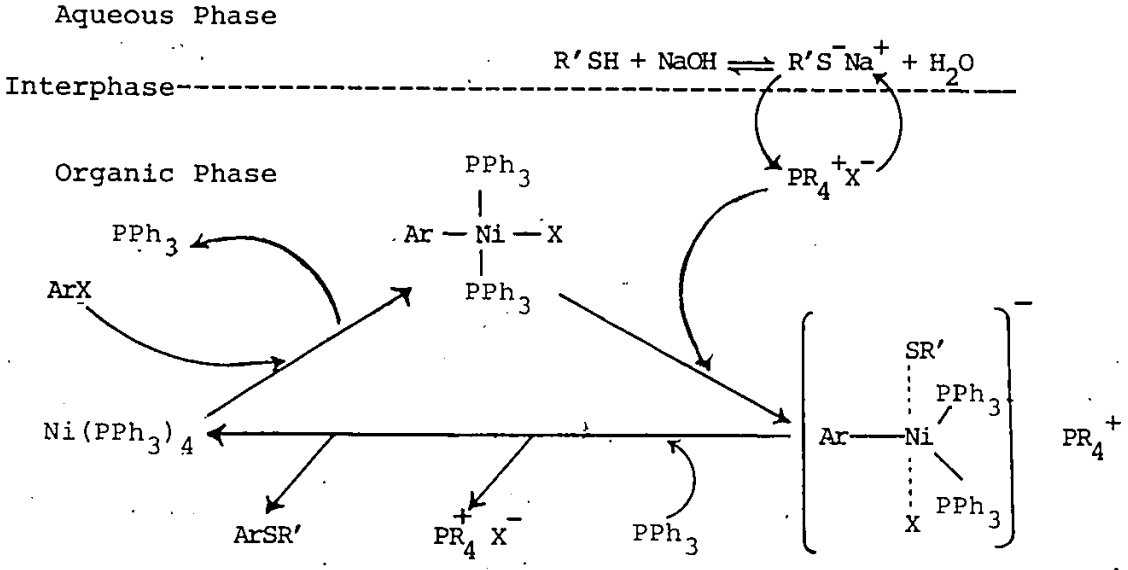
This conjugate addition type reaction may accommodate a wide variety of functional groups. Thus aryl units containing electron donating and electron withdrawing substituents such as -Me, -Cl, -CHO, -COMe, -COOMe, -COOH, -OH, -OMe, -NHCOMe and $-NO_2$ were successfully transferred to the β carbon atom of the α,β-unsaturated ketone and 3-formylphenyl mercury chloride gives the corresponding β-(3-formylphenyl) derivatives. The main limitation seem to arise from the steric hindrance in the starting α,β enone system.[103]

Sulfide synthesis

Aryl and alkenyl sulfides can be conveniently prepared from the corresponding halides and alkali thiolates under phase transfer conditions in the presence of σ-aryl-Ni$(PPh_3)_2Cl$ or σ-aryl-Pd$(PPh_3)_2Br$.[104]

$$RX + R'S^-M^+ \xrightarrow[\sigma\text{-aryl-Ni}(PPh_3)_2Cl,\ \text{or}\ \sigma\text{-aryl-Pd}(PPh_3)_2Br]{\text{Aq. NaOH/Toluene , Onium Salt}} RSR' + NaX$$

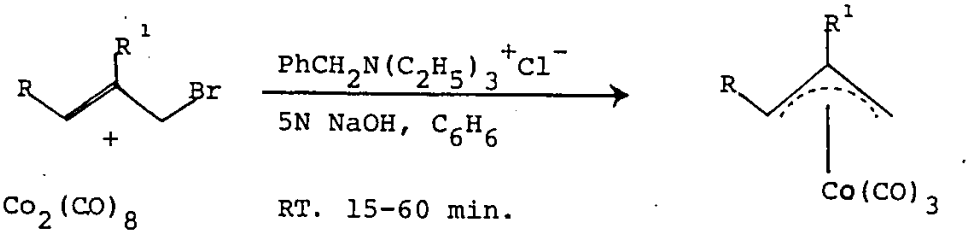
Scheme 5 illustrates a possible mechanism for this reaction.



Scheme 5

Cobalt Tetracarbonyl anion

In catalytic processes one of the most important metal carbonyl anions is the cobalt tetracarbonyl anion, $Co(CO)_4^-$. To establish that the anion is actually formed under phase transfer conditions allyl bromides were reacted at room temperature with a stoichiometric quantity of $Co_2(CO)_8$, sodium hydroxide (5N), benzene and benzyltriethyl-ammonium chloride as the phase transfer catalyst.[79] Good yields (70%-80%) of the π-allylcobalt tricarbonyl complexes were obtained by the use of short reaction times (15-60 min). This method is superior to methods described in the literature.[105-107]



$Co_2(CO)_8$ RT. 15-60 min.

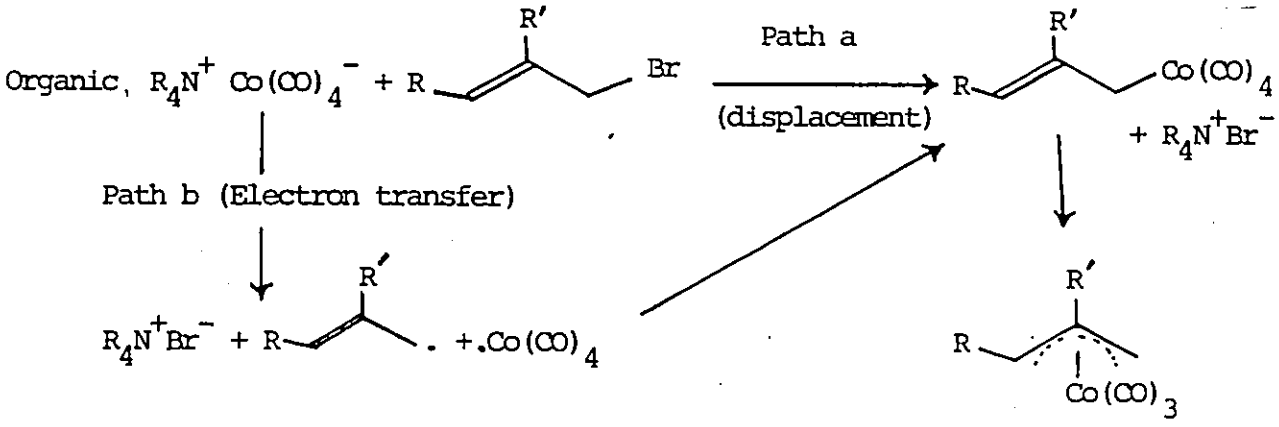
Under a nitrogen atmosphere cobalt carbonyl would be experiencing some disproportionation by base to give the $Co(CO)_4^-$. The subsequent reaction of this anion with the allyl bromide could take place along two pathways to give the π-allyl complex. The mechanism for this reaction is

outlined in Scheme 6.

Aqueous $R_4N^+X^- + NaOH \rightleftharpoons R_4N^+OH^- + Na^+X^-$

Organic $32\, R_4N^+OH^- + 11\, Co_2(CO)_8 \longrightarrow 20\, R_4N^+\, Co(CO)_4^- + 6(R_4N)_2CO_3 + 16\, H_2O + 2\, Co^{2+} + 2\, CO_3^{2-}$

Aqueous $2\, Co^{2+} + 8OH^- \longrightarrow 2\, Co(OH)_4^{2-}$

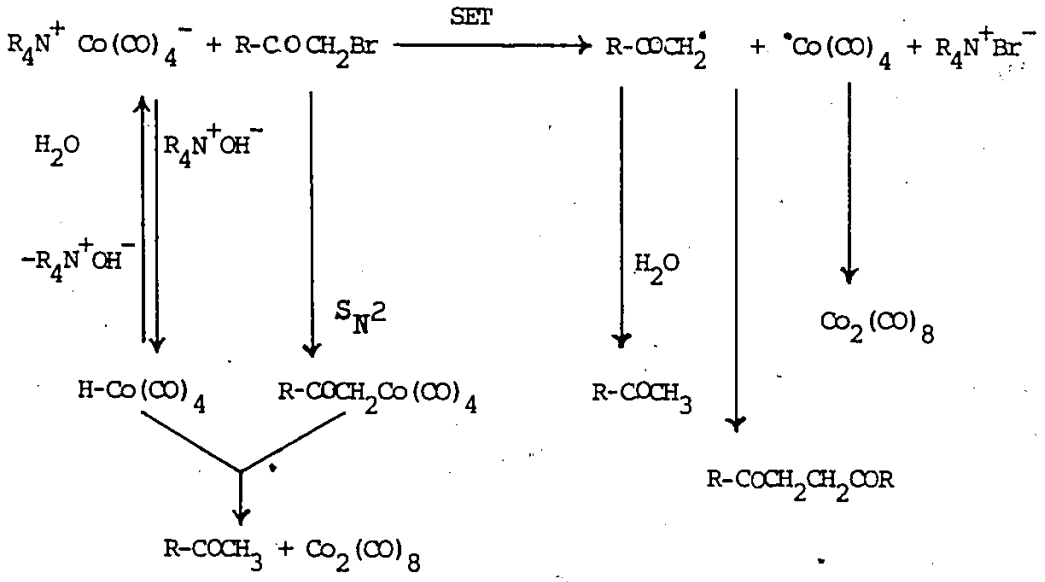


Scheme 6

It has also been described that crown ethers catalyze the generation of $Co(CO)_4^-$ in hydrocarbon solvents or in ether.[108]

The anion with 2,3-bis(bromomethyl)naphthalene in tetrahydrofuran gives a bis π-allyl complex, and ketones were isolated when monocyclic dibromides were used.

α-Bromo ketones can be dehalogenated in the presence of catalytic amount of both $Co_2(CO)_8$ and $PhCH_2N(C_2H_5)_3^+ Cl^-$. Monoketones and in some cases diketones are formed. These products arise by single electron transfer from cobalt tetracarbonyl anion, to the α-halo ketone. (Scheme 7)



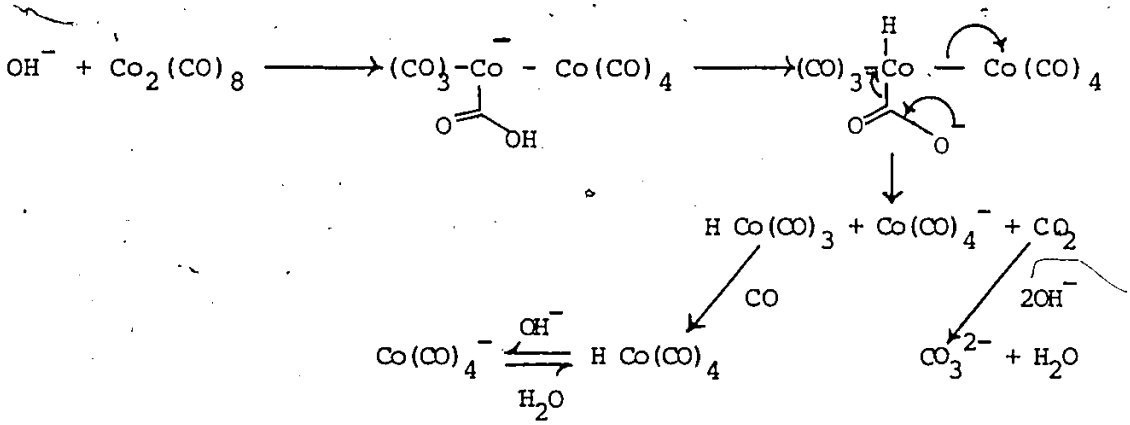
Scheme 7

Use of a carbon monoxide rather than a nitrogen atmosphere results in quantitative conversion of $Co_2(CO)_8$ to $Co(CO)_4^-$.

A balanced equation could be written for this reaction.

$$Co_2(CO)_8 + CO + 4OH^- \longrightarrow 2Co(CO)_4^- + CO_3^{2-} + 2H_2O$$

A stepwise pathway is outlined in Scheme 8.



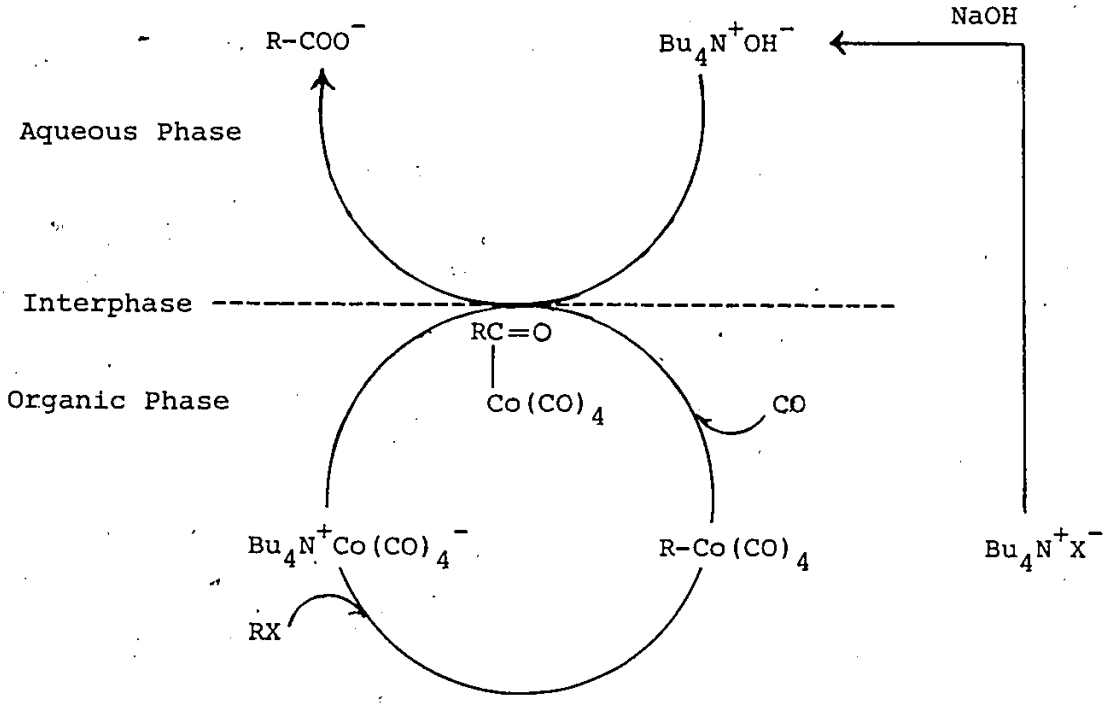
Scheme 8

Carbonylation reactions

The $Co_2(CO)_8$ catalyzed carbonylation of halides to carboxylic acids is a process of genuine synthetic importance. The phase transfer technique is a remarkably mild method for this conversion (room temperature and atmospheric pressure). The yields are good, e.g. benzyl bromide or chloride gives phenylacetic acid in 85% yield.[110,111] Alkyl and acylcobalt carbonyls are the likely intermediates. The acylcobalt carbonyl can be isolated by use of preformed $Co(CO)_4^-$ and water instead of NaOH.[112] Optically active acids were produced

using appropriate optically active, phosphine substituted, cobalt carbonyl catalysts.[113]

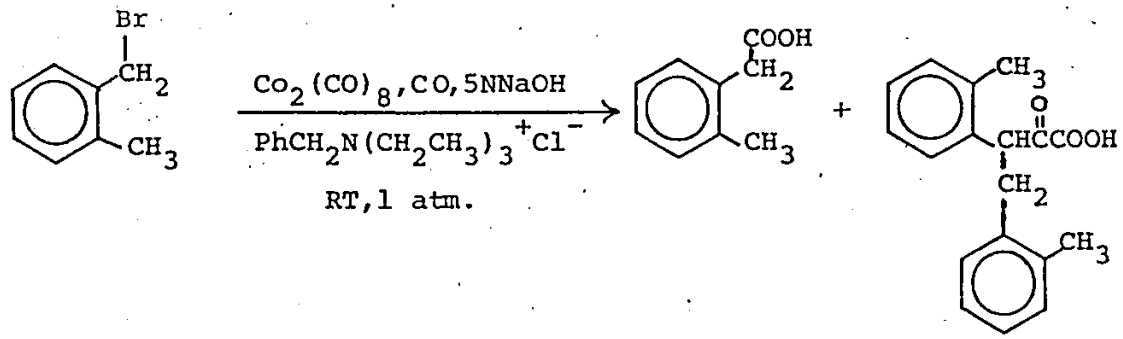
des Abbayes and coworkers after studying the carbonylation of benzyl bromide in the biphasic liquid-liquid system showed that the catalytic ion pair Bu_4N^+ $Co(CO)_4^-$ stays in the organic layer, and the carbonylated product $C_6H_5CH_2\overset{O}{\overset{\|}{C}}O^-$ is in the aqueous one.[114] The mechanism proposed is shown in Scheme 9.



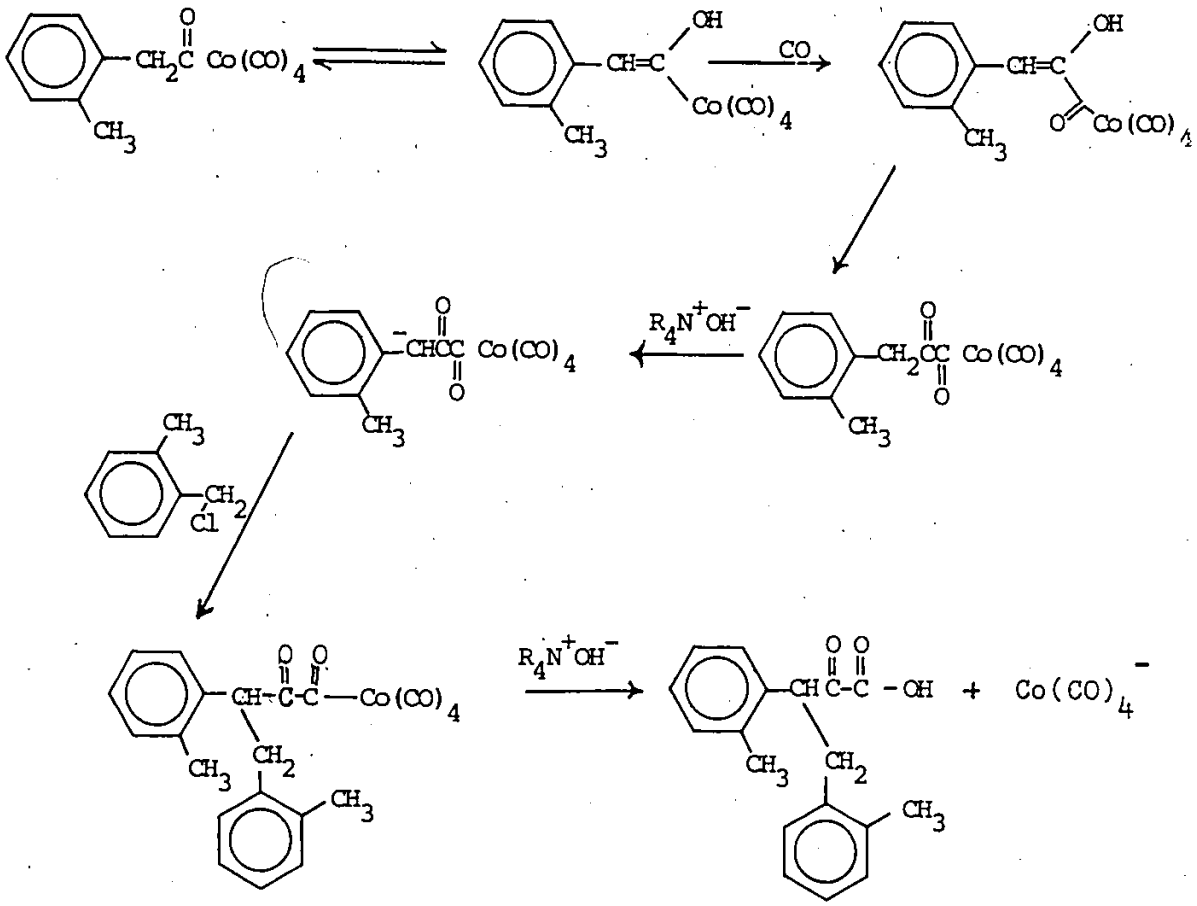
Scheme 9

Evidence for this mechanism includes the fact that the phase transfer reaction is significantly dependent on the speed of stirring. Real phase transfer processes do not depend on the stirring speed after a minimum stirring but interfacial ones strongly do. Therefore it can be concluded that the cleavage of the key intermediate, acylcobalt tetracarbonyl, occurs at the interphase.

In the case of o-methylbenzylbromide a substantial amount of alkylated phenyl pyruvic acid derivative was formed along with the anticipated phenylacetic acid.[110]



Enolization of the intermediate acylcobalt tetracarbonyl would be the key to this double carbonylation reaction. A possible mechanism is given in Scheme 10.



Scheme 10

The phase transfer catalyzed, cobalt carbonyl catalyzed carbonylation (1 atmosphere pressure) of aryl and vinyl bromides under photo stimulation (350 nm) affords the

corresponding unsaturated acids in high yields.[115]

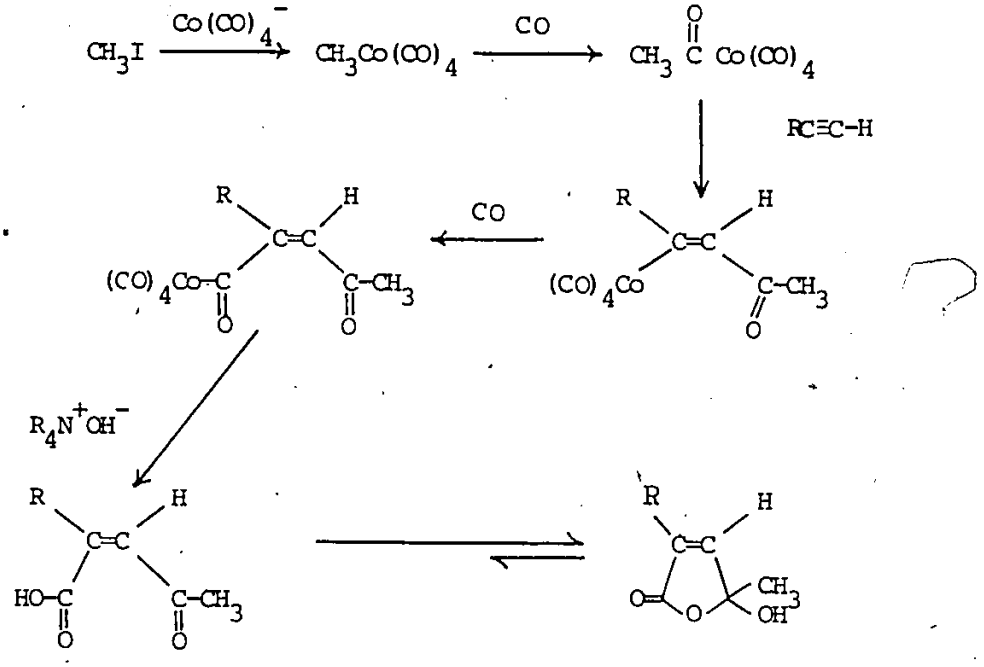
$$ArX + CO + 2NaOH \xrightarrow[NaOH,\ C_6H_6]{Co_2(CO)_8,\ Bu_4^+NBr^-} ArCOONa + NaX + H_2O$$

$h\nu$. 350 nm.

The reactions are generally quantitative and the reactions are highly catalytic toward cobalt. The only observed side reaction, which is the reduction of the aryl halide, was never significant except for o-bromoanisole. A clear explanation could not be given for this observation.

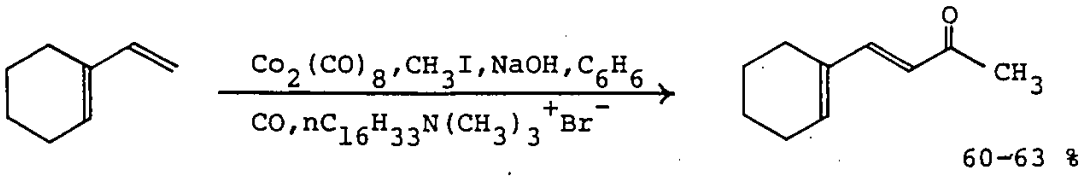
Under these conditions carbonylation did not occur with chlorobenzene. This lack of reactivity has been used for the selective carbonylation of p-chlorobromobenzene to p-chlorobenzoic acid. It has to be noted that during classical S_RN1 reaction performed with dihalobenzene this kind of selective monosubstitutions were not possible.[116]

The acylcobalt tetracarbonyl intermediate can be trapped by carrying out the reaction in the presence of unsaturated compounds. Cobalt carbonyl can catalyze the reaction of alkynes with carbon monoxide and methyl iodide as the halide under phase transfer conditions to give the pharmacologically active 2-butenolides.[117] This regiospecific reaction may proceed via the mechanism shown below. (Scheme 11)



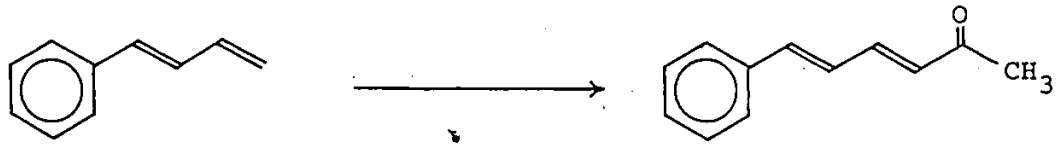
Scheme 11

When a diene or triene is used instead of an alkyne to react with methyl iodide and a catalytic amount of cobalt carbonyl then the (E) conjugated enone is formed in a highly regiospecific manner.[118] This reaction is much milder than those reported using standard conditions [50-85°, 50-130 psi]. The yields are also higher.

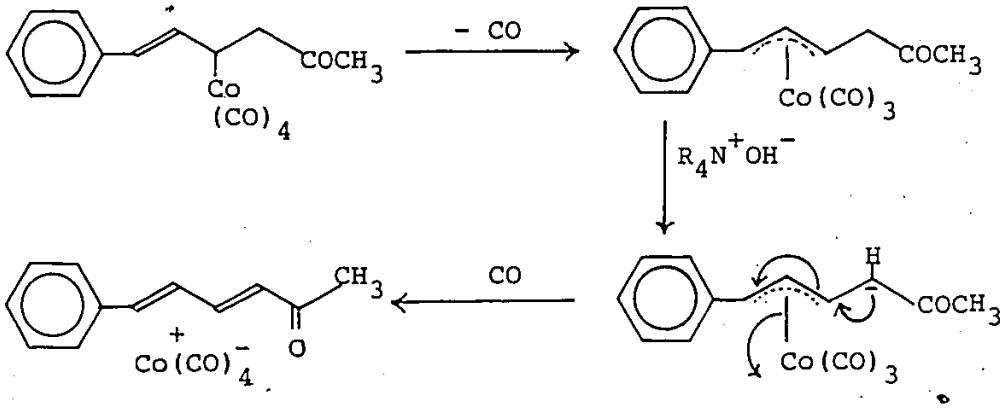


60-63 %

RT. 1 atmosphere



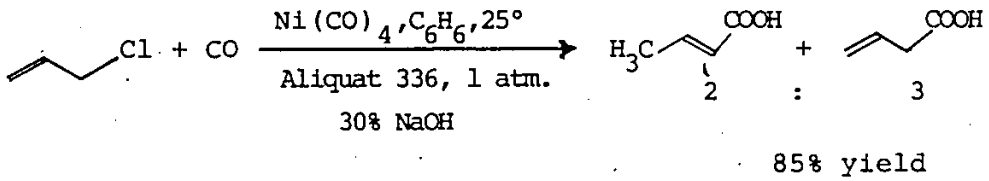
There is some but not conclusive, evidence for 1,2, addition of acylcobalt tetracarbonyl to the least substituted double bond of the diene or triene giving a σ-allyl complex which would then convert to the π-allyl and subsequently to the (E)-dienone. (Scheme 12)



Scheme 12

Also of importance is the fact that the phase transfer catalyst itself can be carbonylated to the carboxylic acids by acylcobalt tetracarbonyl. This is a slow but high yield reaction that occurs for quaternary ammonium salts that are capable of forming reasonably stable free radicals or carbonium ions. Phenylacetic acid is formed in 95% yield from benzyltriethylammonium chloride. These results as well as the pathways for the generation of $Co(CO)_4^-$ are suggestive of the possible participation of free radicals in certain organometallic phase transfer processes. For sluggish cobalt catalyzed reactions, benzylic, naphthylmethyl, or related ammonium halides should not be used as phase transfer catalysts.[120]

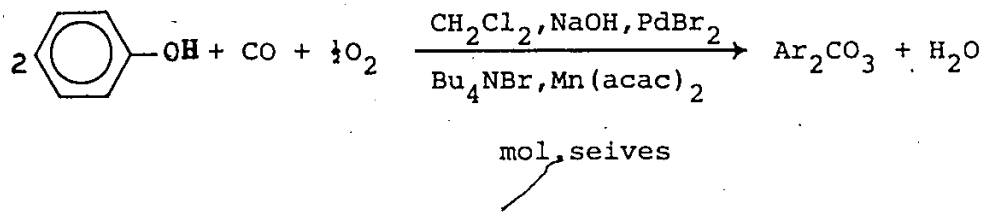
Another organometallic reagent that can be used as a catalyst for the phase transfer carbonylation of halides is bis(triphenylphosphene)palladium chloride $(Ph_3P)_2PdCl_2$.[121] The conditions are 95°C, 5 atmospheres. These are much more drastic conditions compared to the use of $Co_2(CO)_8$. The carbonylation of allyl chloride can be catalyzed by nickel tetracarbonyl giving isomeric mixtures of butenoic acids.[121(a)]



85% yield

When this carbonylation reaction was done in the presence of an alkyne, acetylene insertion did not take place.

Aqueous sodium hydroxide in combination with a phase transfer catalyst was found to be an effective base for the palladium catalyzed synthesis of diphenyl carbonate from phenol, carbon monoxide, and oxygen. The use of small quantities of sodium hydroxide with the phase transfer catalyst resulted in higher reaction rates than that observed previously with a tertiary amine.[122]

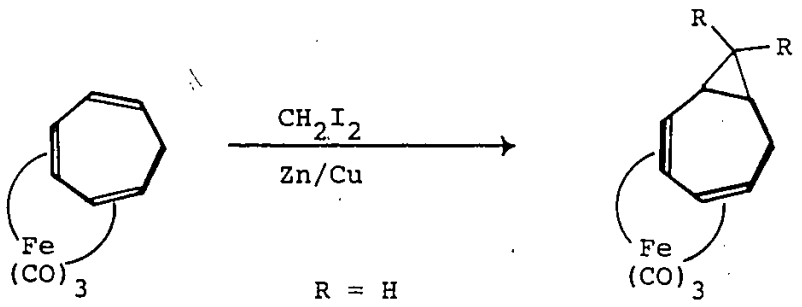


There were no side products observed in this reaction. An interesting observation was that neither sodium nor potassium phenoxide was an effective base when used in the place of sodium hydroxide.

1.6 Aims of research

Carbene insertion into organometallic complexes.

The formal addition of carbene to an uncoordinated double bond of a polyolefin-transition metal complex using the Simmons-Smith reagent was described in 1975 by Reger and Gabrielli.[123]

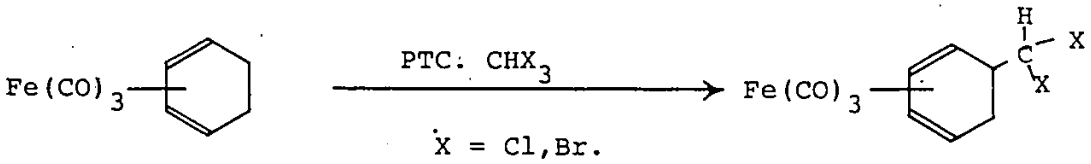


(1) (2)

More recently Taylor has demonstrated the addition of dichlorocarbene generated from chloroform and potassium t-butoxide to (1) to give (2) (R=Cl) and to other polyene complexes.[124]

There has been, to our knowledge, no examples of the insertion of dichlorocarbene into a saturated carbon hydrogen bond of a transition metal organometallic complex.

Our aim was to determine if a carbene, generated by phase transfer catalysis, would insert into a carbon hydrogen bond of a diene-iron carbonyl complex.



Catalytic reduction and carbonylation of nitro compounds

The application of phase transfer catalysis to the stoichiometric reduction of nitro compounds to anilines by triiron dodecacarbonyl in a nitrogen atmosphere was described in 1977.[80] It was later observed that the yields were substantially lower when the deoxygenation was effected in an atmosphere of carbon monoxide.[83]

It has been shown by Ford and coworkers[134] that triruthenium dodecacarbonyl is a good catalyst for the water gas shift reaction. Pettit and coworkers[135] showed that nitrobenzenes can be reduced to anilines by means of the water gas shift reaction at 100°C temperature and 500 psi pressure. Calderazzo and coworkers[136] described the triruthenium dodecacarbonyl catalyzed reduction of nitrobenzene to aniline under homogeneous conditions with carbon monoxide and hydrogen. They had also observed that diphenyl urea is formed as a minor product at $CO:H_2$ ratio greater than

one. This shows that carbon monoxide insertion takes place with triruthenium dodecacarbonyl.

Our aim was to investigate the ruthenium catalyzed reactions of nitro compounds under phase transfer conditions in a carbon monoxide atmosphere. We could expect catalytic reduction of nitro compounds to anilines and/or the insertion of carbon monoxide to give ureas or other carbonyl compounds, under mild conditions i.e. room temperature and atmospheric pressure.

Carbonyl insertion into imines using dicobalt octacarbonyl.

It has been found by Alper and Currie[112] that dicobalt octacarbonyl can catalyze the reaction of alkynes with carbon monoxide, and methyl iodide as the halide, under phase transfer conditions, to give the 2-butenolides. When a diene or triene is used instead of an alkyne (E) conjugated enones are obtained in a highly regiospecific manner.[113] In addition to these results a number of other publications have appeared on the chemistry of the carbon-carbon double bond system, but relatively little work has been done on the carbon-nitrogen double bond system. Therefore, it seemed of interest to determine the effect of a nitrogen atom on the diene system and more generally the reaction of dicobalt octacarbonyl under phase transfer conditions with Schiff bases. As little has been done on the homogeneous reaction of $Co_2(CO)_8$ with Schiff bases it was also of interest to investigate this reaction as well.

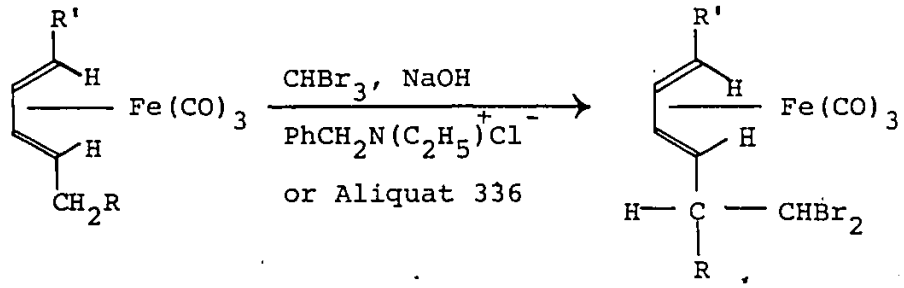
C H A P T E R II

2. RESULTS AND DISCUSSION

2.1 Carbene insertion into diene-iron carbonyl complexes under phase transfer conditions.

Diene-iron carbonyl complexes are an important class of compounds[126], being useful as synthetic intemediates. One function of the iron carbonyl moiety is to act as a protecting group. In this manner pheromones have been synthesized by a simple reaction sequence.[146]

Since the complexation of a diene would inhibit addition of dihalocarbene to one or both double bonds it was anticipated that carbon-hydrogen bond insertion would occur. Therefore, a study was made of the reaction of dihalocarbene generated by phase transfer catalysis with diene-iron tricarbonyl complexes.



Reaction of diene-iron tricarbonyl complexes with bromoform (as reactant and solvent), sodium hydroxide and benzyltriethylammonium chloride as the phase transfer catalyst, (Method A) afforded the dibromomethyl complex as a bright yellow viscous oil. Acyclic as well as cyclic diene-iron complexes, and those which contain secondary or tertiary carbon hydrogen bonds, experienced dibromocarbene insertion. The results are shown in Table 1. As anticipated 1,4-diphenyl-1,3-butadiene-iron tricarbonyl (6),a compound devoid of saturated carbon atoms failed to react with dibromocarbene.

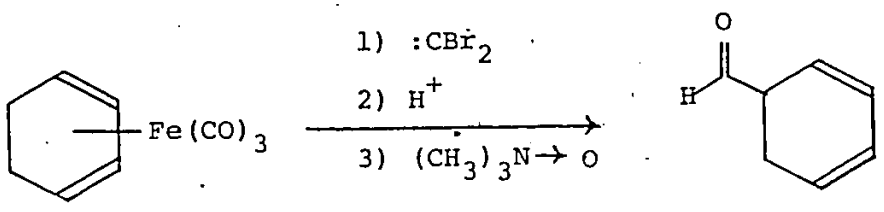
There was no insertion on 1 when chloroform was used as reactant and solvent. This agrees with the excellent work of Dehmlow and coworkers who demonstrated that $:CBr_2$ is more reactive than $:CCl_2$ under phase transfer conditions.[60]

When Aliquat 336 was used as the phase transfer catalyst, methylene chloride as the organic phase (Method B), and cyclohexadieneiron tricarbonyl as the substrate, there was a significant improvement in the yield of the inserted product (Table 1 :14%-- 31%). The structures of these insertion products are supported by analytical and spectral data which are given in Table 2.

Infrared spectra of 7-9, 11 displayed two medium-strong terminal metal carbonyl stretching bands at 2100-1950 cm^{-1}. The mass spectra of 7 and 11 showed molecular ion peaks followed by successive loss of carbonyl ligands.

The highest mass fragments for 8 and 9 were due to the organic ligand. The nuclear magnetic resonance spectra were also in accord with the assigned structure. The nuclear magnetic resonance spectra of compound 7, ^{1}H NMR($CDCl_3$) 1.95(m,3H, protons on saturated ring carbons), 3.00(m,2H, protons on terminal carbons of diene unit), 5.50(m, 2H, protons on internal carbons of diene unit), 6.05(m,1H,$CHBr_2$); ^{13}C NMR($CDCl_3$) 29.11, 29.50(methylene carbons), 51.05($CHBr_2$), 57.61, 59.33, 85.33,85.37(unsaturated carbons).

The yields (27-54%) obtained in the dibromocarbene insertion reactions are good, particularly when compared with those reported for other insertion reactions into organic substances (except adamantanes). This method provides a simple entry into organic and organometallic functionalized dienes since, for example, acid or base treatment will convert the dibromomethyl function to an aldehyde. The diene aldehyde 15 formed on decomposition would be nonconjugated as far as the aldehyde and diene units are concerned.



1 15

Table 1 : The Products and the Yields of the Dihalocarbene Insertion Reaction.

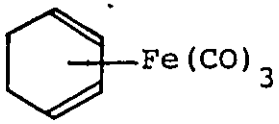
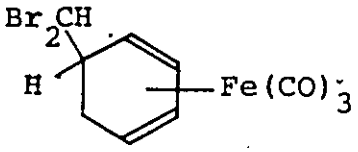
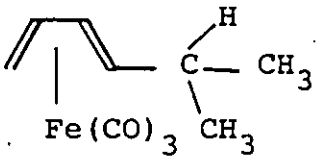
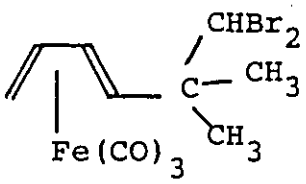
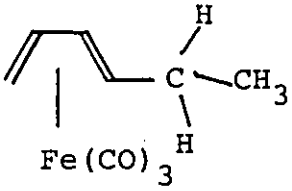
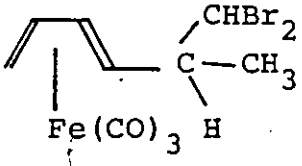
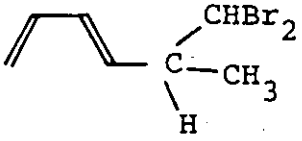
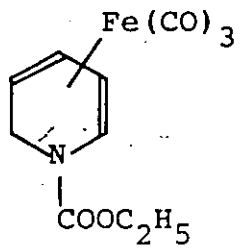
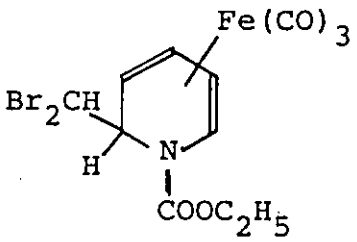
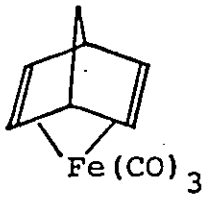
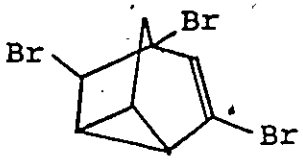
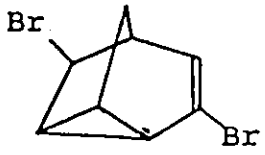
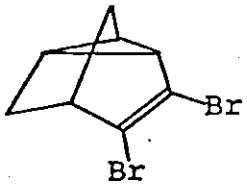
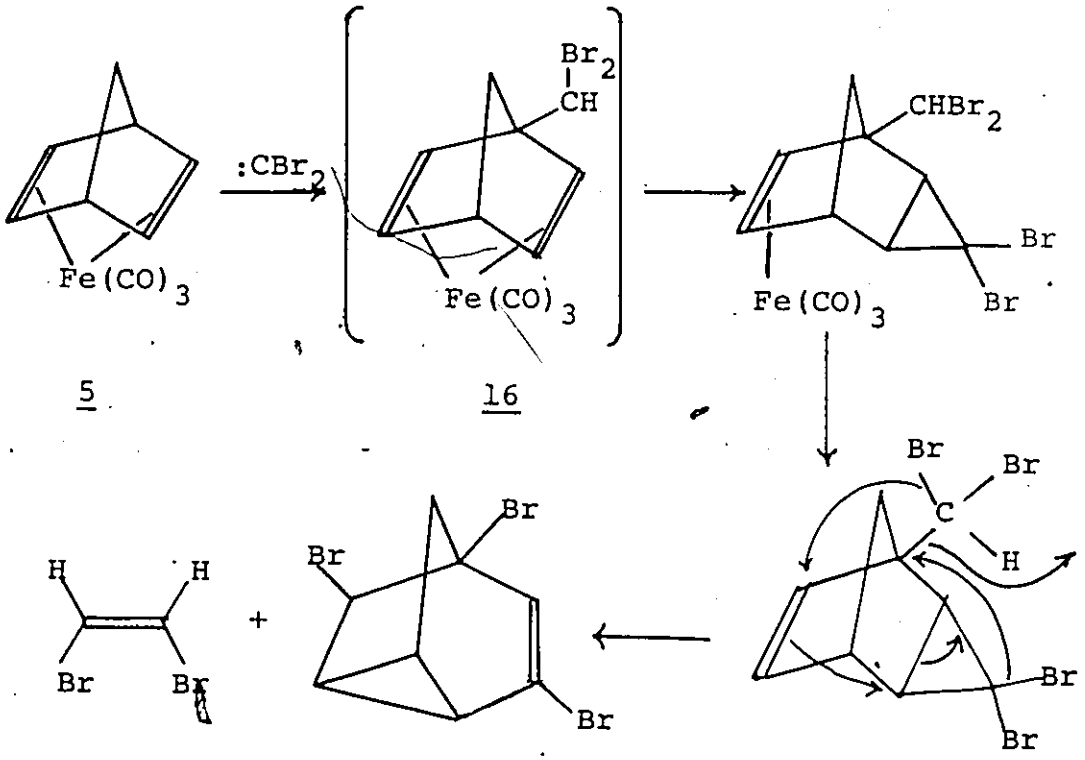
Diene–iron carbonyl complex	Product		Method	Yield %
 1		7	A	14
			B	31
 2		8	A	17
			B	27
 3		9	A	14
			B	40
		10	A	12
 4		11	B	54

Table 1 : (cont'd)

Diene iron carbonyl complex	Product		Method	Yield %
 5		12	A	3
		13	A	7
		14	A	4

The reaction of tricarbonylnorbornadieneiron (5) with dibromocarbene was different from the rest of the diene complexes, with three organic products being formed. According to work by Jefford, de los Heros and Burger[147] who studied the reaction of dibromocarbene with norbornadiene two of the unstable colourless thick oils 13 and 14 could be the rearranged products of the norbornadiene ligand with a dibromocarbene inserted into one carbon-carbon double bond. As compound 12 had three bromine atoms according to its mass spectrum, it is conceivable that dibromocarbene

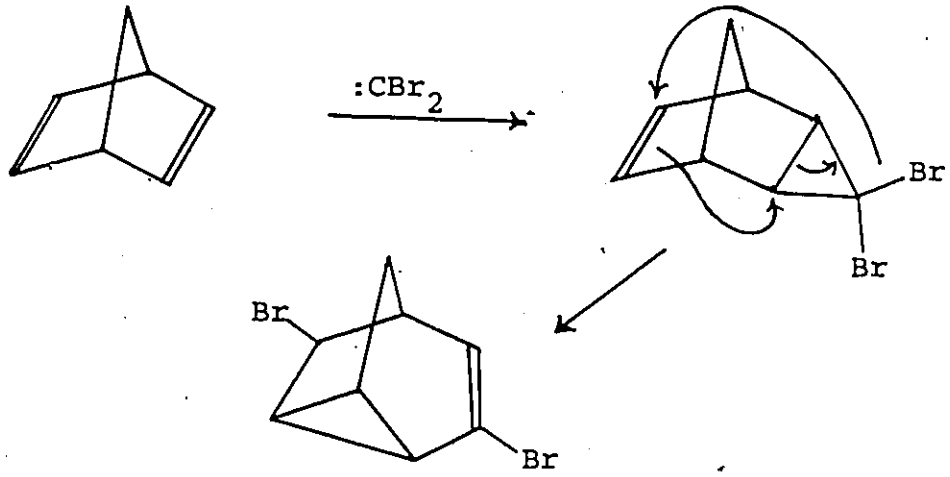
inserted into a carbon-hydrogen bond as well as added to a carbon-carbon double bond. Another possibility is the insertion of a dibromocarbene into both of the double bonds, but evidence to support the first pathway is provided by the mass and nuclear magnetic resonance spectra of compound 16, which could be an intermediate in the formation of 12. The latter could be obtained by the loss of a :CHBr group. The possible mechanisms for the formation of 12, 13 and 14 are outlined in Schemes 13 and 14.



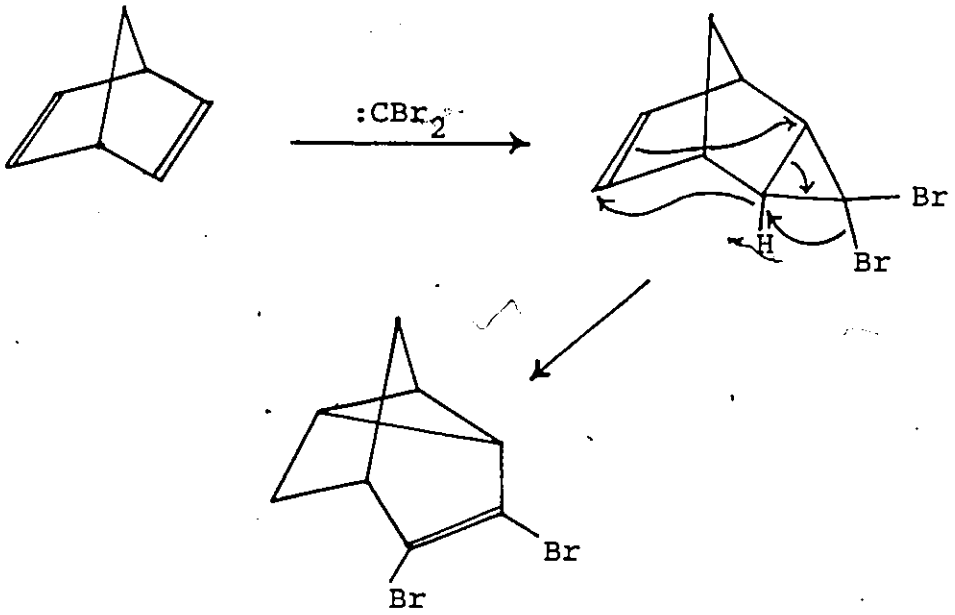
5 16 12

Scheme 13

Dibromides 13 and 14 could be formed by the insertion of a carbene into a carbon-carbon double bond of the diene ligand.



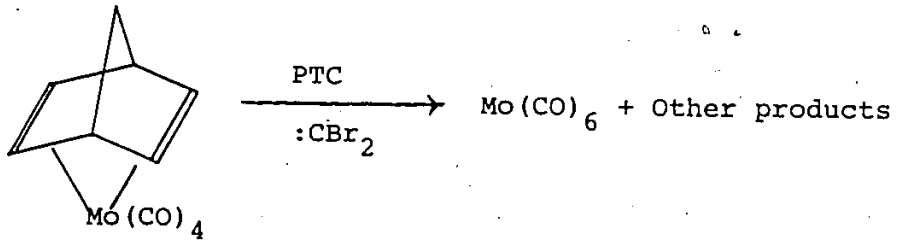
13



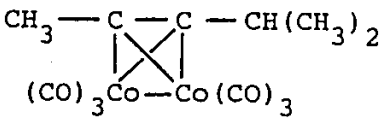
14

Scheme 14

(Norbornadiene) molybdenum tetracarbonyl 17 decomposed under phase transfer conditions giving molybdenum hexacarbonyl and other products which could not be identified. These products were isolated in very low yield.



17



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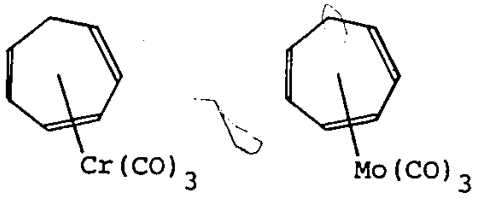
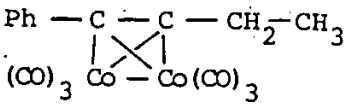


18 19



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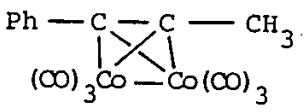


22

Compounds 18-22 when subjected to the carbene insertion reaction according to procedure B afforded numerous products in low yields. These products were isolated in minute quantities and could not be characterized successfully.

Table 2

Analytical and Pertinent Spectral Data for the Carbene Inserted Products of Diene-iron Carbonyl Complexes

Product	— Anal. Calcd. (found) — C	H	Br.	IR, ν_{CO} cm^{-1}	MS m/e	NMR, δ ppm	^{13}C NMR δ
7	30.63(30.41)	2.00(2.01)	40.72(40.92)	2048(w) 2038(s) 2015(w) 1990(vs)	392 $[M]^+$ 364 336 308	1.95(m,3H) 3.00(m,2H)5.50 (m,2H),6.05 (m,1H)	29.11, 29.50,51.05 57.61,59.33 85.33,85.37
8	32.45(32.76)	2.98(3.59)	39.45(39.70	1990(s) 2040(m) 2050(w)	267 $[M-Fe(CO)_3]^+$ 187, 107	0.28(m,1H),0.60 (m,1H),1.02(S,3H) 1.07(S,3H),1.70 (m,1H),5.10 (m,1H),5.18)(m,1H) 5.80(m,1H)	
9	30.50(30.69)	2.56(2.74)	40.86(40.58)	2018(s) 2038(w) 2058(m) 2078(w)	253 $[M-Fe(CO)_3]^+$ 173 93	0.50-2.10(m,3H) 1.38(d,3H)2.38 (M,1H),5.18 (m,2H),5.86 (m,1H)	
10					253 $[M-Fe(CO)_3]^+$ 173,93		

Table 2 (Cont'd)

Product	Anal. Calcd. (found) C	H	Br.	IR, ν_{CO} cm^{-1}	MS m/e	NMR, δ ppm	^{13}C NMR δ
11	30.97(30.72)	2.37(2.49)	34.41(34.28)[a]	1980(s)[b] 2058(m)	465 $[M]^+$ 437,409 381,324	1.30(t,3H),3.55 (m,1H),3.96(m,1H) 4.30(q.2H),5.10 (m,1H)5.85(m,1H) 6.20(d,1H)	
12	27.94(28.10)	2.37(2.47)	69.71(69.37)		344 $[M]^+$ 264,184,104		
13	36.40(36.87)	3.05(3.07)	60.54(60.05)		264 $[M]^+$ 185,104		
14	36.40(36.73)	3.05(2.99)	60.54(60.02)				
16						1.2(m,2H)3.15 (m,4H),5.50 (m,1H)	

[a] N Calculated 3.01 ; found 2.59

[b] $\nu_{C=O}$ 1711 cm^{-1}

2.2 Triruthenium dodecacarbonyl catalyzed reduction and carbonylation of nitro compounds.

2.2.1 Phase transfer catalyzed reduction of nitro compounds

As noted in the introduction, triiron dodecacarbonyl can stoichiometrically reduce nitro compounds to amines by phase transfer methods. Carbon monoxide has an inhibiting effect on this reaction.

It was of interest to learn what influence the metal would have on the reduction process effected under a carbon monoxide or nitrogen atmosphere. Therefore, triruthenium dodecacarbonyl was employed in place of triiron dodecacarbonyl with gratifying results.

$Ru_3(CO)_{12}$ can catalyze the reduction of nitro compounds by phase transfer methods at room temperature and atmospheric pressure. The behaviour of triruthenium dodecacarbonyl is the reverse of that of triiron dodecacarbonyl, when the reactivity in nitrogen or carbon monoxide atmosphere is considered.

Reaction of a nitro compound with a catalytic quantity of $Ru_3(CO)_{12}$, benzyltriethylammonium chloride as the phase transfer catalyst, sodium hydroxide (5N), benzene containing a small amount of 2-methoxyethanol and carbon monoxide, at room temperature and atmospheric pressure, affords the corresponding amine.[145] The reaction times and product yields are listed in Table 3.

$$RNO_2 \xrightarrow[CH_3OCH_2CH_2OH,\ PhCH_2N(C_2H_5)_3^+Cl^-]{CO,\ Ru_3(CO)_{12},\ 5N\ NaOH,\ C_6H_6} RNH_2$$

Under the phase transfer conditions the initial reaction in the organic phase would involve the attack by hydroxide ion at a metal carbonyl carbon to give an anion bearing a hydroxycarbonyl ligand 23 or the conversion of $Ru_3(CO)_{12}$ to $Ru_3(CO)_{11}^{2-}$ by the quaternary ammonium hydroxide. The former type of complex is analogous to species obtained from the phase transfer catalyzed reaction of group VI metal carbonyls with hydroxide ion.[148]

$$M_3(CO)_{12} + R_4N^+OH^- \longrightarrow \underset{\underline{23}}{R_4N^+M_3(CO)_{11}COOH^-} \xrightarrow{-CO_2} \underset{\underline{24}}{R_4N^+\ HM_3(CO)_{11}^-}$$

Loss of carbon dioxide from 23 would generate the trinuclear metal hydride 24 which is the key species in the iron reaction and may or may not be so in the case of ruthenium. The purpose of the phase transfer catalyst is to accelerate the rate at which the presumed benzyltriethylammonium carbonyl ruthenate cluster intermediate, $[PhCH_2N(C_2H_5)_3][HRu_3(CO)_{11}]$ is formed with 2-methoxyethanol increasing the solubility of this anionic cluster in the organic phase. The presence of other cluster anions in the aqueous phase/organic solution

such as $Ru_6(CO)_{18}^{-2}$, $HRu_6(CO)_{18}^{-}$ and $H_3Ru_4(CO)_{12}^{-}$ is also conceivable.[149] Reaction will occur in the absence of 2-methoxyethanol but at the expense of both reaction rates and product yields. The concentration of sodium hydroxide used (5N) is important since the amines were formed in lower yields at either lower or higher base concentrations.

Table 3: Phase transfer catalyzed Reduction of Nitro Compounds by $Ru_3(CO)_{12}$.

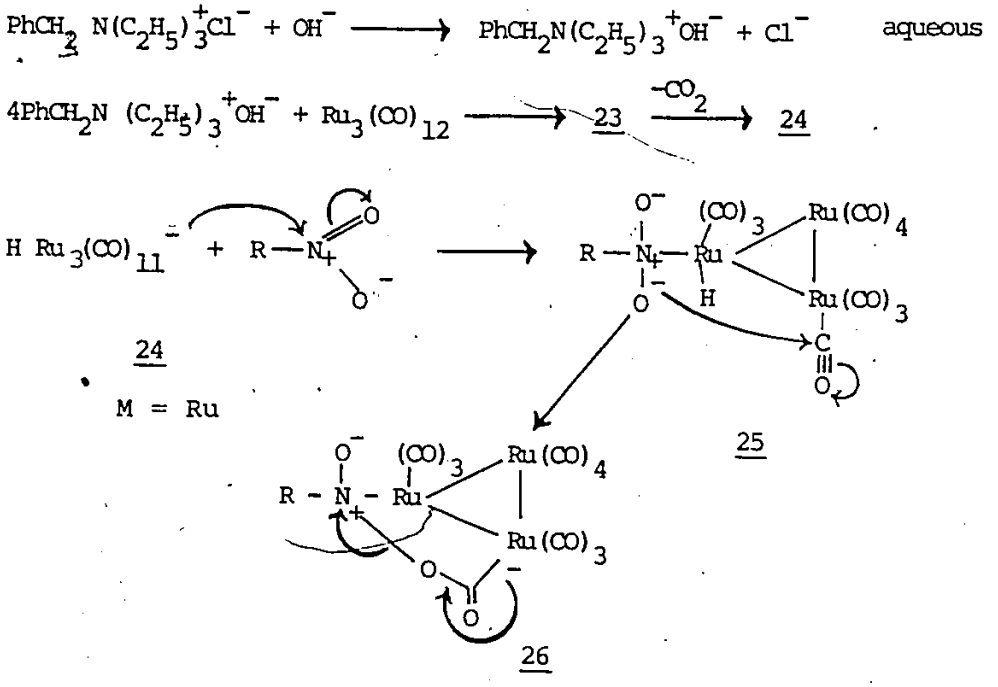
Nitro compound	Reaction time hr.	Product	% Yield[c]
Nitrobenzene	9.0	Aniline	100
p-Nitrotoluene	8.0	p-Toluidine	94
p-Nitroanisole	7.0	p-Anisidine	84
p-Chloronitrobenzene	3.0	p-Chloroaniline	100
p-Nitrobenzophenone	4.5	p-Aminobenzophenone	100
2,6-Dimethylnitrobenzene	25.0	2,6-Dimethylaniline	8
2-Nitrofluorene	20.0	2-Fluorenylamine	95
1-Nitropropane	17.0	1-Propylamine	85[d]

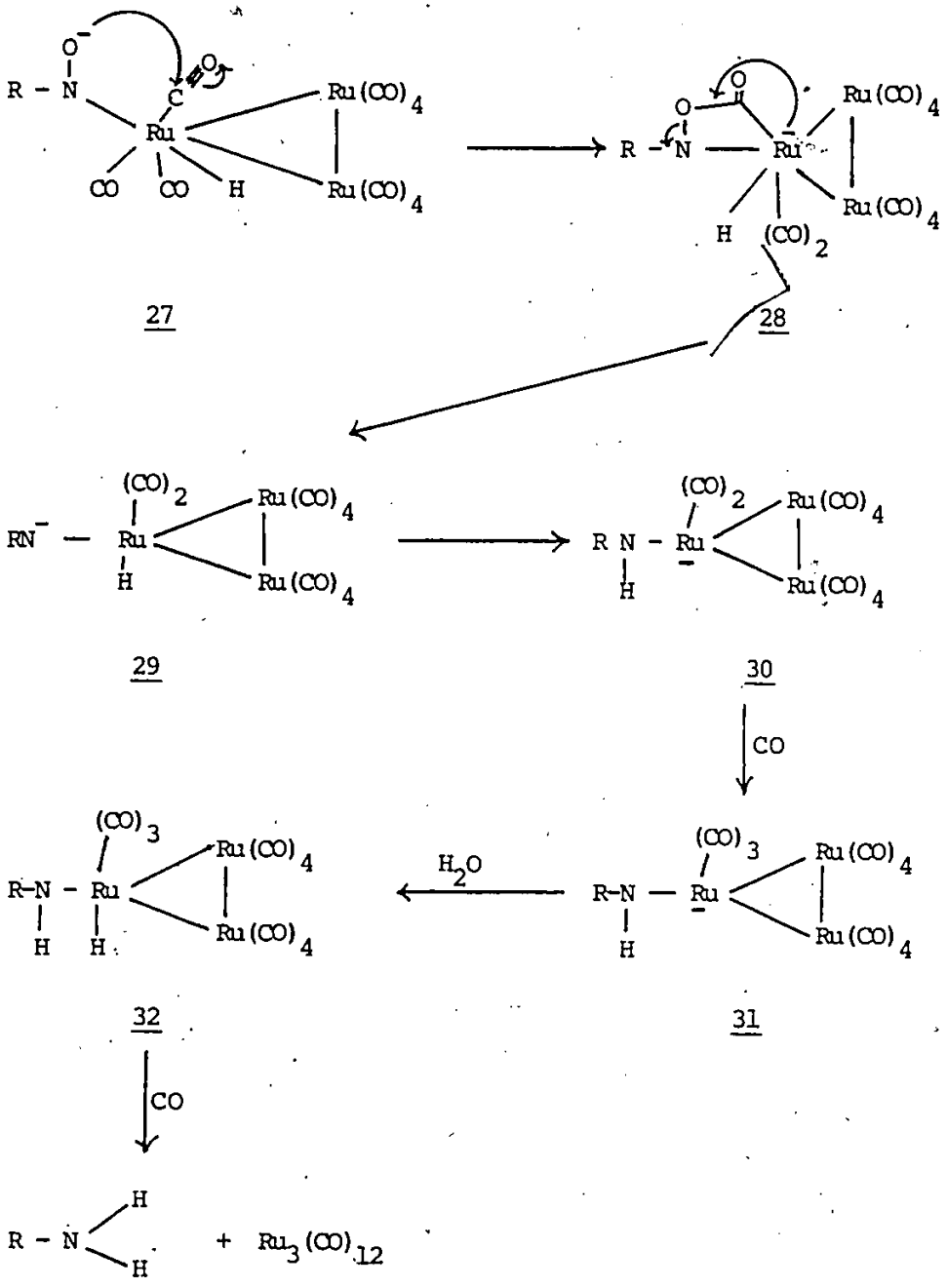
[c]Isolated yields [d]GLC yield

The amines were identified by comparing their melting points IR and NMR spectra to those of authentic samples. The yield of amines was excellent, with the exception of the hindered nitro compound 2,6-dimethylnitrobenzene. The presence of electron withdrawing groups (e.g. chloro, carbonyl) increases the rate of reduction of nitroarenes. Note that the selective

reduction of the nitro function occurs in the presence of a carbonyl group. This reduction can also be done on aliphatic nitro compounds with high yields of the amine obtained. This method is significantly milder than that using water gas shift reaction conditions [100°C, 500 psi pressure]. Since the triruthenium dodecacarbonyl catalyzed phase transfer process occurs at atmospheric pressure, it is also less drastic than when iron pentacarbonyl was employed as the catalyst for the reduction of nitro compounds by carbon monoxide and water [1700 psi pressure].[150]

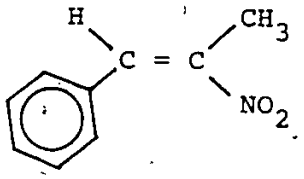
A possible mechanism for this catalytic reduction is shown in Scheme 15.




R – N
O
C
O
Ru
Ru(CO)4
CO
CO
H
Ru(CO)4
R – N
O
O
Ru
Ru(CO)4
H
(CO)2
Ru(CO)4
27
28
RN
(CO)2
Ru
Ru(CO)4
H
Ru(CO)4
R N – Ru
(CO)2
Ru(CO)4
H
Ru(CO)4
29
30
CO
R–N – Ru
(CO)3
Ru(CO)4
H
H
Ru(CO)4
H2O
R–N – Ru
(CO)3
Ru(CO)4
H
Ru(CO)4
32
31
CO
R – N
H
H
+ Ru3(CO)12

Scheme 15

The amines are formed in about 5 times greater yield using a carbon monoxide rather than a nitrogen atmosphere. This is because (as indicated in Scheme 15) CO is required at several stages in the process and therefore is important in assisting in the generation of the catalyst.



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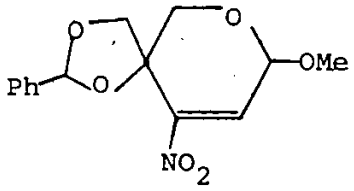
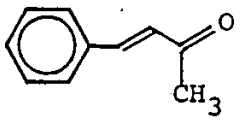


34

α,β Unsaturated nitro compounds (e.g. 33,34) are unstable under phase transfer reducing conditions and numerous products were formed none of which was the expected amine.



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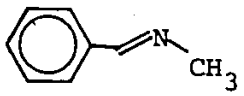

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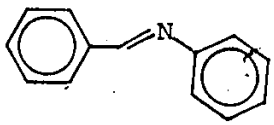

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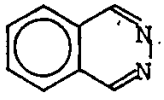

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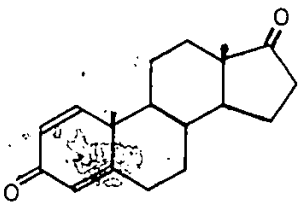
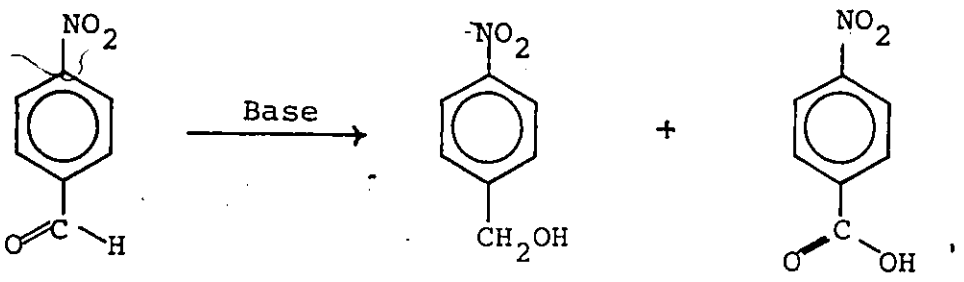


39

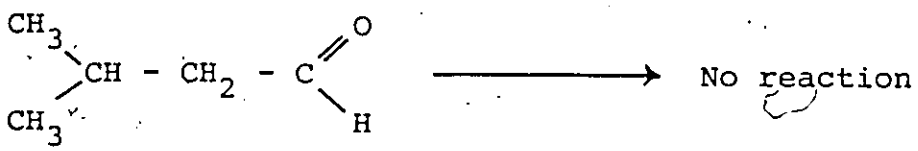
When the reaction was carried out with compounds 35 - 39 starting material was recovered after 48 hours of reaction time. These experiments show that the carbon-carbon and carbon-nitrogen double bonds, and conjugated or nonconjugated carbonyl groups are not reduced under these conditions.

In the case of p-nitrobenzaldehyde 40 the Cannizzaro reaction took place instead of reduction. p-Nitrobenzyl alcohol and p-nitrobenzoic acid were obtained in high yield.



40

A blank reaction was carried out on 40 without $Ru_3(CO)_{12}$ which gave the same products. To determine if there was a small amount of reduction taking place on the aldehyde, to give the alcohol the same reaction was carried out on isovaleraldehyde 41, as the Canizzaro reaction does not take place for aliphatic aldehydes. Therefore if any alcohol is formed then it is produced by $Ru_3(CO)_{12}$ catalysis.



41

However no reaction occurred showing that the aldehyde is not reduced to the alcohol with $Ru_3(CO)_{12}$ under phase transfer conditions.

Other phase transfer catalysts were used to determine the effect on the reduction of nitro to amino groups. When tetrabutylammonium bromide and Aliquat 336 were used as the phase transfer catalysts, there was no significant difference in the yield, reaction time or products (p-chloroaniline was obtained in 100% yield after 4 hours). The reaction, carried out with 18-crown-6 and solid KOH, gave p-chloroaniline in 100% yield in 45 minutes. This shows that 18-crown-6 is a much better phase transfer catalyst for this reaction, but because of its high toxicity it was not used in any other reaction.

The use of other metal catalysts for the phase transfer catalyzed reduction of nitro compounds was also examined, actually prior to the study with $Ru_3(CO)_{12}$. When chlorodicarbonyl rhodium (I) dimer, $[Rh(CO)_2Cl]_2$ was used as the catalyst p-chloroaniline was obtained in 73% yield from p-chloronitrobenzene [65 hours; RT , no 2-methoxy-ethanol]. When the same reaction was carried out at 40-50°C the yield dropped to 44% but the reaction time was shorter [48 hours]. These experiments show that $[Rh(CO)_2Cl]_2$ catalyses the nitro-amino reaction similar to $Ru_3(CO)_{12}$, but in a much less efficient manner.

Bis(benzonitrile)palladium dichloride [$PdCl_2(\phi CN)_2$], tetrakis(triphenylphosphine)palladium [$Pd(PPh_3)_4$], palladium acetate [$Pd(OAc)_2$] or dicobalt octacarbonyl [$Co_2(CO)_8$] under basic phase transfer conditions gave no reaction with p-nitrotoluene. Similarly the use of acidic phase transfer conditions with palladium chloride and palladium acetate, as catalysts resulted in the recovery of starting material using p-nitrotoluene as the substrate.

The phase transfer catalyzed reactions in basic medium were carried out with 50% sodium hydroxide, with these different catalysts (i.e. other than $Ru_3(CO)_{12}$). It was later found out that increasing the base concentration from 5N to 12.5 N (50%) in the $Ru_3(CO)_{12}$ catalyzed process causes a reduction in the yield of p-anisidine from 84% to 25%. Therefore the reason that there was no reaction when $PdCl_2(\phi CN)_2$, $Pd(PPh_3)_4$, $Pd(OAc)_2$ and $Co_2(CO)_8$ were used as catalysts could be partly a consequence of the high base concentration.

The effect of added $Fe(CO)_5$ on the $Ru_3(CO)_{12}$ catalyzed reduction was briefly investigated. When excess $Fe(CO)_5$ and a catalytic amount of $Ru_3(CO)_{12}$ was used in the reaction with p-nitrotoluene, p-toluidine was obtained in 74% yield after 22 hours. As this reaction was carried out in the absence of 2-methoxyethanol, there was a significant improvement in the yield when compared to the

reaction done with $Ru_3(CO)_{12}$ alone. [47% in 72 hours]. When 2:1 $Fe(CO)_5$ to $Ru_3(CO)_{12}$ was used there was little change from the results of the previous experiment. [70% in 20 hours]. When this reaction was carried out with 50% sodium hydroxide instead of 5N the yield dropped from 70% to 15% after 20 hours of reaction.

As the effect of the base was so significant a study of the variation in base concentration was done using p-nitrotoluene as the substrate. The reaction time was 72 hours in all cases and the results are given in Table 4.

Table 4: Variation of the Yield of p-Toluidine with Base Concentration.

Base Concentration N	% Yield of p-toluidine
12.5 (50%)	26
5	47
2	22
6.5	12

This shows that higher and lower base concentrations reduce the yield. It could be that higher base concentrations decompose the metal carbonyl, and lower base concentrations are not sufficient to form the anionic species.

To determine the effect of temperature three reactions were carried out at different temperatures with p-nitrotoluene as the substrate (no 2-methoxyethanol). The reaction time was 72 hours in all cases. (Table 5).

Table 5: Variation of the Yield of p-Toluidine with Temperature.

Reaction Temperature °	% Yield of p-toluidine
0	3
5 - 8	8
25	47
70	15

The yield of p-toluidine is reduced considerably at higher and lower temperatures. In the presence of 2-methoxyethanol the reaction at 0° is slower (8 hours ⟶ 48 hours) but the yield of p-toluidine is the same (95%) as for the reaction done at room temperature (94%).

Different phase transfer catalysts were employed instead of benzyltriethylammonium chloride, for the $Ru_3(CO)_{12}$ catalyzed reaction effected in the absence of 2-methoxy-ethanol. [47% yield of p-toluidine]. When 18-crown-6 and solid KOH was used after 72 hours 55% of p-nitrotoluene was recovered, but interestingly 17% of the N,N'-di-p-tolylurea was isolated (mass $m/_e$ = 240). The yield of p-toluidine was very low (3%). When Aliquat 336 was used as the phase

transfer catalyst in the presence of 50% sodium hydroxide the yield of p-toluidine [26.5%] was approximately the same as when benzyltriethylammonium chloride was used [26%] with 50% NaOH as the aqueous phase.

2.2.2 Carbonylation of nitro compounds with triruthenium dodecacarbonyl

Metal carbonyl induced reductive carbonylation is a process of considerable industrial importance. The nitro functionality has played a major role in this chemistry.

Under phase transfer conditions it has already been shown that a ruthenium hydride is likely formed from $Ru_3(CO)_{12}$ thereby giving the reduction of the nitro compounds in quantitative yields. If on the other hand the anion was not hydridic, carbonylation should take place in an atmosphere of carbon monoxide. Therefore it was of interest to determine the effect of an organic base on these reactions.

The reaction of nitroarenes with a catalytic amount of $Ru_3(CO)_{12}$ in anhydrous benzene using sodium methoxide instead of aqueous sodium hydroxide as the base (50°C), in an atmosphere of carbon monoxide afforded the formamide as the only product. (Table 6). There was only one exceptional case where the azoxy compound was also produced.

When the possible mechanism is considered if

$Ru_3(CO)_{11}^{-2}$ was generated, then one could observe little that had not already been noted in the reaction involving hydroxide ion. However, if methoxide ion attacked the metal carbonyl carbon then the anionic species 42 would be formed, which unlike $Ru_3(CO)_{11}COOH^-$ cannot easily

$$Ru_3(CO)_{12} + {}^-OMe \longrightarrow Ru_3(CO)_{11}COOCH_3^-$$

42

eliminate carbon dioxide. It has been reported[151] that when triiron dodecacarbonyl is used under a synthesis gas (1:1 CO/H_2) atmosphere the carbamate ester is formed. This reaction could be proceeding via different intermediates.

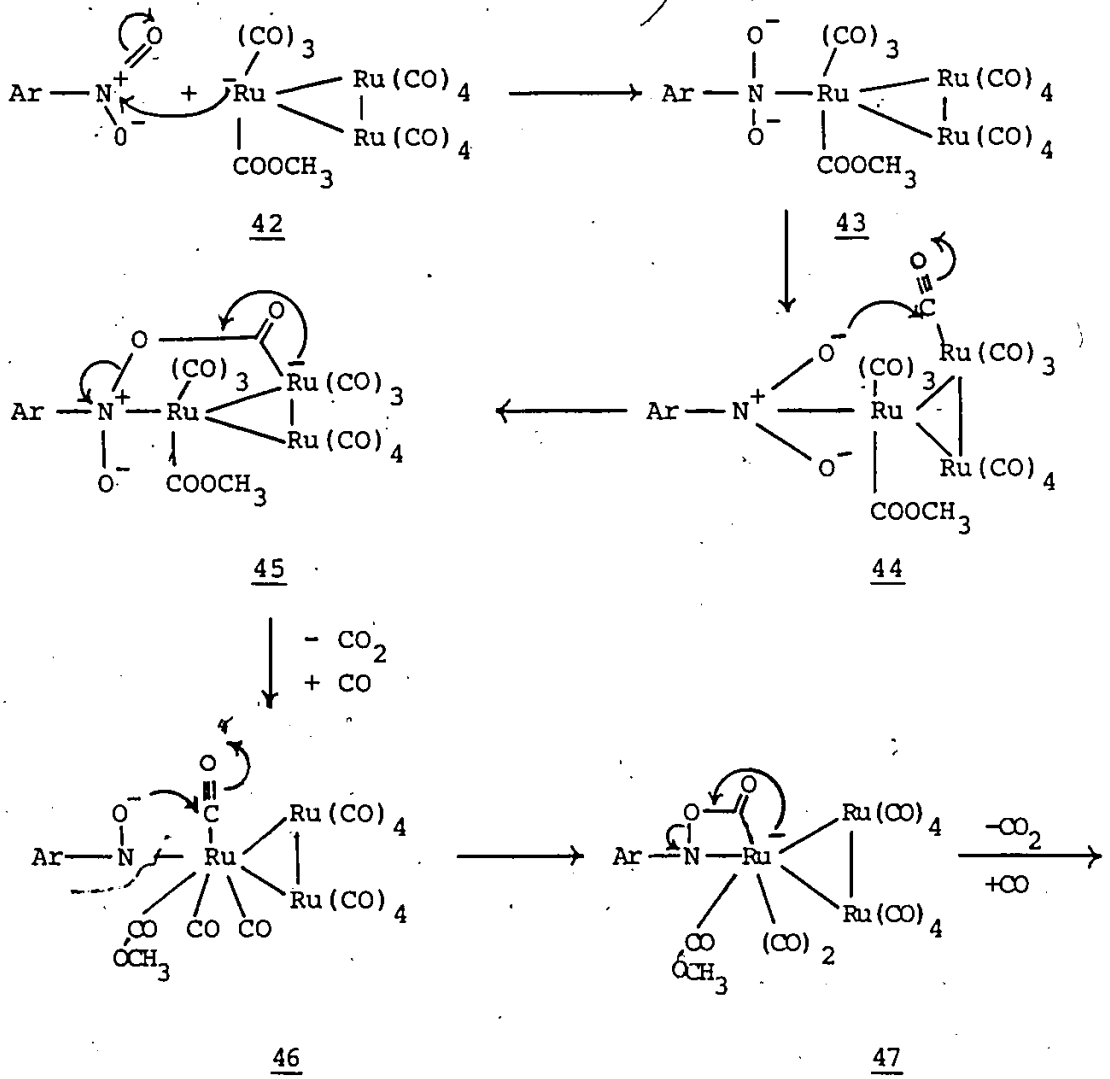
$$Fe_3(CO)_{12} + OMe^- \longrightarrow Fe_3(CO)_{11}\,COOMe^- + Ar\,NO_2$$

$$\downarrow$$

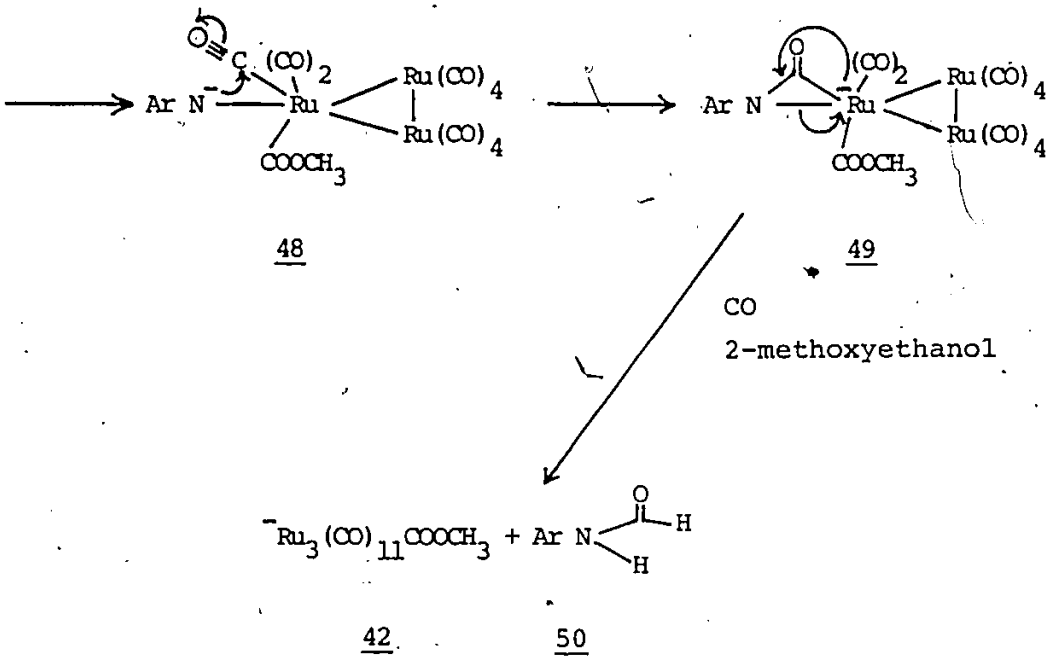
$$Ar\,NH\,COOMe$$

In the ruthenium catalyzed reaction none of the carbamate ester was formed. The difference between the ruthenium and iron reactions is a consequence of the fact that the iron species $Fe_3(CO)_{11}\,COOCH_3^-$ collapses to $Fe(CO)_4\,COOCH_3^-$ in the presence of CO and methoxide ion; the ruthenium complex $Ru_3(CO)_{11}\,COOCH_3^-$ does not undergo declusterification.[152] In the reaction of p-chloronitrobenzene, in addition to the formamide, an azoxy compound was also formed. A

possible mechanism for this carbonylation reaction is shown in Scheme 16.



42 43 44 45 46 47



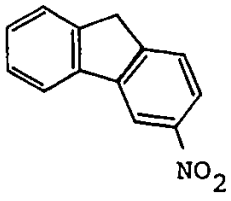
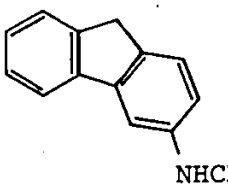
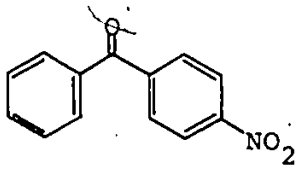
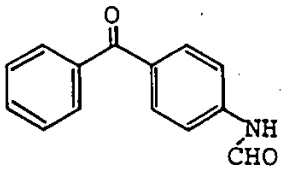
Scheme 16

It was also shown that formamides and amines were formed using the $Ru_3(CO)_{12}$ and $Fe_3(CO)_{12}$ under a synthesis gas atmosphere. Therefore it is conceivable that in such cases the $Ru_3(CO)_{12}$ and $Fe_3(CO)_{12}$ catalyzed reactions proceed via the amine. According to Table 6 it can be seen that no amine is formed from any of the nitro compounds. Therefore when the reaction is carried out in the presence of 2-methoxyethanol it does not proceed via the amine.

It proved difficult to separate the formamide from the residual ruthenium. Attempts to estimate the yield of the crude product by GLC failed. If a method of binding of the ruthenium catalyst on a solid support (eg. polymer, silica, or alumina) is available this reaction could be

carried out to obtain high yields of the formamides, as the separation of the ruthenium residue is by filtration only. The formamide would be the only compound in the liquid phase.

Table 6: Carbonylation of Nitro Compounds by Triruthenium Dodecacarbonyl.

Nitro compound	Reaction time hr.	Formamide 50	Yield %[e]
$p\text{-}CH_3C_6H_4NO_2$	8	$p\text{-}CH_3C_6H_4NHCHO$	11
$p\text{-}CH_3OC_6H_4NO_2$	6	$p\text{-}CH_3OC_6H_4NHCHO$	31
$p\text{-Cl}\ C_6H_4NO_2$	1	$p\text{-Cl}\ C_6H_4NHCHO$	34[f]
	5		25
	7		14

[e]Purified yield. The crude yield from chromatographic analysis was quantitative except for p-chloronitrobenzene which had 50% of the azoxy compound formed.

[f]50% of the azoxy compound was isolated.

Reactions different from the general procedure were carried out on p-chloronitrobenzene to determine if there was any improvement on the yield of the amide. When a catalytic amount of $Fe_3(CO)_{12}$ was used instead of $Ru_3(CO)_{12}$, it took a longer time for the generation of the anion which could be seen from the colour change of dark green to reddish brown. After a reaction time of 72 hours the nitro compound was recovered in 90% yield, and the amine was formed in very low yield (2%). As $Fe_3(CO)_{12}$ was completely soluble in benzene, 2-methoxyethanol was not added. This could be a possible reason (lack of proton source) why there was no reaction.

In the reaction of p-chloronitrobenzene with $[Rh(CO)_2Cl]_2$ in the presence of sodium methoxide, 15-crown-5, in benzene under an atmosphere of carbon monoxide, the nitro compound was recovered in 80% yield after 48 hours. The formamide was separated in 6% yield. The reason for this low conversion could again be attributed to the lack of a proton source.

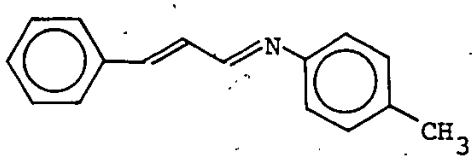
The substitution of potassium t-butoxide for sodium methoxide in benzene gave a lower yield (22.5%) of p-chloroformamide, and 10-13% of p-chloroaniline and 40% of the azoxy compound was separated after 72 hours of reacting. The same reaction in methylene chloride afforded the recovered nitro compound in 90% yield with only 2% of the formamide isolated. Adding 18-crown-6 to the reaction carried out in benzene lowered the yield of formamide from 22.5% $\longrightarrow$ 12% but the other products were the same.

2.3 Dicobalt octacarbonyl catalyzed carbonylation and reaction of organoboranes with imines.

2.3.1 Phase transfer catalyzed reductive acylation of azadienes.

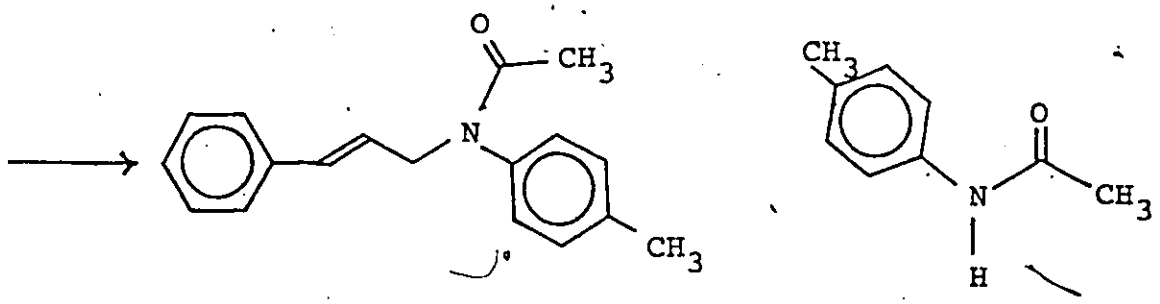
Azadienes, which are easily prepared by the condensation of α,β-unsaturated carbonyl compounds with amines, are well known, stable compounds. The study of the effect of the nitrogen heteroatom of the azadiene, on the phase transfer catalyzed acylation reaction proved to be interesting.

Treatment of the azadiene 51 with methyl iodide, carbon monoxide, benzene, water, benzyltriethylammonium chloride as the phase transfer catalyst, and $Co_2(CO)_8$ as the metal catalyst (10:1 ratio of 51 to $Co_2(CO_8)$ at room temperature for sixty hours, afforded the allyl amide 53 (data in Table 9) in 17% yield with 80% of recovered starting material. When the ratio of 51 to $Co_2(CO)_8$ was increased to 1:1 the allylic amide 53 was formed in good yield (65%) and the amide 52 was isolated in 33% yield.



51

$Co_2(CO)_8/CO\ /CH_3I$
$PhCH_2N(C_2H_5)_3^+Cl^-$
1 atm. RT.
H_2O, C_6H_6



53 65% 52 33%

Compounds 52 and 53 were obtained in the same yields when the reaction was repeated in the dark. The reaction was very fast at 60° (2 minutes) but the yield of 53 decreased to 40% and 52 was isolated in 39% yield. It is conceivable that an intermediate involved in the formation of 53 is unstable at elevated temperatures.

A variety of reaction conditions were used with the substrate 51 in order to determine the effect of the phase transfer catalyst, metal carbonyl, organic phase, and base concentration on the yield of the allylic amides. In the absence of a phase transfer catalyst the yield of the allyl amide decreased from 65% to 21% (18 hours reaction time), while p-methylacetanilide was formed in 61% yield. Benzyltriethylammonium chloride is a better phase transfer agent than Aliquat 336, since the reaction using the latter was slower (18 hours) and afforded the allyl amide in 41% yield. When solid KOH and 18-crown-6 was used there was no reaction after 18 hours. Only starting material was recovered when the

reaction was run in the absence of $Co_2(CO)_8$, but in the presence of benzyltriethylammonium chloride. Methylene chloride can be used as the organic phase in place of benzene, but the yield of 53 was poor (12%) while the less important 52 was isolated in 60% yield. When the reaction was carried out under homogeneous conditions [i.e. without water and a phase transfer catalyst] no allyl amide was formed. Rather 52 was obtained in 35% yield with the remainder being recovered starting material. The extra hydrogen in 52 arises during work up of the reaction mixture.

This phase transfer reaction shows an interesting dependence on the base concentration of the aqueous phase [Table 7]. At very high base concentration, i.e. 12.5 N NaOH, only 52 was formed. At 5N NaOH, a small amount of 53 was obtained, the major product being 52. As the concentration of the base was decreased, the yield of the allylic amide increased to reasonable levels, and 52 the product of cleavage of the azadiene, was obtained in reduced yields.

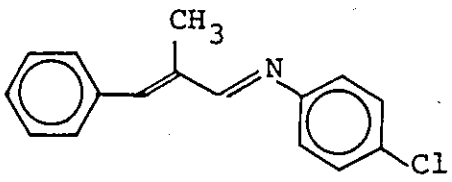
Table 7 : Effect of Base Concentration on the Phase Transfer Catalyzed Reaction of Azadiene 51 with $Co_2(CO)_8$, CH_3I and CO

NaOH concentration N	Reaction time hr.	% yield	
		53	52
12.5	18		48[g]
5.0	3	8	88
2.0	8	22	71
0.5	8	48	36
0.1	6.5	56	38
H_2O	6.0	65	33

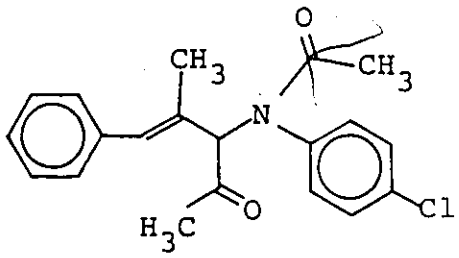
[g] 50% of 51 was recovered.

Substitution of methanol for water or aqueous NaOH gave 53 in only 20% yield (and 52 in 61% yield). One can use an acid phase transfer catalyst, p-toluenesulfonic acid, for the conversion of 51 to 53 (water as the aqueous phase), the yield being somewhat lower (51%) than when a quaternary ammonium salt was employed as the catalyst. Using a stoichiometric amount of methyl iodide or decreasing the amount of water from 20 ml to 1 ml did not have a beneficial effect on the yield of 53. There was no reaction when $CH_3(CH_2)_5Br$ was used instead of CH_3I.

On the basis of the above results, the highest yield of allylic amide 53 was realized using water as the aqueous phase, benzene as the organic phase, and benzyltriethylammonium chloride as the phase transfer catalyst. These conditions were then applied to the reactions of a series of azadienes with carbon monoxide, methyl iodide and dicobalt octacarbonyl. Fair to good yields (Table 8) of the allyl amides were obtained in all but one reaction. The products were identified on the basis of analytical and spectral data [Table 9]. The exceptional case was 66 where 67 an unanticipated product of diacylation of the azadiene was formed. With this one exception the reaction was quite rapid particularly at 60°C.

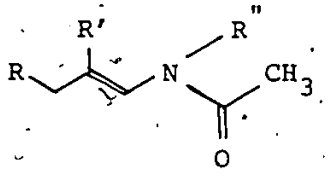


66

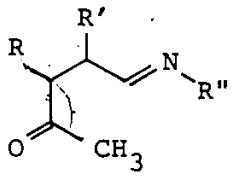


67

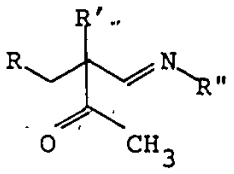
What makes the conversion of azadiene to allylic amides a useful one is its complete regiospecificity. Neither enamides 68 nor isomeric iminoketones 69, 70 were detected in any of these reactions.



68



69



70

Table 8: Reaction of Azadienes with $CO/CH_3I/Co_2(CO)_8/H_2O/C_6H_6/PhCH_2N(C_2H_5)_3^+Cl^-$

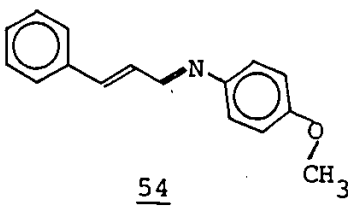
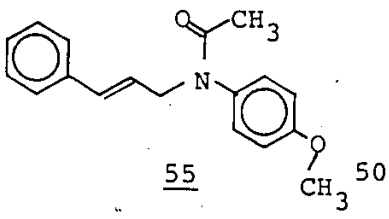
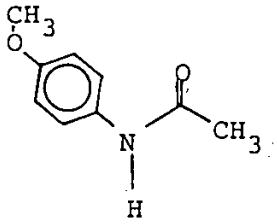
Azadiene	Reaction temp. °C	Reaction time	Product	Yield %
51	R T	6 hrs.	53	65
			52	32
	60	2 min.	53	40
			52	39
 54	R T	8 hrs.	 55	50
			 56	33

Table 8: (Cont'd)

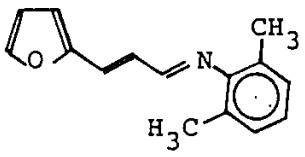
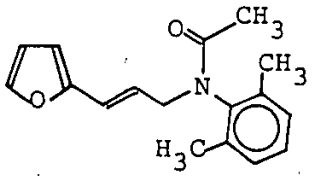
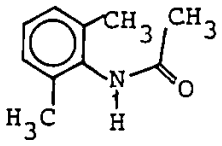
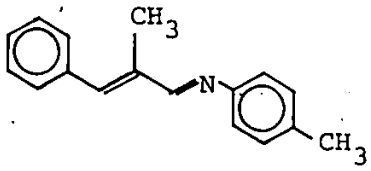
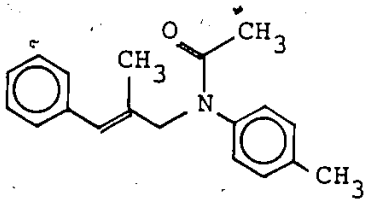
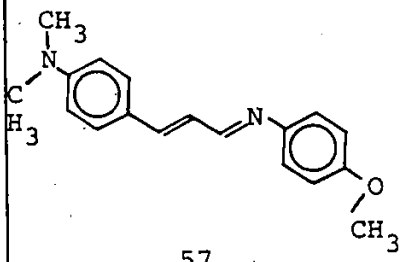
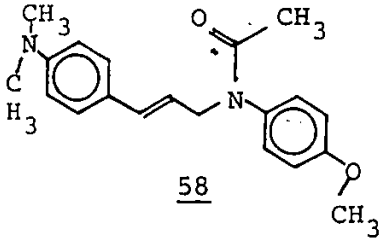
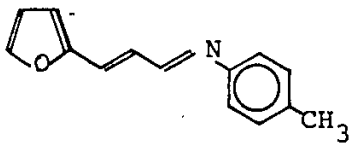
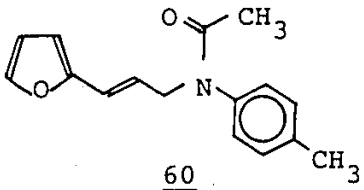
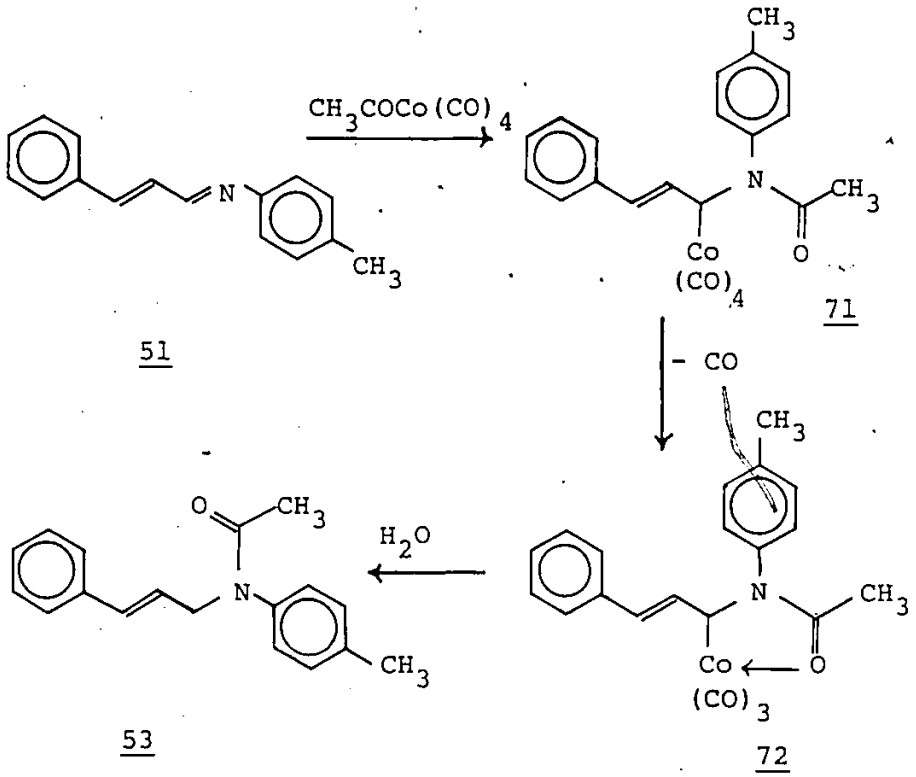
Azadiene	Reaction temp. °C	Reaction time	Product	Yield %
 61	R T	3 hrs.	 62	50
			 63	50
 64	60	8 hrs.	 65	41
			52	50

Table 8: (Cont'd)

Azadiene	Reaction temp. °C	Reaction time	Product	Yield %
 57	R T	8 hrs.	 58	59
			56	39
	60	6 hrs.	58	45
			56	53
 59	R T	2 hrs.	 60	62
			52	34
	60	2 min.	60	31
			52	66
66	R T	6 hrs.	-	-
	60	6 hrs.	66	50
			67	50

A possible mechanism for allylic amide formation is outlined in Scheme 17.

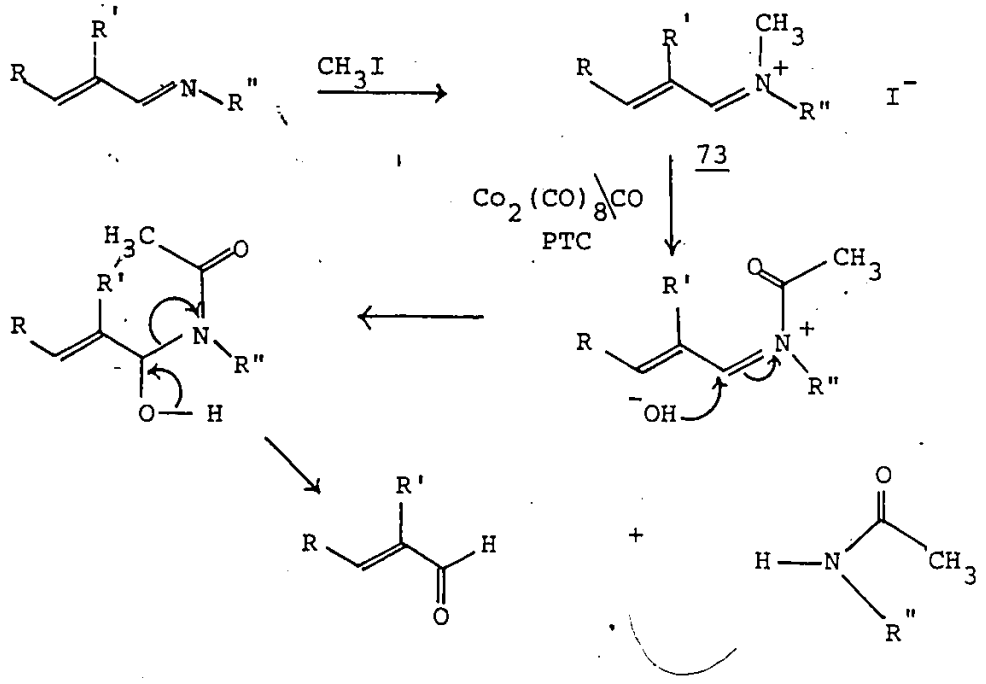


Scheme 17

1,2-Addition of the in situ generated acetylcobalt tetracarbonyl to the carbon nitrogen double bond of 51 would give the σ-allylcobalt complex 71. Such a 1,2-addition likely occurs at the least substituted double bond of a 1,3-diene affording a σ-allyl complex which is convertible to a π-allyl complex on subsequent loss of carbon monoxide.[61] Rather than form an analogous π-allyl complex on loss of carbon monoxide, coordination

of the amide oxygen of 71 to the metal may occur to give 72. The oxygen of an amide is more basic than that of a ketone. [The intermediate π-allyl complex, formed using 1,3-dienes as substrates, contains a ketone functionality]. The allylic amide can then arise by hydrolytic cleavage of the carbon-cobalt bond of 72. Although the generation of a π-allyl intermediate cannot be ruled out, one would have expected, in such an event, the enamide 68 to have been formed along with 53.

The mechanism of the cleavage and carbonylation of 51 ⟶ 52 is not known. One possibility is that it proceeds via an iminium salt; as shown in Scheme 18.



Scehme 18

This mechanism was disapproved by a reaction carried out with 51 in the absence of $Co_2(CO)_8$ under phase transfer conditions. If the initial imine salt 73 is made, as there is no $Co_2(CO)_8$ for further reaction, it will undergo hydrolysis affording the aldehyde and amine. The anticipated hydrolysis did not take place. After 48 hours of reaction the azadiene 51 was recovered quantitatively. The other possibility is that the imine is first hydrolyzed to give the amine and cinnamaldehyde. The amine would then undergo carbonylation affording the p-tolyl derivative of acetanilide. In every reaction the α-β unsaturated aldehyde was isolated in low yield. The presence of this compound shows that some hydrolysis of the azadiene is taking place under phase transfer conditions.

Table 9

Melting Points, Analytical, and Pertinent Spectral Data for the Allylic Amides

Product	Mp.°C	Anal. Calcd. (found)			IR,[i] ν_{CO}	MS	NMR, δ[j]
		C	H	N	cm^{-1}	m/e	ppm
53	212-215	81.47(81.10)	7.22(7.01)	5.28(5.11)	1655	265$[M]^+$ 222$[M-COCH_3]^+$	1.87(s,3H,$COCH_3$),2.43 (s,3H,CH_3),3.90(m,2H,CH_2) 6.20(m,1H,CH=),6.50-7.50 (m,10H,aromatic and olefinic protons).
55	188-190	76.84(76.81)	6.81(6.58)	4.98(4.89)	1655	281$[M]^+$ 238$[M-COCH_3]^+$	1.73(s,3H,$COCH_3$)1.83(s,3H $COCH_3$),3.82(s,3H,OCH_3), 3.85(s,3H,OCH_3),3.93(m, 2H,CH_2),6.30(m,1H,CH=), 6.40-7.40(m,10H, aromatic and olefinic protons).[k]
58	100-104	74.04(74.56)	7.46(7.51)	8.63(8.24)	1655		1.70(s,3H,$COCH_3$),2.83(s, 6H,$N(CH_3)_2$),3.70(m,2H,CH_2) 3.75(s,3H,OCH_3),6.20(m,1H CH=),6.30-7.35(m,9H, aromatic and olefinic protons).

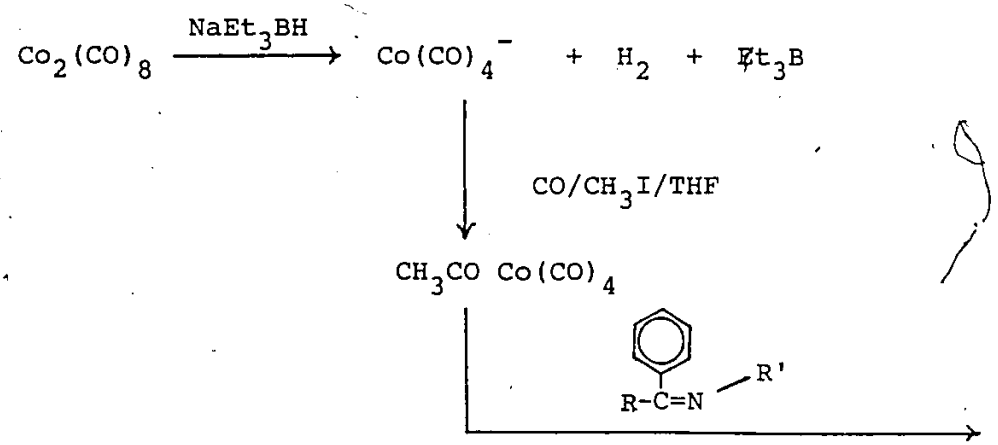
Table 9 (Cont'd)

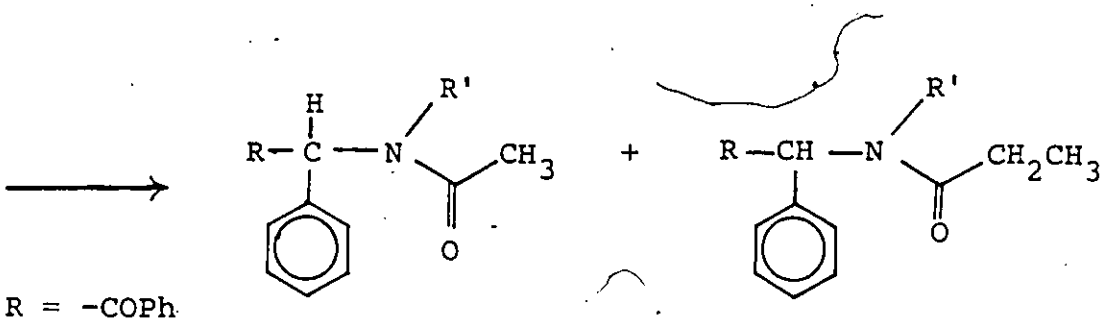
Product	Mp. °C	Anal. Calcd. (found) C	H	N	[i] IR, ν_{CO} cm^{-1}	MS m/e	[j] NMR, δ ppm
60	184 dec.	75.27(74.98)	6.71(6.66)	5.48(5.71)	1645	[a] 255 $[M]^+$ 212 $[M-COCH_3]^+$	1.78(s,3H,$COCH_3$),2.45(s,3H,CH_3),3.98(m,2H,CH_2),5.63(d,1H,J=3.0 Hz,H3 of furan)6.10(m,1H,CH=),6.75-7.45 (m,7H, remaining protons).
62	130 dec.	75.81(75.32)	7.11(6.97)	5.20(5.22)	1655		1.96(s,3H,$COCH_3$),2.35(s,3H,CH_3,2.38(s,3H,CH_3),3.95(m,2H,CH_2),5.63(d,1H,J=3.5 Hz,H-3 of furan),6.08(m,1H,CH=),6.75-7.49 (m,6H, remaining protons)
65	Oil	81.68(82.00)	7.58(7.42)	5.01(4.80)	1650		1.85(s,3H,$COCH_3$),2.12(s,3H,CH_3C=),2.32(s,3H,CH_3),3.63(m,2H,CH_2),6.80-7.50(m,10H, aromatic and olefinic protons).
67	Oil	70.27(70.64)	5.90(5.89)	4.10(4.02)	1720 1650	343,341 $[M]^+$ 300,298 $[M-COCH_3]^+$	1.63,(s,3H,$COCH_3$),1.87(s,3H,$COCH_3$),2.27(s,3H,CH_3C=),5.70(s,1H,$CHOCOCH_3$) 6.77-7.43(m,10H, remaining protons).

[i] In $CHCl_3$. [j] $CDCl_3$ with tetramethylsilane (TMS) as internal standard. [k] Mixture of cis and trans isomers.

2.3.2. Homogeneous reductive acylation of imines.

As the phase transfer reductive acylation of aza-dienes showed a remarkable dependence on the concentration of the base it seemed of interest to determine the nature of the reaction under homogeneous conditions; even though the more expensive and difficult to handle reagent sodium triethylborohydride had to be employed. Cobalt tetracarbonyl anion can be generated by the reaction of dicobalt octacarbonyl with the triethylborohydride anion according to the procedure by Gladysz and coworkers.[141,142] They had also stated that the by-products of the reaction were hydrogen gas and triethylborane (Et_3B) both of which were evolved in the reaction and did not participate in any subsequent reaction. Therefore it was very surprising to observe the production of the ethyl amide as a minor product in the reaction which gave the anticipated methyl amide as the major product.





R = -COPh

R'= Ph

When this reaction was carried out with an azadiene as the starting material it gave a large number of products. Simple imines as well as α-keto imines underwent regeospecific reductive acylation in the presence of a stoichiometric amount of $Co_2(CO)_8$, CH_3I and carbon monoxide in anhydrous tetrahydrofuran at 60°C. This reaction was tried on a series of simple and α-keto imines. The products, their yields and the reaction times are given in Table 10. Products were identified on the basis of elemental analysis (C,H,N,), IR, NMR and mass spectral data (Table 13).

Table 10: Reaction of Simple and α-Keto Imines with, $CH_3I/Co_2(CO)_8/NaEt_3BH/CO$ in THF at 60°

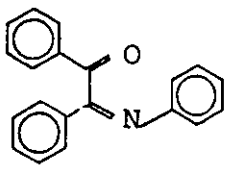
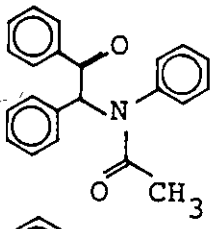
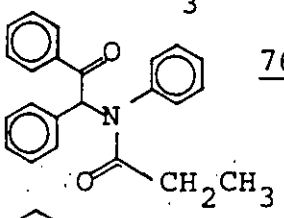
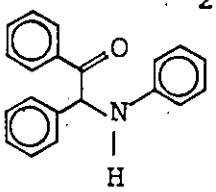
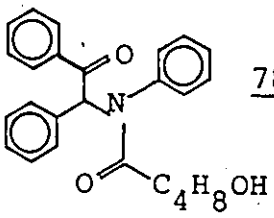
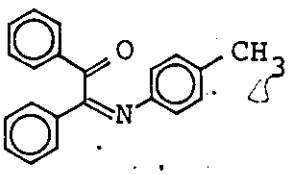
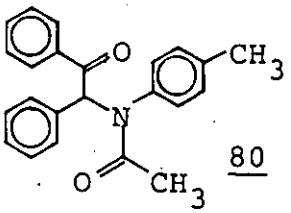
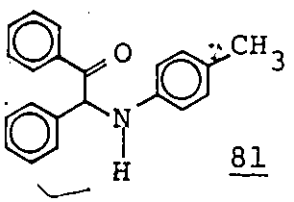
Imine	Reaction time hr.	Product	Yield %
 74	24	 75	44
		 76	32
		 77	12
		 78	8
 79	24	 80	74
		 81	12

Table 10: (Cont'd)

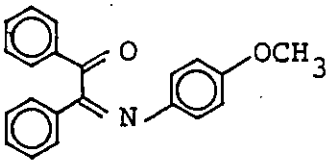
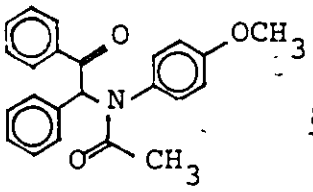
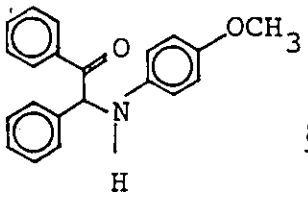
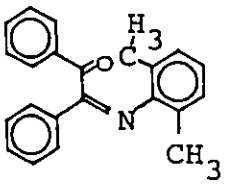
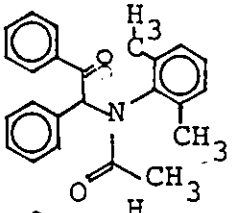
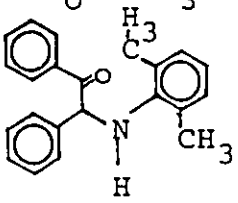
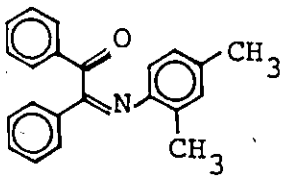
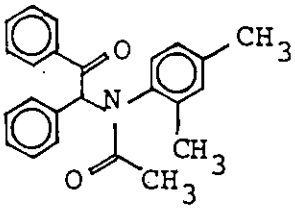
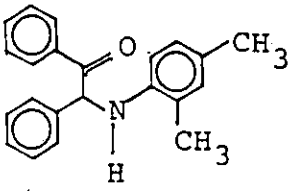
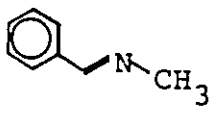
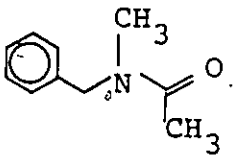
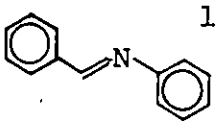
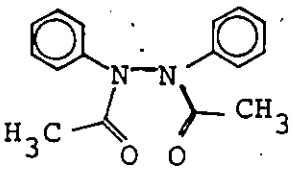
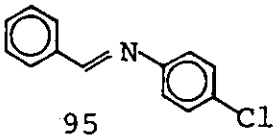
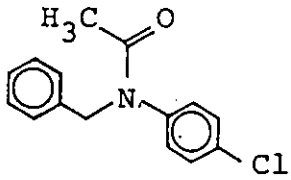
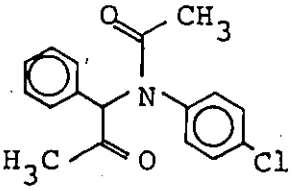
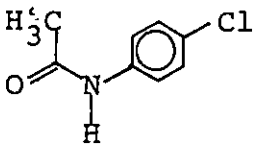
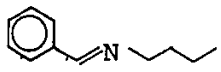
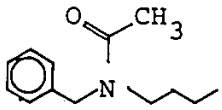
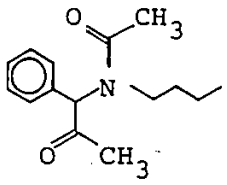
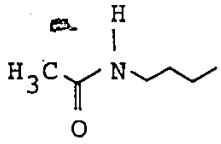
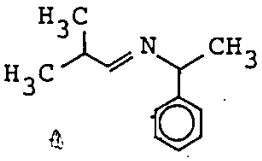
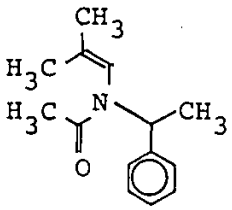
Imine	Reaction time hr.	Product	Yield %
 82	7	 83	88
		 84	11
 85	120	 86	20
		 87	43
 88	72	 89	77
		 90	10

Table 10: (Cont'd)

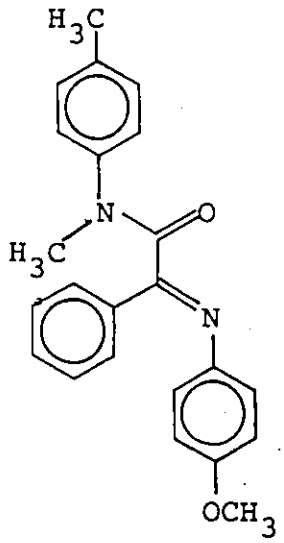
Imine	Reaction time hr.	Product		Yield %
			92	40
91	48			
 [1]			94	28
93	48			
			96	23
95	72			
			97	6
			98	15

[1] This reaction when carried out with $LiEt_3BH$ (superhydride) gave the same product (32% yield).

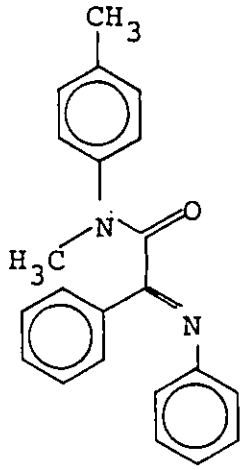
Table 10: (Cont'd)

Imine	Reaction time hr.	Product	Yield %
 99	72	 100	30
		 101	40
		 102	15
 103	24	 104	80

As the keto imines reacted so well to give the keto amides it was of interest to determine if iminoamides would give the diamides. For this, compound 105 was prepared and subjected to the reductive acylation reaction. After four days of reaction the reaction mixture consisted principally the starting imine. There were minute amounts of a number of other compounds formed, none of which could be isolated in pure form. As compound 105 has an amino hydrogen it was possible this interfered in the reaction.



105



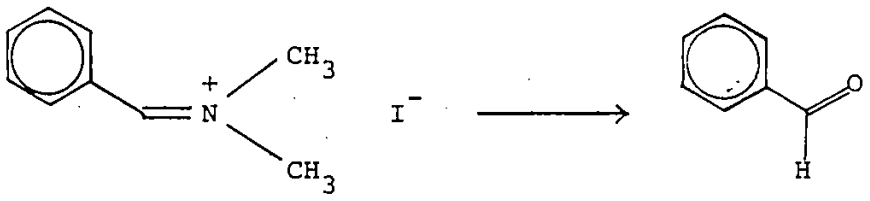
106

Therefore, the tertiary amide 106 was subjected to the reductive acylation reaction. The starting material was recovered in almost quantitative yield (after 4 days). This shows that the amido group deactivates the carbon nitrogen double bond to such an extent that it does not

react with the acylcobalt tetracarbonyl species.

In order to find out if a simple olefin would undergo reductive acylation under these conditions vinyl cyclohexane was used as the substrate. After three days of reaction time vinylcyclohexane was recovered in almost quantitative yield.

Since the homogeneous method gives reductive acylation it seemed conceivable that such a process could also occur under phase transfer conditions. Several α-keto imines were subjected to phase transfer catalyzed reductive acylation. However, as seen from the data in table 11 the anticipated methyl amide was formed in much lower yield than in the homogeneous reaction. This phase transfer reaction was also carried out on the iminium salt of N-benzylidene-methylamine (107).



107

Only benzaldehyde was recovered when the reaction was complete. This shows that 107 is not an intermediate for the methyl amide synthesis.

Table 11: Phase Transfer Catalyzed Reductive Acylation of α-Keto Imines.

Starting imine	Yield and reaction time of the methyl amide			
	Phase transfer conditions		Homogeneous	
	Yield %	Reaction time hr.	Yield %	Reaction time hr.
82	10	120	88	7
79	20	120	74	24
74	18	120	44	24

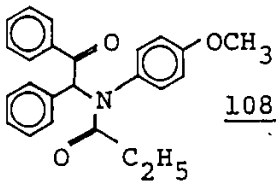
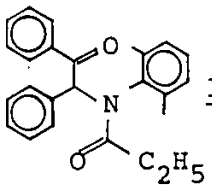
The phase transfer catalyzed reductive acylation reaction, when carried out in an atmosphere of CO/H_2, gave 5% of phenylacetic acid with N-benzylidinemethylamine (91). This was after three days of reaction. (91 was recovered in 90% yield).

When the homogeneous reductive acylation reaction was carried out on 74 in the absence of $Co_2(CO)_8$ the reduced product 77 was isolated in 5% yield and 90% of 74 was recovered after three days of reaction. When $(CH_3)_2$ CHCOCl was employed instead of CH_3I in the presence of $Co_2(CO)_8$ 74 was recovered in 92% yield (after 48 hours).

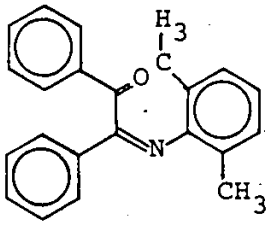
As indicated in table 10, 74 gave 10% of the ethyl amide, which indicates the unprecedented participation of triethylborane in these reactions. Therefore in the absence of methyl iodide the ethyl amide should be the only product. When the reaction was carried out in the absence of methyl

iodide it produced the ethyl amide in fair yield as shown in Table 12. These compounds were identified by their IR, NMR, mass spectral data and C,H,N analytical data (Table 13).

Table 12: Reaction of α-Keto Imines with $Co_2(CO)_8$/ $NaEt_3BH$/CO in THF at 60°C in the absence of CH_3I.

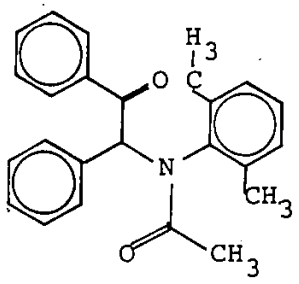
Imine	Reaction time hr.	Product	Yield %
82	24	 108	40
74	24	76	45
85	24	 109	60

It is interesting to note that the steric effect is more pronounced when the reaction is carried out in the presence, rather than in the absence of methyl iodide. This can be seen from the reaction times and yields for the formation of ethyl and methyl amides from the N-2,6-dimethylphenyl substituted keto imine 85. Such dramatic effects were not found when steric factors were of minimal importance (e.g. 74 ⟶ 76).



$Co_2(CO)_8/NaEt_3BH/CO/THF$

CH_3I

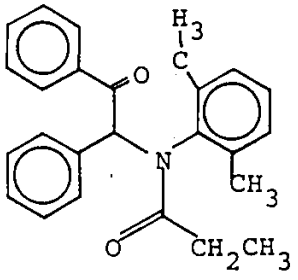


86

20% 120 hrs.

No CH_3I

$Co_2(CO)_8/NaEt_3BH/CO/THF$



109 60% 24 hrs.

Table 13

Melting Points, Analytical, and Pertinent Spectral data for the simple and Ketoamides.

Product	Mp. °C	— Anal. Calcd. (found) — for new compounds			IR, $\nu_{C=O}$ cm^{-1}	MS	NMR, δ
		C	H	N		m/e	ppm
75	151-153	80.37(80.22)	5,78(5.81)	4.20(4.25)	1660(s) 1710(s)		1.83(s,3H),7.12-7.42 (m,14H),7.95-8.10(m,2H)
76	118-119	80.48(80.06)	6.12(6.11)	4.08(4.06)	1643(s) 1705(s)		1.1(t,3H,J=8Hz),2.12 (q,2H,J=8Hz),7.0-7.45 (m,14H),7.85-8.15(m,2H)
78	137-138	76.92(77.49)	6.57(6.50)	3.43(3.61)	1648(s) 1703(s)	369 $[M-H_2O]^+$	1.55(m,4H),2.00(t,2H, J=7Hz),3.55(t,2H,J=7Hz) 7.10-7.5(m,14H)7.88-8.05(m,2H)
80	144-145	80.44(79.99)	6.16(6.03)	4.08(4.01)	1650(s) 1705(s)		1.85(s,3H),2.20(s,3H), 6.9-7.5 m,(13H),7.90-8.10(m,2H)
83	125-126	76.86(76.78)	5.89(5.55)	3.90(3.82)	1650(s) 1700(s)		1.9(s,3H),3.8(s,3H), 6.71-7.60(m,13H),7.82-8.15(m,2H)
86	103-105	80.67(80.75)	6.44(6.45)	3.92(3.88)	1650(s) 1690(s)		1.80(s,3H),2.12(s,3H) 2.72(s,3H),6.65-7.55 (m,12H),7.95-8.18(m,2H)

Table 13 (Cont'd)

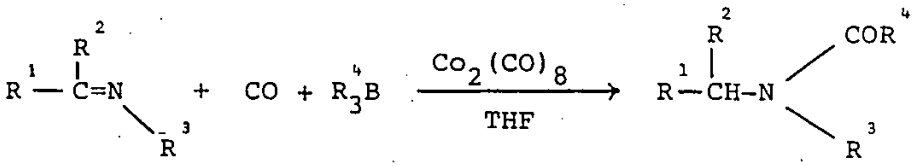
Product	Mp. °C	— Anal. Calcd. (found) — for new compounds C	H	N	IR, $\nu_{C=O}$ cm^{-1}	MS m/e	NMR, δ ppm
89	125-126	80.67(80.74)	6.44(6.63)	3.92(3.57)	1645(s) 1695(s)		1.90(s,3H) 1.92(s,3H), 2.10(s,3H), 7.10-7.52 (m,12H) 7.82-8.10 (m,2H).
92	Oil				1680	163 $[M]^+$ 120, 105,91	2.21(s,3H), 2.80(s,3H) 4.66(m,2H) 7.45(m,5H)
94							2.20(s,6H) 7.20-7.91 (m,10H)
96	Oil				1660(s)	259 $[M]^+$ 216 $[M-COCH_3]$ 105, 91	1.83(s,3H), 4.85(m,2H), 6.8-7.6(m,9H)
97	Oil				1663(s) 1733(s)	305 $[M]^+$ 259 $[M-COCH_3]^+$ 216 $[-COCH_3]$ 183	2.00(s,3H), 2.40(s,3H), 6.82(m,1H), 7.40(m,9H)
100	Oil				1645(s)		0.82(t,3H) 1.65(m,4H), 2.20(s,3H) 3.15(m,2H), 4.42(m,2H), 7.38(m,5H)

Table 13 (Cont'd)

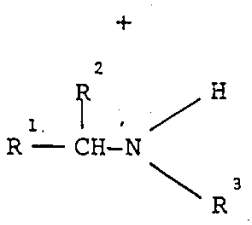
Product	Mp. °C	— Anal. Calcd.(found) — for new compounds C	H	N	IR, $\nu_{C=O}$ cm^{-1}	MS m/e	NMR, δ ppm
101	Oil				1670 1735(s)	247 $[M]^+$ 204 $[M-COCH_3]^+$ 161 $[-COCH_3]$	0.90(t,3H),1.75(m,4H), 2.1(s,3H)2.2(s.3H),3.3 (t,2H)7.0(m,1H)7.5 (s,5H)
104	Oil				1645(s)	217 $[M]^+$ 202 141, 113	1.45(s,3H),1.5(d,3H,J= 6Hz)1.75(s,3H),2.0(s, 3H)3.50(m,1H),6.0(m,1H 7.20(s,5H)
108	Oil	77.19(76.80)	6.21(6.63)	3.75(3.87)	1650(s) 1700		1.0(t,3H,J=7Hz) 2.10(q,2H,J=8Hz)3.70 (s,3H),6.65-7.4(m,13H), 7.75-8.0(m,2H)
109	154-154.5	80.83(80.74)	6.78 (6.63)	3.77(3.87)	1645(s) 1695		0.8(t,3H,J=5Hz) 1.85(q,2H),2.02(s,3H) 2.45(s,3H)6.45-7.23 (m,12H),7.62-7.98 (m,2H)

2.3.3 Dicobalt octacarbonyl catalyzed reaction of organoboranes with imines.

As previously noted α-ketoimines will react with sodium triethylborohydride and cobalt carbonyl in THF, under carbon monoxide (in the absence of methyl iodide), to give the ethyl amide. It seemed conceivable that triethylborane, formed during the generation of cobalt tetracarbonyl anion, participates in the reaction that gives the ethyl amide. If this reasoning is correct then the reaction of α-keto-imines (or other Schiff bases) with organoboranes and carbon monoxide should afford a variety of β-keto amides. However no reaction occurred under these conditions. Nevertheless, it was found that the presence of catalytic amounts of dicobalt octa-carbonyl does indeed result in the reductive carbonylation and alkylation of Schiff bases by organoboranes and carbon monoxide.



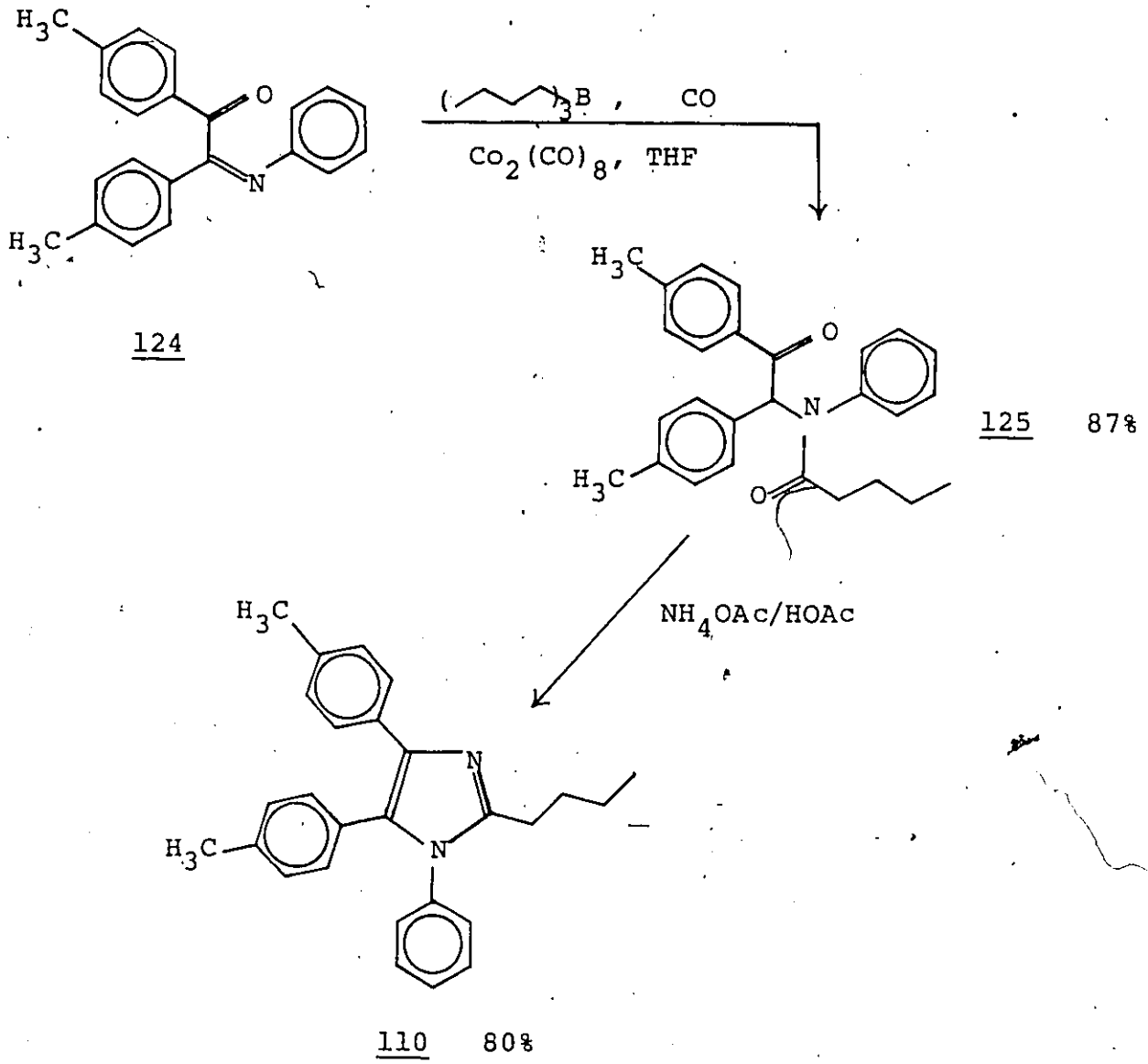
(A) (B) (C)



(D)

Carbonylation of a Schiff base (A) with an equimolar amount of an organoborane (B) and a catalytic quantity of dicobalt octacarbonyl affords the amides (C) in good yields. [Table 14] This reaction can be effected in tetrahydrofuran, methylene chloride or hexane, under mild conditions. (60°C, 1 atm. pressure). The reaction is faster in THF than in hexane or methylene chloride and the product yields are higher in THF. The saturated amine (D) was also formed in some instances.

As the results in Table 14 indicate, the metal carbonyl catalyzed reaction is a versatile one since variation can be made on the nature of both the organoborane and the Schiff base. It is applicable to aliphatic and aromatic organoboranes and to simple as well as to α-keto imines. The organoborane when not commercially available, was generated from the appropriate olefin by hydroboration, and therefore one can convert olefins to amides in this manner. The reaction is regiospecific and in the case of α-keto imines ((A), R^2= carbonyl containing group), gives β-keto amides. These compounds are of considerable use in the synthesis of 1,3 azoles [153]. For example treatment of 124, which was obtained by the reaction of the appropriate Schiff base with tributylborane, $Co_2(CO)_8$ under carbon monoxide in THF, when reacted with ammonium acetate in acetic acid afforded 2-n-butyl-1-phenyl-4,5-di-p-tolylimidazole 110 in 80% yield.



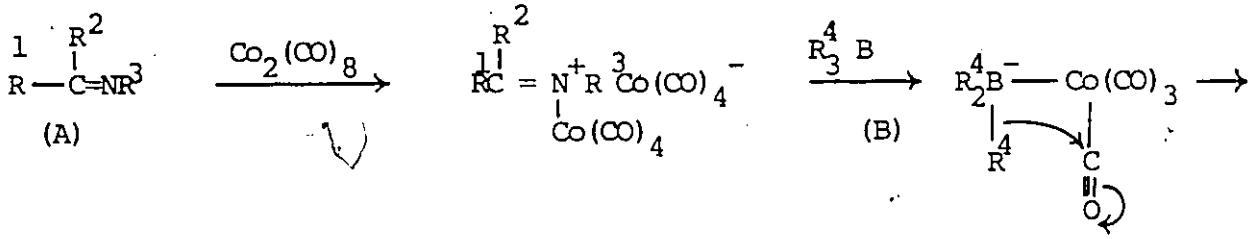
124

125 87%

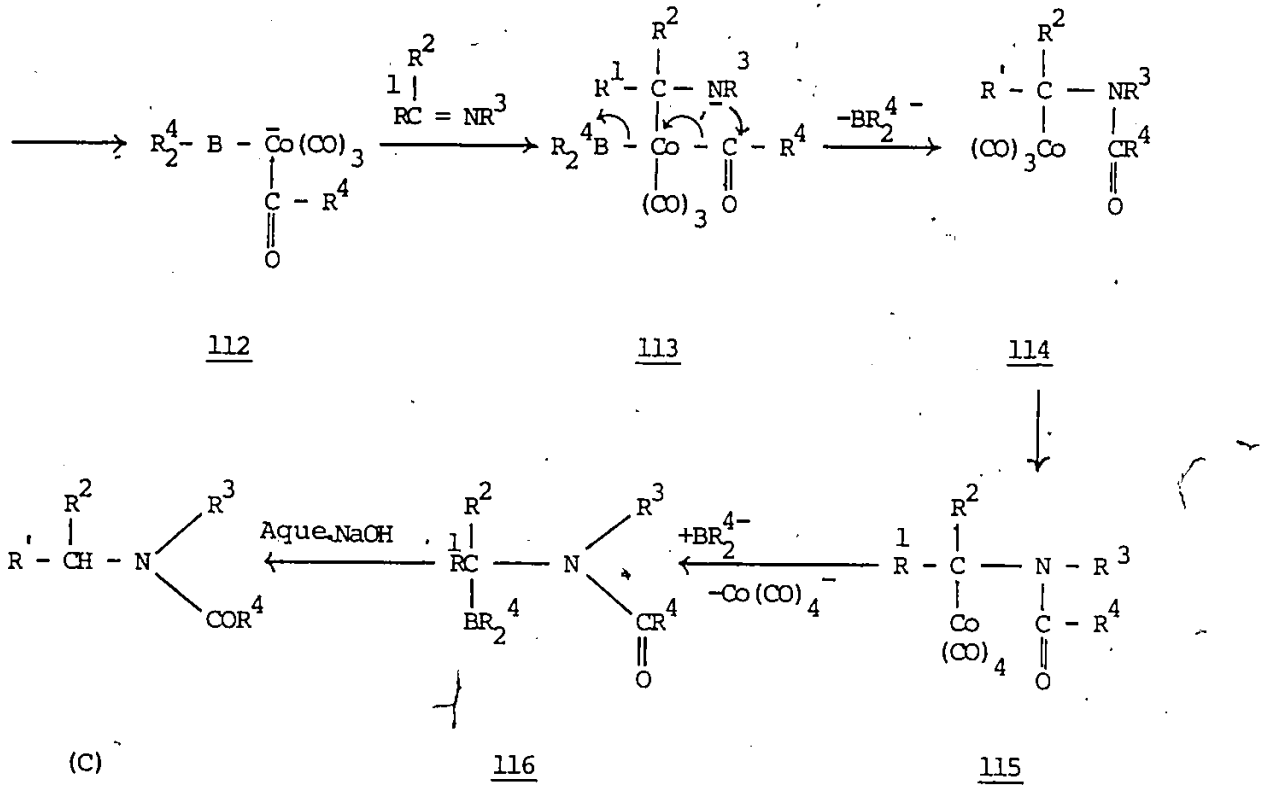
110 80%

A possible pathway for the dicobalt octacarbonyl catalyzed-organoborane-imine-carbon monoxide reaction is outlined in Scheme 19. Reaction of (A) with the catalyst may give an ion pair, the anionic component being the cobalt

tetracarbonyl anion. The latter may then interact with the organoborane (B) to give 111. A strong interaction between the organoborane and $Co(CO)_4^-$ is not required; in fact there is evidence against such an interaction on exposure of triphenyl borane to $Co(CO)_4^-$ in an argon atmosphere.[154] All that is necessary is a weak interaction of sufficient duration under a carbon monoxide atmosphere, to enable migration of an alkyl or aryl group to occur from boron to a carbonyl carbon to give 112. Addition of 112 to the imine (to give 113) and subsequent acyl transfer and elimination of dialkyl or diarylboron anion would afford 114. Carbonylation of 114 to 115 and then regeneration of $Co(CO)_4^-$ by displacement by $R^4_2B^-$ would give 116. As these reactions are worked up in aqueous sodium hydroxide boron-carbon bond cleavage will take place affording the amide (C).



111



Scheme 19

Repeated attempts were made to isolate the intermediate anion by trapping with bis(triphenylphosphine)iminium chloride (PPN^+Cl^-). A PPN^+ salt was isolated from the reaction of tributylborane with a stoichiometric amount

of $Co_2(CO)_8$ under carbon monoxide. This was a pale green solid which in THF gave a bright lime green solution. The NMR of this complex showed the presence of an ethyl group. When the imine 74 was added to a THF solution of this salt and left to react, the starting imine 74 was isolated in 100% yield. No definitive experimental evidence could be obtained for the mechanism of this reaction. Therefore it must be stressed that Scheme 19 simply provides a working hypothesis for rationalizing the catalytic process. The emphasis of this research has been on the synthetic aspects of the chemisty.

Table 14: The $Co_2(CO)_8$ Catalyzed Reaction of Imines with Organoboranes and CO in THF at 60°C.

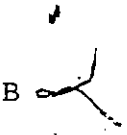
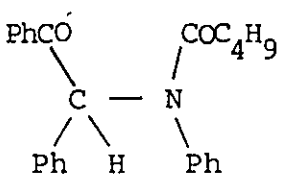
Imine (A)	Organoborane (B)	Reaction time hr.	Product	Yield %
74		24	76	50
R^1= Ph R^2= -COPh R^3= Ph	$(C_2H_5)_3B$		77	48
	$(C_4H_9)_3B$ 	36		
			117	82
			77	18

Table 14 (Cont'd)

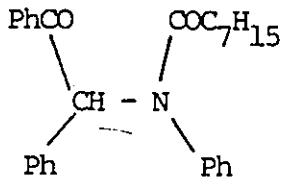
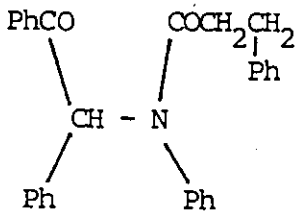
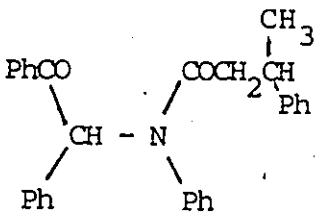
Imine (A)	Organoborane (B)	Reaction time hr.	Product	Yield %
74	$(C_7H_{15})_3B$	48		
			118	55
			77	22
	$(PhCH_2CH_2)_3B$	48		
			119	60
			77	10
	$(PhCH(CH_3)CH_2)_3B$	48		
			120	30
			77	40

Table 14 (Cont'd)

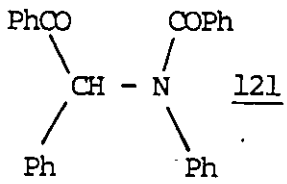
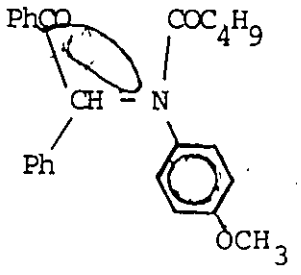
Imine (A)	Organoborane (B)	Reaction time hr.	Product	Yield %
74	$(Ph)_3B$	18	 121	67[n]
			77	10
	$(CH_3CH_2\underset{\displaystyle CH_3}{\underset{\vert}{CH}})_3B$	120	—	—
82	$(C_2H_5)_3B$	48	108	33
R^1= Ph R^2= -CPh (=O) R^3= p-$CH_3OC_6H_4$			84	65
	$(C_4H_9)_3B$	48		
			122	76

Table 14 (Cont'd)

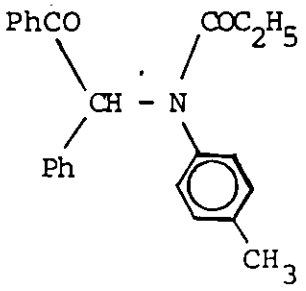
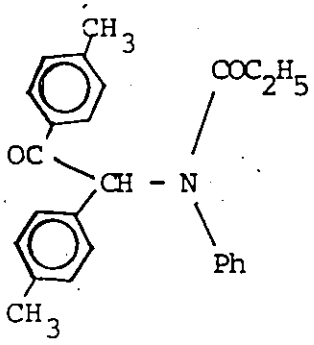
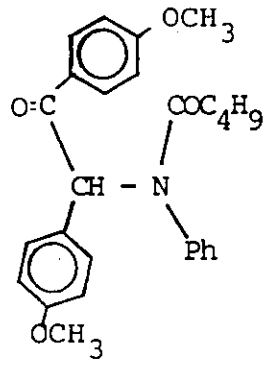
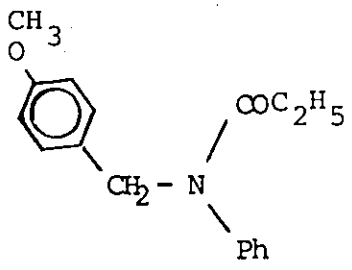
Imine (A)	Organoborane (B)	Reaction time hr.	Product	Yield %
79 R^1= Ph R^2= COPh R^3= p-CH_3 C_6H_4	$(C_2H_5)_3B$	72		
			123	37
			81	60
124 R^1= p-CH_3 C_6H_4CO R^2= p-CH_3 C_6H_4 R^3= Ph	$(C_4H_9)_3B$	48		
			125	87

Table 14 (Cont'd)

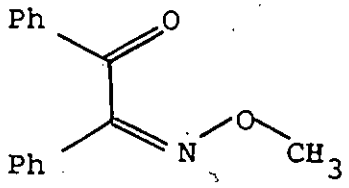
Imine (A)	Organoborane (B)	Reaction time hr.	Product	Yield %
126 R^1= p-CH_3O C_6H_4CO R^2= p-CH_3O C_6H_4 R^3= Ph	$(C_4H_9)_3B$	72	 127	74
128 R^1= p-CH_3O C_6H_4CO R^2= H R^3= Ph	$(C_2H_5)_3B$	72	 129	62

[m] Yields are of pure products.

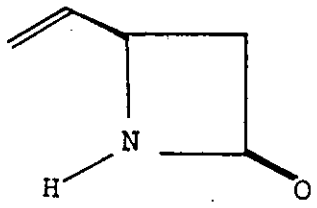
[n] Yield was 44%, using hexane as the solvent.

[o] The yield of 118 decreased to 51%, and the yield of the saturated product (77) was 1%. The remainder being recovered starting material. (When the reaction was carried out under an atmosphere of CO/H_2).

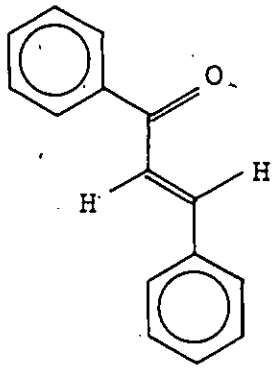
As anticipated 74 when reacted with 9-BBN (9[borabicyclo (3.3.1) nonane]) afforded 77 in 50% yield but no amide was formed. There was no reaction between 74 and tri-sec-butylborane . It appears that the secondary organoborane is not sterically favourable for the reaction. The oxime O-methyl ether 130 reacted with triethylborane but 65% of 130 was recovered after 120 hours and the small amount of products isolated could not be identified. When the organoborane of 4-vinylazetidine-2-one 131 was reacted with 74, 131 was recovered in quantitative yield as 131 could not be hydroborated to the organoborane.



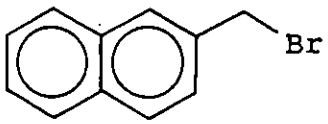
130



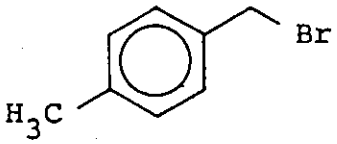
131



132

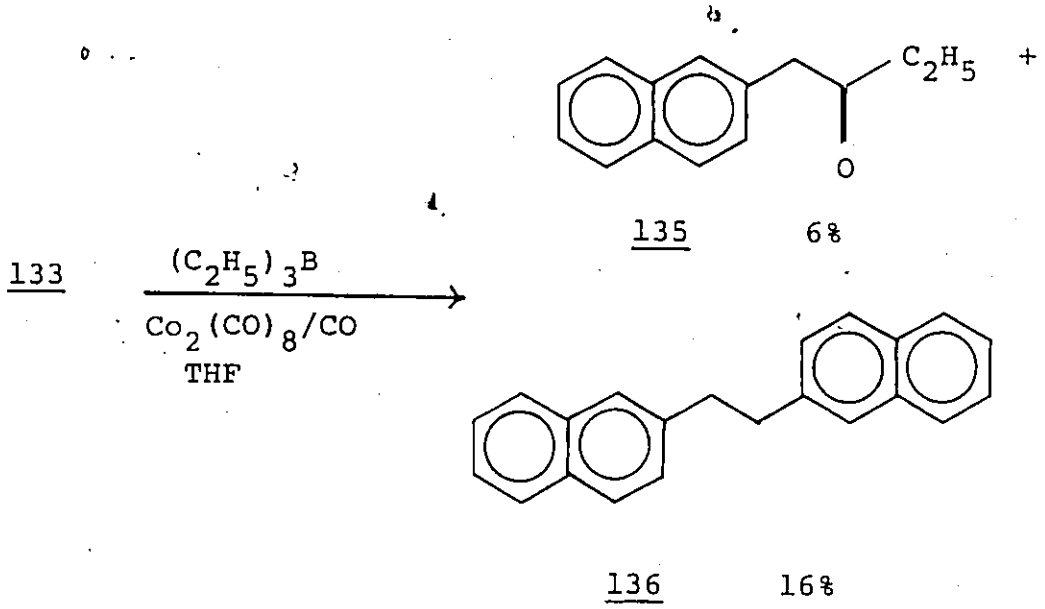


133



134

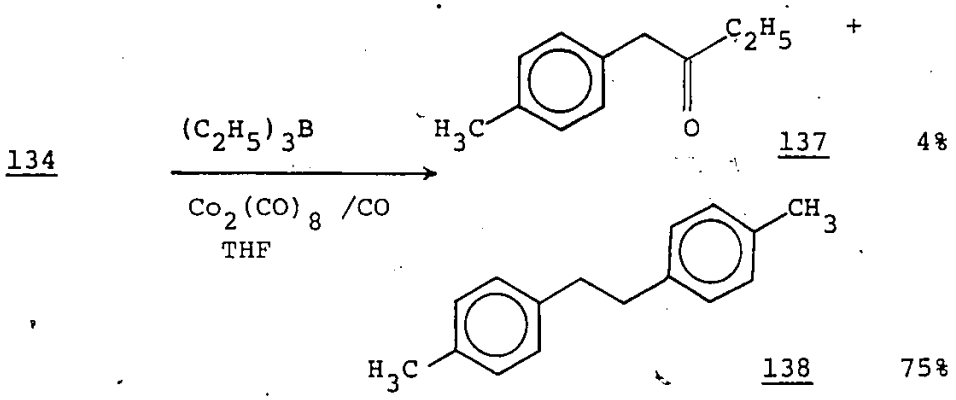
Reaction of 132 with triethylborane gave recovered starting material. Treatment of 133 and 134 with triethylborane gave the ethyl ketones in low yield.



135 6%

136 16%

Recovered 133 70%

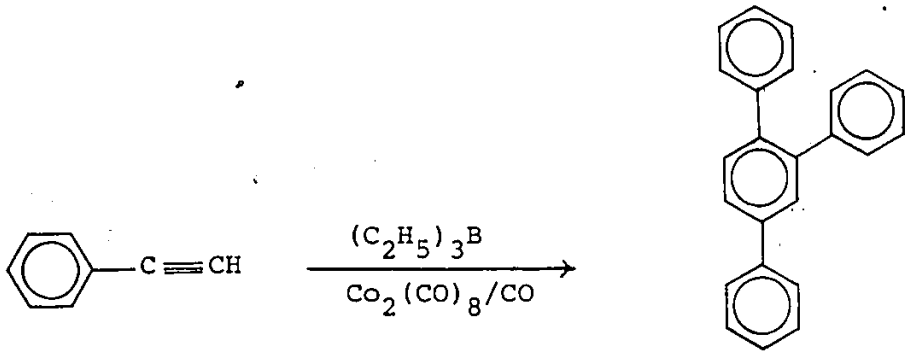


134 → 137 4%

138 75%

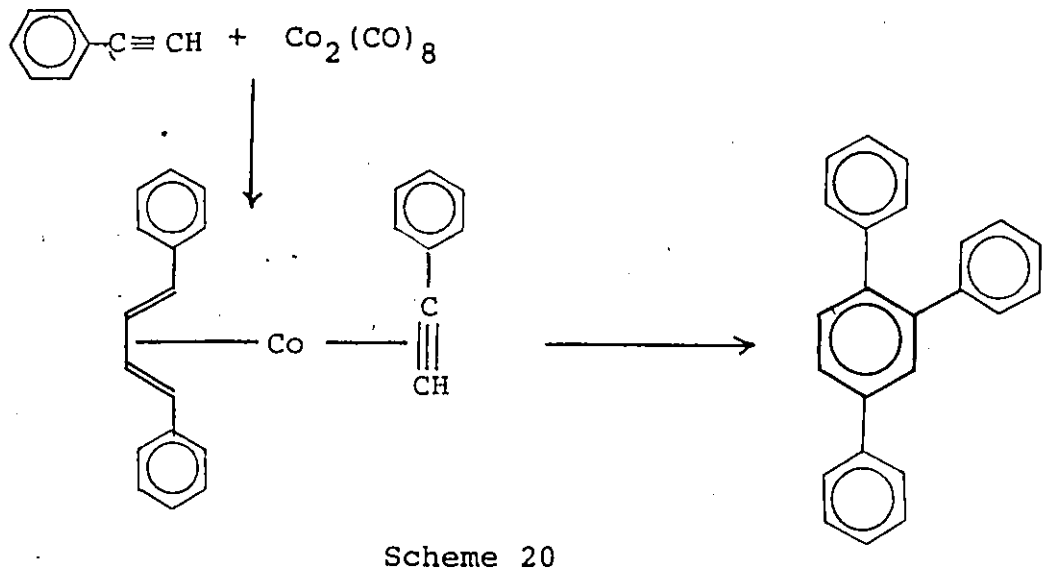
Recovered 134 18%

When phenylacetylene was reacted with triethylborane it gave 1,2,4-triphenylbenzene 140 in 100% yield after one hour of reaction.



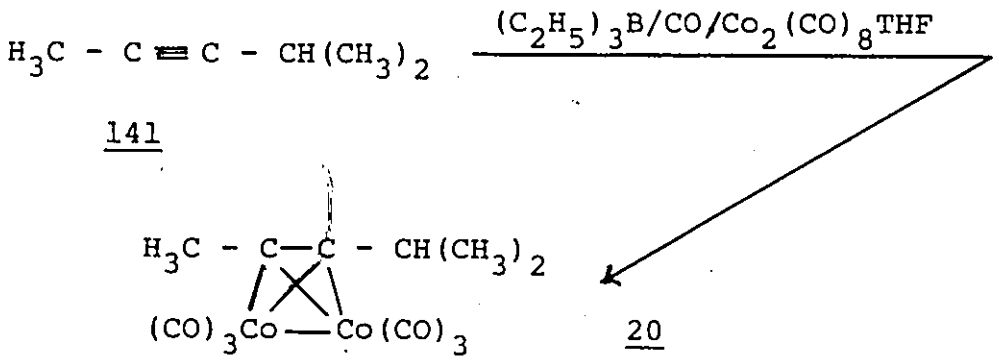
139 → 140 100%

As the ethyl group is not present in the product it is possible that only $Co_2(CO)_8$ is reacting. This reaction is interesting as it gives only one isomer. The intermediate could be a diene-cobalt complex as shown in Scheme 20.



Scheme 20

When an internal alkyne 141 was used as the starting material none of the expected benzene derivative was produced.



141

20

20 15 %, Recovered 141 75 %

Compounds 135, 136, 137, 138, 140 were identified by comparing their melting points IR, NMR and mass spectral data to those of authentic samples.

Table 15

Melting Points, Analytical and Pertinent Spectral data for the Products of the Reaction of Imines with Organoborane and Carbon Monoxide in Tetrahydrofuran

Product	Mp.°C	— Anal. Calcd. (found) — for new compounds			IR, $\nu_{C=O}$ cm^{-1}	MS m/e	NMR, δ ppm
		C	H	N			
117	77-78	80.83(80.55)	6.78(7.07)	3.77(3.95)	1645(s) 1702		0.88(t,3H,J=6.Hz)1.39 (m,4H),2.1(t,2H J=6Hz) 7.03- 7.33(m,14H)7.82- 8.02(m,2H)
118	Oil	81.32(81.69)	7.56(7.55)	3.39(3.51)	1650(s) 1695		0.88(t,3H,J=3Hz)1.15 (m,10H),2.75(t,2H,J= 6Hz)7.02-7.43(m,14H) 7.8-8.08(m,2H)
119	114-115.5	83.03(82.52)	6.01(5.80)	3.34(3.29)	1650(s) 1700	419 $[M]^+$ 314 $[M-CH_2CH_2Ph]^+$	2.38(t,2H,J=7Hz)2.95 (t,2H,J=7Hz)7.0-7.40 (m,19H)7.85-8.04) (m,2H)
120	133-135				1650 1700		1.25(d,3H,J=6Hz)2.00 (m,1H),2.33(d,2H,J= 7Hz)7.0-7.45(m,19H)7.85 8.05(m,2H)

Table 15 (Cont'd)

Product	Mp.°C	Anal. Calcd. (found) for new compounds C	H	N	IR, $\nu_{C=O}$ cm^{-1}	MS m/e	NMR, δ ppm
121	144-145				1655(s) 1710	391 $[M]^+$	7.0-7.50(m,17H) 7.80-8.05(m,4H)
122	Oil	77.71(77.78)	7.30(6.78)	3.30(3.49)	1641 1695		0.84(t,3H,J=8Hz)1.31 (m,2H),2.15(t,2H,J= 7Hz)3.65(s,3H),6.55- 7.40(m,13H)7.8-8.0(m.2H
123	112-113				1645(s) 1695		1.1(t,3H,J=7Hz)2.08 (q,2H,J=6Hz)2.2(s,3H), 6.9-7.45(m,13H),7.75- 7.95(m,2H)
125	115-116	81.17(81.18)	7.32(7.29)	3.50(3.47)	1650(s) 1692		0.83(t,3H),1.40(m,4H) 2.07(s,3H),2.10(t,2H) 2.15(s,3H),6.95-7.15 m,12H),7.87(d,2H,J= 8Hz)

Table 15 (Cont'd)

Product	Mp.°C	Anal. Calcd. (found) for new compounds C	H	N	IR, $\nu_{C=O}$ cm^{-1}	MS m/e	NMR, δ ppm
127	84-84.5				1650(s) 1695	431[M]$^+$ 296,219	0.83(t,3H,J=6Hz)1.45 (m,4H),2.02(t,2H),J= 8Hz)3.63(s,3H),3.75 (s,3H),6.90(m,12H), 7.88(d,2H)1.05
129	Oil	75.81(75.93)	7.11(7.32)	5.20(4.81)	1655(s)	269[M]$^+$ 212[M-Bu]$^+$ 135,121	1.05(t,3H,J=7Hz)2.06 (q,2H,J=8Hz)3.75(s,3H), 4.82(s,2H),6.7-7.5 (m,9H)

C H A P T E R III

3. EXPERIMENTAL

General Data

Melting point determinations were made by using a Fisher-Johns apparatus and are uncorrected. Infrared spectra were obtained by use of a Unicam SP-1100 spectrometer equipped with a calibration standard. A Nicolet MX-1, FT spectrometer was used for recording some infrared spectra. Varian T60, EM360A and Varian HA100 spectrometers were used for proton magnetic resonance determinations. Carbon magnetic resonance spectra were recorded in the fully and partially decoupled modes with a Varian FT-80 spectrometer. Elemental analysis were carried out by Canadian Microanalytical Service, Vancouver, Canada and by M-H-W Laboratories, Phoenix, Arizona. Silica gel was used for column and for thin layer chromatography. Gas liquid chromatography was performed on a Gow Mac 550 gas chromatograph with Carbowax 20 on chromosorb G (40-45°) or Versamide on chromosorb G (200-250°).
Mass spectra were determined on an AEI MS902 spectrometer. Solvents were purified and dried by standard methods. All reactions were run under an atmosphere of prepurified nitrogen unless otherwise stated.

Triiron dodecacarbonyl was purchased from Pressure Chemical Co., and was dried in vacuo prior to use. Diiron enneacarbonyl,palladium acetate and palladium chloride were purchased from Alfa Inorganics and were used as received. Chromium hexacarbonyl, molybdenum hexacarbonyl, iron pentacarbonyl, triruthenium dodecacarbonyl, chlorodicarbonylrhodium(I) dimer, and dimanganese decacarbonyl were purchased from Pressure Chemical Co. and were used as received. Dicobalt octacarbonyl was purchased from Strem Chemical Inc., dichloro(dibenzonitrile)palladium(II) was a gift from Prof. Alper and tetrakis(triphenylphosphine)palladium(0) was a gift from Dr. Tanaka.

All phase transfer catalysts were commercially available and were used as received. All dienes were commercial products except N-carboethoxy-1,2-dihydropyridine which was a gift from Prof. Alper. The vinyl nitro compound 33 was a gift from Mike Hrystak and the nitro sugar 34 was a gift from Dr. Zeher Hanna. 4-Vinylazetidine-2-one was a gift from Dr. Gunda Georg.

Reagent grade methyl iodide was passed through a short column of alumina before adding to the reaction mixture.

3.1 Carbene insertion into organometallic complexes under phase transfer conditions.

3.1.1. Preparation of diene-iron carbonyl complexes

Cyclohexa-1,3-dieneiron tricarbonyl (1)[125]

A mixture of cyclohexa-1,3-diene(40 g., 50 mmol) triiron dodecacarbonyl (7.5 g., 15 mmol) and benzene (75 ml.) was refluxed for four hours under nitrogen. The solution was cooled and filtered through celite to remove particles of iron. Removal of the solvent in vacuo gave a brown oil. This was taken up in pentane and filtered through a column of alumina, grade 'O'. Removal of the solvent gave the pure product as a canary yellow viscous oil [4.24 g., 43%] IR $\nu_{CO}(CHCl_3)$ 1980(s), 2060 (m) cm^{-1}. ^1H NMR ($CDCl_3$)δ 1.65(S,4H), 3.20 (m,2H), 5.30 (m,2H)ppm.

1,3-Hexadieneiron tricarbonyl (3)[126]

1,3-Hexadiene (3.3 g., 40 mmol) and triiron dodecacarbonyl (6 g., 12 mmol) were refluxed in benzene (50 ml). The reaction was effected as described for cyclohexa-1,3-dieneiron tricarbonyl. The final purified [2.35 g., 30% yield] canary yellow viscous oil was obtained. IR, ν_{CO} ($CHCl_3$) 1990 (s), 2075 (m) cm^{-1}. ^1H NMR($CDCl_3$)δ 0.31 (m,2H), 1.1(t,3H J=6Hz), 1.88 (m,3H), 5.3(m.2H) ppm.

Bicyclo-[2,2,1]-hepta-2,5-dieneiron tricarbonyl (5)[127]

Bicyclo[2,2,1]hepta-2,5-diene (norbornadiene) (4 g., 43 mmol) and triiron dodecacarbonyl (5 g., 10 mmol) were refluxed in benzene for one hour. The work up was the same as for the previous compounds. The final purified product was a dark orange, viscous oil [1.37 g., 20%] IR $\nu_{CO}(CHCl_3)$ 1985 (s), 2065 (m) cm^{-1}. ^1H NMR ($CDCl_3$) δ1.3 (t, 2H), 3.0 (m,6H) ppm.

1,4-Diphenyl-1,3-butadieneiron tricarbonyl (6)

A mixture of 1,4-diphenyl-1,3-butadiene (2 g., 10 mmol) and triiron dodecacarbonyl (1.6 g., 3.2 mmol) was refluxed in benzene for four hours. When cooled bright orange crystals separated from the filtrate. These were recrystallized from chloroform. The yield of purified product was 1.3 g., [40% yield] IR $\nu_{CO}(CHCl_3)$ 2000(s), 2065(m) cm^{-1}. ^1H NMR ($CDCl_3$) δ 2.35(m,2H, protons on terminal carbons of diene units), 5.85(m,2H, protons on internal carbon of diene unit). 7.20(s,10H, aromatic protons), Mass (m/e) 346,318,290,262,206.

(N-Carboethoxy-1,2-dihydropyridine)iron tricarbonyl (4)[128]

A solution of N-carboethoxy-1,2-dihydropyridine (2.3 g., 15 mmol) and triiron dodecacarbonyl (5.46 g., 15 mmol) was stirred at room temperature for 52-78 hours in benzene. The reaction mixture was filtered and subjected to column chromatography on silica gel. Elution with hexane gave recovered starting material. Elution with benzene gave the diene-iron tricarbonyl

complex as a thick yellow oil. [1.32 g., 30% yield] IR ν_{CO} $(CCl)_4$ 2058, 1980, $\nu_{C=O}$ 1711 cm.$^{-1}$, ^{1}H NMR ($CDCl_3$) δ 1.26 (t,3H) 2.65-3.50 (m,3H), 4.27 (q,2H) 5.0 (d,1H), 5.5 (m,2H) ppm. MS(m/e) 293,265,237,209,153,84,56.

Bicyclo-[2,2,1]-hepta-2,5-dienemolybdenum tetracarbonyl (17)[130]

Bicyclo[2,2,1]-hepta-2,5-diene (6.8 g., 74 mmol) was added dropwise to a solution of molybdenum hexacarbonyl (5.28 g., 20 mmol) in methyl cyclohexane (50 ml) at its boiling point (110°C). The final pure product was obtained by sublimation of the crude precipitate formed when the filtrate was cooled to -78°C. The yield of the pure yellow crystalline complex was 0.85 g.(14%). IR ν_{CO}($CHCl_3$) 2028, 1980-1923, 1869 cm.$^{-1}$ ^{1}H NMR ($CDCl_3$) δ 1.3 (2H,m), 3.78(2H,m), 4.85(4H,m).

3.1.2. Preparation of cycloheptatriene complexes.

Cycloheptatrienemolybdenum tricarbonyl (19)[131]

Molybdenum hexacarbonyl (5.28 g., 20 mmol) and cycloheptatriene (10 ml-excess) were refluxed in ethylcyclohexane (50 ml). The mixture was cooled, filtered under nitrogen, and the filtrate was kept at -78°C for several hours. The red crystals that separated were dried and purified by sublimation. The yield was 1.9 g., (35%). IR ν_{CO}($CHCl_3$) 2005(s), 1930(s) 1895(s) cm.$^{-1}$ ^{1}H NMR ($CDCl_3$) δ 2.4 (m,2H), 3.6 (m,2H), 4.9 (m,2H) 6.1 (m,2H) M_p 100-101°C.

Cycloheptatrienechromium tricarbonyl (18)[132]

A mixture of chromium hexacarbonyl (5 g., 23 mmol) and cycloheptatriene (6 g., 60 mmol) was refluxed in acetonitrile (40 ml) for 20 hours. The work up used was the same as that for the analogous molybdenum complex. The yield of pure red crystalline product was 1.15 g., (22%). ^1H NMR ($CDCl_3$) δ 2.10 (m,2H), 3.20 (m,2H), 4.70 (m,2H), 5.90 (m,2H).

3.1.3. Preparation of alkyne cobalt complexes.[138]

$Co_2(CO)_8$ (13 mmol) and the alkyne (17 mmol) were stirred under nitrogen in pentane (50 ml) overnight at room temperature. The solution was filtered under nitrogen and the solvent was evaporated. Recrystallization from methanol afforded the pure products.

1-Phenyl-1-propyne-dicobalt hexacarbonyl (22)

Long reddish black needle like crystals. Final purified yield 2.76 g., 54%. Mp 36°C. IR ν_{CO}($CHCl_3$) 2040(s), 2055(m) 2115(w) cm^{-1}. ^1H NMR ($CDCl_3$) δ 2.95(s,3H), 7.50(m,5H aromatic) m/e Mass 402,374,346,318,290,262,234.

4-Methyl-2-pentyne-dicobalt hexcarbonyl (20)

Needle like brown crystals which decompose at 80 °C. Final purified yield: 3.39 g.(71%), IR ν_{CO}($CHCl_3$) 2055(s), 2070(m), 2110(w) cm^{-1}. ^1H NMR($CDCl_3$) δ 1.2(s,3H), 1.40(s,3H), 3.10 (m,1H) 2.70 (s,3H). m/e Mass 368, 340, 312, 284, 256, 228,200.

1 Phenyl-1-butyne dicobalt hexacarbonyl (21).

Thick reddish black oil. Final purified yield 4.05 g., (75%). IR $\nu_{CO}(CHCl_3)$2050(s),2075(m),2115(w) cm^{-1}. ^1H NMR ($CDCl_3$)δ 1.41(t,3H),3.15(q,2H),7.40(m,5H aromatic).

3.1.4. General procedure for the carbene insertion reaction.

3.1.4.1 Benzyltriethylammonium chloride as the phase transfer catalyst (Method A).

A mixture of the organometallic complex (5 mmol), bromoform (50 mmol), 30% NaOH (25 mmol) and benzyltriethylammonium chloride (0.2 mmol) was vigorously stirred at room temperature under nitrogen for 24-72 hours. Then the reaction mixture was added to excess distilled water (200-250 ml). The organic phase was separated with the aid of methylene chloride. This was then dried ($MgSO_4$) and the solvent was evaporated in vacuo. The resulting crude brown oil was distilled under reduced pressure (4 mm). The excess bromoform was collected at 50°C bath temperature. The remaining thick brown oil was worked up in the following manner for the various reactions. Products and their yields are given in Table 1. Spectral data are given in Table 2.

Cyclohexa-1,3-dieneiron tricarbonyl (1)

The remaining thick brown oil was dissolved in a small amount of chloroform and filtered through a column of silica gel with chloroform as the solvent. Evaporation of the solvent gave 0.51 g.,(26%) of the dibromo complex as a thick yellow oil.-

1,3-Hexadieneiron tricarbonyl (3)

The remaining crude brown oil was dissolved in a small amount of chloroform and filtered through a silica gel column with chloroform as the solvent. The resulting yellow oil showed two spots on thin layer chromatography. The yellow oil was again chromatographed on a silica gel column using 1:1 hexane-benzene as eluant. Two fractions were separated. Fraction one (bright yellow) was the dibromoiron complex [0.274 g., 14%]. Fraction two was the dibromo ligand, [0.151 g., 12%], 5 dibromomethyl-1,3-hexadiene.

5-Methyl-1,3-hexadieneiron tricarbonyl (2)

The remaining thick brown oil was filtered through a column of silica gel using benzene as the solvent. The resulting yellow product was analytically pure dibromoiron complex . Yield [0.35 g., 17%].

Bicyclo-[2,2,1]-hepta-2,5-dieneiron tricarbonyl (5)

The remaining thick brown oil was filtered through a silica gel column using carbon tetrachloride as the solvent.

The bright yellow eluant was collected and concentrated in vacuo. This was streaked on a prepared tlc plate and run with hexane. Three fractions were separated. All three were colourless oils and weighed 0.0065 g.,(3%), 0.150 g., (7%), 0.09 g., (4%).

1,4-Diphenyl-1,3-butadieneiron tricarbonyl (6)

Thin layer chromatography of the crude product showed that there were no new products formed. The starting diene-iron carbonyl complex was recovered in quantitative yield.

3.1.4.2. Aliquat 336 as the phase transfer catalyst (Method B).

A mixture of the organometallic complex (7.5 mmol), bromoform (0.15 mmol), Aliquat 336 (0.75 mmol), ice cold 50% NaOH (o.3 mmol), methylene chloride (30 ml) and ethanol (1.5 ml.) was vigorously stirred at room temperature for one hour, and then at 50°C for five hours. After cooling to room temperature the reaction mixture was added to excess distilled water (250 ml.) and the organic layer was separated with the aid of additional methylene chloride. The organic phase was dried ($MgSO_4$) and the solvent was evaporated in vacuo. The resulting crude brown thick oil was dissolved in some methylene chloride and a small amount of silica gel was added. The methylene chloride was evaporated in vacuo. The silica gel coated with the crude compound was added on top of a silica gel column. This was worked up

in the following manner for the various reactions. Products and their yields are given in Table 1. Spectral data are given in Table 2.

N-Carboethoxy-1,2-dihydropyridineiron tricarbonyl. (4)

Hexane (250 ml.) was passed through silica gel which carried with it the unreacted bromoform. Then benzene was passed through and two fractions were separated. Fraction one was the dibromoiron complex, a thick yellow oil [1.84 g., 54%]. Fraction two was the unreacted starting material [0.61 g., 28%].

1,3-Cyclohexadieneiron tricarbonyl. (1)

Elution with hexane gave three fractions. Fraction one contained unreacted bromoform. The second fraction was unreacted starting material [0.22 g., 14%]. The third fraction, on the evaporation of the solvent gave the dibromoiron complex [0.88 g., 32%] as a thick yellow oil.

1,3-Hexadieneiron tricarbonyl. (3)

Unreacted bromoform was separated by eluting with hexane. The dibromoiron complex was then eluted with 1:1 benzene-hexane. On evaporation of the solvent the dibromo complex was obtained as a thick yellow oil [0.784 g., 40%]. None of the ligand was present.

5-Methyl-1,3-hexadieneiron tricarbonyl. (2)

Unreacted bromoform was separated by eluting with hexane. The dibromoiron complex was then separated by using benzene as the solvent. There was no unreacted starting material or the free ligand. On evaporation of the solvent the dibromoiron complex was obtained as a thick yellow oil. [0.556 g., 27%].

Bicyclo-[2,2,1]-hepta-2,5-dienemolybdenum tetracarbonyl. (17)

When an IR spectrum of the colourless oil was taken, it showed that only bromoform and molybdenum hexacarbonyl was present. There was no starting material and no products. The complex had collapsed under these conditions.

Cycloheptatrienemolybdenum tricarbonyl. (19)

Thin layer chromatography of the crude product showed a large number of inseparable compounds, none of which seemed to be the major product.

Cycloheptatrienechromium tricarbonyl. (18)

Elution with hexane separated the unreacted bromoform. A mixture of hexane:methylene chloride (3:1 ratio) when passed through the column separated four products, each of which was obtained in less than 10 mg.

1-Phenyl-propyne dicobalt hexacarbonyl. (22)

Thin layer chromatography of the crude dark red oil showed that there was only the starting material present. When this oil was passed through a column of silica gel with chloroform as the solvent the pure starting material was obtained in 92% yield.

4-Methyl-2-pentyne dicobalt hexacarbonyl. (20)

Eluting with hexane separated the unreacted bromoform and unreacted starting material [1.42 g., 70%]. Two more fractions were separated with benzene-hexane (1:1). Spectral data of the major fraction; (0.028 g.) ; ^1H NMR ($CDCl_3$)δ :1.60(s,3H), 1.75(s,3H), 1.95(s,3H), 6.08(s,1H). IR$\nu_{C=O}$ cm^{-1} ($CHCl_3$) 1770 (s) , MS (m/e) 281,253, 173, 93. The second fraction was obtained in less than 10 mg.

These two compounds could not be identified successfully.

1-Phenyl-1-butyne dicobalt hexacarbonyl. (21)

Eluting with hexane separated the unreacted bromoform and unreacted starting material. [1.43 g., 78%] Two more fractions were separated with a mixture of benzene;hexane (1:1) . Spectral data of the major product(0.042 g.); ^1H NMR ($CDCl_3$)δ :1.05(d,3H), 1.25(m,1H), 6.05(d,1H), 6.15(s,5H). IR $\nu_{C=O}$($CHCl_3$):1730(s) cm^{-1}. MS m/e: 329, 301, 249, 169. The second fraction was obtained in less than 10 mg. These two compounds could not be identified successfully.

3.2 Catalytic reduction and carbonylation of nitro compounds by triruthenium dodecacarbonyl.

3.2.1 General procedure for the reduction of nitro compounds with triruthenium dodecacarbonyl under phase transfer conditions.

To $Ru_3(CO)_{12}$ (0.03 mmol) in benzene (20 ml.) containing 2-methoxyethanol (5 ml.) was added benzyltriethylammonium chloride (0.25 mmol) in 5N sodium hydroxide (10 ml.) The reaction mixture was stirred for one hour under an atmosphere of carbon monoxide. During this time the colour of the reaction mixture changed from orange to bright wine red. The nitro compound (5.0 mmol) in benzene (5 ml.) was added and stirring was continued until the reaction was complete (tlc). The organic phase was separated, and the aqueous phase was acidified to pH 6 with dilute hydrochloric acid and the amine was extracted with ether. The latter was added to the organic phase which was then dried ($MgSO_4$). Evaporation of the solvent gave the crude amine which was worked up in the following manner for the various compounds. The yields and reaction times are given in Table 3.

Nitrobenzene.

The crude oil was taken up in 1:1 hexane-ethyl acetate and passed through a column of silica gel. Evaporation of the solvent gave pure aniline [0.446 g., 97%] which was identified by comparison of spectral data (IR, NMR), R_f value and the boiling point with authentic material.

p-Nitrotoluene.

The crude black solid was dissolved in a small amount of methylene chloride and streaked on four preparative thin layer silica gel plates. Methylene chloride was used to develop the plates. The amine was separated from the small amount of ruthenium impurity. The pure crystalline product was identified as p-toluidine by comparing its spectral data (IR, NMR), R_f value and melting point with literature data for p-toluidine (yield 0.503 g., 94%).

2,6-Dimethylnitrobenzene

The crude black solid was dissolved in a small amount of methylene chloride and coated on a small amount of silica gel. This was added to a column of silica gel. Two fractions were separated with hexane:ethyl acetate (1:4). Fraction one contained unreacted starting material. [0.68 g., 90%]. Fraction two contained the pure amine [0.048 g., 8%]. This pure oily product was identified by comparing its spectral data (IR, NMR) and R_f values to literature data for 2,6-dimethylaniline.

p-Nitroanisole.

The crude solid was dissolved in a small amount of ethyl acetate and streaked on four preparative thin layer silica gel plates. A mixture of 4:1 ethyl acetate-hexane was used to develop the plates. The amine was separated as white crystals. This product was identified as p-anisidine by comparing its spectral data (IR NMR), R_f value and melting point to literature data for p-anisidine. Yield (0.517 g., 84%).

p-Chloronitrobenzene.

The crude black solid was dissolved in a small amount of methylene chloride and streaked on four preparative thin layer plates. The plates were developed with a 1:4 mixture of hexane:ethyl acetate. A white crystalline amine was obtained [0.62 g., 98%]. The product was identified by comparing its spectral data (IR, NMR), R_f value and melting point with that of authentic p-chloroaniline.

2-Nitrofluorene.

The crude black solid was dissolved in a small amount of methylene chloride and streaked on four preparative thin layer plates. Methylene chloride was used to develop the plates. The pure amine was separated from the ruthenium impurity [0.86., 95%]. The buff coloured crystals were identified by comparing its spectral data (IR, NMR) to those given in the literature for 2-aminofluorene.

4-Nitrobenzophenone.

The crude black solid was dissolved in a small amount of methylene chloride and streaked on four preparative thin layer plates. Methylene chloride was used to develop the plates. The pure amine was separated from the ruthenium impurity[0.95 g., 97%]. The compound was identified by comparing its spectral data (IR, NMR) with that of authentic 4-aminobenzophenone.

1-Nitropropane.

While the reaction is proceeding small samples of the organic phase was injected into a carbowax column at 40-45°C. The completion of the reaction was determined when the peak for nitropropane disappeared. By comparing the retention time of the product to that of commercially available 1-propylamine the compound was identified and the yield was found to be 85%.

This reduction was tried on vinyl nitro coumpounds 33 and 34 , and also on other substances (35-39).

A few reactionswere carried out on the nitro compounds with variations on the general procedure.

Without the phase transfer catalyst.

p-Nitrotoluene was subjected to reduction by the general procedure in the absence of the phase transfer catalyst, benzyltriethylammonium chloride. The work up was the same as described for p-nitrotoluene.

Reaction under a nitrogen atmosphere.

p-Nitrotoluene was subjected to reduction by the general procedure in an atmosphere of nitrogen instead of carbon monoxide. The work up was the same as in the general procedure for p-nitrotoluene.

With 50% sodium hydroxide.

p-Nitrotoluene was subjected to reduction by the general procedure in the presence of 50% sodium hydroxide instead of the 5N sodium hydroxide (20%). The work up was the same as in the general procedure for p-nitrotoluene.

With tetrabutylammonium bromide as phase transfer catalyst.

p-Nitrotoluene was subjected to reduction by the general method in the presence of tetrabutylammonium bromide (0.25 mmol) instead of benzyltriethylammonium chloride. Work up was the same as in the general procedure for p-nitrotoluene.

With Aliquat 336 as the phase transfer catalyst.

p-Chloronitrobenzene was subjected to reduction by the general procedure in the presence of Aliquat 336 (0.25 mmol) instead of benzyltriethylammonium chloride. Work up was the same as in the general procedure for p-chloronitrobenzene.

With 18-crown-6 as the phase transfer catalyst.

$Ru_3(CO)_{12}$ (0.19 g., 0.3 mmol) was dissolved in tetrahydrofuran (60 ml.) and 2-methoxyethanol (5 ml.) was added. To this solution solid powdered potassium hydroxide (1.25 g.) was added and the solution was stirred for fifteen minutes with 18-crown-6 (0.08 g., 0.3 mmol). p-Chloronitrobenzene (2.35, 15 mmol) was then added and the reaction mixture was stirred at room temperature. When complete (followed by this layer chromatography) the reaction mixture was added to 100 ml. of distilled water and the amine was extracted with CH_2Cl_2 and purified according to the general procedure for p-chloronitrobenzene.

Before the general procedure for reduction of nitro compounds was discovered, a number of reactions were carried out on the nitro system to determine if any carbonyl insertion or reduction took place.

Using different metal catalysts

Chlorodicarbonylrhodium(I) dimer

To a solution of p-chloronitrobenzene (0.78 g., 5 mmol) in methylene chloride (25 ml.) and 8N sodium hydroxide (20 ml.) was added benzyltriethylammonium chloride (0.23 g., 2 mmol) and chlorodicarbonylrhodium(I) dimer (0.077 g., 0.2 mmol). The reaction mixture was stirred under carbon monoxide at 25-30 °C for 65 hours. Distilled water was then added and the amine was extracted with methylene chloride, and purified according to the general procedure of p-chloronitrobenzene.

The reaction was also effected in the same manner, at 45-50 °C.

$PdCl_2(PhCN)_2$

The palladium complex (0.5 mmol) was stirred under carbon monoxide at room temperature in benzene for ten minutes. Then 50% sodium hydroxide (10 ml.) was added along with benzyltriethylammonium chloride (0.5 mmol). p-Nitrotoluene (5 mmol) was added, the reaction mixture was stirred at room temperature overnight , and then worked up as usual.

$Pd(PPh_3)_4$

Tetrakis(triphenylphosphine)palladium (0.5 mmol) was stirred under carbon monoxide at room temperature in benzene for ten minutes. Then 50% sodium hydroxide (10 ml.) was added along with benzyltriethylammonium chloride (0.5 mmol). p-Nitrotoluene (5 mmol) was added and the reaction mixture stirred at room temperature overnight. The work up was the same as given in the general procedure.

$PdCl_2$

To a stirred solution of p-nitrotoluene (o.466 g., 3.4 mmol) in methylene chloride (6.5 ml.) was added a 3N solution of hydrochloric acid (4.0 ml.) and benzyltriethl-ammonium chloride (0.073 g., 0.34 mmol) and $PdCl_2$(0.17 mmol). This reaction mixture was stirred at room temperature for five hours. The work up was the same as for the general procedure.

$Pd(OAc)_2$)

Palladium acetate was substituted for $PdCl_2(PhCN)_2$ and $PdCl_2$ in the above procedure using basic and acidic conditions respectively.

$Co_2(CO)_8$

Methylene chloride was degassed and then the flask was charged with carbon monoxide. To this was added 50% sodium hydroxide (25 ml.) and carbon monoxide was bubbled through

the solution at a fast rate. Dicobalt octacarbonyl (0.27 g., 0.8 mmol) was added and the solution was stirred for 2 hours. To this mixture p-nitrotoluene (1.096 g., 8.0 mmol) was added and the reaction was followed by thin layer chromatography. Workup was the same as described in the general procedure.

$Ru_3(CO)_{12}/Fe(CO)_5$ (excess).

To $Ru_3(CO)_{10}$ (0.19 g., 0.3 mmol) in benzene (15 ml.) was added benzyltriethylammonium chloride (0.068 g., 0.3 mmol) and 5N sodium hydroxide (10 ml.). When the solution turned red $Fe(CO)_5$ (0.784 g., 4 mmol) was added followed ten minutes later by p-nitrotoluene (o.685 g., 5 mmol). The reaction was followed by thin layer chromatography. Work up was the same as described in the general procedure.

$Ru_3(CO)_{12}/Fe(CO)_5$ (1:2 ratio).

The procedure above was followed but instead of 4 mmol of $Fe(CO)_5$, only 0.6 mmol was used.

Using different base concentrations.

To $Ru_3(CO)_{12}$ (0.19 g., 0.3 mmol) in benzene (20 ml.) was added benzyltriethylammonium chloride (0.057 g., 0.25 mmol) in 0.5N, 2N, 5N, and 50% NaOH (10 ml) in five different reactions. The reaction mixtures were stirred for one hour under carbon monoxide. The nitro compound, p-nitrotoluene (0.685 g., 5 mmol), was added and stirring was continued overnight. The work up for all five reactions was the same as for

the general procedure. The results are given in Table 4.

At different reaction temperatures.

To $Ru_3(CO)_{12}$ (0.19 g., 0.3 mmol) in benzene (20 ml.) was added benzyltriethylammonium chloride (0.057 g., 0.25 mmol) in 5N sodium hydroxide (10 ml.). The mixture was stirred for one hour under carbon monoxide, p-nitrotoluene (0.685 g., 5 mmol) was then added and stirring was continued for 6 hours at 0°C,5°C and 70°C in three different reactions. The work up in each case was the same as for the general procedure. The results are given in Table 5.

Using different phase transfer catalysts.

18-Crown-6

$Ru_3(CO)_{12}$ (0.19 g., 0.3 mmol) was dissolved in tetrahydrofuran (60 ml.). Solid potassium hydroxide (1.25 g.) and 18-crown-6 (0.08 g., 0.3 mmol) were then added and stirred for fifteen minutes. p-Nitrotoluene (2.05 g., 15 mmol) was added in portions to the vigorously stirred solution. After one hour it was heated to reflux for 48 hours. Work up was the same as for the general procedure.

Aliquat 336

To $Ru_3(CO)_{12}$ (0.38 g., 0.6 mmol) in methylene chloride (50 ml.), was added 50% sodium hydroxide (2.5 ml.) and Aliquat 336 (0.43 g., 0.6 mmol). Then p-nitrotoluene (1.37 g., 10 mmol) was added and stirring was continued for 48 hours at room temperature. Work up was the same as for the general procedure.

3.2.2. General procedure for the carbonylation of nitro compounds with triruthenium dodecacarbonyl.

To a mixture of $Ru_3(CO)_{12}$ (0.3 mmol) in benzene (50 ml.) and 2-methoxyethanol (10 ml.) was added sodium methoxide (30 mmol), and the reaction mixture was stirred under carbon monoxide for one hour. The nitro compound (5 mmol) dissolved in benzene (5 ml.), was then added and the reaction mixture was warmed to 50°C (oil bath temperature). The reaction was followed by thin layer chromatography and when all the starting material had reacted the reaction mixture was added to distilled water to remove any unreacted sodium methoxide. The organic layer was separated and the aqueous layer was extracted several times with 25 ml. portions of ether. These were added to the organic phase and dried ($MgSO_4$). Evaporation of the solvent gave the crude product which contained the amide as the major species. This was worked up in the following manner for the various reactions. Yields and reaction times are given in Table 6.

p-Nitrotoluene

The crude black solid was dissolved in a small amount of methylene chloride and coated on silica gel. This was added to the top of a column of silica gel. Elution with

hexane:ether (2:3) gave the amide as a pale buff coloured solid [0.72 g., 11%]. The product was identified by comparison of spectral data (IR NMR), R_f value and melting point with literature data.

p-Nitroanisole

The crude black solid was dissolved in methylene chloride and coated on a small amount of silica gel. This was added on top of a silica gel column. Elution with hexane:ether (1:4) gave the formamide [0.186 g., 31%]as a buff coloured solid, identified by comparing spectral data, R_f and melting point with literature data.

p-Chloronitrobenzene

The crude black solid was dissolved in a small amount of methylene chloride and coated on silica gel. This was added on top of a column of silica gel and eluted with hexane:ether (2:3). The first fraction was the azoxy compound [0.322 g., 50%]. The second fraction was the amide [0.212 g., 34%]. The azoxy compound and the amide were identified by comparing their spectral data (IR, NMR), R_f and melting points with authentic samples.

2-Nitroflourene

The crude black solid was dissolved in a small amount of methylene chloride and coated on silica gel. This was added on top of a silica gel column and eluted with

hexane:ether (2:3). The formamide was obtained as a pale brown solid [0.276 g., 25%], identified by comparing its spectral data (IR and NMR), R_f value and melting point with authentic material.

4-Nitrobenzophenone

The crude black solid was coated on a small amount of silica gel and added to the top of a silica gel column. Elution with a mixture of hexane:ether (1:4 ratio) gave the amine [0.125 g., 14%] as a light brown solid, which was identified by comparing its spectral data (IR, NMR), R_f value and melting point to that of authentic material.

$Fe_3(CO)_{12}$/Sodium methoxide

To a solution of $Fe_3(CO)_{12}$ (0.15 g., 0.3 mmol) in benzene (50 ml) was added sodium methoxide (1.6., 30 mmol) and the reaction mixture was stirred under carbon monoxide for 8 hours until the colour changed from deep green to reddish brown. p-Chloronitrobenzene (0.628 g., 5 mmol) was added and stirring was continued at 50°C for 72 hours. Work up was the same as for a the general procedure. Note that 2-methoxyethanol was not added as $Fe_3(CO)_{12}$ was completely soluble in benzene.

$[Rh(CO)_2Cl]_2$/Sodium methoxide/15-crown-5.

To p-chloronitrobenzene (0.628 g., 5 mmol) in benzene (50 ml) was added 15-crown-5 (0.05 ml., 0.3 mmol) followed by sodium methoxide (0.6 g., 30 mmol) and $[Rh(CO)_2Cl]_2$ (0.77 g., 0.2 mmol). The reaction was stirred for 48 hours

(monitored by thin layer chromatography) and then worked up as described in the general procedure.

$Ru_3(CO)_{12}$/Potassium t-butoxide.

To a solution of $Ru_3(CO)_{12}$ (0.19 g., 0.3 mmol) in THF (50 ml.) and 2-methoxyethanol (5 ml.) was added potassium t-butoxide (3.48 g., 30 mmol) and 18-crown-6 (0.21 g.,1.2 mmol). After stirring for one hour p-chloronitrobenzene (0.628 g., 5 mmol) in THF (5 ml.) was added and the reaction was run for 24 hours. Work up was the same as for the general procedure for p-chloronitrobenzene. The reaction was also repeated in the absence of crown ether catalyst. This reaction with crown ether was carried out in benzene and in methylene chloride to determine the effect of the different solvents.

3.3 Dicobalt octacarbonyl catalyzed reductive acylation and reaction of organoboranes with imines.

3.3.1. Phase transfer catalyzed reductive acylation of azadienes.

Preparation of azadienes.

The α,β-unsaturated aldehydes and the amines were commercially available and used as received. The azadienes were prepared according to the procedure given by Cardaci and Bellachioma.[137] An ether solution of the amine (20 mmol) was added dropwise to an ether solution of the α,β-unsaturated aldehyde (20 mmol). The reaction mixture was stirred for one hour, dried ($MgSO_4$), and the solvent was evaporated. The crude azadiene was purified by recrystallization from a mixture of hexane and methylene chloride.

1-p-Anisoyl-4-phenyl-1,3-azadiene. (54)

Obtained as bright yellow crystals, yield 3.69 g. (78%). ^1H NMR ($CDCl_3$)δ 3.75(s, 3H), 6.80-7.60(m, 1H), 8.20-8.35 (t, 1H J=2Hz).

1-p-Tolyl-4-phenyl-1,3-azadiene. (51)

Bright yellow crystals, yield 3.09 g. (70%). ^1H NMR ($CDCl_3$)δ 2.4 (s,3H), 7.0-7.7 (m, 11H), 8.2-8.45 (t, 1H J=2Hz).

1-p-Tolyl-3-methyl-4-phenyl-1,3-azadiene. (64)

Bright dark yellow crystals. Yield was 2.91 g. (62%) ^1H NMR ($CDCl_3$)δ. 2.11(s,3H), 6.95-7.18(m,10H).8.05(s,1H).

1-p-Chlorophenyl-3-methyl-4-phenyl-1,3-azadiene. (66)

Dark yellow long crystals. Yield was 3.57 g., (70%). ^{1}H NMR ($CDCl_3$) δ. 2.11(s,3H), 6.95-7.18(m,10H).8.05(s,1H).

1-p-Tolyl-4-(2 furyl)-1,3-azadiene. (59)

Dark brown crystals. Yield was 1.055 g., (50%). ^{1}H NMR ($CDCl_3$) δ. 2.32(s,3H), 6.47(m,2H) 6.83-7.42(m,7H), 8.05(m,1H).

1-(2,4-Dimethylphenyl)-4 -(2 furyl)-1,3-azadiene. (61)

Dark brown crystals. Yield was 1.125 g., (50%). ^{1}H NMR ($CDCl_3$) δ. 2.28 (s,6H), 6.39(m,2H), 6.73-7.35 (m,6H), 8.03(m,1H).

1-p-Anisoyl-4-(4-dimethylaminophenyl)-1,3-azadiene. (57)

Dark orange coloured crystals. Yield was 0.672 g., (24%). ^{1}H NMR ($CDCl_3$) δ 2.92(s,6H), 3.75(s,3H), 6.55-7.43 (m,10H), 8.05 (m, 1H).

General procedure for the reductive acylation of azadienes under phase transfer conditions.

Nitrogen gas was passed, for a period of one hour through a mixture of anhydrous benzene (20 ml.), distilled water (20 ml.) and benzyltriethylammonium chloride (0.5 mmol). The gas was changed to carbon monoxide, and dicobalt octacarbonyl (2.0 mmol) was added along with methyl iodide (1 ml.). This mixture was stirred overnight at room temperature. The

azadiene (20 mmol) was added under a fast stream of carbon monoxide. The reaction mixture was stirred at room temperature or 60°C until the solution became bright red indicating the completion of the reaction. The organic layer was separated and the aqueous layer was extracted several times with 25 ml. portions of methylene chloride. The methylene chloride extracts were combined with the organic layer, dried ($MgSO_4$) and concentrated by rotary evaporation. The resulting crude product was worked up in the following manner for the various reactions. Yields and reaction times are given in Table 8. Spectral data melting points and analysis (C,H,N) are given in Table 9.

Azadiene 51

The crude dark red thick oil was dissolved in some methylene chloride and coated on a small amount of silica gel. This was then added on top of a silica gel column and eluted with 1:1 hexane-ether. Three fractions were separated. Fraction one contained cinnamaldehyde [0.51 g., 22%]. Fraction two contained pure white crystalline allyl amide [0.336 g., 65%]. The third fraction contained the p-tolyl derivative of acetanilide [0.10 g., 33%].

Azadiene 54

The crude dark red thick oil was dissolved in some methylene chloride and coated on a small amount of silica gel. This

was then added to the top of a silica gel column and eluted with ether-hexane (1:1). Three fractions were separated. Fraction one contained cinnamaldehyde[0.065 g., 28%]. Fraction two contained pure white crystalline allyl amide [0.284 g., 50%]. Fraction three contained the p-anisoyl derivative of acetanilide [0.120 g., 33%].

Azadiene 64

The crude dark red thick oil was dissolved in some methylene chloride and coated on a small amount of silica gel. This was then added to the top of a silica gel column and eluted with ether-hexane (1:1). Four fractions were separated: 64 [0.18 g., 40%], 2-methyl cinnamaldehyde [0.06 g., 25%], allyl amide [0.147 g., 25%], as a thick dark yellow oil and the p-tolyl derivative of acetanilide [0.095 g., 30%.] When the yields were calculated according to the starting material reacted, the allyl amide was formed in 41% yield while the p-tolyl derivative of acetanilide was formed in 50% yield.

Azadiene 66

The crude dark red thick oil was dissolved in some methylene chloride and coated on a small amount of silica gel. This was then added on top of a silica gel column and eluted with ether-hexane (1:1). Two fractions were separated: starting azadiene 66[0.205 g., 50%] and allyl keto amide 67[0.342 g., 50%]; as a thick pale yellow oil. Calculated yield compared to starting material reacted is 100%. When

the reaction was carried out at room temperature for 72 hours, four fractions were separated; 2-methylcinnamaldehyde [0.093g., 32%], 66 [0.238 g., 47%] allyl ketoamide 67 [0.070 g., 10%] and the p-chloro derivative of acetanilide [0.137 g., 40%].

Azadiene 59

The dark red solid was dissolved in some methylene chloride and coated on a small amount of silica gel. This was added on top of a silica gel column and eluted with hexane-ether (1:1). The following fractions were separated: β-(2-furyl)-acrolein [0.073 g., 30%]; allyl amide as white crystals [0.316 g., 62%]; and the p-tolyl derivative of acetanilide [0.103 g., 34%]. The allyl amide was recrystallized from hexane-methylene chloride.

Azadiene 61

The dark red solid was dissolved in some methylene chloride and coated on a small amount of silica gel. This was then added on to a column of silica gel and eluted with ether-hexane (1:1). The following fractions were separated: β-(2-furyl)acrolein [0.109 g., 45%], allyl amide as white crystals [0.256 g., 50%]; and the 2,4-dimethylphenyl derivative of acetanilide [0.179 g., 50%]. The allyl amide was recrystallized from hexane-methylene chloride.

Azadiene 57

The dark red solid was dissolved in some methylene

chloride and coated on a small amount of silica gel. This was then added on top of a silica gel column and elution with 1:1 hexane ether gave three fractions: 4-dimethylaminocinnamaldehyde [0.098 g., 30%], allyl amide as light brown crystals [0.305 g., 49%], and the p-anisoyl derivative of acetanilide [0.133 g., 39%]. The allyl amide was re-crystallized from hexane and methylene chloride.

A number of reactions were carried out on 51 (1-p-tolyl-4-phenyl-1,3-azadiene) with variations on the general procedure.

Catalytic $Co_2(CO)_8$

Only 0.2 mmol of $Co_2(CO)_8$ was used instead of 2 mmol. The reaction and work up was the same as for the general procedure for (1-p-tolyl-4-phenyl-1,3-azadiene) 51.

Blank reactions

(a) Without $Co_2(CO)_8$. Reaction and work up was the same as for the general procedure for 51.

(b) Without the phase transfer catalyst. Reaction and work up was the same as for the general procedure for 51.

In the dark

The reaction was carried out according to the general procedure but the reaction flask was covered with aluminum foil.

With Aliquat 336

Instead of benzyltriethylammonium chloride (0.5 mmol)

Aliquat 336 (0.5 mmol) was used as the phase transfer agent. The reaction and work up was the same as for the general procedure for 51.

CH_3I:Azadiene, 1:1(Stoichiometric amount of methyl iodide).

2 mmol of CH_3I was used instead of the excess 1 ml. The reaction and work up was the same as the general procedure for 51.

Using methanol instead of water.

Methanol (20 ml.) which was freshly distilled over magnesium (under nitrogen) was used in place of distilled water. With (a) 1:2 ratio of azadiene to methyl iodide(0.57 g., 4 mmol) (b) Excess methyl iodide. (1 ml.)
No phase transfer catalyst was used in these reactions. Once the reaction mixture turned red indicating the completion of the reaction the solvents were evaporated by rotary evaporation and worked up similar to the general procedure for 51.

$CH_3(CH_2)_5Br$ instead of CH_3I.

A stoichiometric amount of $CH_3(CH_2)_5Br$ (0.328 g., 2 mmol) was used instead of excess CH_3I. Reaction and the work up was similar to the general procedure for 51.

Methylene Chloride as solvent.

Instead of benzene (20 ml.) methylene chloride (20 ml.) was used. Methylene chloride was freshly distilled. Reaction

and work up was carried out in the usual manner for 51.

Homogeneous reaction

Reaction was carried out in freshly distilled anhydrous benzene in the absence of water. No phase transfer catalyst was added. Work up involved the concentration of the reaction mixture by evaporating benzene and separation as described in the general procedure for 51.

Different base concentrations

(a) 12.5 N NaOH (20 ml.).

(b) 5 N NaOH (20 ml.).

(c) 2 N NaOH (20 ml.).

(d) 0.5 N NaOH (20 ml.).

(e) 0.1 N NaOH (20 ml.) was used instead of 20 ml. of distilled water. Reaction and work up same as for the general procedure for this particular azadiene. The results of this study are given in Table 7.

Using solid KOH and 18-crown-6

Solid KOH (1 g.) and 18-crown-6 was used instead of water. The reaction and the work up was the same as the general procedure for this particular azadiene.

Under acidic phase transfer conditions.

A mixture of pentane (20 ml.), distilled water (20 ml.) and toluenesulfonic acid (0.172 g., 1 mmol) was degassed for one hour by passing nitrogen through the solution. The gas was changed to carbon monoxide, $Co_2(CO)_8$ (0.68 g., 2 mmol) and CH_3I (1 ml.) were added and the solution was stirred for four hours. To this mixture was added azadiene (2 mmol) and the solution was stirred overnight. The workup was the same as for the general procedure for this particular azadiene.

3.3.2. Homogeneous reductive acylation of imines.

The simple imines were synthesized according to the procedure of Campbell et al.[138] The ketoimines were synthesized according to the procedure of Knovenagel.[139] The iminoamides were prepared as described below. N-methylaniline was used instead of toluidine for the phenylmethylimino amide. Dichloromethyl methyl ether (3.6 g., 30 mmol) was added dropwise to stirred benzoyl formic acid (4.5 g., 30 mmol). After the evolution of hydrochloric acid the reaction mixture was heated in an oil bath for 30 minutes at 50°C. The resulting α-keto acid chloride was distilled off at 110°C/4 mm and collected at -20°C. To this, an ether solution of toluidine (3.2 g., 30 mmol) was added slowly.

The ketoamide formed was recrystallized from ethanol. The final purified pale yellow crystalline ketoamide was obtained in 2.25 g.,(32%).[140] The ketoamide (1.0 g., 4.5 mmol) was dissolved in benzene (25 ml.) and p-anisidine (0.55 g., 4.5 mmol), and iodine (0.1 g.,) were added. The solution was warmed to 60°C for 30 minutes. The solvent was evaporated and the crude iminoamide was recrystallized from ethanol which gave 0.72 g.,(30%) of bright yellow cristals.Mp 109-112°C.

All the imine compounds were identified by their ^1H NMR, IR and in some cases mass spectra.

Cobalt tetracarbonyl anion was prepared according to the procedure of Gladysz and coworkers.[141,142]

General procedure for the reductive acylation of imines under homogeneous conditions.

$NaCo(CO)_4$ was formed by stirring a mixture of $Co_2(CO)_8$ (2.0 mmol) and 5.0 ml. of sodium triethylborohydride (1 M in tetrahydrofuran) in tetrahydrofuran (50 ml) for fifteen minutes. Methyl iodide (1.0 ml - carbon monoxide atmosphere) was added, the reaction mixture was warmed to 60°C, and after fifteen minutes the imine (2.0 mmol) was added. The reaction was monitored by thin layer chromatography and when complete, the solution was cooled to room temperature and to it was added 5N sodium hydroxide (20 ml.). Ether was then added to the separated organic phase. The solution was acidified (pH 6) washed with water, dried ($MgSO_4$) and

concentrated. The resulting crude product was dissolved in a small amount of methylene chloride and coated on some silica gel. This was added on top of a silica gel column and fractions separated in the following manner for the different imines. The yields and reaction times are given in Table 10. Spectral data (NMR, IR, mass), melting points and analytical data of the products are listed in Table 11.

Ketoimine 74

Elution with hexane gave the unreacted 74 [0.114 g., 20%]. Use of 2:1 hexane-ether afforded the ethyl amide 76 as a white solid [0.068 g., 10%]. Elution with 1:1 hexane-ether gave the ring opened tetrahydrofuranyl amide [0.065 g., 17%] and the methyl amide [0.286 g., 44%].

Ketoimine 79

Elution with hexane gave two fractions. The first fraction was the saturated product [0.072 g., 12%] as an oil and the second fraction was the methyl amide [0.505 g., 74%]which was a white solid. Recrystallization from ether-hexane gave the pure product.

Ketoimine 82

Elution with hexane gave the saturated product [0.069 g., 11%] as a thick oil. Elution with 1:1 hexane-ether and subsequent recrystallizations gave the methyl amide [0.628 g., 88%] as a pure white solid.

Ketoimine 85

Elution with hexane gave the starting material [0.094 g., 15%] and the saturated product [0.279 g., 43%] as a thick pale yellow oil. Elution with 2:1 ether-hexane afforded the amide 86 [0.143 g., 20%] as pure white crystals.

Ketoimine 88

Elution with hexane gave unreacted starting material [0.250 g.,40%] and the saturated product [0.063 g., 10%] as a thick pale yellow oil. Elution with 2:1 ether-hexane gave the amide 89 [0.327 g., 46%] as pure white crystals.

Iminoamide 105

Elution with 1:1 ether-hexane gave unreacted starting material [0.619 g., 90%]. No products were isolated.

Iminoamide 106

Elution with 1:1 hexane gave unreacted starting material [0.512 g., 78%] and an unidentified product with high molecular weight, fragments of which were seen by mass spectroscopy.

Imine 91

Elution with 1:2 pentane-ether afforded the methyl amide [0.157 g., 40%] as a thick pale yellow oil. It was identified by mass, NMR and IR spectra.

Imine 93

Elution with 1:2 hexane-ether gave the white crystalline compound 94 [0.11 g., 25%].

Imine 95

Elution with hexane-ether (1:1) gave three fractions. Fraction one was the keto amide 97 [0.036 g., 6%], fraction two was the p-chloro derivative of acetanilide [0.078 g., 15%] and fraction three was the methyl amide [0.122 g., 23%].

Imine 99

Elution with 1:2 hexane-ether afforded three fractions. Fraction one was the n-butylmethylamide [0.185 g., 30%], fraction two was the ketoamide 101 [0.225 g., 45%] and fraction three was the aliphatic amide 102 [0.083 g., 15%]. All three compounds were oils.

Imine 103

Elution with hexane-ether (1:1) gave the allyl amide [0.350 g., 80%] as a thick pale yellow oil.

Vinyl cyclohexane

Elution with ether-hexane (2:1) gave the starting material [0.176 g., 80%]. No products were isolated.

Once the general procedure for reductive acylation was established some variations were made to determine if improvements could be made to the reaction.

Under phase transfer conditions.

A mixture of distilled benzene (25 ml.), 5N sodium hydroxide (20 ml) and benzyltriethylammonium chloride was degassed for one hour by nitrogen. Dicobalt octacarbonyl (2 mmol) was then added with methyl iodide (1 ml.). After two hours the imine (2 mmol) was added and the reaction mixture was stirred under an atmosphere of carbon monoxide. The reaction was monitored by thin layer chromatography. When complete the reaction mixture was added to distilled water (100 ml.), the organic phase extracted with ether, dried ($MgSO_4$) and concentrated and coated on a small amount of silica gel. This was added to the top of a silica gel column. Elution with 1:1 hexane-ether gave unreacted starting material followed by the methyl amide. The yields and reaction times are given in Table 11.

Phase transfer reaction under an atmosphere of CO/H_2.

This reaction was run like the carbon monoxide phase transfer reaction, but instead of carbon monoxide a mixture of carbon monoxide and hydrogen was used. N-benzylidinemethylamine 91 was used as the starting material. After three days the reaction was terminated. The aqueous layer when acidified (dil. HCl) gave phenylacetic acid [0.049 g., 5%]. The organic layer contained the starting material.

Blank reaction.

This reaction was carried out similar to the general

procedure but in the absence of dicobalt octacarbonyl, with 74 used as the starting material. The reaction was followed by thin layer chromatography. After 72 hours the reaction was stopped, and worked up using the general procedure to give unreacted starting material [0.5 g., 90%], and the saturated product [0.022 g., 5%] was also isolated.

Isobutyryl chloride instead of methyl iodide.

The reaction was the same as the general procedure but instead of excess methyl iodide a stoichiometric amount of isobutyryl chloride $(CH_3)_2CHCOCl$ (0.213 g., 2 mmol) was added. The imine used was 74 . After 48 hours there was no reaction and the starting material was recovered [0.524 g., 92%].

In the absence of methyl iodide.

Reactions were carried out as in the above general procedure but in the absence of methyl iodide. Column chromatography with 1:1 hexane-ether gave the starting material as the first fraction, and the ethyl amide as the second fraction. Reaction times and yields are given in Table 12. Spectral data (NMR, IR, mass), melting points and analysis are listed in Table 13.

Using lithium triethylborohydride.

The cobalt tetracarbonyl anion was generated by lithium triethylborohydride; (5 ml. in THF) instead of

sodium triethylborohydride. 93 was used as the starting material. When the reaction was over the crude product was worked up using the same procedure as above. Column chromatography on silica gel with 1:2 hexane-ether gave 94 [0.14 g., 32%] as a white solid.

Using an iminium salt.

The iminium salt of 91 was synthesized according to literature methods.[143] This salt (0.524 g., 2 mmol) was added to a solution of cobalt tetracarbonyl generated by sodium triethylborohydride. When the reaction was complete (monitored by thin layer chromatography) the iminium salt had decomposed to give benzaldehyde.

3.3.3. Dicobalt octacarbonyl catalyzed reaction of organoboranes with imines.

General procedure for the reaction of imines with commercially available boranes.

The organoborane was added to freshly distilled tetrahydrofuran (50 ml.) and this mixture was degassed for half an hour. Then dicobalt octacarbonyl (0.068 g., 0.2 mmol) was added under a fast stream of carbon monoxide. After ten minutes the imine was added and the reaction mixture was heated to 60°C. The reaction was monitored by thin layer chromatography, and when complete the solution was cooled to room temperature and to it was added 5N sodium hydroxide (20 ml.). Ether was then added to the separated organic phase. The aqueous

phase was extracted several times with 25 ml. portions of ether. The organic extracts were combined, dried ($MgSO_4$), and concentrated. The crude product was dissolved in a small amount of methylene chloride, deposited on some silica gel, added on top of a silica gel column and the products were separated in the following manner for the various compounds. The yields and reaction times are given in Table 14. Spectral data, melting points and analysis data are listed in Table 15.

The reaction of ketoimine 74 with -

(a) Triethylborane

Elution with 1:1 hexane-ether gave 0.28 g. (48 %)of the white crystalline saturated compound. When 1:3 hexane-ether was used as the eluant the amide was collected [0.343 g., 50%].

(b) Tributylborane

Elution with 1:1 hexane-ether gave the starting material [0.113 g., 19%] followed by the saturated compound [0.103 g., 18%]. Elution with 1:4 hexane-ether gave the amide as white crystals [0.495 g., 67% ;82% based on the amount of 74 reacted] .

(c) Triphenylborane

Elution with 1:1 hexane-ether gave three fractions:

unreacted starting material [0.144 g., 24%]; saturated product [0.116 g., 20%]and the pure white crystalline amide [0.42 g., 56%;67% based on the amount of 74 reacted].

(d) Tri-sec-butylborane

Elution with 1:3 hexane-ether gave two fractions: Unreacted starting material [0.463 g., 81%] and an unidentified product [0.041 g.] which was not the amide.

(e) 9-[Borabicyclo(3:3:1)nonane]

Elution with 1:1 hexane-ether gave unreacted starting material [0.100 g., 18%]; the saturated compound [0.228 g., 50%] and an unidentified product [0.135 g.].

Reaction of ketoimine 82 with -

(a) Triethylborane

Elution with 1:1 hexane-ether gave unreacted starting material as the first fraction [0.013 g., 2%]. Elution with 1:4 hexane-ether gave the saturated product [0.407 g., 65%] as a thick pale yellow oil, and the amide [0.245 g., 33%].

(b) Tributylborane

Elution with 1:2 hexane-ether gave starting material [0.263 g., 42%] followed by the amide [0.351 g., 44%]. No saturated product was isolated. The yield of the amide when calculated based on the imine reacted was 76%.

Reaction of ketoimine 79 with triethylborane.

Elution with 1:1 hexane-ether gave three fractions: the unreacted starting material [0.081 g., 12%]; the saturated compound [0.408 g., 60%] and the ethyl amide [0.255 g., 32%]. The yield of the amide when calculated based on the imine reacted was 37%.

Reaction of the ketoimine 124 with tributylborane.

Elution with 1:3 hexane-ether gave two major products. Fraction one contained unreacted starting material [0.20 g., 31%], and fraction two contained the amide [0.488 g., 60%] calculated based on the imine reacted, the yield of the amide was 87%.

Reaction of the ketoimine 126 with tributylborane.

Elution with 1:2 hexane-ether gave unreacted starting material [0.44 g., 68%] followed by the amide [0.18 g., 23%] Yield of amide when calculated based on the amount of imine reacted was 74%.

Reaction of the imine 128 with triethylborane.

Elution with 1:1 ether-hexane gave unreacted starting material [0.14 g., 35%] followed by the amide [0.28 g., 38%]. The yield of the amide when calculated based on the amount of imine reacted was 62%.

Reaction of the oxime 130 with tributylborane.

Elution with 1:1 hexane-ether gave three fractions: the unreacted starting material [0.310 g., 65%]and two other products [0.08 g. and 0.06 g.] which could not be identified.

General procedure for the reaction of in situ generated organoboranes with imines.

The olefin (8.0 mmol) was dissolved in tetrahydrofuran (5 ml.) in a 50 ml. nitrogen flushed round bottom flask equipped with a magnetic stirrer, septem inlet and reflux condenser. The solution was cooled to 0°C and BH_3-THF (2 mmol) was added via a syringe. The solution was stirred at 0°C for one hour under nitrogen.[144] Then tetrahydrofuran (40 ml.) (distilled under N_2 and added via a syringe) was added and the gas was changed to carbon monoxide. Dicobalt octacarbonyl (0.2 mmol) was then added followed after ten minutes, by the imine (2.0 mmol) and the reaction mixture was warmed to 60°C. The reaction was monitored by thin layer chromatography. When complete the solution was cooled to room temperature and extracted in the same way as the previous procedure. The products were separated in the following manner for the various reactions. The yields and reaction times are given in Table 14. Spectral data (NMR, IR, mass), melting points and analytical data are listed in Table 15.

Reaction of the ketoimine 74 with -

(a) The borane generated from styrene (triphenethylborane).

Elution with 1:1 hexane-ether gave three fractions: unreacted starting material [0.10 g., 18%], saturated compound [0.05 g., 10%] and the amide [0.40 g., 48%] as pure white crystals. The yield of amide when calculated based on the amount of imine reacted was 60%.

(b) The borane generated from α-methylstyrene

Elution with 1:1 hexane-ether gave unreacted starting material followed by the saturated product and the amide.

(c) The borane generated from n-heptene (tri n-heptylborane).

Elution with 1:1 hexane-ether gave unreacted starting material [0.11 g., 19%], saturated compound [0.126 g., 22%] and then the amide [0.35 g., 43%] as a thick pale yellow oil. The yield of the amide when calculated based on the amount of imine reacted was 55%.

(d) The borane generated from 4-Vinyl-azetidine-2-one.

Elution with 1:1 hexane gave the unreacted starting material and the unreacted 4-vinyl azetidine-2-one. This shows that the organoborane was not formed by this olefin. Some of 74 was reduced to the saturated product by the unreacted BH_3.THF.

Reaction of phenylacetylene (139) with triethylborane.

The reaction was carried out in an identical manner to the general procedure but phenylacetylene(2 mmol) was used instead of the imine (2 mmol). The crude product after work up contained 1,2,4-triphenylbenzene in 100% yield. This crude product was passed through a short column of silica gel using 1:1 hexane-ether. The pure 1,2,4-triphenylbenzene was obtained in 90% yield as a white solid. Identified by comparing the melting point and spectral data with an authentic sample.

Reaction of 4-methyl-2-pentyne (141) with triethylborane.

Reaction was carried out in essentially the same manner as the general procedure but with 4-methyl-2-pentyne substituted for the imine. After work up thin layer chromatography of the crude product showed that almost all the starting material was present and a small amount of an alkyne cobalt complex was formed. This was separated on a silica gel column using 2:1 hexane-ether. IR and NMR of this dark red oil showed that it was the alkyne cobalt complex [0.081 g., 15%], identified by comparing the melting point and spectral data with those of the alkyne cobalt complex 20.

Reaction of 2-bromomethylnaphthalene (133) with triethylborane.

Reaction was carried out in essentially the same manner as the general procedure but 2-bromomethylnaphthalene was used instead of the imine. After work up the crude product was coated on some silica gel and loaded on a silica gel column. Elution with hexane-ether (1:3) gave unreacted

starting material [0.30 g., 70%], the dimer [0.04 g., 16%], and the ethyl ketone [0.024 g., 6%].

Reaction of p-methylbenzyl bromide (134) with triethylborane.

Reaction was carried out in essentially the same manner as the general procedure but with p-methylbenzyl bromide instead of the imine. After work up the crude product was coated on a small amount of silica gel and loaded on to a silica gel column and eluted with 1:2 hexane-ether. The first fraction was the unreacted starting material [0.069 g., 18%], followed by the coupled product [0.315 g., 75%] and the ethyl ketone [0.013 g., 4%].

Reaction of PhCOCH = CHPh (132) with triethylborane.

Reaction was the same as the general procedure but using PhCOCH = CHPh instead of the imine. Thin layer chromatography of the crude product showed that there was no new product.

Variations on the general procedure were made to determine if any improvement could be made. The ketoimine 74 was used as the starting material for these reactions.

Under an atmosphere of CO/H_2 gas with tributylborane.

The reaction was carried out and worked up in essentially the same manner as the general procedure but under an atmosphere of 1:1 CO/H_2 gas instead of carbon monoxide. Three

fractions were separated: recovered starting material [0.126 g., 22%], saturated compound [0.006 g., 1%] and the butylamide [0.379 g., 51%].

Using hexane as solvent with triethylborane in hexane.

The reaction was carried out like the general procedure, but using hexane instead of THF, and triethylborane in hexane, instead of triethylborane in THF. Work up was effected according to the general procedure for this imine and triethylborane. Three fractions were separated: unreacted starting material [0.068 g., 12%], saturated product [0.20 g., 40%], ethyl amide [0.20 g., 30%].

Using methylene chloride as the solvent with triethylborane in THF.

The reaction was carried out and worked up in essentially the same manner as the general procedure but using methylene chloride instead of tetrahydrofuran. Separation gave unreacted starting material [0.43 g., 72%], saturated compound [0.045 g., 8%] and the ethyl amide [0.082 g., 12%].

Generating the cobalt tetracarbonyl anion under nitrogen.

A mixture of triethylborane (2 mmol) and $Co_2(CO)_8$ (0.2 mmol) in THF (50 ml.) was stirred at 60°C under a nitrogen atmosphere for 30 minutes. Then the imine (2 mmol) was added and the flask was charged with carbon monoxide. Usual work up conditions gave the saturated compound [0.281 g., 50%] and the ethyl amide [0.314 g., 46%].

Adding $Co_2(CO)_8$ last.

To triethylborane in THF was added the starting imine. The reaction mixture was stirred under carbon monoxide at 60°C for fifteen minutes. $Co_2(CO)_8$ (0.068 g., 0.2 mmol) was then added and the reaction was continued until completion. Work up gave recovered starting material [0.295 g., 52%] and the ethyl amide [0.26 g., 38%].

Reaction of triphenylborane in anhydrous hexane.

The reaction was carried out in exactly the same way as the general procedure but using anhydrous hexane instead of THF. Work up gave unreacted starting material [0.09 g., 30%], and the phenyl amide [0.122 g., 31%].

Cyclization of a ketoamide.

The ketoamide (0.2 g., 0.5 mmol) was refluxed in concentrated acetic acid (15 ml.) with excess ammonium acetate (3 g.). When the reaction was complete (monitored by thin layer chromatography) it was added to distilled water (100 ml.), neutralized with sodium carbonate (50%, 5 ml.) and the organic phase was extracted with ether, dried ($MgSO_4$), and concentrated. The 1,3 azole 110 was obtained [0.152 g., 80%]. This was identified by its spectral data.

^1H NMR ($CDCl_3$) δ 0.8(t,3H J=5Hz), 1.62(m,4H) 2.35(s,6H), 2.85(t,2H,J=6Hz), 7.05-7.7(m,13H), mass m/e380, 351, 319, 305, 276, 263, 248, 221, 179, 117.

The attempted trapping of the $[Co - B]^-$ species with PPN^+Cl^-

Triethylborane (10 ml. , 10 mmol) was added to THF (50 ml.). After half an hour $Co_2(CO)_8$ (3.4 g., 10 mmol) was added and the solution was left overnight under an atmosphere of carbon monoxide. Solid PPN^+Cl^- (11.48 g., 20 mmol) was then added and the resulting blue solid was filtered and separated. When the THF was evaporated it afforded a pale green solid (7.0 g.), the NMR spectrum of which showed the presence of an ethyl group.

C H A P T E R IV

4. SUMMARY

4.1. Conclusion

The research described herein has resulted in the discovery of new phase transfer catalyzed organometallic reactions. The dibromocarbene inserted diene-iron carbonyl complexes (7 - 11) show potential as intermediates for organic synthesis.

The phase transfer catalyzed triruthenium dodecacarbonyl catalyzed reduction of nitro compounds is a great improvement to that using water gas shift reaction conditions.

The dicobalt octacarbonyl catalyzed reaction between an organoborane and a Schiff base is the first example of metal carbonyl catalysis of an organoborane reaction. By this method simple as well as α-ketoimines can be converted to substituted amides and β-ketoamides, and subsequently to 1,3 azoles, thiazoles and oxazoles. As the organoborane is synthesized by the hydroboration of olefins this reaction can also be considered as a method to convert olefins to amides.

4.2. Further Research

There are several interesting aspects of this work that seem worthy of investigating,

(i) If the carbene insertion reaction is carried out under an atmosphere of CO and/or $CO:H_2$ there could be an insertion of CO in addition to the insertion of carbene.

(ii) Fixing $Ru_3(CO)_{12}$ on a solid support (e.g. silica gel, alumina, polymer) for the reaction of a nitro compound and sodium methoxide. There is a possibility of obtaining quantitative yields of formamides from nitro compounds.

(iii) Are there any other metals much more efficient than $Co_2(CO)_8$ in catalyzing the organoborane reaction with Schiff bases?

(iv) What other compounds would give carbonylation with organoboranes and carbon monoxide in addition to Schiff bases?

(v) Would organoaluminum and organotin compounds react with Schiff bases and carbon monoxide, catalyzed by metal complexes?

4.3. Claims To Original Research

- Phase transfer catalyzed dibromocarbene insertion into diene-iron tricarbonyl complexes.

- The ruthenium carbonyl catalyzed reduction of nitro compounds by phase transfer catalysis.

- The ruthenium carbonyl carbonylation of nitro compounds under homogeneous conditions.

- The selective reductive acylation of imines under homogeneous conditions.

- Metal carbonyl catalysis of organoborane reactions: cobalt carbonyl catalyzed reductive carbonylation of Schiff bases.

- The regiospecific phase transfer catalyzed reductive carbonylation of azadienes.

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(i) Phase transfer catalyzed dibromocarbene insertion into diene-iron tricarbonyl complexes.
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A paper titled, Phase transfer catalyzed reductive acylation of Schiff bases, was presented at the 8th Canadian Symposium on Catalysis in May 1982, Waterloo, Ontario. The author is also a recipient of a Commonwealth Scholarship.

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