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LIST OF ABBREVIATIONS

<u>Symbol/Abbreviation</u>	<u>Name</u>
$\text{Fe}_3(\text{CO})_{12}$	Triiron dodecacarbonyl
$\text{Co}_2(\text{CO})_8$	Dicobalt octacarbonyl
$\text{Mo}(\text{CO})_6$	Molybdenum hexacarbonyl
$\text{Pd}(\text{PPh}_3)_4$	Tetrakis (triphenylphosphine) palladium
$\text{Pd}(\text{dba})_2$	Bis (dibenzylideneacetone) palladium
$\text{Pd}(\text{dpe})_2$	Bis[bis (1,2-diphenylphosphino) -ethane] palladium
IR	Infrared
vs	very strong
s	strong
m	medium
w	weak
br.	broad
NMR	Nuclear Magnetic Resonance
s	singlet
d	doublet
t	triplet
q	quartet
qt	quintet
dd	doublet of doublet
m	multiplet
MS	Mass Spectra
PTC	Phase transfer catalysis
mM	millimole

ABSTRACT

After a brief look into the pros and cons of employing a homogeneous versus heterogeneous process, the classification of supported organometallics along with examples of their current applications are described. In this context, the nature of refractory oxide (silica and alumina) and a reaction model to explain the adsorption of metal carbonyls on alumina are given. A review of studies of metal carbonyls immobilized on inorganic supports is followed by another review of the work done by organometallic reagents under liquid-liquid phase transfer catalysis.

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

Triiron dodecacarbonyl was stirred with alumina to generate a red trinuclear hydride. Nitroarenes were reacted with it to study its reductive potential. As a result, a mild and selective method was developed to reduce nitroarenes to anilines. The red hydride can be generated on neutral alumina also and it can deoxygenate azoxybenzenes and heterocyclic N-oxides in 59-86% yield.

The formation of a cobalt hydride by immobilization of dicobalt octacarbonyl on alumina is described. This species is capable of reducing nitroarenes and can dehalogenate α -halosulfoxides selectively without affecting the sulfoxide functionality.

A subcarbonyl species generated by activation of molybdenum hexacarbonyl on inorganic oxide has been found to be useful for deoxygenation and desulfurization reactions. Molybdenum hexacarbonyl on refractory oxide were reacted with sulfur containing compounds. The reaction was utilized for desulfurization of crude oil. This metal carbonyl on florisil has been found to be the most active for such desulfurization reactions.

The reactions run under phase transfer catalysis in carbon monoxide medium are divided into two parts. In part (a), a mononuclear cobalt carbonyl bearing a stabilizing cyclopentadienyl ligand was reacted with benzyl bromides under phase transfer catalysis. The products formed were compared with that of the reported carbonylation of benzyl bromides with other cobalt carbonyls.

In part (b), first report of palladium (0) catalyzed dicarbonylation of vinylic dibromides, under phase transfer condition, has been presented. While these products are formed in tert-amyl alcohol medium, use of a less polar solvent - benzene - results in diyne as the major product.

The procedures used to conduct the experiments have also been described in detail.

CHAPTER I

INTRODUCTION

Why metal carbonyls?

Commercially available or readily synthesized transition metal carbonyls^{1,2} have well characterized bonding and structural properties³. The carbonyl ligand can be removed by ligand substitution without forming any side product due to the fact that carbon monoxide is a gas. Metal carbonyl clusters may be utilized for carrying-out reactions which require multiple metal sites and also for generating highly dispersed metal particles on refractory oxides. Thus far, metal carbonyls have been shown to catalyze reactions which produce higher molecular weight organic molecules via olefin and carbon monoxide insertion⁴.

Can we use metal carbonyls as reagents or catalysts for developing new, useful and simple reactions in organic chemistry? In the field of organic synthesis, reactions involving these organometallics have generally been effected in homogeneous media. Recently, there has been considerable interest in applying heterogeneous conditions to these reactions, the goals being the use of mild reaction conditions and the realization, in certain instances, of different reaction pathways in

Comparison with the conventional methods.

The present work describes some applications of two such heterogeneous processes in metal carbonyl chemistry:

1. the deposition of metal carbonyls on refractory oxides (solid-liquid), and
2. phase transfer catalysis (liquid-liquid).

Homogeneous vs Heterogeneous Processes

Bench scale processes to convert olefin to aldehydes and alcohols by hydroformylation were developed by using organometallic catalysts soluble in the reaction medium (homogeneous catalysis). But these methods could not be utilized as large scale industrial processes due to the following problems associated with such catalysts⁵.

1. Separation and recovery of the catalysts from the reaction medium poses problems.
2. Some homogeneous catalyst solutions are corrosive to the reactors.
3. Often the catalyst systems are unstable.

At times, these disadvantages make it impractical to utilize homogeneous catalysis in spite of some benefits including:

1. High selectivity: the ability to produce pure products in high yield.
2. Regulation of catalytic properties by variation in electronic and steric properties by change of ligands or composition of metal complexes.
3. Reproducible preparation of catalysts.
4. Effective control of the nature of active centers and well interpreted catalytic cycles. The active sites are well defined.

5. They are active under mild reaction conditions and usually have all of the metal available for catalysis.

One goal during the past twenty years was to find ways to combine the advantages of the heterogeneous and homogeneous catalytic systems by means of immobilizing highly active and selective homogeneous catalysts on organic and inorganic supports.

Such attachment processes provide the following advantages^{6,7}:

1. Enhanced thermal and mechanical stability is imparted to the catalytic system.
2. The catalyst can be easily separated and recovered from the reaction medium. In industrial processes, packed and fluidized beds are commonly used for quick separation of reaction products. Employment of an immobilized catalyst does not need any additional change in the system per se.
3. The equilibrium between the metal species and ligands are altered and thus stereochemistry around the metal atom can be changed.
4. The catalytically active but normally unstable structures can be stabilized⁸.
5. Due to the bulk of the support, it is possible to generate preferred orientations in the catalysts.
6. The heterogeneous catalysts are known to be active for various types of reactions including large-scale processes.

It should be pointed out that heterogeneous catalysts have drawbacks as well, such as:

1. The industrial processes utilizing heterogeneous catalysis normally work under drastic conditions (at high temperatures and pressures). This is undesirable in the present time when conservation of energy is important.
2. The active sites of the support are not clearly characterized. This limits the possibilities of designing new catalysts and improving upon them.
3. Confinement of the catalyst on the support may reduce its accessibility and effectiveness.
4. Control of catalyst and ligand concentration on the support may require specific condition.
5. The mechanistic details of heterogeneous catalysis are not well understood.

Is it possible to strike a balance by incorporating the attributes of both these systems? The concept of hybrid catalysts evolves from this idea of the preparation of "an ideal" catalyst and the pursuit to achieve it imparts an impetus for new research in this area.

Classification of Supported Organometallics

Supported organometallics may be classified⁹ based on: I. type of immobilization, II. type of support or III. nuclearity of attached complexes (Table 1).

Important features of different types of reagents under the preceding heads are outlined along with the examples of their usage.

Table 1. Classification of Supported Organometallics.

I. Type of Immobilization

- (1) Complexes in the volume of a matrix
- (2) Complexes on the surface of a matrix
 - A in a non-volatile solvent or as a melt
 - B without chemical bonding to the surface
 - C with chemical bonding on the surface

II. Type of Support

- (1) Organic polymer
- (2) Inorganic compounds functioning as anchoring sites

III. Nuclearity of Anchored Complexes

- (1) Mononuclear
- (2) Binuclear complexes or clusters with a known number of metal atoms
- (3) Polynuclear species with an indefinite number of metal atoms

I. TYPE OF IMMOBILIZATION

(1) Complexes in the volume of a matrix

Organometallic complexes can be incorporated in the volume of a matrix, which is itself insoluble in the reaction medium. For example, polymer gels have been utilized for stabilization of dispersed metallic particles¹⁰. Such catalysts are active for ethylene polymerization and olefin dimerization^{9,11}. On the other hand, transition metal organometallics can be sandwiched between the layers of inorganic materials having layered structures (mica type silicates, graphite or dichalcogenides). In analogy with this is the reported activity of lamellar compounds of metals with graphite¹² towards dehydrogenation, ammonia synthesis and the Fischer-Tropsch process.

(2) Complexes on the surface of a matrix

Generally complexes are anchored on the surface of a matrix having a large surface area and sufficient pore size for allowing the diffusion of reagents to the catalyst. Surface immobilized complexes can be further subdivided based upon their interaction with the support.

(2A) Complexes on the surface of matrix: in a non-volatile solvent or as melt

The pores of the support are filled either with a solution of an organometallic complex in a non-volatile solvent¹³ or the active component is added in a molten state to prepare this supported liquid-phase catalyst. At present, a melt of vanadium compounds on silica is used for the oxidation of SO_2 to SO_3 ¹⁴.

(2B) Complexes on the surface of the matrix: without chemical bonding to the surface

This class of catalysts can be prepared by mixing a solution of the complex with the support which does not contain anchoring sites, followed by removal of the solvent and activation of the catalyst¹⁵. Hydroformylation of propylene¹⁶ and carbonylation of methanol¹⁷ have been carried out by employing such catalysts.

Grinding the metal carbonyls with the inorganic support in an inert atmosphere can be used for impregnating the support but the heat generated during grinding can lead to the decomposition of the metal carbonyl³.

The second method of preparing this type of catalyst is by reacting adsorbed metal with ligands or organometallics to prepare the organometallic reagent in situ on the surface¹⁸. Ziegler Natta type catalysts (made from titanium chloride on silica and its subsequent reaction with organoaluminum cocatalysts) are highly active in olefin polymerization¹⁹.

In yet another method, metal carbonyls can be sublimed onto the support in a flow of inert gas²⁰.

(2C) Complexes on the surface of the matrix: with chemical bonding on the surface

Supports having ligands (L) on the surface are reacted with the metal (M) to form $[S] + L-M-X$ type complexes, where X represents ligands not coordinated to the surface. Such compounds may yield a wide variety of catalysts as the metal and both types of ligands can be varied. This approach may result in "an ideal" catalyst if all metal atoms are

converted to homogeneous active centers possessing the same properties and which are regenerated after each catalytic cycle.

In such complexes, the structure of the initial homogeneous catalyst is most likely maintained.

Complexes on the surface of a support can be immobilized by using organic or inorganic functions as anchoring sites..

II. TYPE OF SUPPORT

(1) Organic polymer

Both synthetic and natural polymers have been used as matrices to anchor organometallics. Among them, crosslinked copolymers of styrene and divinylbenzene stand out as the most commonly used polymers. The aromatic ring of styrene can be easily functionalized and that in turn can serve as ligands to anchor the metal complexes²¹. Various functionalities have been reported for anchoring the active complex on such copolymers²².

Functional groups can be introduced also by grafting prefunctionalized side chains on the main polymer²³. The third method of obtaining functionalized polymers is by copolymerizing monomers carrying functional groups²⁴.

Straight chain polymers are soluble, but crosslinked polymers do not dissolve in the reaction medium. The rigidity, flexibility and swelling capacity is related to the degree of crosslinking²⁵.

As the swollen crosslinked polymer is a dynamic environment²⁵, the variation of ligand to metal ratio can alter the concentration of the complex and thereby its catalytic properties. Such a phenomenon

has been observed during hydroformylation of olefins by rhodium tri-phenylphosphine complexes on supports²⁶. It was found that the yield of normal straight chain products increased by increasing the surface phosphine:rhodium ratio. The reason for this has been attributed to the mobility of the low crosslinked polymer chains. The phosphine ligands on its surface fill the coordination environment of the metal and thereby prevent it from being coordinatively unsaturated and thus the reactivity of the complexes is reduced.

The mobility and flexibility of the swellable polymer may deactivate the catalyst due to polycoordination. By employing inorganic supports such deactivation can be prevented.

(2) Inorganic compounds functioning as anchoring sites

The matrix surface of inorganic supports is rigid and this prevents many surface functionalities from entering the site of coordination in an anchored complex. Normally only one or two ligands serve as anchoring sites.

The added advantages of using inorganic supports over polymer supports are:

1. Most inorganic oxide supports inherently possess surface groups for anchoring metals. Surface hydroxyl groups or siloxane bridges directly react with carbonyls and immobilize them by binding them to the surface.
2. The thermal stability of complexes on inorganic supports depends upon the stability of the complex itself, which may be over 300°C in some cases²⁷, whereas the thermal stability

of polymer supports (macroreticular resins) is only about 160°C. The anchoring process on inorganic supports enhances the thermal stability of the organometallics per se.

3. Methods for large-scale production of inorganic supports with the required surface area and pore volume are available. Due to their fixed surface area and pore volume, inorganic supports normally have stable diffusional characteristics²⁷. In contrast, polymer swelling may be variable under different reaction conditions and this may make it difficult to control its diffusional properties.

Oxide supports are most common among the inorganic substrates.

Complexes are immobilized on them (i) by binding directly to the surface hydroxyl groups, (ii) via formation of a heteroatomic metal-metal bond²⁸. Sometimes, undesirable side reactions may occur on the surface of oxide supports. To overcome this, the surface hydroxyl groups are made lipophilic by silylation²⁹ and thus the desorption of products from the surface is enhanced without reducing the catalytic activity. This approach is found in gas chromatography. (iii) The third approach is by using organic functionalities as anchoring sites.

Clearly, homogeneous catalysts bound to silica or alumina are better than those supported on organic polymers. However, the potential advantages are offset by more serious problems involving synthesis and characterization. As a result, silica is less frequently used as a support³⁰.

III. NUCLEARITY OF ANCHORED COMPLEXES

(1) Mononuclear

Most of the studies reported with immobilized catalysts have been carried out with mononuclear complexes. When such complexes react with other reagents, the resulting intermediate species (Fig. 1)³¹ generated is similar to that obtained from soluble mononuclear complexes. Therefore, mononuclear supported complexes have the potential to catalyze reactions known to occur using soluble complexes².

Organometallics which do not solubilize in the reaction medium or cannot be generated in homogeneous media are conveniently employed on solid supports. One obvious limitation of such a catalyst is that those reactions which require the formation of different types of intermediate species (Fig. 2)³¹ and need the participation of more than one transition metal cannot be realized with mononuclear anchored complexes.

(2) Binuclear complexes or clusters with a known number of metal atoms

Binuclear complexes have two metal atoms which may be linked by metal-metal bonds or by bridging atoms. On the other hand, clusters possess three or more metal atoms which are bound to each other by metal-metal bonds in a polyhedral arrangement.

Anchored binuclear complexes are prepared by (i) supporting individual binuclear complexes on the surface, (ii) reacting an anchored mononuclear complex with another suitable complex in solution. An example of the former approach is support of $\text{CpNi}(\text{CO})_2$ on unmodified silica⁹.

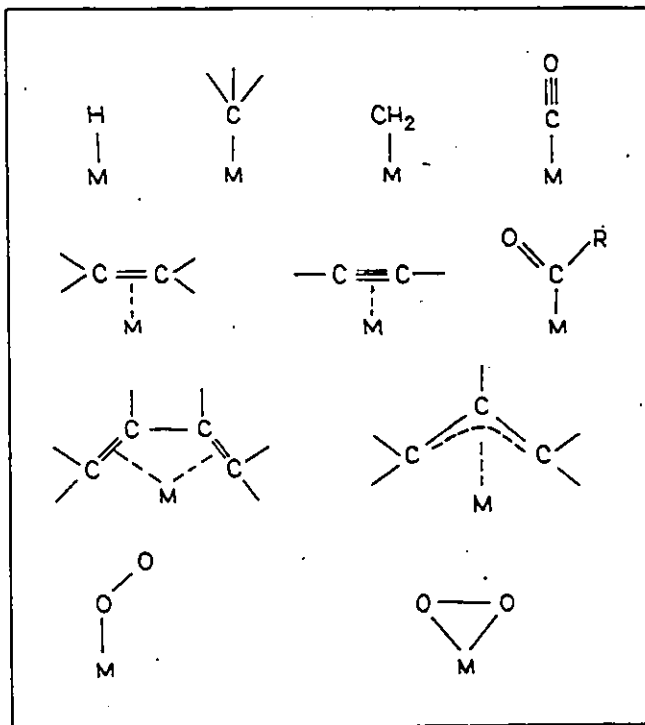


Fig. 1. Functionalities formed by the reaction of various reagents with mononuclear complexes (Ref. 31).

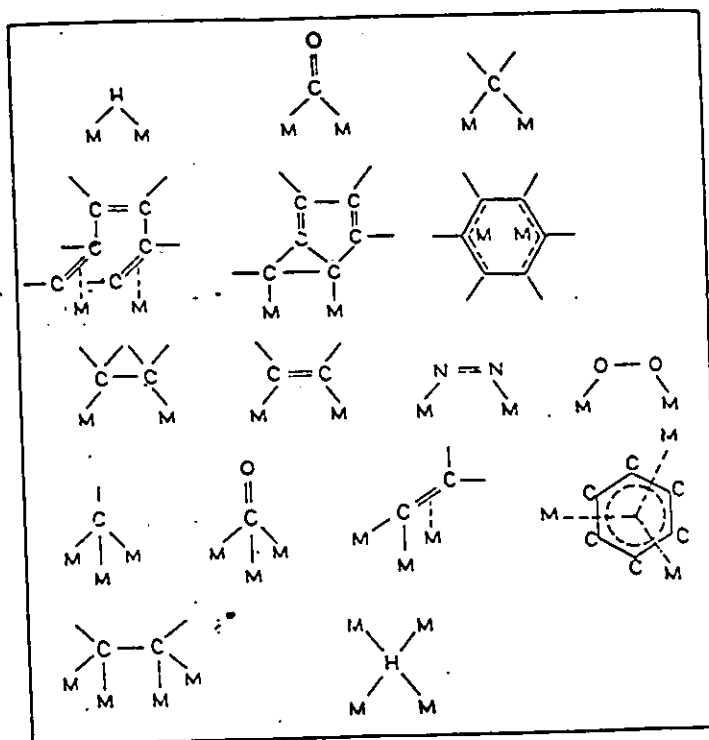


Fig. 2. Functionalities that may possibly be formed by the reaction of reagents with metal surfaces or polynuclear complexes (Ref. 31).

The anchored binuclear complexes are important because they make it possible to activate two different reagents simultaneously or different parts of a single reagent molecule by utilizing the coordination spheres of two transition elements at one instant.

Similarly, anchored clusters gain importance as they can activate different parts of a molecule or different reagents on their multinuclear active centers. Furthermore, clusters are useful models for studying the adsorption and catalytic activity of various reagents on metallic surfaces³². It has been shown by Muetterties^{31,33} that intermediate species (Fig. 2) generated on clusters are the same as those obtained by adsorbing the reagents on metallic surfaces.

As an improvement over mononuclear anchored complexes which do not catalyze the hydrogenolysis of the carbon-carbon bond, soluble clusters can effect hydrogenolysis of acetylenes, olefins and carbon monoxide^{33,34}.

The clusters in solution may be regarded as poisoned metallic particles due to the saturation of its coordination sphere by strongly bound ligands³⁴. The activation of such soluble clusters by increase in temperature may lead to their agglomeration instead of generating new coordinatively unsaturated centers. The limitation of soluble cluster complexes can be overcome by anchoring them on a surface. On heating the clusters bound on a surface, their coordination sphere can be activated without any interaction among themselves and possible agglomeration.

Individual cluster complexes are anchored directly to prepare surface polynuclear compounds. Various metal carbonyls [e.g., $\text{Fe}_3(\text{CO})_{12}$]³⁵,

$\text{Co}_4(\text{CO})_{12}$ ³⁶ and carbonyl clusters of rhodium with various nuclearity³⁷ have been immobilized. However, the initial nuclearity of the cluster on a support may change or the cluster may even fragment under the reaction conditions. The second method of preparation of surface polynuclear clusters has been reported in the preparation of polynuclear palladium complexes on silica⁹. In this method, metal atoms are introduced one by one in successive steps until the desired number of metal atoms have been incorporated.

(3) Polynuclear species with an indefinite number of metal atoms

Surface polynuclear species with an indefinite number of metal atoms are normally obtained by decomposing group 8 organometallics on oxide supports. Such catalysts contain highly dispersed particles or species which are stabilized by interacting with the surface functionalities.

Re/Pt/SiO_2 is prepared by reducing anchored rhenium (III) alkoxide to form low valent rhenium first, followed by its reaction with platinum compound. Such supported catalysts have been shown to possess higher catalyst stability and yet are useful in petroleum refining at lower pressures³⁸.

The preparation of functionalized polymers, and its properties, have been recently reviewed²⁴. The nature of inorganic supports, namely silica and alumina, will now be considered.

Nature of Silica

The physical and chemical nature of the silica surface has been studied for sometime³⁹⁻⁴¹. There are three kinds of species present on

the silica surface (Fig. 3):

- (i) isolated hydroxy (silanol) groups
- (ii) pairs of hydrogen bonded silanol groups; and
- (iii) siloxane bridges.

The vicinal hydroxyl pairs (ii) are less reactive than free silanol groups (i), which are believed to be the principal sites at which the silica surface may be functionalized. Maximum concentration of such groups as (i) is roughly one per 100\AA^2 on a surface area of 300 m^2 per gram. Silica has a large surface area, rigid matrix and is thermally stable.

Nature of the Transition Alumina Surface

Both η - and γ - alumina^{42,43}, commonly termed as active or transition alumina, have a cubic closed-packed lattice of oxide ions. η -Alumina differs from γ -alumina because it has a more acidic surface and exhibits higher catalytic activity in many reactions.

The lattice of both forms is related to spinel, MgAl_2O_4 . The arrangement of Al^{3+} ions among the octahedral and tetrahedral sites of the unit cell, just below the surface, is not clear. Nevertheless, the x-ray diffraction pattern shows that its lattices are strongly disordered.

Activated aluminas are widely used for adsorption and catalysis where their large surface area, pore structure and surface chemistry play an essential role. They are obtained from various hydrated aluminas by controlled heating so as to remove most of the water of composition. On heating alumina up to 200°C , all water remaining in it is in the form of hydroxyl groups⁴⁴. On heating above 200°C , the hydroxyl groups are

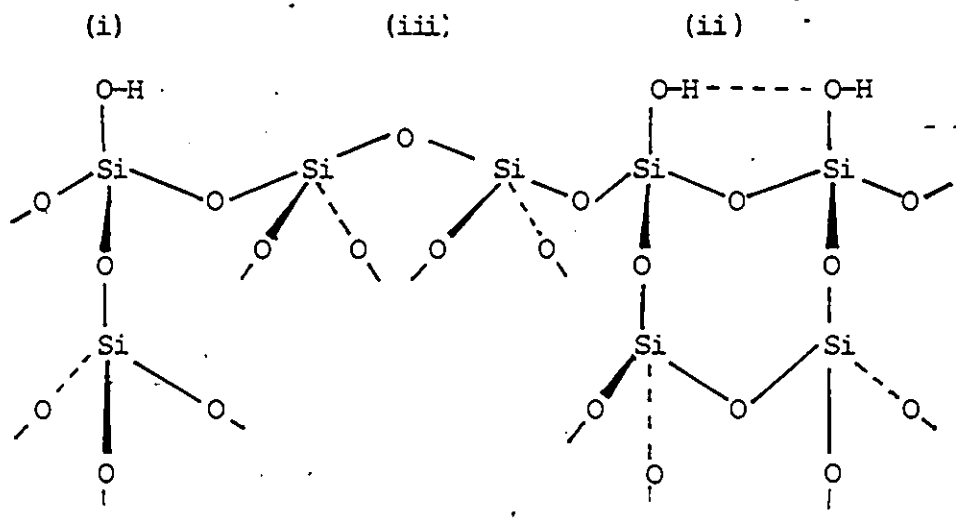


Fig. 3. Bulk silica..



gradually expelled as H_2O , but some hydroxyl groups remain on the surface even after heating to $1000^\circ C$. Therefore, the alumina surface contains some mixture of oxide and hydroxide ions along with coordinatively unsaturated Al^{3+} .

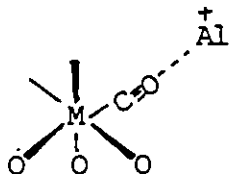
The surface of alumina possesses both acidic and basic sites. Alumina can act as a base towards Lewis acids or electrophiles, e.g., adsorption of CO_2 forms bicarbonates and carbonates on the surface⁴⁵. Due to its acidic character, alumina reacts with bases like pyridine and ammonia. An IR study of adsorbed pyridine has been reported to be useful for the characterization of different Lewis acid sites present on alumina⁴⁶. Similarly, carbon monoxide chemisorption studies⁴⁷ indicate the presence of two kinds of acid sites on both η and γ alumina.

Reaction of Metal Carbonyl Compounds with the Surface of Alumina: A Reaction Model

Based upon the available published work on transition metal carbonyls supported on oxide surfaces, simple reaction models have been developed by Brown⁴⁸. His model can explain the adsorption of metal carbonyls on alumina and can successfully interpret various types of chemical reactions observed for these adsorbed species. The proposed hypothesis is based on an interpretation of the reactions observed on solid surfaces as compared to the chemical behavior of analogous organometallic species in solution.

The highlights of this study are:

1. The mononuclear species $\text{Mo}(\text{CO})_3(\text{ads})$ formed by decarbonylation of $\text{Mo}(\text{CO})_6/\text{Al}_2\text{O}_3$ at 100°C is stabilized on alumina due to strong interaction between the terminal carbonyl with a coordinatively unsaturated Al^{3+} site on the surface^{49,50}.



Such interaction requires that steps and other irregularities exist on the surface of alumina.

2. The mobility of metal carbonyl fragments on the oxide surface is due to the relatively facile cleavage of the M-O linkage as compared to dissociation of CO ⁵¹. After a metal-oxy bond is ruptured, the resulting unsaturated and the surrounding OH or oxide group then acts as a donor toward the metal center. This explains the formation of $\text{Rh}_6(\text{CO})_{16}$ from adsorption of $\text{Rh}_4(\text{CO})_{12}$ on alumina^{52,53} and $\text{Fe}_3(\text{CO})_{12}$ from $\text{Fe}(\text{CO})_4$ in HY zeolite⁵⁴.
3. Mechanistic details are given to explain CO_2 and H_2 formation. Carbon dioxide is formed via nucleophilic attack of a surface hydroxyl at the metal bound CO [e.g., in $\text{Fe}_3(\text{CO})_{12}$] followed by loss of CO_2 to afford $\text{HFe}_3(\text{CO})_{11}^-$ ⁵⁵. Hydrogen formation is accompanied by oxidation of the metal center. This occurs via oxidative addition of surface hydroxide on the metal⁵⁶ followed by reductive elimination of hydrogen.
4. Detailed mechanistic schemes are presented to account for hydrocarbon formation from H_2 and CO and under temperature programmed

thermal decomposition (TPDE) of $\text{Mo}(\text{CO})_3(\text{ads})$ in hydrogen or helium flow. These reactions involve the intermediacy of Mo (IV) alkylidene species which accounts for the olefin metathesis activity⁵⁷ observed by supported molybdenum carbonyl.

Studies of Metal Carbonyls on Inorganic Supports

A summary of selected publications on transition metal (Mo, Fe, Co) carbonyls, immobilized on inorganic support is presented in a tabular form (Table 2)⁵⁸⁻⁷⁸.

It is evident from the Table that attempts thus far to utilize these carbonyls on supports have been made for metathesis, polymerization, hydrogenation of olefins, and hydrocarbon production. The use of $\text{Mo}(\text{CO})_6/\text{SiO}_2$ as desulfurization reagents and $\text{Co}_2(\text{CO})_8$ on modified silica for olefin hydroformylation are the only other examples reported which are of synthetic importance.

Since a review⁷⁹ on the subject has already appeared, the following is a brief account of developments in this area.

Immobilized Group 6 Carbonyls

Chromium

Temperature-programmed decomposition studies by Brenner and Hucul⁸⁰ show that complete decarbonylation of $\text{Cr}(\text{CO})_6$ on alumina required temperatures of more than 300°C. The extent of decarbonylation depends upon the temperature of activation. On heating the carbonyl at low temperature, only carbon monoxide is lost but on increasing the temperature the remaining carbonyls are eliminated along with hydrogen from the surface.

Table 2

Metal Carbonyl	Support Used	Structure of Supported Complex	Possible Utilization	Remarks	Ref.
$\text{Mo}(\text{CO})_6$	$\gamma\text{-Al}_2\text{O}_3$ SiO_2 $\text{SiO}_2\text{-Al}_2\text{O}_3$		metathesis, polymerization and cyclization of ethylene		58
$\text{Mo}(\text{CO})_6$	SiO_2		metathesis and hydrogenation of propene	TPDE	59
$\text{Mo}(\text{CO})_6$	Al_2O_3		polymerization of acetylene and ethylene, metathesis of olefins		60,61
$\text{Mo}(\text{CO})_6$	$\gamma\text{-Al}_2\text{O}_3$ SiO_2 MgO		metathesis of propene	IR, TPDE, effect of O_2 and CO	62
$\text{Mo}(\text{CO})_6$	$\gamma\text{-Al}_2\text{O}_3$	$\text{Mo}(\text{CO})_3\text{ ads;}$ $\text{Mo}(\text{CO})_2\text{O}_2\text{ ads}$	propene metathesis	TPDE, effect of O_2	63,64
$\text{Mo}(\text{CO})_6$	SiO_2		dehydrodimerization of propylamine	Ph_3Bi cocatalyst	65
$\text{Mo}(\text{CO})_6$	chloromethylated SiO_2		metathesis of nonyne	phenol cocatalyst	66,67
$\text{Mo}(\text{CO})_6$	SiO_2		desulfurization		68
$\text{Mo}(\text{CO})_6$	Al_2O_3		dehalogenation		69

Table 2 (cont'd)

Metal Carbonyl	Support Used	Structure of Supported Complex	Possible Utilization	Remarks	Ref.
Mo(CO) ₆	γ- and δ-Al ₂ O ₃	Mo(CO) ₆ ads, Mo in O, 2 ⁺ , 4 ⁺ oxidation state	reduction of CO by H ₂	preparation of Mo ⁰ and Mo ²⁺	70
Mo(CO) ₆	γ-Al ₂ O ₃	Mo(CO) ₆ ads	metathesis of propylene, polymerization of ethylene	IR, effect of NO, CO and propylene	71
Fe(CO) ₅ and Fe ₃ (CO) ₁₂	La ₂ O ₃ , MgO, SiO ₂ and γ-Al ₂ O ₃		reduction of CO by H ₂		72
K ₂ Fe(CO) ₄	η-Al ₂ O ₃		reduction of CO by H ₂	IR, x-ray diffraction, CO chemisorption cocatalyst	73, 74
Co ₂ (CO) ₈ and Co ₄ (CO) ₁₂	γ-Al ₂ O ₃ ZnO		formation of hydrocarbon hydroformylation of olefins		75 36 76
Co ₂ (CO) ₈	phosphinated SiO ₂	[(Si-O-Si-C ₂ H ₄ PR ₂) ₂ Co(CO) ₃] ₂ [(Co(CO) ₄) ₂] ₂ [(Si-O-Si-C ₂ H ₄ PR ₂) ₂ Co(CO) ₃] ₂	hydrogenation of cyclododecatriene	IR	77
Co ₂ (CO) ₈	C ₅ H ₅ modified SiO ₂	Si-O-Si-CpCo(CO) ₂	hydroformylation of olefins	IR	78

This suggests that the metal is oxidized during high temperature decarbonylation.

The adsorption of NO on $\text{Cr}(\text{CO})_6/\text{Al}_2\text{O}_3$ forms the same species as that formed on conventional chromia-alumina catalysts⁸¹. Infrared and electron paramagnetic resonance (EPR) studies⁸² by Kasusaka and Howe demonstrate that the displacement of CO by NO and oxidation of Cr(0) to Cr^{2+} and Cr^{3+} occurs, when catalysts are pretreated at 25°C. Treatment of the catalyst at higher temperatures results in the oxidation of chromium due to reaction with surface hydroxyl groups and subsequent reaction with NO yields Cr^{2+} and Cr^{3+} nitrosyl species. Silica-supported $\text{Cr}(\text{CO})_6$ gives similar results⁵⁹.

Little work has been carried out to utilize the immobilized $\text{Cr}(\text{CO})_6$. Ethylene can be polymerized^{60,61} by catalytic amounts of $\text{Cr}(\text{CO})_6$ on alumina or silica-alumina at 121-127°C and propylene can be hydrogenated by $\text{Cr}(\text{CO})_6/\text{Al}_2\text{O}_3$ at 195°C⁵⁹.

Molybdenum

Howe, Davidson and Whan⁸³ have reported that activation of $\text{Mo}(\text{CO})_6$ on a support leads to decarbonylation, the extent of which depends on the abundance of hydroxyl groups on the support. The resulting subcarbonyl species is stabilized on alumina and magnesia but not on silica. They postulated that such catalysts can act as a source of Mo(0) which could be oxidized to form catalysts for the metathesis of olefins.

Infrared studies of surface bonded $\text{Mo}(\text{CO})_6$ indicate that oxygen can destroy the immobilized metal carbonyl as no adsorptions appeared in the carbonyl region⁸⁴. During this study, Davie, Whan and Kembell have

pointed out that heating for one hour to 100°C under vacuum is needed for propene metathesis activity. An x-ray photoelectron study⁸⁵ of $\text{Mo}(\text{CO})_6/\text{Al}_2\text{O}_3$ provided evidence for the loss of carbonyl ligands during activation and electron paramagnetic resonance spectroscopy⁸³ identified the oxidation states of molybdenum during such activation. It was then confirmed that metal oxidation occurs during activation. This shows that the active metathesis species is some oxidized form of Mo. Support outgassing and activation temperatures also influence the activity of $\text{Mo}(\text{CO})_6$ ⁸⁶.

The temperature programmed thermal decomposition (TPDE) study and CO mass balance with temperature variation were carried out by Brenner and Burwell^{63,64,87,88}. They found that treatment of $\text{Mo}(\text{CO})_6$ on alumina at 53°C gives $\text{Mo}(\text{CO})_3$ (ads) which is not a good catalyst for propene metathesis but at higher temperature loss of CO occurs and metathesis activity increases. This study by Brenner et al⁸⁷ shows that decarbonylation occurs without hydrogen evolution at low temperature and a zero valent subcarbonyl species is formed, whereas at high temperature, hydrogen evolution is accompanied by a concurrent oxidation of the transition metal.

During activation of $\text{Mo}(\text{CO})_6/\text{Al}_2\text{O}_3$ from -17° to 1000°C, the original zerovalent metal is oxidized to $\text{Mo}(6+)$ ²⁰. On using fully dehydroxylated alumina, molybdenum remains in the zerovalent state. Mo clusters are shown to be formed similarly by Bowman and Burwell⁷⁰. These clusters were found to be a mixture of Mo^{2+} and $\text{Mo}(0)$ species in which the delocalized charge is balanced by surface Al-O^- groups.

Supported $\text{Mo}(\text{CO})_6$ is active for isotopic exchange between an alkane and deuterium⁸⁹. It can also polymerize ethylene and acetylene as well as hydrogenate olefins^{60,61}. Dehalogenation⁶⁹ and desulfurization⁶⁸ are other reactions which have been observed using $\text{Mo}(\text{CO})_6$ /alumina or silica.

Tungsten

Less attention has been accorded to $\text{W}(\text{CO})_6/\text{Al}_2\text{O}_3$ as compared to its molybdenum counterpart. Infrared studies⁹⁰ of $\text{W}(\text{CO})_5\text{L}$ (where $\text{L}=\text{CO}, \text{PR}_3$) on η -alumina suggests that CO is coordinated to the Lewis acid center on the alumina surface to generate an intermediate $\text{W}-\text{C}=\text{O}-\text{Al}$ during the first step of activation. This decreases the electron density on tungsten due to more ($d\pi-p\pi$)back donation of electrons to the π^* orbitals of CO.

The findings of TPDE studies performed by Brenner and Hucul⁹¹ indicates that $\text{W}(\text{CO})_3$ (ads) is formed at 135°C, whereas W^{6+} is generated at higher temperature (>400°C) on hydroxylated alumina. On a dehydroxylated support, only $\text{W}(\text{O})$ is formed. Immobilized and activated $\text{W}(\text{CO})_6$ catalyzes metathesis^{92,93}, hydrogenation⁵⁹ and polymerization of olefins⁶⁰.

Immobilized Group 7 Carbonyls

Manganese

Shriver et al.⁹⁴ reported that initial adsorption of $\text{Mn}(\text{Me})(\text{CO})_5$ on alumina is accompanied by methyl migration. The formation of the resulting cyclic product needs both Lewis acid and base sites of the alumina surface. Manganese carbonyl and TiCl_4 as cocatalyst have been impregnated on chlorinated alumina for the polymerization of ethylene⁹⁵.

Rhenium

Activated rhenium carbonyl on controlled pore glass is useful for selectively reducing the carbonyl functionality of unsaturated aldehydes to afford unsaturated alcohols^{96,97}. A bimetallic reforming catalyst⁹⁸ is formed on decomposing $\text{Re}_2(\text{CO})_{10}$ on $\text{Pt}/\text{Al}_2\text{O}_3$ under a hydrogen atmosphere. This catalyst shows more selectivity for C_5 and higher hydrocarbons than the traditional $\text{Pt-Re}/\text{Al}_2\text{O}_3$ catalyst in a hydrocarbon reforming process.

Immobilized Group 8 Carbonyls

Iron

Based on their TPDE studies^{99,100} of $\text{Fe}(\text{CO})_5$, $\text{Fe}_2(\text{CO})_9$, and $\text{Fe}_3(\text{CO})_{12}$ on alumina, Brenner and Hucul suggested that the chemistry of surface bonded materials depends on the nuclearity of the carbonyl initially employed. Later, Basset et al.⁵⁵ found that both $\text{Fe}(\text{CO})_5$ and $\text{Fe}_3(\text{CO})_{12}$ on alumina or magnesia forms $[\text{HFe}_3\text{CO}_{11}]^-$ possibly via nucleophilic attack of the hydroxyl group on a carbonyl ligand.

Zerovalent subcarbonyl species are formed when iron carbonyls on alumina are activated below 150°C , whereas above 300°C hydrogen evolution is accompanied by the oxidation of iron. Brenner and Hucul reported that alumina stabilizes the subcarbonyl species and prevents the formation of a metal mirror on the surface because a wider temperature range is needed to decompose the carbonyls as compared to unsupported carbonyls.

It is possible to prepare a more dispersed metal catalyst from immobilized iron carbonyls than by conventional high temperature calcina-

tion and reduction of Fe^{3+} . Such catalysts are active for the hydrogenation of olefins and for methane formation¹⁰⁰.

The decomposition of iron carbonyls on a dehydroxylated support gives catalysts active in the Fischer-Tropsch synthesis (180-270°C). Such catalysts are more selective for ethylene and propylene production as compared to those prepared by impregnation with $\text{Fe}(\text{NO}_3)_3$ ⁷².

By decomposing $\text{K}_2\text{Fe}(\text{CO})_4$ on alumina and silica under a hydrogen atmosphere, a better Fischer-Tropsch catalyst is obtained^{73,74}. These catalysts are unstable in an oxygen atmosphere. Carbon monoxide chemisorption studies indicated that these K/Fe catalysts have higher surface area than conventional catalysts.

A higher degree of dispersion is found on alumina than on silica. $\text{Fe}_3(\text{CO})_{12}/\text{SiO}_2$, activated at 100°C in He or H_2 , is reported to be active for CO reduction. Guzzi et al. decomposed $\text{Fe}_3(\text{CO})_{12}$ and $\text{Ru}_3(\text{CO})_{12}$ together to obtain bimetallic catalysts¹⁰¹.

Iron carbonyls were put on zeolites^{102a} to obtain a Fischer-Tropsch catalyst but they are less selective for olefins as compared to those derived from iron carbonyls supported on alumina or silica. The photochemical decomposition of $\text{Fe}(\text{CO})_5$ in HY zeolite forms highly dispersed pyrophoric iron^{102b}.

On heating $\text{Fe}(\text{CO})_5$ on pretreated graphite at 105°C, metallic iron as thin rafts forms along the edges and steps of graphite¹⁰³. Prolonged heating at 177°C causes sintering and produces iron carbides.

Ruthenium

Decomposition of $\text{Ru}_3(\text{CO})_{12}$ on alumina produces hydrocarbons^{75,104}. At 180°C, methane is produced with 49% selectivity⁷². The decomposition of $\text{K}_2\text{Ru}_3(\text{CO})_{12}$ on $\eta\text{-Al}_2\text{O}_3$ forms highly dispersed ruthenium particles, which gives 32% methane selectivity⁷³. However, these catalysts give higher conversion of carbon monoxide than iron or iridium complexes. The degree of hydroxylation of alumina governs the extent of adsorption of ruthenium carbonyls¹⁰⁵.

Silica bonded $\text{Ru}_3(\text{CO})_{12}$ is active for olefin isomerization and hydrogenation¹⁰⁶. $\text{Ru}_3(\text{CO})_{12}$ on silica, after decarbonylation in helium, gives dispersed metal crystallites which are more active for the reduction of carbon monoxide than those produced by reducing the anchored cluster in a hydrogen atmosphere. Guzzi¹⁰¹ suggested that metal agglomeration is prevented by the carbon content of the catalyst.

Osmium

Hydrocarbons are formed on decomposing $\text{Os}_3(\text{CO})_{12}$ and $\text{Os}_6(\text{CO})_{18}$ on alumina thermally^{75,104}. $\text{Os}_3(\text{CO})_{12}$ on alumina is active for the reduction of carbon monoxide whereas $\text{Os}_3(\text{C}_6\text{H}_8)(\text{CO})_{10}/\text{Al}_2\text{O}_3$ catalyzes the hydrogenation of ethylene¹⁰⁷.

Oxidative addition of the surface hydroxyl of silica on $\text{Os}_3(\text{CO})_{12}$ yields $\text{HOs}_3(\text{CO})_{10}(\text{OSi}\equiv)$ at 200°C. This catalyst shows 85.5% methane selectivity in Fischer-Tropsch processes⁷².

A variety of anchored metal carbonyl clusters can be formed by immobilizing the cluster on functionalized inorganic supports, e.g., $\text{H}_2\text{Os}_3(\text{CO})_{10}$ reacts with phosphinated silica to afford $[\text{Si}]-\text{O}-\text{Si}-\text{C}_2\text{H}_4\text{PPh}_2$

$[\text{H}_2\text{Os}_3(\text{CO})_9]$. Although this catalyst is inactive for the hydrogenation of olefins, it does isomerize 1-butene¹⁰⁸.

Cobalt

There has been little investigation of species obtained from cobalt carbonyls on inorganic supports. Albeit $\text{Co}_4(\text{CO})_{12}/\text{ZnO}$ is less active for the hydroformylation of olefins than supported rhodium catalysts, it is more selective for normal aldehyde formation^{76,109}. Catalysts obtained from $\text{Co}_2(\text{CO})_8$ on silica show activity for the synthesis of saturated hydrocarbons ($\text{C}_1\text{-C}_{30}$) from synthesis gas¹¹⁰.

Alumina is reported to be a more reactive support for the decarbonylation of cobalt carbonyl than silica or NaY zeolite¹¹¹.

Dicobalt octacarbonyl forms a mononuclear complex when anchored to silica through a cyclopentadienyl ligand⁷⁸. Anchored cobalt carbonyl phosphine complexes catalyze the hydrogenation of cyclododecatriene⁷⁷.

Photochemistry of surface confined $[\text{S}]\text{-Co}(\text{CO})_4$ has been studied by Reichel and Wrighton¹¹². Their heterogeneous photocatalysts give the same product distribution as analogous homogeneous precursors, but the oxide supported reagent is more easily isolated and handled and is more durable than $\text{R}_3\text{SiCo}(\text{CO})_4$.

Rhodium

Immobilized rhodium carbonyl on γ -alumina and silica has been studied by Smith and coworkers⁵². They reported that $\text{Rh}_6(\text{CO})_{16}$ is adsorbed physically on γ -alumina under a CO atmosphere, and exposure to oxygen results in the evolution of carbon dioxide and formation of small metal aggregates at the surface. Decarbonylated $\text{Rh}_4(\text{CO})_{12}$ or $\text{Rh}_2(\text{CO})_4\text{Cl}_2$

on alumina, on exposure to carbon monoxide generates $\text{Rh}_6(\text{CO})_{16}/\text{Al}_2\text{O}_3$. The rearrangement of $\text{Rh}_4(\text{CO})_{12}$ on silica or η -alumina to $\text{Rh}_6(\text{CO})_{16}$ is retarded by carbon monoxide, nevertheless it indicates a high surface mobility of zerovalent rhodium carbonyl⁵³.

$\text{Rh}_6(\text{CO})_{16}$ loses its molecular character and is oxidized when supported on alumina or magnesia but it can be stabilized on finely divided silica. $\text{Rh}_6(\text{CO})_{16}/\text{SiO}_2$ is not decarbonylated at room temperature but on rapid heating such decarbonylation is observed. Silica bonded clusters of $\text{Rh}_4(\text{CO})_{12}$ and $\text{Rh}_6(\text{CO})_{16}$ can be oxidized to $[\text{Rh}^1(\text{CO})_2]$ species at 100° in the absence of water^{53,113,114}.

Ichikawa¹¹⁵⁻¹¹⁸ studied a variety of supported rhodium carbonyls [$\text{Rh}_4(\text{CO})_{12}$, $\text{Rh}_6(\text{CO})_{16}$, $\text{Rh}_7(\text{CO})_{17}$ and $(\text{Rh}_{13}(\text{CO})_{23}\text{H}_{2-3})^{2-}$] surface bonded to TiO_2 , ZrO_2 , ThO_2 , CeO_2 , La_2O_3 , ZnO , MgO , BeO , Al_2O_3 , SiO_2 , CaO , and activated carbon for the reduction of carbon monoxide with hydrogen and olefin hydroformylation⁷⁶. The catalysts supported on ZnO , BeO and CaO favor methanol formation¹¹⁵. The use of La_2O_3 , TiO_2 , ZrO_2 , ThO_2 or CeO_2 results in the preferential formation of ethanol^{116,117} over methanol but Al_2O_3 and SiO_2 yields mostly methane¹¹⁵.

Anchored $\text{Rh}_6(\text{CO})_{16}$ has been shown to be active for olefin and alkyne hydrogenation as well as for isomerization and Fischer-Tropsch synthesis^{119,120,72}. Catalysts prepared from monophosphinated silica are effective for the hydrogenation of benzene¹²¹.

Iridium

The surface chemistry of $\text{Ir}_4(\text{CO})_{12}/\text{Al}_2\text{O}_3$ and SiO_2 has been studied by Howe et al.^{37,122,123}. Similar to other metal carbonyls, the

carbonyl is initially physically adsorbed onto the surface of hydroxylated alumina¹²². Decarbonylation occurs on heating under reduced pressure and on prolonged heating (at 350°C) iridium crystallites are formed^{37,123}.

$\text{Ir}_4(\text{CO})_{12}$ on silica behaves similarly. Immobilized $\text{Ir}_4(\text{CO})_{12}$ has been utilized for the hydrogenolysis of paraffins and in Fischer-Tropsch chemistry. Supported $\text{KIr}(\text{CO})_4$ after reduction also exhibits catalytic activity in the Fischer-Tropsch process^{73,74}.

Nickel

As early as 1965, Parkyn¹²⁴ proposed that at room temperature $\text{Ni}(\text{CO})_4$ initially adsorbs on alumina, decomposes on evacuation to small carbonylated metal clusters, and rapidly reacts with oxygen. Silica is less effective in catalyzing such decomposition and oxidation.

The surface chemistry of $\text{Ni}(\text{CO})_4/\text{Al}_2\text{O}_3$ was investigated by Bjorklund and Burwell¹²⁵. They reported that on partially dehydroxylated alumina, carbon monoxide, hydrogen and carbon dioxide evolution occurs, while no hydrogen evolution or metal oxidation is found on dehydroxylated alumina. Supported nickel alkyl-oligomerization catalysts have been prepared on γ -alumina¹²⁶.

On anchoring nickel carbonyl to phosphinated silica¹²⁷, its stability is enhanced. Heating to 220°C is required for complete decarbonylation of the anchored reagent prepared from $\text{Ni}(\text{CO})_2 - [\text{PPh}_2(\text{CH}_2)_2\text{Si}(\text{OC}_2\text{H}_5)_3]_2$ and silica.

Platinum

Metal crystallites obtained from platinum carbonyl cluster anions catalyze the reduction of carbon monoxide with hydrogen¹²⁸ and the

dehydrocyclization¹²⁹ of n-hexane to methylcyclopentane.

Thermal decomposition^{128,129} of $[\text{Et}_4\text{N}]_2[\{\text{Pt}_3(\text{CO})_6\}_n]^{2-}$ (n=1-5) on γ -alumina, silica, ZnO, and MgO in vacuo or under H_2 or He forms catalysts which show a higher rate of CO conversion and greater alcohol selectivity as compared to conventional platinum catalysts¹¹⁵.

Immobilized Bimetallic Carbonyls

Catalysts derived from $\text{Co}_2\text{Rh}_2(\text{CO})_{12}/\text{Al}_2\text{O}_3$ are more dispersed as metal particles when compared with materials prepared by conventional (cobalt nitrate and rhodium chloride) method³⁷. The bimetallic carbonyl is initially adsorbed on γ -alumina with loss of bridging carbonyls; the remaining carbonyls are lost when it is heated. Dispersion is enhanced in oxygen as compared to nitrogen. This suggests that oxidative decarbonylation occurs^{130,131}. The catalysts are better than conventionally prepared Co or Rh catalysts for dehydrocyclization of n-hexane¹³¹. It is suggested that the cobalt monolayer is formed on a rhodium enriched matrix at 220-320°C. The same catalysts were shown to be more effective for hydrogenolysis than their silica counterparts due to the higher surface concentration of rhodium on alumina.

Rhodium cobalt carbonyl catalysts on ZnO are useful for hydroformylation^{76,109}. Whereas linear isomer selectivity increases with cobalt content, specific activity decreases in the following order: $\text{Rh}_4(\text{CO})_{12} > \text{Rh}_2(\text{Co})_2(\text{CO})_{12} > \text{RhCo}_3(\text{CO})_{12} > \text{Co}_4(\text{CO})_{12}$ due to a decrease in rhodium content.

The bimetallic clusters $\text{HFeCo}_3(\text{CO})_{12}$ and $\text{Co}_2\text{Rh}_2(\text{CO})_{12}$ were used by Kaesz et al.¹³² to generate mixed metal crystallites. Mossbauer studies of iron-cobalt carbonyl on alumina indicates the presence of oxidized iron on the surface and ESCA studies of supported cobalt-rhodium carbonyl do not show any surface cobalt.

Fragmentation of the surface bonded clusters during activation or poisoning of the group 6 metal atom by carbon from the cyclopentadienyl ligand is posulated to be the reason for a lack of improvement in the activity for CO reduction on using $(\eta^5\text{-C}_5\text{H}_5)\text{WOs}_3(\text{CO})_{12}\text{H}$ and $(\eta^5\text{-C}_5\text{H}_5)\text{MoOs}_3(\text{CO})_{12}\text{H}$ instead of $\text{Os}_3\text{CO}_{12}$ on alumina¹³³. Finally, anchored $[\text{HAuOs}_3(\text{CO})_{10}\text{Ph}_2\text{PSi}(\text{OSi})]$ is found to be inactive for the hydrogenation of propylene but it can isomerize 1-butene at 110°C ¹⁰⁸.

Liquid-Liquid Phase Transfer Catalysis

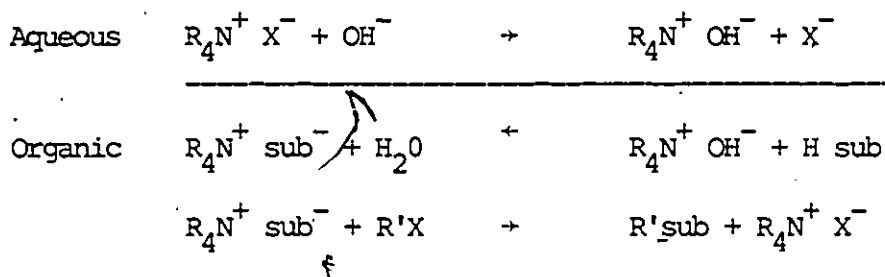
At times, chemists carry out reactions using organic compounds, soluble in an organic solvent, with water-soluble reagents. This is done by increasing the rate of such two-phase reactions by rapid agitation (Ultrasound¹³⁴ has been employed recently), the use of appropriate mutual solvents¹³⁵ or by addition of a catalytic amount of a reagent which can transfer the water-soluble reagent to the organic phase. A homogeneous reaction can then occur in that phase.

The last process is called phase transfer catalysis (PTC). These reactions are run in an aqueous-organic two-phase system with an ammonium or phosphonium salt or crown ether as the catalyst. For solid-liquid two-phase systems, crown ethers are the catalysts of choice.

Phase transfer reactions are usually mild and facile and subsequent workup is easy.

This technique is not new in itself. Examples were reported¹³⁶ as early as 1926 but it gained recognition when Makosza¹³⁷ published his work and Starks¹³⁸ proposed the mechanism of nucleophilic substitution under phase transfer catalysis.

Scheme 1



Anion exchange of a water-soluble quaternary ammonium salt generates the quaternary ammonium hydroxide which can deprotonate the organic substrate (H sub) in the organic phase. The homogeneous reaction of this ion-pair with alkyl halide regenerates the quaternary ammonium salt and forms R' sub.

There have been several reviews¹³⁹⁻¹⁴⁴ and books^{145,146} which describe the usefulness of this technique. The recent application of phase transfer catalysis to organometallic chemistry has also been reviewed^{147,148}.

The following is a summary of developments in three areas of organometallic phase transfer catalysis:

- I. Organometallic synthesis
- II. Stoichiometric organic reactions, and
- III. Catalytic organic reactions.

I. ORGANOMETALLIC SYNTHESIS

1. Ligand Substitution

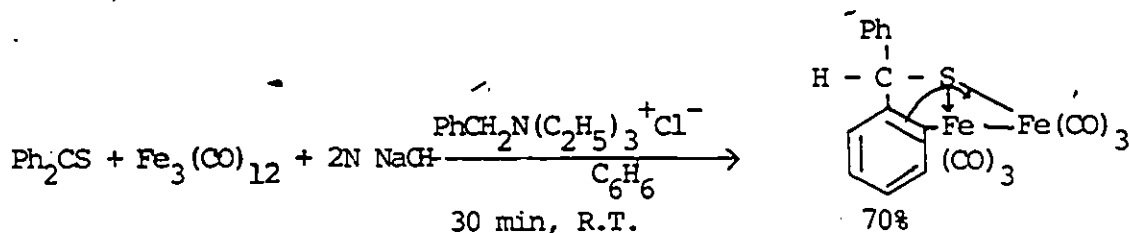
Under phase transfer catalysis, hydroxide ion attacks the carbonyl ligand of a metal carbonyl to form a $[M(CO)_n C(=O)OH]^-$ intermediate. It was reported that this hydroxycarbonyl ligand can make a cis CO group more labile¹⁴⁹. Darensbourg¹⁵⁰ investigated this point and concluded that the tendency for carbon dioxide elimination and M-H bond formation is reduced when the metal is electron rich.

One or more ligands of a Group 6 metal carbonyl can be substituted by nitrogen, phosphorus and arsenic ligands to form the product $M(CO)_n Lx$ in 51-94% yield¹⁵¹. Similarly isonitrile substitution provides an efficient route to the monosubstituted complexes¹⁵².

Bridging hydroxo complexes of platinum are synthesized via KOH and crown ether catalysis from bridging chloro complexes. Such halide displacement is shown for a phosphorus donor ligand cycloplatinated complex in which internal crown ether moiety encapsulates the sodium ion to enhance the nucleophilicity of the iodide anion¹⁵³.

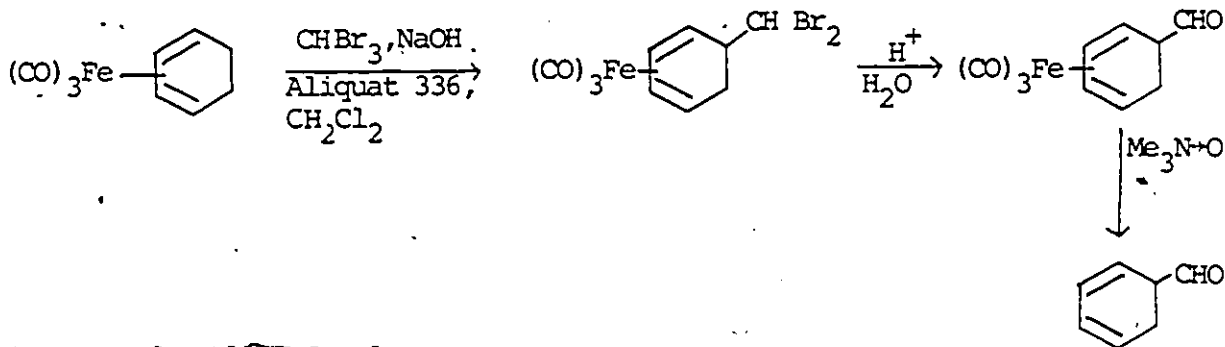
2. Arene Complexes

The first application of phase transfer catalysis in organometallic chemistry was reported by Alper and DesRoches¹⁵⁴. Employing phase transfer catalysis enables one to synthesize sulfur-donor ligand ortho-metalated complexes within an hour and in good yields. These complexes are of use in organic synthesis¹⁵⁵.



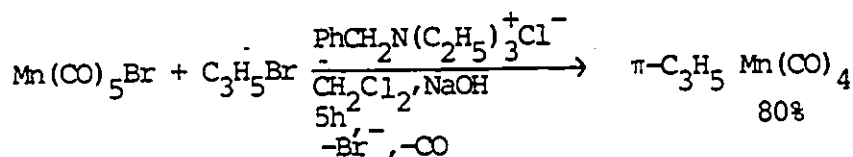
3. Diene-Iron Tricarbonyl Complexes: Dibromocarbene Insertion

Generation of dihalocarbenes from haloform under phase transfer condition is well-known¹³⁴. These in situ generated carbenes can insert into a saturated C-H bond of a 1,3-diene where the double bonds are protected by complexation of iron tricarbonyl¹⁵⁶. Dibromomethyl-substituted complexes, the reaction products, are of genuine utility in organic synthesis because they are convertible to dienals where the diene is not conjugated to the aldehyde function.



4. σ - and π -Allyl Complexes

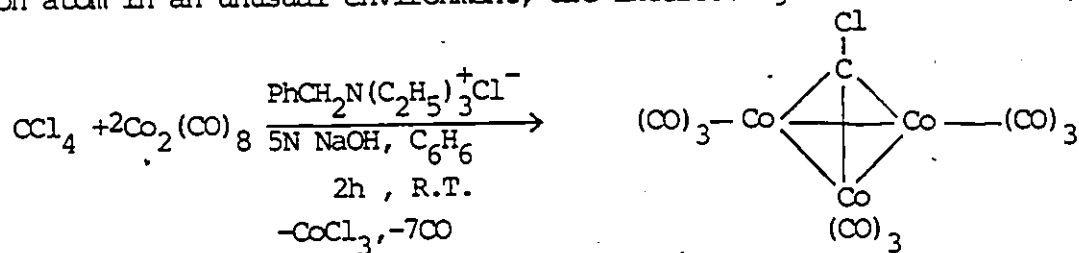
Allyl bromide reacts with a stoichiometric amount of $\text{Co}_2(\text{CO})_8$ under phase transfer conditions to generate π -allyl cobalt tricarbonyl complexes in fine yields. But this method is not applicable to other metals, e.g., $\text{Mn}_2(\text{CO})_{10}$ gave only 20-30% yields of products. Gibson et al.¹⁵⁷⁻¹⁵⁹ reported that the reaction of metal carbonyl halides with allyl halides under phase transfer catalysis provides an efficient route to the synthesis of π - and σ -allyl complexes of manganese, molybdenum, iron and ruthenium.



σ -allyl and benzyl complexes are also formed in some instances.

5. Clusters

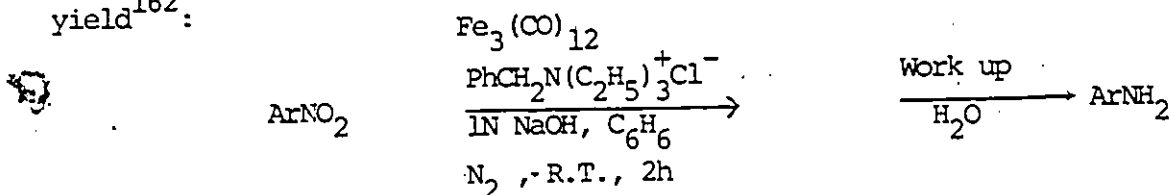
Cobalt carbonyl reacts with carbon tetrachloride to afford alkylidynetricobalt nonacarbonyl complexes¹⁶⁰. Other tri and tetrahaloalkanes form analogous complexes. These novel complexes¹⁶¹, possessing a carbon atom in an unusual environment, are interesting in themselves.



II. STOICHIOMETRIC ORGANIC REACTIONS

1. Nitro Compounds

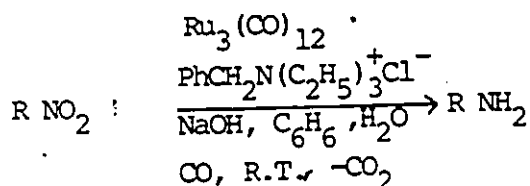
The reaction of triiron dodecacarbonyl with nitroarenes under phase transfer catalysis produces the corresponding anilines in 60-92% yield¹⁶²:



Hydridoundecacarbonyltriferrate anion $\text{H Fe}_3(\text{CO})_{11}^-$ was proposed to be the active species in this process¹⁶³. Recently, Alper and Damude¹⁶⁴ successfully trapped and characterized this species as a bis(triphenylphosphine) iminium (PPN) salt. They showed that this reduction can be effected with a catalytic amount of fluoride ion instead of aqueous sodium hydroxide.

Phase transfer catalyzed reaction of nitro compounds with $\text{Fe}_3(\text{CO})_{12}$ under carbon monoxide atmosphere forms amines and organometallic complexes $(\text{RN})_2\text{Fe}_3(\text{CO})_9$ and $(\text{RN})_2\text{Fe}_2(\text{CO})_6$ in small amounts¹⁶⁵.

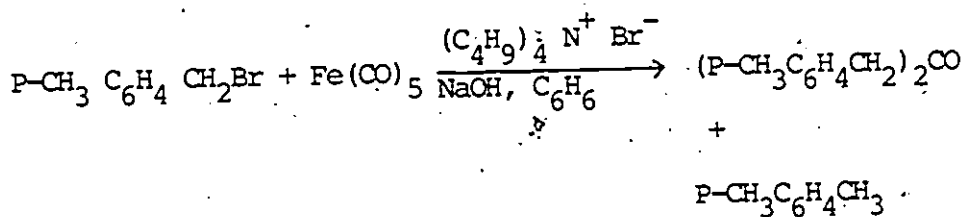
However, catalytic amounts of ruthenium carbonyl under phase transfer conditions is able to reduce both aromatic and aliphatic nitro compounds to amines in a carbon monoxide atmosphere¹⁶⁶.



With $(\text{Ph}_3\text{P})_3\text{RuCl}_2$ amines are formed in higher yield under a 'CO and H_2 ' atmosphere than in ether CO, H_2 or N_2 ¹⁶⁷.

2. Halides

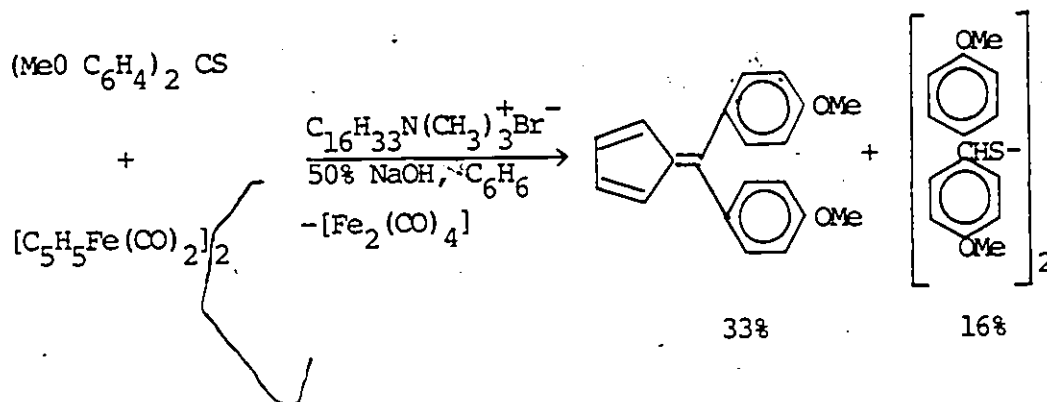
Iron pentacarbonyl under phase transfer conditions converts benzyl bromides to ketones. Hydrocarbons are formed as low yield by-products, when the concentration of the base was high¹⁶⁸.



It is believed that tetracarbonylferrate $\text{Fe}(\text{CO})_4^{2-}$ is formed when very concentrated (33%) sodium hydroxide is used, whereas on employing the base in low concentration (2%) $\text{HFe}(\text{CO})_4^-$ is generated. Nonetheless, $\text{HFe}(\text{CO})_4^-$ has actually been isolated in small amounts on reacting $\text{Fe}(\text{CO})_5$ with strong sodium hydroxide (50%) under PTC¹⁶⁹.

3. Thiobenzophenones

Cyclopentadienyl metal carbonyl anions of Mo, W or Fe react with thiobenzophenones under phase transfer catalysis to afford fulvenes in 30-50% yields¹⁷⁰. Sodium hydroxide and $C_{16}H_{33}N(CH_3)_3^+ Br^-$ as well as KOH and crown ether can be used for this conversion.



4. Metal Carbonyl Anion

Phase transfer catalyzed reduction of metal carbonyls and metal carbonyl halides by quaternary ammonium borohydride affords metal carbonyl anions¹⁷¹ from $Br Mn(CO)_5$, $C_5H_5Mo(CO)_3Cl$, $Fe_3(CO)_{12}$ and $Co_2(CO)_8$ and the corresponding hydrides from $Br Mn(CO)_4 PPh_3$ and $C_5H_5Ru(CO)_{12}Br$.

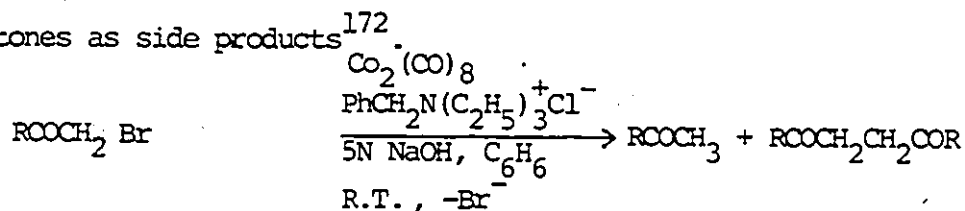
Cobalt carbonyl anion $Co(CO)_4^-$ is important for catalytic processes. It can be generated along with $Co(II)$ ion under nitrogen atmosphere. However, it can be formed almost quantitatively from $Co_2(CO)_8$ under a carbon monoxide atmosphere by using phase transfer catalysis¹⁴⁷.

III. CATALYTIC ORGANIC REACTIONS

1. Dehalogenation

As noted before, $Co_2(CO)_8$ when stirred with sodium hydroxide (5N), benzene and benzyltriethylammonium chloride (PTC) under a CO atmosphere

forms the mononuclear $\text{Co}(\text{CO})_4^-$ anion. This in situ generated reagent can dehalogenate activated halides, such as α -bromo ketones. Single electron transfer has been envisaged to account for the formation of 1,4-diketones as side products¹⁷².

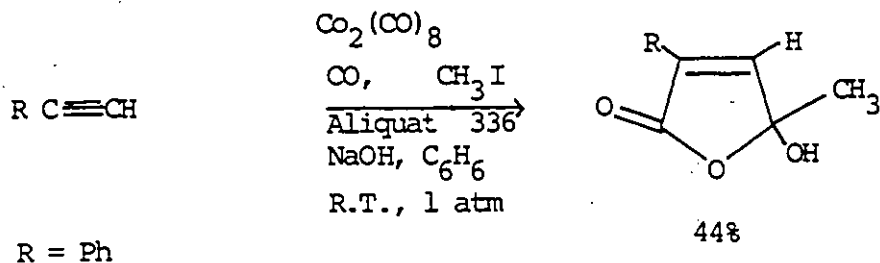


2. Carbonylation Reactions

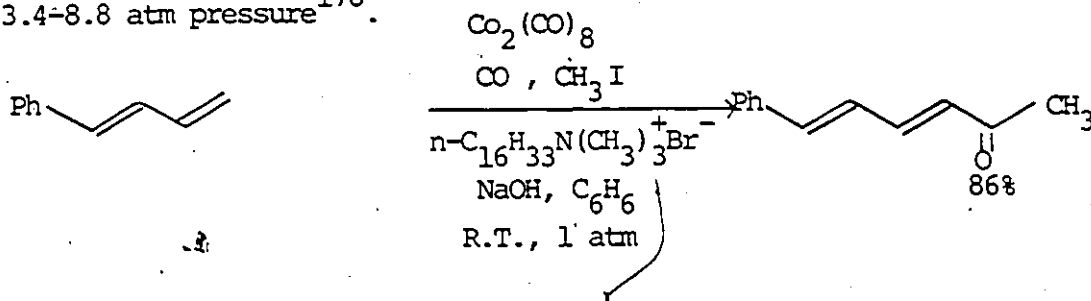
Cobalt carbonyl under phase transfer catalysis is a valuable catalyst for carbonylating halides to carboxylic acids^{173,174}. This mild method enables one, for example, to convert benzyl bromide to phenyl acetic acid in 85% yield under ambient conditions. With *o*-methyl benzyl bromide, an alkylated phenyl pyruvic acid is formed as a by-product¹⁷³.

A kinetic study of the carbonylation of benzyl bromide in a biphasic liquid-liquid system has revealed that the catalytic ion-pair $\text{Bu}_4\text{N}^+\text{Co}(\text{CO})_4^-$ stays in the organic layer and the carbonylated product in the aqueous one¹⁷⁵. Alkyl and acyl cobalt tetracarbonyls are likely intermediates in these reactions. The latter has been intercepted by carrying out this carbonylation in the presence of alkynes or dienes¹⁴⁷.

Reaction of methyl iodide with catalytic amounts of cobalt carbonyl under a carbon monoxide atmosphere affords acetylcobalt tetracarbonyl. This in situ generated species under phase transfer catalysis reacts with alkynes regiospecifically to form 2-butenolides, several derivatives of which are pharmacologically useful¹⁷⁶.



Similarly, the use of dienes or trienes as unsaturated substrates produces (E)-conjugated enones in good yields under mild conditions¹⁷⁷. The earlier reported method for this conversion required 50-85°C, and 3.4-8.8 atm pressure¹⁷⁸.



The phase transfer catalyzed carbonylation of aryl and vinyl bromides by cobalt carbonyl has also been reported. This reaction requires photostimulation (350 nm) and affords the corresponding unsaturated acids in high yields¹⁷⁹.

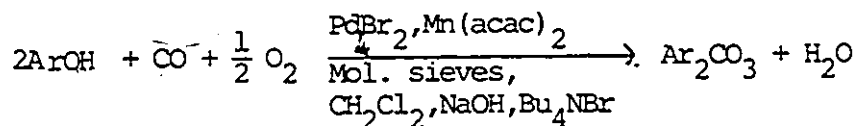
Nickel tetracarbonyl has been employed as a catalyst for preparing butenoic acids from allyl chlorides. Foa and Cassar¹⁸⁰ have proposed polynuclear nickelates as the intermediates in this phase transfer process.

Phase transfer carbonylation of halides by catalytic amount of $(\text{Ph}_3\text{P})_2\text{PdCl}_2$ requires strong conditions (95°C, 5 atm)¹⁸¹. But use of palladium (0) catalyst can carbonylate benzyl bromides at room temperature¹⁸². This reaction is dependent upon the nature of ligands attached

to the metal, e.g., Pd(dpe)₂ gave carbalkoxylation.

		% Yield			
		Ln=(PPh ₃) ₄	(dba) ₂	(dpe) ₂	
ArCH ₂ X + CO	$\xrightarrow[\text{Pd Ln,}]{(\text{C}_6\text{H}_{13})_4\text{N}^+\text{HSO}_4^-}$	Ar CH ₂ COOH	84	2	24
	$\text{CH}_2\text{Cl}_2 \text{ or } \text{C}_6\text{H}_6,$	+ Ar CH ₃	4	66	
Ar = 2Np	$5\text{N}^-\text{NaOH, 1 atm}$	+ ArCH ₂ CO O CH ₂ Ar	1		65

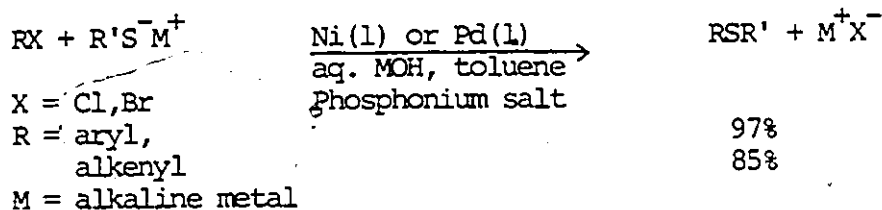
Aqueous sodium hydroxide in combination with a phase transfer catalyst was found to be an effective base for the palladium catalyzed synthesis of diphenyl carbonate from phenol, carbon monoxide, and oxygen¹⁸³.



3. Substitution

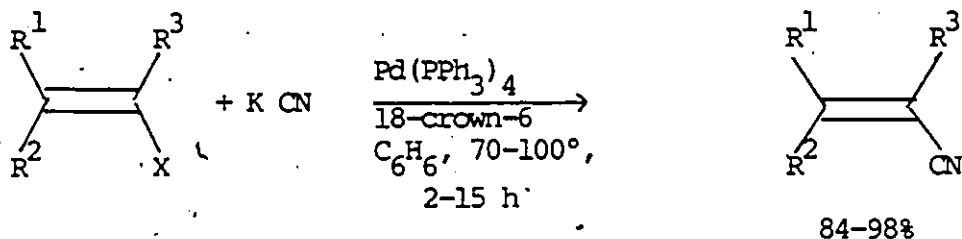
(i) Synthesis of sulfide

In the presence of σ-aryl-Ni(PPh₃)₂Cl or σ-aryl-Pd(PPh₃)₂Br, aryl or alkenyl halides react with thiolate anion under phase transfer conditions to give the corresponding sulfides¹⁸⁴.



(ii) Synthesis of cyanides

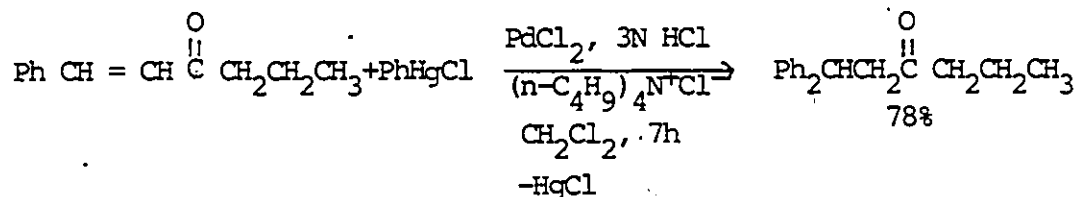
Crown ether catalyzed cyanation of vinyl halides is possible in the presence of tetrakis(triphenylphosphine) palladium (0) catalyst¹⁸⁵.



Tris (triphenylphosphine) nickel (0) has been recommended as the catalyst for substituting the halogen of aromatic halide by cyanide under liquid-liquid phase transfer catalysis¹⁸⁶.

4. Phenylation

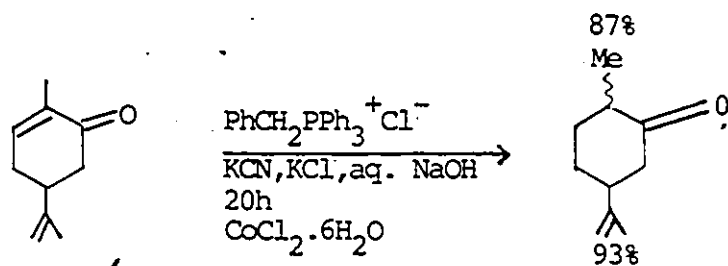
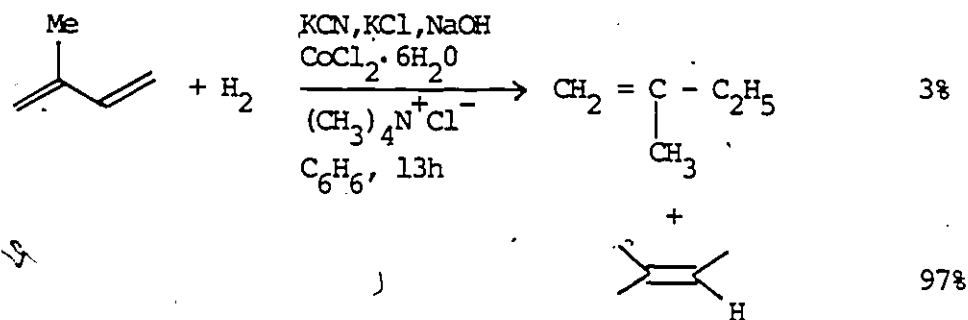
Conjugate addition of phenyl group at the β position of α, β -unsaturated ketones is possible by using phenyl mercuric chloride or tetraphenyl tin as a source of the phenyl group. This reaction needs an acidic solution of palladium chloride in catalytic amounts and works only with disubstituted double bonds¹⁸⁷.



5. Hydrogenation

The double bond of water-soluble olefins can be reduced by using Wilkinson's catalyst $[(Ph_3P)_3RhCl]$ in a water-benzene two-phase system¹⁸⁸. The hydrogenation of organic-soluble cyclohexene can be catalyzed by water-soluble rhodium complexes. These complexes carry sulfonated triphenylphosphine ligands which make the catalyst water-soluble.

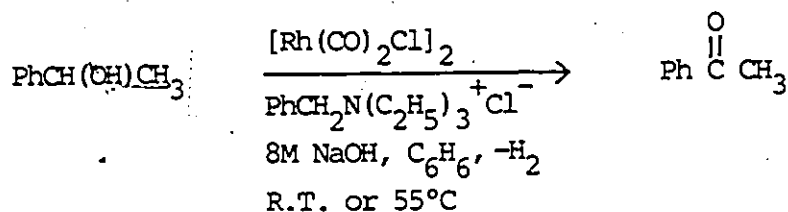
Hydridopentacyanocobaltate anion H Co(CN)_5^{3-} can catalyze the hydrogenation of conjugated dienes to mono olefins and of α,β -unsaturated to saturated ketones¹⁸⁹⁻¹⁹¹. The reagent is generated by stirring hydrated cobalt chloride, potassium cyanide, potassium chloride with a phase transfer catalyst under a hydrogen atmosphere.



The effect of micelles on the reduction of dienes and methyl sorbate has been studied by Reger and Habib^{192,193}.

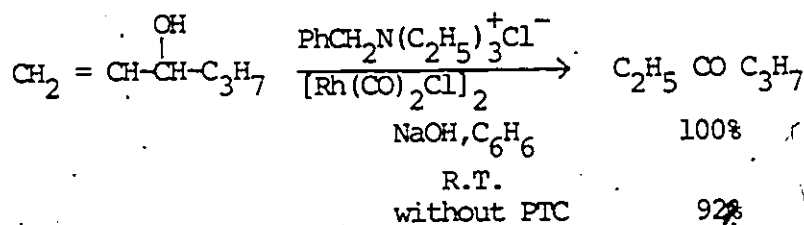
6. Dehydrogenation

Benzylic alcohols can be dehydrogenated to the corresponding carbonyl compounds by using chlorodicarbonyl rhodium (I) dimer as a catalyst under phase transfer conditions¹⁹⁴. It is possible to oxidize secondary alcohols in the presence of primary because the primary alcohols react very sluggishly under the reaction conditions, e.g., only secondary alcohol of $\text{PhCH(OH)CH}_2\text{CH}_2\text{OH}$ is dehydrogenated.



7. Isomerization

Allyl alcohols are isomerized by Rh(I) under phase transfer catalysis¹⁹⁵. This conversion can be carried out even in the absence of phase transfer catalyst in excellent yield. Hydroxy- π -allylrhodium complexes have been postulated as intermediates in these reactions.



μ_3 -Oxo-triruthenium acetate gives lower product yields and requires heating to 120°C for the same conversion¹⁹⁶.

It should be kept in mind that certain phase transfer catalysts may react with the active species generated under phase transfer catalysis^{179,197}. For example, acetylcobalt tetracarbonyl can carbonylate benzyltriethylammonium chloride to give phenyl acetic acid (via benzyl radical) in 95% yield. No such reaction occurs with tetra n-alkyl-ammonium bromide salts.

CHAPTER II

AIMS OF RESEARCH

A. Metal Carbonyls on Inorganic Supports

While, as noted in the Introduction, there are many studies of the nature of metal complexes on inorganic supports, relatively few publications have described synthetic applications of these systems. One aim of this research was to carry out exploratory investigations of the reagent capabilities of metal carbonyls on refractory oxides. The focus of this work is on reduction reactions, involving deoxygenation, dehalogenation, or desulfurization processes. While the reactions which were examined did not involve particularly difficult transformations, the results nevertheless demonstrate the capabilities of metal carbonyls on oxide supports as reducing systems.

B. Phase Transfer Catalysis

The cobalt carbonyl catalyzed carbonylation of benzylic halides to acids is one of the most useful organometallic phase transfer reactions. It seemed of interest to learn the effect of a stabilizing ligand, specifically the cyclopentadienyl ligand, on this carbonylation reaction.

The use of vinylic dibromides as substrates for phase transfer catalyzed carbonylation reactions has not been investigated. It was of significance to determine whether carbonylation, or other reactions, would be preferred for such substrates.

CHAPTER III

RESULTS AND DISCUSSION

Section I. $\text{Fe}_3(\text{CO})_{12}$ on Alumina

(a) Reaction with Nitrobenzenes

During our investigation of the use of metal carbonyls deposited on inorganic solid supports (silica, alumina), for effecting deoxygenation and/or carbonyl insertion reactions, publications by Basset, Chauvin, and co-workers⁵⁵ appeared indicating the formation of the red hydridoundecacarbonyltriferrate anion, $[\text{HFe}_3\text{CO}_{11}]^-$, by interaction of triiron dodecacarbonyl with alumina and magnesia. Chemisorption of $\text{Fe}_3(\text{CO})_{12}$ on a support such as magnesia or alumina results in nucleophilic attack of a hydroxyl group of the support on a carbonyl ligand coordinated to the cluster framework. This leads to the formation of the anionic hydrido cluster linked to the surface $[\text{HFe}_3(\text{CO})_{11}]^- \text{M}^+$, $\text{M}^+ = \text{Al}^+(\text{O}^-)_x$, $\text{Mg}^+(\text{O}^-)_y$.

It was suggested that a hydroxyl group (in alumina or magnesia) rather than molecular water is responsible for the formation of the anionic cluster, and silica did not promote the formation of anionic clusters but gave only physisorption.

It was anticipated that as the hydroxyl group on silica is slightly acidic as compared to the hydroxyl of magnesia or alumina, use of basic alumina should promote the rapid formation of the hydrido species.

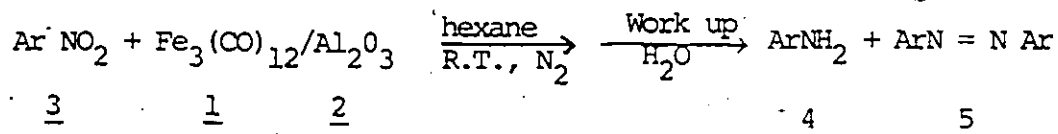
In a typical experiment (details are given in the Experimental Section, Chapter IV), basic alumina was heated overnight at 150°C under

reduced pressure. Triiron dodecacarbonyl in degassed, dry hexane and activated alumina were then stirred at room temperature under nitrogen. Within two hours, the initially green solution became colorless and the solid turned deep red. After removal of hexane, the surface species was extracted into a solution of tetraethylammonium chloride in methylene chloride. After stirring for one hour at 25°C under nitrogen, the solid became colorless and the solution deep red. An infrared spectrum of the solution showed carbonyl stretching bands at 2071w, 2002s, 1970m, 1945w, and 1715m cm^{-1} . This agreed with the reported infrared data for $\text{Et}_4\text{N}^+[\text{HFe}_3(\text{CO})_{11}]^-$. Lit. 2070w, 2000 vs, 1972 s, 1946 m, 1718 m cm^{-1} .¹⁹⁸

The ultraviolet (UV) spectrum of the same solution showed an absorption maximum at 543 nm, which is in good agreement with the reported UV of $\text{Et}_4\text{N}^+[\text{HFe}_3(\text{CO})_{11}]^-$ ¹⁹⁹ and $[\text{PPN}]^+[\text{HFe}_3(\text{CO})_{11}]^-$ ¹⁶⁴.

It was of interest to study the reductive potential of triiron dodecacarbonyl on basic alumina, as the intermediate species has a metal-hydrogen bond.

The reduction of nitrobenzenes to anilines was examined as a basis for determining the utility of $\text{Fe}_3(\text{CO})_{12}/\text{Al}_2\text{O}_3$ as a reagent system in synthesis. The trinuclear hydride, $[\text{HFe}_3(\text{CO})_{11}]^-$, generated by stirring a hexane solution of $\text{Fe}_3(\text{CO})_{12}$ with basic alumina, was treated with an equimolar amount of a nitro compound (3) overnight at room temperature.



The supernatant (hexane) did not show the presence of either nitrotoluene or toluidine indicating that the reaction occurs on the surface of the solid. Workup by trituration of the solid with ether, followed by silica gel chromatography, gave the pure aromatic amines (4) in 40-79% yields (Table 3). By-products of these reactions were the azo compounds (5, 4-8% yield). The amines were characterized by comparison with the authentic material. (Refer to Table 5 for melting point, NMR and IR data of amines and Table 6 for melting point and NMR of azo compounds and heterocyclic amines.)

Table 3. Yields of Aromatic Amines from Nitro Compounds and $\text{Fe}_3(\text{CO})_{12}/\text{Al}_2\text{O}_3$

<u>3</u> , Ar =	Product	Yield ^a , %
p- $\text{CH}_3\text{C}_6\text{H}_4$	p-Toluidine	64
m- $\text{CH}_3\text{C}_6\text{H}_4$	m-Toluidine	40
o- $\text{CH}_3\text{OC}_6\text{H}_4$	o-Anisidine	51
p- $\text{CH}_3\text{OC}_6\text{H}_4$	p-Anisidine	73
p- ClC_6H_4	p-Chloroaniline	70
p- $\text{C}_6\text{H}_5\text{COC}_6\text{H}_4$	p-Aminobenzophenone	68
2-Fluorene	2-Aminofluorene	79

^a The quoted yields are of the pure, isolated products and are not gas chromatography yields.

Nuclear magnetic resonance spectroscopy and thin layer chromatography (tlc) were found most useful for the identification of the amino compounds. In the IR spectra of nitroarenes, bands at 1350 and 1560 cm^{-1}

were characteristic of asymmetric and symmetric nitro stretching absorptions. Characteristic infrared absorptions of the product amines occurred at 3400 and 3500 cm^{-1} , which are due to NH stretching vibrations.

When the reaction of p-nitrotoluene was performed in the absence of $\text{Fe}_3(\text{CO})_{12}$, unreacted starting material was recovered. The homogeneous reaction (without alumina) occurs in refluxing benzene (10-17 h)¹⁶³. Thus, the heterogeneous reaction occurs under significantly milder conditions and the isolation of pure products is much simpler.

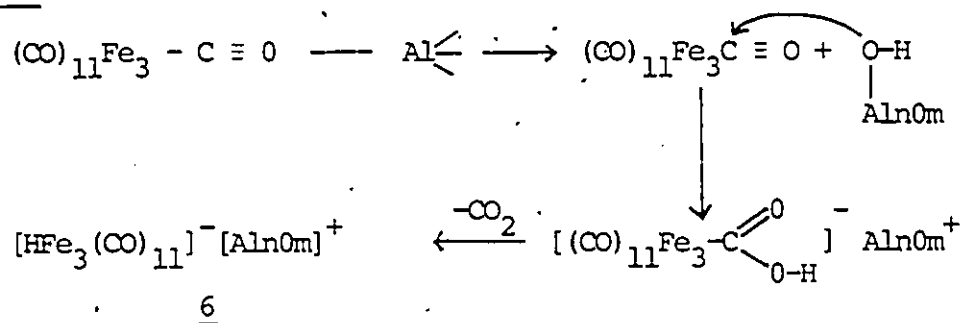
Experiments were carried out to test whether the in situ generated hydride species is selective for the reduction of nitro compounds or, in other words, to find what other common reducible groups can be tolerated. The reaction with p-nitrobenzophenone showed that the carbonyl functionality is not affected. Similarly, double bond, α,β -unsaturated ketone, alkyne, vinylic dibromide, azo, imine, amide and dibenzothiophene containing compounds were recovered unreacted after the reaction.

The reaction with p-nitrobenzoic acid was not of use since the product amino acid was adsorbed on basic alumina and could not be abstracted. Nitro compounds bearing the aldehyde or epoxide functionality did not afford the corresponding amine cleanly as these groups react with alumina itself. In addition 1-nitrooctane, 2-nitropropane and 1-nitroadamantane did not give the reduced product on reaction with $\text{Fe}_3(\text{CO})_{12}/\text{Al}_2\text{O}_3$. It is known that alumina itself reacts with aliphatic nitro compounds to yield carbonyl compounds²⁰⁰.

Studies of the reaction of hydroxide ion with metal carbonyls in hydrocarbon solvents under phase transfer conditions¹⁵⁰ reveal some points of interest. By analogy, one can propose a hypothesis about the steps involved in the formation of $[\text{HFe}_3(\text{CO})_{11}]^-$ on alumina and attempt to account for the observed behavior of a particular metal carbonyl on the surface of the inorganic support.

Initially, one carbonyl of triiron dodecacarbonyl interacts with a Lewis acid site on the alumina surface. The adjoining hydroxyl group on the surface can then attack this most electrophilic carbonyl to generate a hydroxycarbonyl iron anion.

Scheme 2



It is known from phase transfer experiments that after the formation of this hydroxycarbonyl, two processes may compete with each other: ¹⁸O exchange catalyzed by OH⁻ (i.e., removal of coordinated CO) and CO₂ elimination together with formation of a metal-hydrogen bond. Hydroxycarbonyl complexes having electron rich metals (coordinated to PPh₃, O⁻ or by its own nature) are less prone to carbon dioxide elimination.

In the case of Fe₃(CO)₁₂, OH⁻ or O⁻ does not displace carbon monoxide from the metal center at room temperature. Instead, the metal

may donate electrons to the π^* orbitals of CO due to $p\pi-d\pi$ back bonding. This renders the metal less electron rich. This point favors carbon dioxide elimination in preference to decarbonylation.

Three factors are known to be responsible for the preference of either ^{18}O exchange (loss of CO) or CO_2 elimination (formation of an M-H bond).

(i) Nature of metal

Comparing Mo with Fe, ^{18}O exchange is much more rapid than CO_2 formation in Group 6B carbonyls, while elimination of CO_2 is the dominant process among Group 8 metal carbonyls.

(ii) Substitution at the metal center

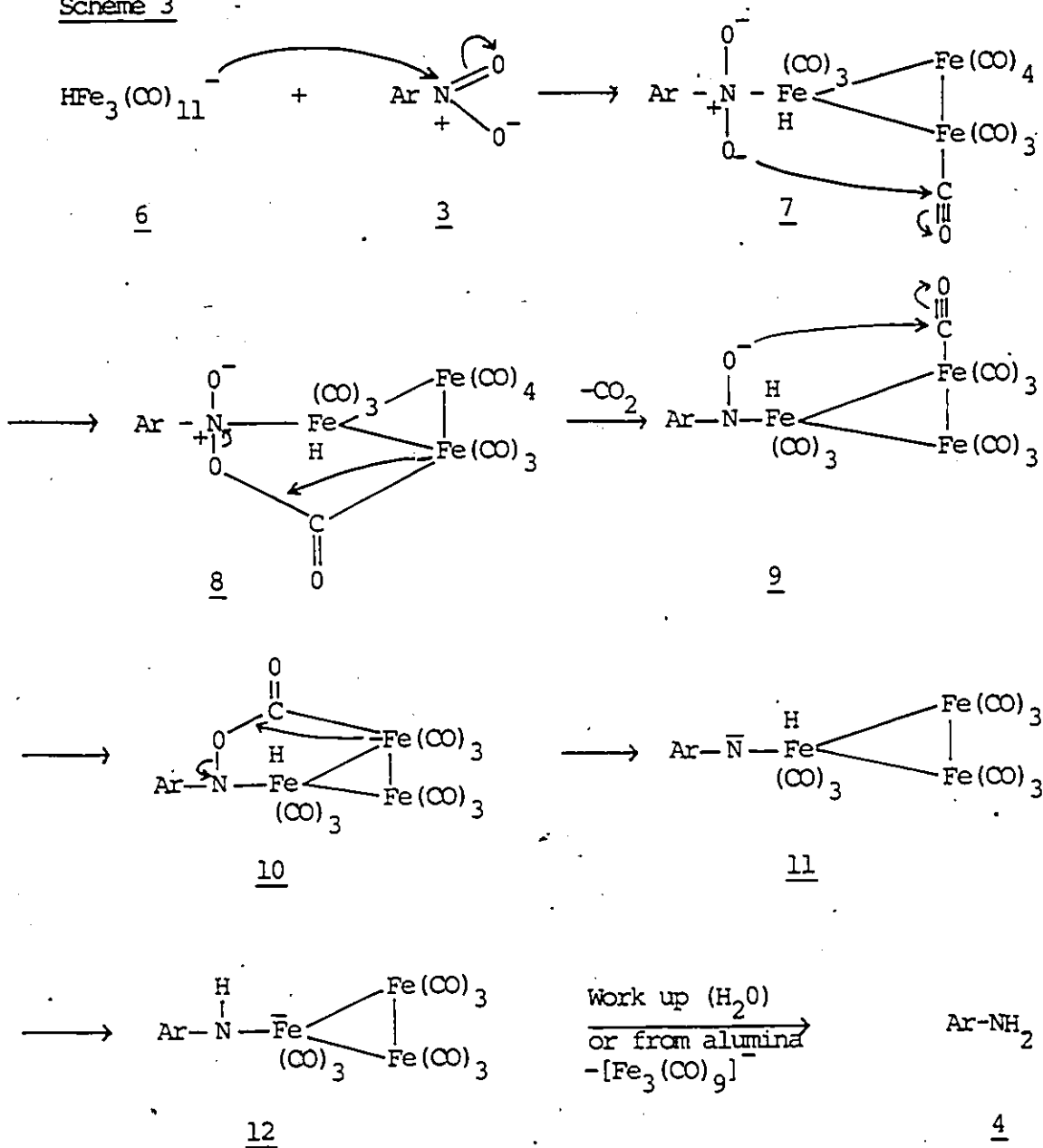
As the red hydrido species has been isolated and characterized, it can be safely concluded that O^- does not attack the metal (under the reaction conditions) and no other coordinated carbonyl is lost.

(iii) Type of support

Strong basic centers on the surface enhance carbon dioxide elimination.

In the present case, these factors favor the formation of hydride species (via CO_2 elimination) in preference to the loss of coordinated carbonyls.

Scheme 3



The pathway by which the nitroarene is converted to the amine by $\text{HFe}_3(\text{CO})_{11}^-$ is not known. A possible scheme is outlined in Scheme 3.

The hydrido undecacarbonyltriferrate anion (6) is more nucleophilic than the nitro compound so it can attack on the nitro group of the nitroarene to generate 7. The nitro then becomes more nucleophilic than the neutral metal carbonyl $\text{Fe}_n(\text{CO})_m$ portion of 7. The negatively charged O^- of nitro then attacks a carbonyl carbon intramolecularly to form the cyclized product 8. Complex 8 eliminates carbon dioxide to afford 9. Repetition of the process (attack on coordinated carbonyl by O^- of nitro) gives 11 (via 10). 11 on β hydrogen migration would form 12, which may give NH_2 by abstracting hydrogen during workup (H_2O) or from alumina.

The other two iron carbonyls, $\text{Fe}(\text{CO})_5$ or $\text{Fe}_2(\text{CO})_9$ also reduce nitro compounds but the generation of a hydride species requires more time and the reaction is not clean (i.e., many products are formed). The yield of amino product is also lower in these cases.

In conclusion, triiron dodecacarbonyl on basic alumina constitutes a simple, mild, and convenient method for reducing nitroarenes to aromatic amines.

(b) Reaction with Azoxybenzenes and N-Oxides

The selective formation of aromatic amines from the reaction of nitroarenes with $\text{Fe}_3(\text{CO})_{12}/\text{Al}_2\text{O}_3$ (basic) led to an investigation of the deoxygenation of other compounds containing an N-O bond. Finally, it was worthwhile knowing whether neutral alumina could be used as the adsorbent.

The red hydrido species was also formed on stirring triiron dodecacarbonyl in hexane with neutral alumina at room temperature under

nitrogen. Treatment of this mixture with azoxybenzene [3/2 ratio of azoxy compound/ $\text{Fe}_3(\text{CO})_{12}$] for twenty hours at room temperature afforded 61% of pure azobenzene. No aniline was formed. The experiment also showed that azobenzene is not the intermediate in the reduction of nitrobenzenes to anilines by $\text{Fe}_3(\text{CO})_{12}/\text{Al}_2\text{O}_3$. If azobenzene is reduced by triiron dodecacarbonyl on alumina, aniline would have been obtained as the major product.

Azoxybenzene (13) bearing other substituents, and heterocyclic N-oxides (14) were reacted with the in situ generated reagent at room temperature to give the corresponding deoxygenated products in 59-86% yield (Table 4).

Table 4. Yield of Azobenzenes and Heterocyclic Amines.

REACTANT <u>13</u> , <u>14</u>	PRODUCT <u>5</u> , <u>17</u>	YIELD, %
Azoxybenzene	Azobenzene	61
4,4'-Azoxyanisole	4,4'-Azoanisole	68
4,4'-Azoxyphenetole	4,4'-Azophenetole	59
Quinoline N-oxide	Quinoline	79
4-Picoline N-oxide	4-Picoline	86

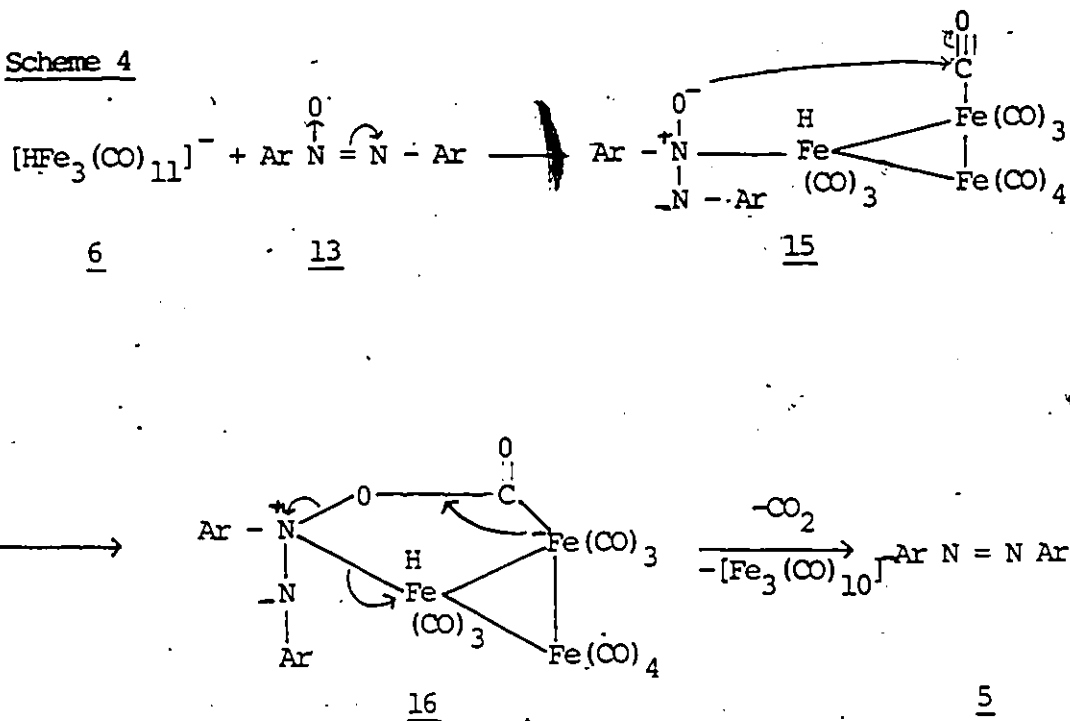
The compounds were characterized by the usual spectroscopic methods. Their infrared spectra, for example, were superimposable in the finger-print region with the spectra of authentic materials.

(Refer to Table 6.)

The product yields obtained by using triiron dodecacarbonyl on alumina are both lower, or in some cases higher, than that for iron pentacarbonyl in butyl ether. However, the latter process requires much more drastic conditions (140°C, 17-24h)^{201a}. The reported deoxygenation of nitroxyl radical with triiron dodecacarbonyl in benzene and methanol also required refluxing and the yield of the amine was 42%^{201b}.

The heterogeneous method is also competitive with, or superior to, the use of other reagents for affecting the same transformations. For example, the recently reported^{202a} deoxygenation of pyridine N-oxides by trimethyl(ethyl)amine sulfur dioxide complexes occurs in refluxing dioxane (~100°C). For 4-picoline N-oxide, the only case for direct comparison, the yield of deoxygenated material is lower (70-75%) using the sulfur dioxide reagent than that realized with $\text{Fe}_3(\text{CO})_{12}/\text{Al}_2\text{O}_3$. Use of triphenylphosphine under photolytic conditions is also inferior to the method described herein because clean deoxygenated product was formed in only 22-29% yield with substituted quinoline N-oxides and the photoisomerization products (59-61%) have to be separated along with triphenylphosphine oxide^{202b}.

Scheme 4



A possible pathway for explaining this deoxygenation of azoxybenzenes or N-oxides is outlined in Scheme 4. The nucleophilic hydridoundecacarbonyltriferrate anion (6) attacks the nitrogen of N-oxide (17) or azoxybenzene (13) to generate 15. The negatively charged oxygen of the azoxybenzene then reacts with the coordinated carbonyl ligand intramolecularly to form the cyclic intermediate 16. This cyclic complex (16) on elimination of carbon dioxide affords the product (5).

Table 5. Properties of Aromatic Amines Obtained from $\text{ArNO}_2 / [\text{Fe}_3(\text{CO})_{12}/\text{Al}_2\text{O}_3]$.

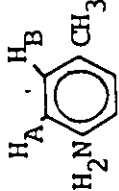
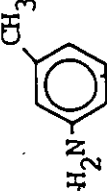
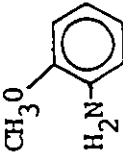
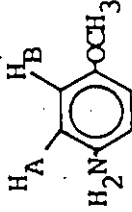
COMPOUND	STRUCTURE	m.p., °C	^1H NMR (CDCl_3), δ	IR (CHCl_3), cm^{-1}
p-Toluidine		42-43	2.23 (s, 3H, CH_3), 3.53 (broad s, 2H, NH_2) 6.57 (d, 2H, H_A , ortho to NH_2 ; J=8 Hz), 6.97 (d, 2H, H_B , ortho to CH_3 ; J=8 Hz)	[3520 (m), 3440 (s), NH str.] [3040 (m), aromatic CH] [2908, 2970 (m), aliphatic CH] [1515, 1625 (s) NH bending], [820 (s), NH out of plane bending]
m-Toluidine		b.p. 203	2.25 (s, 3H, CH_3), 3.51 (broad s, 2H, NH_2), 6.31-6.68 (m, 3H, aromatic CH), 6.85-7.21 (m, 2H, aromatic CH)	3450 (m), 3380 (s), NH str.
o-Anisidine		b.p. 224	3.80 (s, 5H, NH_2 and OCH_3), 6.75 (s, 4H, aromatic CH)	3480 (m), 3390 (w), NH str.
p-Anisidine		57-59	3.47 (broad s, 2H, NH_2), 3.73 (s, 3H, OCH_3), 6.68 (s, 4H, aromatic CH)	3460 (m), 3380 (s), NH str.

Table 5 (cont'd)

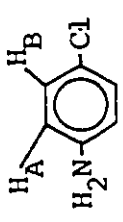
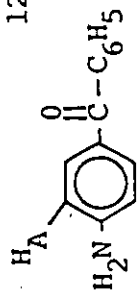
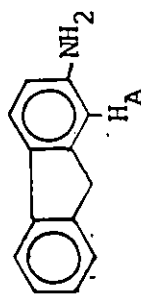
COMPOUND	STRUCTURE	m.p., °C	¹ H NMR (CDCl ₃), δ	IR (CHCl ₃), cm ⁻¹
p-Chloroaniline		69-72	3.61 (s, 2H, NH ₂), 6.57 (d, 2H, H _A ortho to NH ₂ , J=8 Hz), 7.11 (d, 2H, H _B ortho to Cl, J=8 Hz)	3450 (m), 3400 (s), NH str.
p-Aminobenzophenone		121-123	4.17 (broad s, 2H, NH ₂), 6.70 (d, 2H, H _A ortho to NH ₂ , J=8 Hz), 7.27-7.87 (m, 7H, aromatic CH)	3418 (m), 3520 (w), NH str.
2-Aminofluorene		125-127	3.63 (broad s, 2H, NH ₂), 3.73 (s, 2H, benzylic), 6.50-6.87 (m, 2H, H _A ortho to NH ₂ , aromatic CH), 7.00-7.97 (m, 5H, aromatic CH)	3450 (m), 3520 (s), NH str.

Table 6. Properties of Azo Compounds and Heterocyclic Amines.

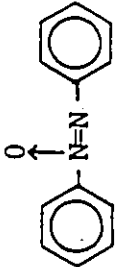
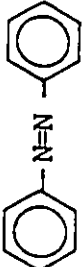
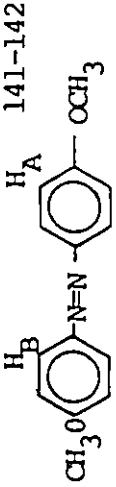
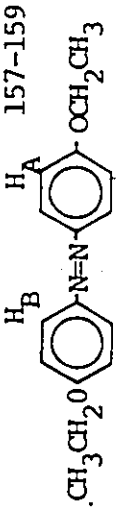
COMPOUND	STRUCTURE	m.p., °C	¹ H NMR (CDCl ₃), δ
Azoxybenzene ^a		36	7.30-7.67 (m, 6H, aromatic CH), 8.0-8.38 (m, 4H, aromatic CH)
Azobenzene		67-68	7.32-7.60 (m, 6H, aromatic CH), 7.71-8.06 (m, 4H, aromatic CH)
4,4'-Azoanisole		141-142	3.93 (s, 6H, OCH ₃), 7.07 (d, 4H, H _A ortho to methoxy, J=9 Hz), 7.97 (d, 4H, H _B ortho to azo, J=9 Hz)
4,4'-Azophenetole		157-159	1.43 (t, 6H, CH ₃ CH ₂ , J=6.5 Hz), 4.10 (q, 4H, CH ₃ CH ₂ , J=6.5 Hz), 6.93 (d, 4H, H _A ortho to ethoxy, J=8 Hz), 7.80 (d, 4H, H _B ortho to azo, J=8 Hz)

Table 6 (cont'd)

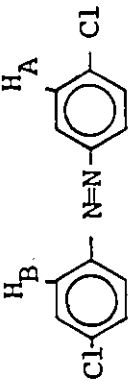
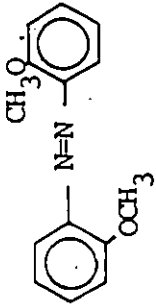
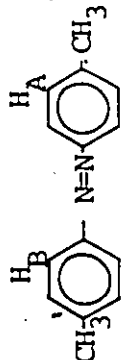
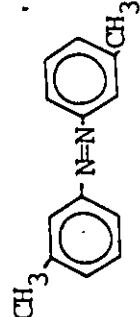
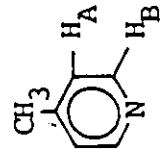
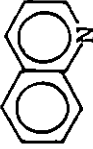
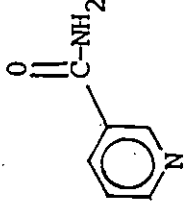
COMPOUND	STRUCTURE	m.p., °C	¹ H NMR (CDCl ₃), δ
4,4'-Dichloroazobenzene		184-185	7.43 (d, 4H, H _B ortho to azo, J=8.5 Hz), 7.83 (d, 4H, H _A ortho to Cl, J=8.5 Hz)
2,2'-Azoanisole		152-153	3.81 (s, 6H, OCH ₃) 6.75 (s, 8H, aromatic CH)
4,4'-Azotoluene		144	2.43 (s, 6H, CH ₃), 7.30 (d, 4H, H _A ortho to CH ₃ , J=8 Hz), 7.80 (d, 4H, H _B ortho to azo, J=8 Hz)
3,3'-Azotoluene ^b		54	2.47 (s, 3H, CH ₃), 7.20-7.50 (m, 4H, aromatic CH), 7.57-7.93 (m, 4H, aromatic CH)
4-Picoline		b.p. 145	2.32 (s, 3H, CH ₃), 7.12 (d, 2H, H _A ortho to CH ₃ , aromatic CH, J=6 Hz), 8.47 (d, 2H, H _B ortho to N, aromatic CH, J=6 Hz)

Table 6. (cont'd)

COMPOUND	STRUCTURE	m.p., °C	¹ H NMR (CDCl ₃), δ
Quinoline		b.p. 238	7.13-7.90 (m, aromatic CH), 7.90-8.33 (m, aromatic CH), 8.83-9.17 (m, aromatic CH)
Nicotinamide		129-130	2.60 (s, 2H, NH ₂), 7.41-7.95 (m, aromatic CH), 8.00-8.60 (m, aromatic CH), 8.70-8.90 (m, aromatic CH), 9.12-9.22 (m, aromatic CH)
a	IR(CHCl ₃) ν _{CH} str. 3042 (m), ν _{C=C} 1600 (w), ν _{N+O} str. 1310 (s)		
b	MS, m/e 210 [M] ⁺ , 134 [M-C ₆ H ₄] ⁺ , 119 [M-C ₆ H ₄ CH ₃] ⁺ , 91 [M-N ₂ C ₆ H ₄ CH ₃] ⁺		
c	NMR was run in DMSO-d ₆ .		
	IR(CHCl ₃) ν _{NH} 3420 (broad, s), 3210 (w), ν _{CO} 1685 (s)		

Section II. $\text{Co}_2(\text{CO})_8$ on Alumina

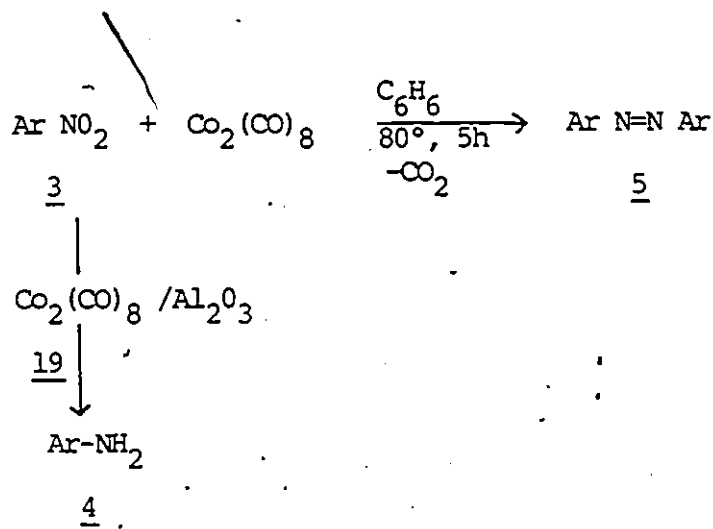
(a) Reaction with Nitrobenzenes

One of the active areas of research in organic chemistry involves the use of reagents supported on porous solids to effect various synthetic transformations. Studies by Posner et al.²⁰³ and by McKillop and Young²⁰⁴ have demonstrated the utility of alumina as a support.

As previously noted, comparatively little work has been done in the area of organic reactions effected by metal carbonyls supported on alumina.

Having found that a trinuclear iron hydride is generated by stirring triiron dodecacarbonyl on basic or neutral alumina and this species $[\text{HFe}_3(\text{CO})_{11}]^-$ is able to deoxygenate nitrobenzenes, azoxybenzenes and N-oxides, it was of interest to see what happens when cobalt carbonyl is put on a refractory oxide such as alumina. The reduction of nitroarenes was chosen for this model study. It is known that nitrobenzenes are converted to azobenzenes with dicobalt octacarbonyl in refluxing benzene²⁰⁵. The next step was to learn the effect of a refractory oxide on the nitroarene-dicobalt octacarbonyl reaction. In other words, is the heterogeneous process similar to, or different from, the homogeneous one?

A rapid color change occurs when a hexane solution of $\text{Co}_2(\text{CO})_8$ is exposed to alumina at room temperature. When p-nitrotoluene was added to it and the reaction mixture stirred overnight at room temperature, p-toluidine was isolated in 60% yield with the azo compound being obtained as a low yield by-product.



The alumina (Fischer adsorption) used in the experiment was dried as usual at 150°C under reduced pressure. The yield of p-toluidine decreased to 35% when the reduction was effected in a carbon monoxide atmosphere. A similar reduction in yield occurred using a nitrogen atmosphere, but first drying the alumina at 550°C instead of 150°C. Other oxides, including silica and florisil, afforded p-toluidine from p-nitrotoluene, but in lower yields than in the case of alumina.

Good yields of aromatic amines were also obtained from a variety of nitroarenes and $\text{Co}_2(\text{CO})_8/\text{Al}_2\text{O}_3$ (Table 7).

When cobalt carbonyl (3 mmol) was stirred with alumina and 1,2-dimethoxyethane, a red colored species characteristic of cobalt was not formed and on its reaction with azoxybenzene (3 mmol), very small amount of azobenzene was obtained and 91% of starting material was recovered. On carrying out the same reaction in hexane, 27% azobenzene was obtained. This shows that hexane is a better solvent for such deoxygenation reaction.

Table 7. Yields of Aromatic Amines from Nitro Compounds and $\text{Co}_2(\text{CO})_8$ /Refractory Oxides.

<u>3</u> , Ar =	Oxide	Product <u>4</u> , <u>5</u>	Yield, %
p- $\text{CH}_3\text{C}_6\text{H}_4$	Al_2O_3	p-Toluidine	60
		4,4'-Azotoluene	6
	Al_2O_3 (550°C)	p-Toluidine	38
	Al_2O_3	p-Toluidine	35 ^a
	SiO_2	p-Toluidine	40
	Florisil	p-Toluidine	35
p- $\text{CH}_3\text{OC}_6\text{H}_4$	Al_2O_3	p-Anisidine	62
		4,4'-Azoanisole	5
	Al_2O_3 (550°C)	p-Anisidine	39
p- ClC_6H_4	Al_2O_3	p-Chloroaniline	62
p- PhCOC_6H_4	Al_2O_3	p-Aminobenzophenone	71
m- $\text{CH}_3\text{C}_6\text{H}_4$	Al_2O_3	m-Toluidine	70
2-Fluorenyl	Al_2O_3	2-Aminofluorene	77

^a Reaction was done in carbon monoxide atmosphere.

Bis(tributylphosphine) dicobalt hexacarbonyl and tetracobalt dodecacarbonyl on alumina were less effective reagents (7-45% yields of p-toluidine) than dicobalt octacarbonyl for the reduction of p-nitrotoluene.

Only starting material was recovered when the nitroarene was exposed to alumina in the absence of dicobalt octacarbonyl.

The following experiment clearly demonstrates that the reduction process is heterogeneous. After stirring the mixture of dicobalt octacarbonyl and alumina in hexane for two hours, the solid and liquid phases were separated by filtration under a nitrogen atmosphere. Each phase was treated separately with p-nitrotoluene in benzene. While p-toluidine was cleanly formed using the solid phase, the liquid phase only afforded recovered nitro compound.

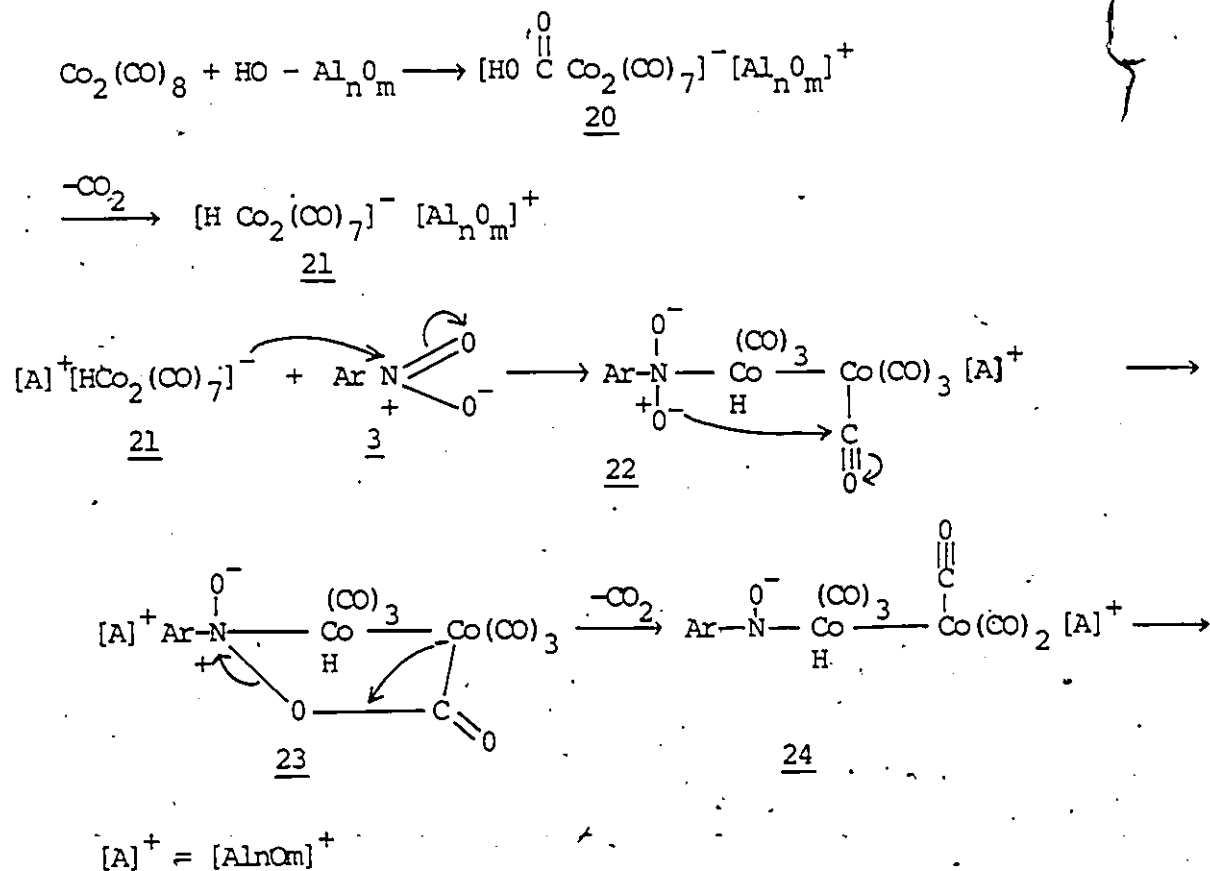
Functionalities such as chloro, ketone, and ether are unaffected under these reaction conditions (Table 7). Experiments were carried out to determine whether the in situ generated reagent is able to reduce other common reducible groups or not. It was found that a double bond, α,β -unsaturated ketone, imine, azo, triple bond, unsaturated halide and sulfoxide are not affected by it. However, one cannot use nitro compounds bearing epoxide, thiol, or thioketone functions since such functionalities react with alumina.

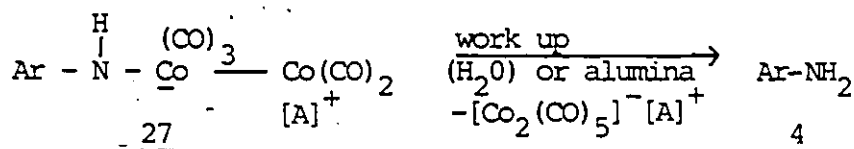
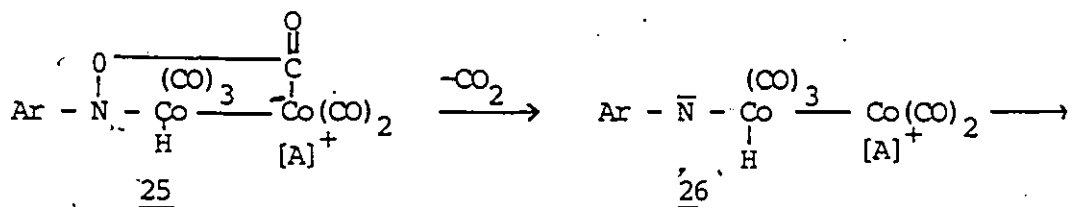
Thus $\text{Co}_2(\text{CO})_8/\text{Al}_2\text{O}_3$ is a specific reagent for the reduction of nitroarenes to amines under very mild conditions.

Clearly, the heterogeneous process is different from the homogeneous pathway. It is therefore likely that the intermediates involved

in the two reactions are not the same. A key observation, noted above, is that an increase in the temperature at which alumina is dried results in a decrease in the yield of amine, indicating that the hydroxyl groups which are present on the surface of the oxide participate in the reaction. There are more such hydroxyl groups present at 150°C than at 550°C. It is conceivable that attack by one of these hydroxyl groups on a cobalt carbonyl carbon would afford 20, which on loss of carbon dioxide generates the binuclear cobalt hydride. The latter can then convert nitroarene to aromatic amine.

Scheme 5





The nucleophilic attack by the oxygen of nitro group in 22 may occur on the carbonyl of other molecules of cobalt hydride (21), instead of intramolecular attack as shown here in Scheme 5. The scheme is similar to the one (Scheme 3) reported for triiron dodecacarbonyl on alumina in Section I(a).

Aliphatic nitro compounds could not be reduced by $\text{Co}_2(\text{CO})_8/\text{Al}_2\text{O}_3$ because such nitro groups are known to react with alumina alone²⁰⁰. Reactions were tried using 1-nitrooctane, nitrocyclohexane, and 1-nitroadamantane as reactants. In none of these cases was the corresponding amino compound formed.

As noted above, product yields are lower using $\text{Co}_2(\text{CO})_6(\text{PBU}_3)_2$ instead of $\text{Co}_2(\text{CO})_8$ as the reagent. This result may be because tributylphosphine is more electron-donating than carbonyl and this will make the attack by hydroxyl of alumina on carbonyl carbon much slower. With this reagent, even after four hours of stirring under nitrogen, the color of alumina was lemon and the hexane solution was light orange. This indicates that the hydride $[\text{HCo}_2(\text{CO})_5(\text{PBU}_3)_2]^-$ is either being

formed much more slowly than $[\text{HCo}_2(\text{CO})_7]^-$, or some other species is produced. On reaction of p-nitrotoluene with the in situ generated species, only 7% of p-toluidine was isolated and the nitro compound was recovered.

It should be noted that a similar observation was made by Darensbourg, Baldwin and Froelich¹⁵⁰ for Group 6 carbonyls. Attachment of phosphine in the place of carbonyl prevented the formation of hydride under phase transfer conditions.

The basicity and thus the reactivity of transition metal complexes can be gauged from the K_a values of the corresponding hydrides acting as acids. Although few accurate K_a values for transition metal hydrides are known due to secondary reactions, air sensitivity, and problems in finding suitable solvents for comparisons, those K_a values which have been reported³⁰ illustrate a strong dependence on both the nature of the metal and the other ligands. For example,

	K_a
H Co(CO)_4	~ 1
$\text{H Co(CO)}_3\text{PPh}_3$	1×10^{-7}
H Fe(CO)_4^-	4×10^{-14}

The less acidic the hydride, the more basic the conjugate base. H Co(CO)_4 shows strongly acidic character. Substitution of the electron-releasing triphenylphosphine ligand for the electron-withdrawing CO (π -acid) ligand causes a change in acidity of the hydride by seven

orders of magnitude. This example shows that a change in metal basicity (reactivity) occurs on altering the ancillary ligand.

On comparison of $[\text{HCo}_2(\text{CO})_7]^-$ -alumina versus $[\text{HCo}_2(\text{CO})_5(\text{PBu}_3)_2]^-$, it is expected that the latter would be a much weaker acid than the red species generated by dicobalt octacarbonyl on alumina. The greater Co-H bond strength will be anticipated in phosphine substituted ligand.

Although a red-brown colored species was generated on stirring dicobalt octacarbonyl with silica or florisil, the yield of p-toluidine was reduced on using these supports instead of alumina. This may be due to the lower abundance of basic hydroxyl (cf. alumina) groups.

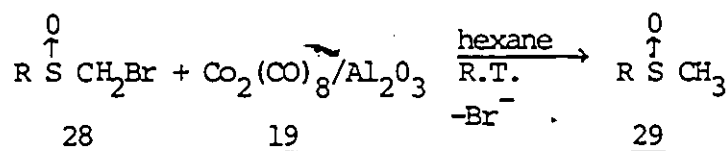
On changing the solvent from hexane to benzene, the red colored species was generated and supernatant became colorless within an hour. But on reducing the amount of alumina to 10 g, instead of the normal 20 g, the color of the supernatant remained red-brown even after 6 hours of stirring. This observation indicated that some dicobalt octacarbonyl was adsorbed on the support, with the rest being in benzene.

In the case of rhodium carbonyl⁵³, it has been shown that on reaction with alumina, larger clusters are formed. This process does not seem probable with $\text{Co}_2(\text{CO})_8$ because on using $\text{Co}_4(\text{CO})_{12}$ (a bigger cluster) the yield of p-toluidine was found to be reduced (to 45%). Had there been formation of a bigger cluster, use of tetracobalt dodecacarbonyl should have resulted in the enhancement of the yield.

(b) Reaction with α -Halosulfoxides

In the last section, it was observed that deoxygenation reactions with dicobalt octacarbonyl supported on alumina can be carried out under gentle conditions, the reactions are simple to workup, and can be selective as well. Simple and mild dehalogenation reactions can be realized by use of $\text{Co}_2(\text{CO})_8/\text{Al}_2\text{O}_3$.

Treatment of dicobalt octacarbonyl adsorbed on alumina with α -bromosulfoxide (28) in hexane at room temperature for twenty hours gives the sulfoxide normally in 80-100% yield. Product yields with several compounds are listed in Table 8.



α -Bromomethyl p-chlorophenyl sulfoxide was recovered unchanged when exposed to alumina in the absence of the metal carbonyl. Similarly, ethyl phenyl sulfoxide was unaffected when allowed to react with $\text{Co}_2(\text{CO})_8/\text{alumina}$ showing that no reaction occurs at the sulfoxide functionality.

Bromides were found to be more reactive than chlorides. With chloromethyl phenyl sulfoxide, the yield of dehalogenated product was 13% but the rest of the starting material could be recovered by chromatography. On using ultrasound^{134,206}, the yield increased slightly (to 23%).

Table 8. Yields of Sulfoxide from α -Halosulfoxide and $\text{Co}_2(\text{CO})_8/\text{Al}_2\text{O}_3$.

α -Halogenosulfoxide, <u>28</u>	Product	Yield, %
$\text{C}_6\text{H}_5\text{S}(\text{O})\text{CH}_2\text{Cl}$	Methyl phenyl sulfoxide	13 ^a
$\text{C}_6\text{H}_5\text{S}(\text{O})\text{CH}_2\text{Br}$	Methyl phenyl sulfoxide	80
	$\text{C}_6\text{H}_5\text{S}(\text{O})\text{CH}_2\text{CH}_2\text{S}(\text{O})\text{C}_6\text{H}_5$	7
$4\text{-ClC}_6\text{H}_4\text{S}(\text{O})\text{CH}_2\text{Br}$	p-Chlorophenyl methyl sulfoxide	100
$\text{C}_6\text{H}_5\text{S}(\text{O})\text{CH}(\text{Br})\text{CH}_3$	Ethyl phenyl sulfoxide	50 ^b
$\text{C}_6\text{H}_5\text{CH}_2\text{S}(\text{O})\text{CH}_2\text{Br}$	Benzyl methyl sulfoxide	100
$2\text{-C}_{10}\text{H}_7\text{S}(\text{O})\text{CH}_2\text{Br}$	Methyl naphthyl sulfoxide	100

a Yield increased to 23% in the presence of ultrasonic irradiation.

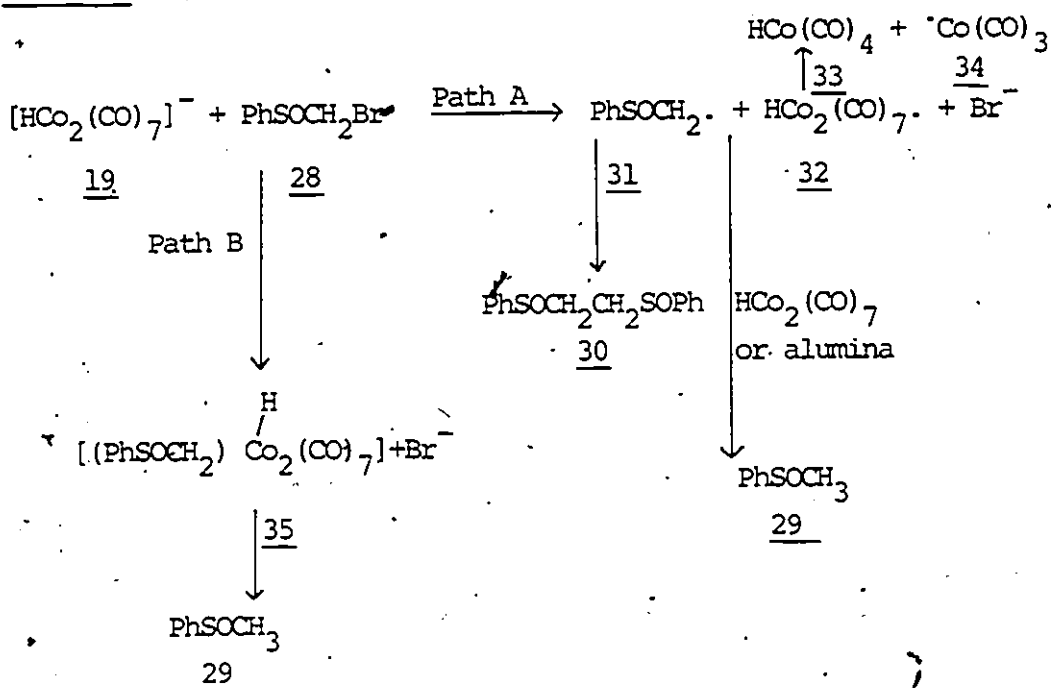
b An unidentified by-product was also formed.

With bromides, the reactions are so clean that no chromatography is required. Only trituration of the solid and filtrations are necessary for workup of the reaction.

The lower yield observed in the case of $\text{PhS}(\text{O})\text{CH}(\text{Br})\text{CH}_3$ is possibly due to dehydrohalogenation as the competing step leading to $\text{PhS}(\text{O})\text{CH}=\text{CH}_2$ as the side product. On using dicobalt octacarbonyl and $\text{PhS}(\text{O})\text{CH}_2\text{Br}$, in a ratio of 1 to 3, the product was formed in 37% yield along with 14% $\text{PhS}(\text{O})\text{CH}_2\text{CH}_2\text{S}(\text{O})\text{Ph}$ and the remaining starting material (49%) was recovered. This shows that the reaction is not catalytic though more than a stoichiometric amount of α -bromosulfoxide can be employed.

In one case, with α -bromomethyl phenyl sulfoxide, the product $C_6H_5S(O)CH_2CH_2S(O)C_6H_5$ was isolated (see Table 9 for characterization by NMR, MS). This indicates that the reaction may proceed via an electron transfer pathway.

Scheme 6



Hyridoheptacarbonyldicobaltate (19) may react with α -halosulfoxide (28) via electron transfer to generate free radical 31 and bromide ion. The coupling of 31 would give 30, whereas reaction of this radical 31 with a hydroxyl group of alumina or hydridoheptacarbonyldicobaltate (19) would account for the formation of α -halogenated sulfoxide 29 (Path A). Complex 32 may collapse to hydridocobalt tetracarbonyl 33 and tricarbonylcobalt radical 34.

Alternatively, the anion 19 can attack 28 to displace the activated bromide and form 35. This, on reductive elimination, will give the product 29 (Path B).

Such reductive elimination is well-known in homogeneous catalysis where an alkyl hydrido complex forms alkane. Reductive elimination (being the reverse of oxidative addition) is favored by ligands which decrease the electron density on the metal. Here PhSOCH_2 and CO both have electron withdrawing character. Decomposition of biradical 35 would give radical 31, which on coupling forms 30. At this stage, the mechanism is not clear, yet some involvement of free radicals cannot be ruled out.

One reaction was tried with an α -haloketone (α -bromo p-methoxyacetophenone) $\text{ArC(O)CH}_2\text{Br}$ and $\text{Co}_2(\text{CO})_8/\text{Al}_2\text{O}_3$ in 1,2-dimethoxyethane at room temperature under nitrogen. The monoketone 4-methoxyacetophenone was formed in 76% yield. On carrying out the reaction in dimethoxyethane on anachemia alumina, 84% 4-methoxyacetophenone was formed. On changing the atmosphere from nitrogen to carbon monoxide, the product was obtained in slightly better yield. Such dehalogenation has earlier been effected by molybdenum hexacarbonyl on alumina⁶⁹. The yield of the ketone from α -bromo p-methoxyacetophenone was 60%.

Table 9. Properties of Sulfoxides and α -Halosulfoxides.

COMPOUND	m.p./bp, °C	^1H NMR (CDCl_3), δ	IR (CHCl_3), cm^{-1}
$\text{C}_6\text{H}_5\text{SOCH}_2\text{Cl}$	bp 78-79 (0.2mm)	4.39 (s, 2H, CH_2), 7.55 (m, 5H, aromatic CH)	1047 (s)
$\text{C}_6\text{H}_5\text{SOCH}_2\text{Br}$		4.20 (d, 1H, $J=10$ Hz), 4.35 (d, 1H, $J=10$ Hz), 7.23-7.77 (m, 5H, aromatic CH; main peak at $\delta 7.50$)	1058 (vs)
4-ClC ₆ H ₄ SOCH ₂ Br		4.23 (s, 2H, CH_2), 7.53 (s, 4H, aromatic CH)	
$\text{C}_6\text{H}_5\text{-CH(Br)SOCH}_3$	61-63	2.35 (s, 3H, CH_3), 5.50 (s, 1H, benzylic proton), 7.37 (s, 5H, aromatic CH)	
$\text{C}_6\text{H}_5\text{CH}_2\text{SOCH}_2\text{Br}^a$	77-78	4.00-4.26 (m, 4H, CH_2 and benzylic proton), 7.37 (s, 5H, aromatic CH)	1080 (vs)
$\text{C}_6\text{H}_5\text{SOCH(Br)CH}_3$		1.83 (d, 3H, CH_3 , $J=6.5$ Hz), 4.77 (q, 1H, CHBr , $J=6.5$ Hz), 7.20-7.83 (m, 5H, aromatic CH; main peak at $\delta 7.53$)	1057 (s)
2-C ₁₀ H ₇ SOCH ₂ Br	91	4.39 (d, 1H, $J=10$ Hz), 4.18 (d, 1H, $J=10$ Hz), 7.23-8.10 [m, 6H, aromatic CH; main peak at 7.33 (d, $J=2.5$ Hz)], 8.22 (s, 1H, aromatic CH)	1050 (vs)
$\text{C}_6\text{H}_5\text{SOCH}_3$	bp 263-264 m.p. 33-34	2.67 (s, 3H, CH_3), 7.53 (broad s, 5H, aromatic CH)	1060 (vs)
4ClC ₆ H ₄ SOCH ₃	46-48	2.70 (s, 3H, CH_3), 7.27-7.77 (m, 4H, aromatic CH; main peak at $\delta 7.53$)	1047 (vs)

Table 9. (cont'd)

COMPOUND	m.p./bp, °C	¹ H NMR (CDCl ₃), δ	IR(CHCl ₃), cm ⁻¹
C ₆ H ₅ CH ₂ SOCH ₃	53-54	2.13 (s, 3H, CH ₃), 4.00 (d, 2H, J=2H), 7.40 (s, 5H, aromatic CH)	1045 (vs)
C ₆ H ₅ SOCH ₂ CH ₃	b.p. 143 (13mm)	1.17 (t, 3H, CH ₃ , J=7.0 Hz), 2.85 [q (subdivided with J=2.0 Hz), 2H, SOCH ₂ CH ₃ , J=7.0 Hz], 7.53 (m, 5H, aromatic CH)	1055 (vs)
2-C ₁₀ H ₇ SOCH ₃	101	2.73 (s, 3H, CH ₃), 7.20-8.27 (m, 7H, aromatic CH)	-
2-C ₁₀ H ₇ SCH ₃	59-60	2.57 (s, 3H, SCH ₃), 7.20-7.97 (m, 7H, aromatic protons)	-
C ₆ H ₅ SOCH ₂ CH ₂ SOCH ₂ C ₆ H ₅ ^b	123	3.03 (s, 4H, CH ₂), 7.57 (m, 10H, aromatic CH)	1090 (s), 1072 (sh)

^a ¹³C NMR (CDCl₃) δ [130.52 (d), 130.14 (d), 129.13 (d), 128.80 (d), 28.26 (d) -aromatic CH],
55.55 (t, SOCH₂Br), 42.22 (t, benzylic carbon)

^b MS, m/e 278 [M⁺]

Section III. $\text{Mo}(\text{CO})_6$ On Alumina

(a) Reaction with Azoxybenzenes and N-Oxides

Molybdenum hexacarbonyl on alumina can catalyze olefin disproportionation and isomerization reactions⁵⁷ and can effect dehalogenation⁶⁹ and desulfurization⁶⁸. In this section, the deoxygenation of azoxy compounds and N-oxides is described.

Alumina was suspended in dry hexane containing molybdenum hexacarbonyl and hexane was removed by rotary evaporation: $\text{Mo}(\text{CO})_6/\text{Al}_2\text{O}_3$ was heated for 1h at 105°C for activation. The N-oxide or azoxy compound was added to the cooled solid along with 1,2-dimethoxyethane and the reaction mixture was stirred at reflux overnight. Simple workup gave the deoxygenated products in 15-71% yields (Table 10).

Table 10. Yield of Azobenzenes and Heterocycle from Deoxygenation by $\text{Mo}(\text{CO})_6/\text{Al}_2\text{O}_3$.

REACTANT <u>13, 14</u>	PRODUCT <u>5, 17</u>	YIELD, %
Azoxybenzene <i>2</i>	Azobenzene	31
4,4'-Azoxyanisole	4,4'-Azoanisole	34
4,4'-Azoxyphenetole	4,4'-Azophenetole	15
Quinoline N-oxide	Quinoline	41
4-Picoline N-oxide	4-Picoline	32
Nicotinamide N-oxide	Nicotinamide	71

Brenner and Burwell²⁰ carried out a temperature programmed thermal decomposition study of $\text{Mo}(\text{CO})_6$ on alumina and characterized

$\text{Mo}(\text{CO})_3$ ads as the active species. The nature of the species produced by the adsorption of molybdenum hexacarbonyl on alumina depends upon the temperature at which the adsorbent was dried and metal carbonyl was activated on the oxide.

The products were identified by comparison with authentic samples. Table 6 lists their melting/boiling point and spectral data.

On using neutral alumina and carrying out the reaction at 55-60°, the yield of azobenzene was found to be 15%. Heating to 90°C (oil bath, under refluxing 1,2-dimethoxyethane) increased the yield of azobenzene to 31%.

Reaction of $\text{Mo}(\text{CO})_6/\text{Al}_2\text{O}_3$ with p-nitrotoluene gave a small amount of p-toluidine but the yield was low and the reaction was not clean. With phenyl isopropyl sulfoxide, this reagent gave phenyl isopropyl sulfide in only 9% yield.

$^1\text{H-NMR}(\text{CDCl}_3/\text{TMS}) \delta 1.28[\text{d}, 6\text{H}, \text{CH}(\text{CH}_3)_2, \text{J}=6.0 \text{ Hz}]$,

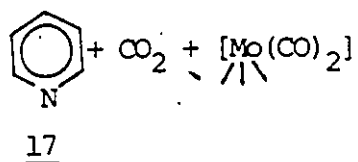
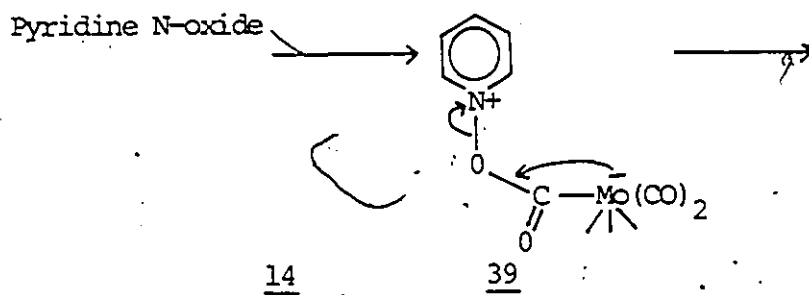
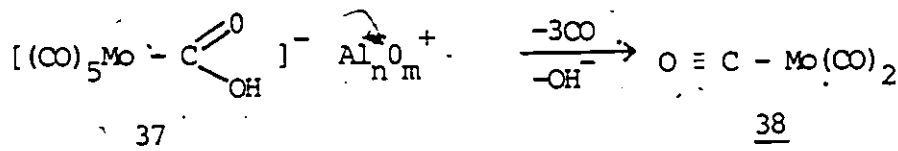
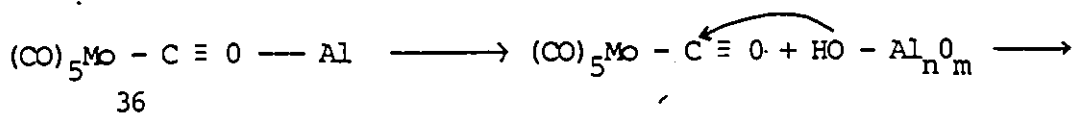
$3.73-3.67[\text{qt}, 1\text{H}, \text{CH}(\text{CH}_3)_2, \text{J}=6.0 \text{ Hz}]$,

$7.13-7.57(\text{m}, 5\text{H}, \text{aromatic CH})$;

MS, m/e $152[\text{M}^+]$, $137[\text{M}-\text{CH}_3]^+$, $109[\text{M}-(\text{CH}_3)_2\text{CH}]^+$.

The mechanism of deoxygenation of azoxybenzene or heterocyclic N-oxides by molybdenum carbonyl on alumina is not known. A possible pathway is outlined in Scheme 7.

Scheme 7



The oxygen of heterocyclic N-oxide (14) can attack the carbon of a carbonyl ligand to form a dipolar intermediate 39. This intermediate can evolve carbon dioxide and form the product heterocycle 17.

b) Desulfurization by Molybdenum Hexacarbonyl on Solid Support

The removal of sulfur from fossil fuels²⁰⁷ is a subject of considerable current interest because the presence of sulfur leads to environmental pollution (e.g., acid rain) and sulfur poisons the metal catalyst²⁰⁸ and thereby reduces the efficiency of certain processes in petrochemical industries.

Various materials employed as desulfurization reagents have met with mixed success²⁰⁹. On using Raney nickel, for example, sulfides are formed from aromatic thiols and the reaction requires high Raney nickel to substrate ratio²¹⁰.

Initial model experiments with metal carbonyls have indicated their potential as desulfurization reagents.

Episulfides, thioanhydrides and thionocarbonate are converted to olefins by using iron carbonyls²¹¹⁻²¹³. Thioketones and thioamides on reaction with hydridotetracarbonylferrate anion form hydrocarbons and amines respectively in good yields. On employing dicobalt octacarbonyl, cobalt tetracarbonyl anion, or cyclopentadienyliron dicarbonyl dimer as reagents, thioketones gave coupled olefins in 45 to 83% yield in refluxing benzene²¹⁴. Modified molybdenum carbonyl species also showed activity for desulfurization of thiols in tetrahydrofuran at 50°C⁶⁸. Recently, triosmium dodecacarbonyl has been shown to cleave alkyl phenyl sulfide to give $\text{HOs}_3(\mu\text{-SR})(\mu_3\text{-}\eta^2\text{-C}_6\text{H}_4)(\text{CO})_9$ ²¹⁵.

In this section are described the results of attempted desulfurization reaction by metal carbonyls on inorganic oxide supports. The substrates chosen were organic molecules bearing sulfur (e.g., thiols, thioketone, thioamide or thiophene) and the reactions were applied for the desulfurization of crude oil and commercial xylene.

Various adsorbents including alumina (different kinds), florisil (magnesium silicate), magnesium oxide and silica were utilized as supports and molybdenum hexacarbonyl, dimanganese decacarbonyl, triiron dodecacarbonyl, dicobalt octacarbonyl and chlorodicarbonyl rhodium (I)

dimer were employed as reagents. Of these, $\text{Mo}(\text{CO})_6$ /florisil showed maximum activity. Various parameters (e.g., amount of support, type of support, gaseous atmosphere of the reaction, amount of reagent and reaction time) were varied in order to determine optimum conditions. The results are listed in a tabular form (Table 11). Several interesting conclusions can be drawn from this study.

From these studies (Table 11), it can be concluded that immobilized molybdenum, iron, and cobalt react with sulfur containing compounds but clean desulfurized product was not obtained except with triphenylmethyl mercaptan.

Disulfide was the major product on reaction of metal carbonyls with 2-naphthalene thiol on most of the supports used, e.g., acidic alumina, basic alumina, neutral alumina, florisil, and modified silica. Maximum amount of disulfide was formed on using molybdenum hexacarbonyl on silica doped with dilute hydrochloric acid. No naphthalene was found in any case. It was observed that neutral alumina doped with boron trifluoride was a better support than acidic alumina containing boron trifluoride because on using the first support, more amount of triphenylmethane was formed.

The yield of disulfide did not decrease on using pretreated (450°C) deactivated alumina as compared to unheated alumina. But an additional unidentified product was isolated from activated alumina experiment.

Alumina activated at 150°C reacted with thioketone to generate the corresponding ketone. Even on heating alumina to 625°C, ketone

Table 11. Reaction with Sulfur Bearing Organic Compounds with Metal Carbonyls on Inorganic Support.

S.N.	Compound	Support	Dried at °C, Treatment	Metal Carbonyl	Activation Temp, °C	Solvent	Reaction Temp, °C	Comment (Product Isolated)
1	2-Naphthalene thiol (2-C ₁₀ H ₇ SH)	Basic alumina	150 (R.P.) ^b	Fe ₃ (CO) ₁₂	25	Hexane	25	Np-S-S-Np
2	"	Acidic alumina	350	Mo(CO) ₆	100	DME	70	NpS-S Np and 3 more
3	"	Acidic alumina Activity III	Not dried and de-activated	"	100	DME	70	NpSSNp (38%)
4	"	Acidic alumina Activity IV	450, then deacti-vated	"	100	DME	70	NpSSNp (38%) + unidentified product
5	"	Acidified silica, Activity IV	HCl, 450	"	100	DME	70	NpSSNp (60%)
6	"	Neutral alumina	BF ₃ , 350	"	100	Toluene	95	NpSSNp
7	"	Florisil		"	100	Hexane	60	No naphthalene
8	"	Fischer alumina	150 (R.P.)	Co ₂ (CO) ₈	25	DME	25	NpSSNp

Table 11. (cont'd)

S.N.	Compound	Support	Dried at °C, Treatment	Metal Carbonyl	Activation Temp, °C	Solvent	Reaction Temp, °C	Comment (Product Isolated)
9	(C ₆ H ₅) ₃ CSH	Acidic alumina	BF ₃ , 400	Mo(CO) ₆	100	Toluene	80	φ ₃ CH (38%)
10	"	Neutral alumina	BF ₃ , 400	"	100	Toluene	80	φ ₃ CH (69%)
11	"	Neutral alumina	-	Blank	100	Toluene	80	φ ₃ CH
12	Dibenzothiophene	Neutral alumina	BF ₃ , 400	Mo(CO) ₆ (10 mmHg)	100	Toluene	80	S.M. recovered
13	"	Neutral alumina	BF ₃ , 400	Mo(CO) ₆ (15 mmHg)	100	m-Xylene	130	S.M. recovered
14	"	Basic alumina	150 (R.P.)	Fe ₃ (CO) ₁₂	25	Hexane	25	S.M. recovered
15	"	Neutral alumina	400	Mn ₂ (CO) ₁₀	100	Hexane+ DME	70	S.M. recovered
16	"	Basic alumina	400	Mo(CO) ₆	100	DME	80	S.M. recovered
17	4,4'-Dimethoxy thiobenzophenone (4-MeOC ₆ H ₄) ₂ C=S	Neutral alumina	150	Co ₂ (CO) ₈ (3mm)	25	Hexane	25	(4MeOC ₆ H ₄) ₂ C=O (76%)

Table 11. (cont'd)

S.N.	Compound	Support	Dried at °C, Treatment	Metal Carbonyl	Activation Temp, °C	Solvent	Reaction Temp, °C	^a Comment (Product Isolated)
18	4,4'-Dimethoxy thiobenzophenone (4-MeOC ₆ H ₄) ₂ C=S	Neutral alumina	150 (R.P.)	Co ₂ (CO) ₈ (6mm)	25	Hexane	25	(4MeOC ₆ H ₄) ₂ C=O (41%)
19	"	Neutral alumina	150 (R.P.)	Blank	25	Hexane	25	(4MeOC ₆ H ₄) ₂ C=O
20	"	Florisil	150 (R.P.)	Blank	25	Hexane	25	4,4'-Dimethoxy thiobenzophenone (S.M.) + small amount of benzo-phenone
21	"	Fischer alumina	625	Co ₂ (CO) ₈	25	Hexane	25	mainly benzo-phenone + small amount of starting material
22	Thiobenzanilide C ₆ H ₅ (C=S)NHC ₆ H ₅	Neutral alumina	150 (R.P.)	Co ₂ (CO) ₈	25	Hexane	25	mainly benzanilide [C ₆ H ₅ (C=O)NH C ₆ H ₅] formed

^a Reaction time was kept constant at twenty hours for all these reactions.

^b R.P. stands for 'at reduced pressure (2-4 mmHg)'.

(4,4'-dimethoxybenzophenone) was the major product but small amount of unreacted thioketone was recovered. Use of florisil as the support gave back most of the unreacted thioketone along with a small amount of ketone after a blank reaction (i.e., without metal carbonyl). This suggests that florisil should prove to be more reliable for such desulfurization studies.

An increase in the amount of molybdenum hexacarbonyl from 10 mmol to 15 mmol or dicobalt octacarbonyl from 3 mmol to 6 mmol did not alter the product ratio. An increase of the reaction temperature from 80 to 130°C for the desulfurization of dibenzothiophene could not improve the reaction.

Experiments were carried out to reduce the sulfur content of crude oil. Though triiron dodecacarbonyl and chlorodicarbonyl rhodium (I) dimer were employed during preliminary runs, the majority of the work was conducted with molybdenum hexacarbonyl on a support, as it had been found to be active for desulfurization⁶⁸.

Alumina (or other support) was activated by heating to 150-650°C and molybdenum hexacarbonyl (1-15 mmol) in hexane was mixed with the support. The solid was activated by heating under nitrogen to generate modified molybdenum carbonyl species. After cooling, crude oil, either alone or in an inert solvent, was added and the reaction mixture was stirred for 18-24 hours under a nitrogen atmosphere. The final mixture was collected in aliquots, filtered and then analyzed for its sulfur content.

The results are presented in Table 12.

Table 12. Reaction of Crude Oil with Metal Carbonyls on Inorganic Support.

S.N.	Oil	Amount, mL	Solvent	% S	Metal Carbonyl	Support	Treatment of Support, °C	Reaction Temp., °C	Found % S
1	Shell-2	50		1.95	Mo(CO) ₆	Silica 30g	400	60	1.49
2	"	50		1.95	"	Silica 15g	400	60	1.67
3	"	50		1.95	"	MgO 20g	400	60	1.30
4	"	50	Hexane	1.73	"	MgO 20g	400	60	1.01
5	"	50		1.95	"	Florisil 30g	400	60	0.28
6	"	50		1.95	Blank	Florisil 30g	400	60	0.43
7	Athabasca	34g	Hexane 70mL	3.82	Mo(CO) ₆ 10mM	Florisil 30g	400	60	1.75
8	"	55	Pentane	4.48	Mo(CO) ₆ 10mM	Fischer alumina	400	60	2.23
9	Shell-1	50		1.56	Mo(CO) ₆ 10mM	Fischer alumina	400	60	0.65
10	"	50	Hexane	1.09	Mo(CO) ₆ 1mM	Fischer alumina	400	60	0.80

Table 12. (cont'd)

S.N.	Oil	Amount, mL	Solvent	% S	Metal Carbonyl	Support	Treatment of Support, °C, Temp.	Reaction Temp., °C	Found % S
11	Shell-1	50	Hexane	1.09	Mo(CO) ₆ 1mM	Fischer alumina	BF ₃ , 400	60	0.88
12	"	50	Hexane	1.09	Mo(CO) ₆ 10mM	Fischer alumina (not dried)	BF ₃ , 400	60	0.62
13	"	50	Hexane	1.09	Mo(CO) ₆ 10mM	Fischer alumina (dried at 600°C)	BF ₃ , 400	60	0.70
14	"	50	Hexane	1.09	Mo(CO) ₆ 10mM	Neutral alumina	BF ₃ , 400	60	1.19
15	"	50*	Hexane	1.09	Mo(CO) ₆ 10mM	Neutral alumina	BF ₃ , 400	60	1.16
15.1 ^b	Shell-2	50	Hexane	1.95	Mo(CO) ₆ 10mM	Florisil 30g	400	50	0.72
15.2	"	50	Hexane	1.95	Mo(CO) ₆ 6mM	Florisil 5g	400	50	0.98
15.3	Atha- basca	34g	Hexane 67mL	1.98	Mo(CO) ₆ 6mM	Florisil 5g	400	50	1.81
16	Shell-2	50	Hexane 50mL	1.73	[Rh(CO) ₂ Cl] ₂	Fischer alumina	150 (R.P.)	60	1.35

Table 12. (cont'd)

S.N.	Oil	Amount, mL	Solvent	% S	Metal Carbonyl	Support Of Support, °C Temp. °C	Treatment Reaction Temp. °C	Found % S	
17	Shell-1	1g	Hexane	1.56	Fe ₃ (CO) ₁₂	Basic alumina	150 (R.P.)	25	0.75
18	Shell-2	50		1.95	Mo(CO) ₆	Florisil	400	60	1.38 ^c
19	Oil	27.5g	n-decane 22.5g	0.47	Mo(CO) ₆ 10mM	Fischer alumina	400	60	0.36
20	"	27.5g	n-decane 22.5g	0.47	Mo(CO) ₆ 10mM	Fischer alumina	400	60	0.35
21	"	27.5g	n-decane 22.5g	0.40	Mo(CO) ₆ 10mM	Fischer alumina	400	50	0.15
22	p-xylene			42ppm	Mo(CO) ₆	Florisil 30g	450	50	<0.1%
23	"	80		30ppm	Mo(CO) ₆	Florisil 30g	450	50	<3ppm
24	"	80		30ppm	Mo(CO) ₆	Florisil 30g	450	50	<2ppm
25	"	80		30ppm	Mo(CO) ₆	Florisil 30g	450	50	<2ppm

^a The reaction time was 20 hours.

^b Experiments listed in S.N. 15.1, 15.2 and 15.3 were carried out by Dr. J. Heveling.

^c Experiment (S.N. 18) was performed in synthesis gas medium. Other experiments were run in nitrogen atmosphere.

The following conclusions can be made from representative experiments listed in Table 12.

1. The best support for desulfurization of crude oil is florisil. The efficiency of supports is listed in an order: Florisil > alumina > alumina - BF_3 > MgO > silica gel. Experiments listed in serial numbers 10 and 11 indicate that alumina is a better support as such than alumina doped with boron trifluoride. Silica gel gave the least satisfactory results with such desulfurization experiments.
2. An increase in the amount of the solid support improves the desulfurization, but not substantially. (Refer to 1 vs 2, 15.1 vs 15.2.)
3. Molybdenum hexacarbonyl on a support is better than $\text{Fe}_3(\text{CO})_{12}$ /basic alumina or $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ /alumina. (Compare 16 and 17 with $\text{Mo}(\text{CO})_6$ experiments.)
4. A decrease in the amount of molybdenum hexacarbonyl does not adversely affect the desulfurization process. Thus, these reactions are catalytic in molybdenum (S.N. 9 vs 10).
5. Nitrogen is a better medium than synthesis gas (S.N. 5 vs 18).
6. An increase in reaction time from 20 to 30 hours has little effect. However, slight improvement in desulfurization is observed.

Many experiments were carried out to check the reproducibility of results. Experiments S.N. 14 vs 15 and 24 vs 25 are just two examples.

These reactions are also successful in reducing the sulfur content of p-xylene, which had only 30-42 ppm sulfur. This indicates that this process may be utilized in petrochemical industries (e.g., nylon) where even such low sulfur contents are undesirable.

The present study clearly shows the potential of modified molybdenum hexacarbonyl on florasil as a reagent for the desulfurization of crude oil. However, scale up experiments preferably at pilot plant scale and study of its economic feasibility would have to be carried out for its proper utilization.

Section IV. Phase Transfer Catalysis.

a) Reaction of CpCo(CO)₂ with Benzyl Bromides

As described in the Introduction, the carbonylation of halides to acids can be catalyzed by dicobalt octacarbonyl under mild conditions (PTC)¹⁷³. It seemed worthwhile to investigate the use of cyclopentadienylcobalt dicarbonyl as the catalyst, and to compare the behavior of this mononuclear complex bearing a donor cyclopentadienyl ligand, with cobalt tricarbonyl nitrosyl, Co(CO)₃NO.

One study²¹⁶ using a mononuclear cobalt carbonyl-cobalt tricarbonyl nitrosyl as the metal catalyst, indicated that the reaction could be more selective than dicobalt octacarbonyl for monoacid formation, although with reduced product yields. The mononuclear catalyst contains a nitrosyl ligand which is a better π-acceptor than carbonyl.

Aqueous sodium hydroxide, benzene and phase transfer catalyst were stirred with cyclopentadienyl cobalt dicarbonyl under carbon monoxide atmosphere to generate the active species. Benzyl bromides were then added and the mixture was stirred at 50°C. After workup, corresponding phenyl acetic acids were isolated from the aqueous phase and the organic phase afforded products which are listed in Table 13.

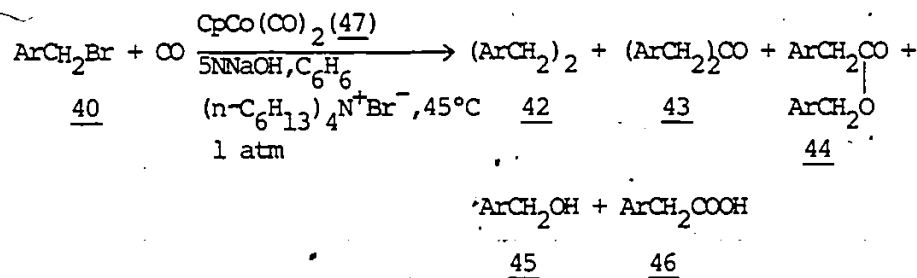


Table 13. Products Obtained from PTC Carbonylation of Benzyl Bromides with CpCo(CO)₂.

ArCH ₂ Br, 40	ArCH ₃ , 41	ArCH ₂ CH ₂ Ar, 42	ArCH ₂ C(CH ₂ Ar) ₂ , 43	ArCH ₂ C(O)OCH ₂ Ar, 44	ArCH ₂ OH, 45	ArCH ₂ COOH, 46
0 - CH ₃ C ₆ H ₄		8	26	17	9	26
p-CH ₃ C ₆ H ₄		24	38			27
p-FC ₆ H ₄		17	31	10	3	15
2-C ₁₀ H ₇	4	11	3	17	15	33
C ₆ H ₅		24	26	21	13	13

Table 14 lists a comparative yield of products obtained on using $\text{CpCo}(\text{CO})_2$, $\text{Co}(\text{CO})_3\text{NO}$ and $\text{Co}_2(\text{CO})_8$.

The results listed in Tables 13 and 14 show that the reaction is much less selective than that using $\text{Co}_2(\text{CO})_8$ or $\text{Co}(\text{CO})_3\text{NO}$ as catalysts. Among the many products obtained were dibenzyl ketones and monoacids. The amount of ketones formed was significantly more than when dicobalt octacarbonyl or cobalt tricarbonyl nitrosyl was used as catalysts. Also isolated were carboxylic esters which were not observed in previous reactions. The phenyl acetic acids were formed in lower yield on using $\text{CpCo}(\text{CO})_2$ as compared to $\text{Co}(\text{CO})_3\text{NO}$ and $\text{Co}_2(\text{CO})_8$. The absence of double carbonylation product with 0-methyl benzyl bromide and aldehyde with benzyl bromide indicate that the active species generated with $\text{CpCo}(\text{CO})_2$ behave differently from the other two cobalt carbonyls.

The reaction products were identified by comparison of their spectral properties (IR, NMR and MS) with the authentic sample (Table 15).

A change of phase transfer catalyst from tetra n-hexylammonium bromide to tetra n-hexylammonium hydrogensulfate did not vary the yield or the product composition significantly. Adding the starting material drop by drop in one hour or increasing the reaction time from 48 to 96 hours also did not give any new product.

Table 14. Comparative Yields of Products Obtained on Using Different Cobalt Carbonyls.

ArCH ₂ Br, Ar=	Products	Yield, %			
		CpCo(CO) ₂	NbCo(CO) ₃	Co ₂ (CO) ₈	
C ₆ H ₅	C ₆ H ₅ CH ₂ COOH	13	58	85	
	(C ₆ H ₅ CH ₂) ₂	11	9	5	
	(C ₆ H ₅ CH ₂) ₂ CO	26	7	10	
	C ₆ H ₅ CHO		4		
	C ₆ H ₅ CH ₂ CO C ₆ H ₅ CH ₂ -O	21			
O-CH ₃ C ₆ H ₄	C ₆ H ₅ CH ₂ OH	13			
	O-CH ₃ C ₆ H ₄ CH ₂ COOH	26	68	30	
	(O-CH ₃ C ₆ H ₄ CH ₂) ₂	8	12	7	
	(O-CH ₃ C ₆ H ₄ CH ₂) ₂ CO	26	10	13	
	O-xylene		4	5	
O-CH ₃ C ₆ H ₄	O-CH ₃ C ₆ H ₄ CH ₂ COOH				34
	O-CH ₃ C ₆ H ₄ CH ₂				
	O-CH ₃ C ₆ H ₄ CH ₂ CO				
	O-CH ₃ C ₆ H ₄ CH ₂ -O				
		17			



Table 14. (cont'd)

ArCH ₂ Br, Ar=	Products	Yield, %		
		CpCo(CO) ₂	NOCo(CO) ₃	Co ₂ (CO) ₈
β-C ₁₀ H ₇	2-C ₁₀ H ₇ CH ₂ COOH	33	44	64
	β-methylnaphthalene	4	6	9
	β-naphthaldehyde		5	
	(β-C ₁₀ H ₇ CH ₂) ₂	11		5
	(β-C ₁₀ H ₇ CH ₂) ₂ CO	3		6
	β-C ₁₀ H ₇ CH ₂ CO β-C ₁₀ H ₇ CH ₂ O	17		
	β-C ₁₀ H ₇ CH ₂ OH	15		

^a Yields with NOCo(CO)₃ and Co₂(CO)₈ are taken from Ref. 216 and 173.

Table 15. Properties of Reaction Products Obtained from the Reaction of CpCo(CO)_2 with Benzyl Bromides.

Compound	$^1\text{H NMR (CDCl}_3), \delta$	IR (CHCl_3), cm^{-1}	MS, m/e
$(\text{O-CH}_2\text{C}_6\text{H}_4\text{CH}_2)^- 2$	2.30 (s, 6H, CH_3), 2.83 (s, 4H, benzylic), 7.13 (s, 8H, aromatic CH)	$\nu_{\text{C}=\text{C}}$ 1602 (m)	238 $[\text{M}]^+$, 105 $[\text{M}-(\text{O-CH}_2\text{C}_6\text{H}_4\text{-CH}_2\text{CO})]^+$
$(\text{O-CH}_2\text{C}_6\text{H}_4\text{CH}_2)_2\text{C}=\text{O}$	2.11 (s, 6H, CH_3), 3.63 (s, 4H, CH_2), 7.04 (s, 8H, aromatic CH)	ν_{CO} 1711 (vs)	254 $[\text{M}]^+$, 149 $[\text{M-CH}_2\text{C}_6\text{H}_4\text{CH}_2]^+$ $\equiv [\text{RCH}_2\text{CO}]^+$, 133 $[\text{M}-(\text{O-CH}_2\text{C}_6\text{H}_4\text{CH}_2\text{O})]^+$ \equiv [Acylium] $^+$, $\equiv [\text{CH}_2\text{C}_6\text{H}_4\text{CH}_2\text{O}]^+$
$\text{O-CH}_2\text{C}_6\text{H}_4\text{CH}_2\text{C}=\text{O}$	2.23 (s, 6H, CH_3), 3.60 (s, 2H, ArCH_2CO), 5.04 (s, 2H, ArCH_2OC), 7.13 (s, 8H, aromatic CH)	ν_{CO} 1728 (vs)	122 $[\text{M}-(\text{CH}_2\text{C}_6\text{H}_4\text{CH}_2\text{CO})]^+$ $\equiv [\text{CH}_2\text{C}_6\text{H}_4\text{CH}_2\text{OH}]^+$, $\equiv [\text{CH}_2\text{C}_6\text{H}_4\text{CH}_2\text{COO}]^+$
$\text{O-CH}_2\text{C}_6\text{H}_4\text{CH}_2\text{O}$			105 $[\text{M}-(\text{CH}_2\text{C}_6\text{H}_4\text{CH}_2\text{COO})]^+$ $\equiv [\text{CH}_2\text{C}_6\text{H}_4\text{CH}_2]^+$
$\text{O-CH}_2\text{C}_6\text{H}_4\text{CH}_2\text{OH}$	2.00 (s, 1H, OH), 2.37 (s, 3H, CH_3), 4.67 (s, 2H, $\text{CH}_2\text{-OH}$), 6.90-7.37 (m, 4H, aromatic CH; main peak at δ 7.13)	ν_{OH} 3425 (br., s), $\nu_{\text{C-O}}$ 1035 (w)	
$\text{O-CH}_2\text{C}_6\text{H}_4\text{CH}_2\text{COOH}$	2.30 (s, 3H, CH_3), 3.67 (s, 2H, CH_2), 7.23 (s, 4H, aromatic CH), 10.26 (s, 1H, COOH)	ν_{OH} 3070 (br., s), ν_{CO} 1710 (vs), $\nu_{\text{C-O}}$ 1300 (s)	

Table 15. (cont'd)

Compound 41-46	¹ H NMR (CDCl ₃), δ	IR (CHCl ₃), cm ⁻¹	MS, m/e
(p-CH ₃ C ₆ H ₄ CH ₂) ₂	2.29 (s, 6H, CH ₃), 2.81 (s, 4H, CH ₂), 7.07 (s, 8H, aromatic CH)	ν _{C=C} 1603 (m)	210 [M] ⁺ , 105 [M-(CH ₃ - C ₆ H ₄ CH ₂)] ⁺
(p-CH ₃ C ₆ H ₄ CH ₂) ₂ C=O	2.31 (s, 6H, CH ₃), 3.52 (s, 4H, CH ₂), 6.51-7.37 (m, 8H, aromatic CH; main peak at δ6.87 and 7.04)	ν _{CO} 1714 (s)	238 [M] ⁺ , 105 [M-(p-CH ₃ - C ₆ H ₄ CH ₂ CO)] ⁺ , 91 [M-(p-CH ₃ C ₆ H ₄ CH ₂ C(O)CH ₂ -)] ⁺
p-CH ₃ C ₆ H ₄ CH ₂ COOH	2.28 (s, 3H, CH ₃), 3.52 (s, 2H, CH ₂), 7.10 (s, 4H, aromatic CH), 10.60 (s, 1H, COOH)		
(p-FC ₆ H ₄ CH ₂) ₂	2.83 (s, 4H, benzylic CH ₂), 7.02 (br. s, 8H, aromatic CH)		
(p-FC ₆ H ₄ CH ₂) ₂ C=O	3.62 (s, 4H, CH ₂), 6.75 (t, 8H, aromatic CH, J=6Hz; main peak at δ6.63, 6.75, and 6.87)	ν _{CO} 1712	
p-FC ₆ H ₄ CH ₂ C=O	3.72 (s, 2H, CH ₂), 5.03 (s, 2H, CH ₂), 6.60-7.00 (m, 8H, aromatic CH; main peak at δ6.78)	ν _{CO} 1730	
p-FC ₆ H ₄ CH ₂ OH	4.51 (s, 3H, CH ₂ and OH), 6.7-7.5 (m, 4H, aromatic CH; main peak at δ7.11)		

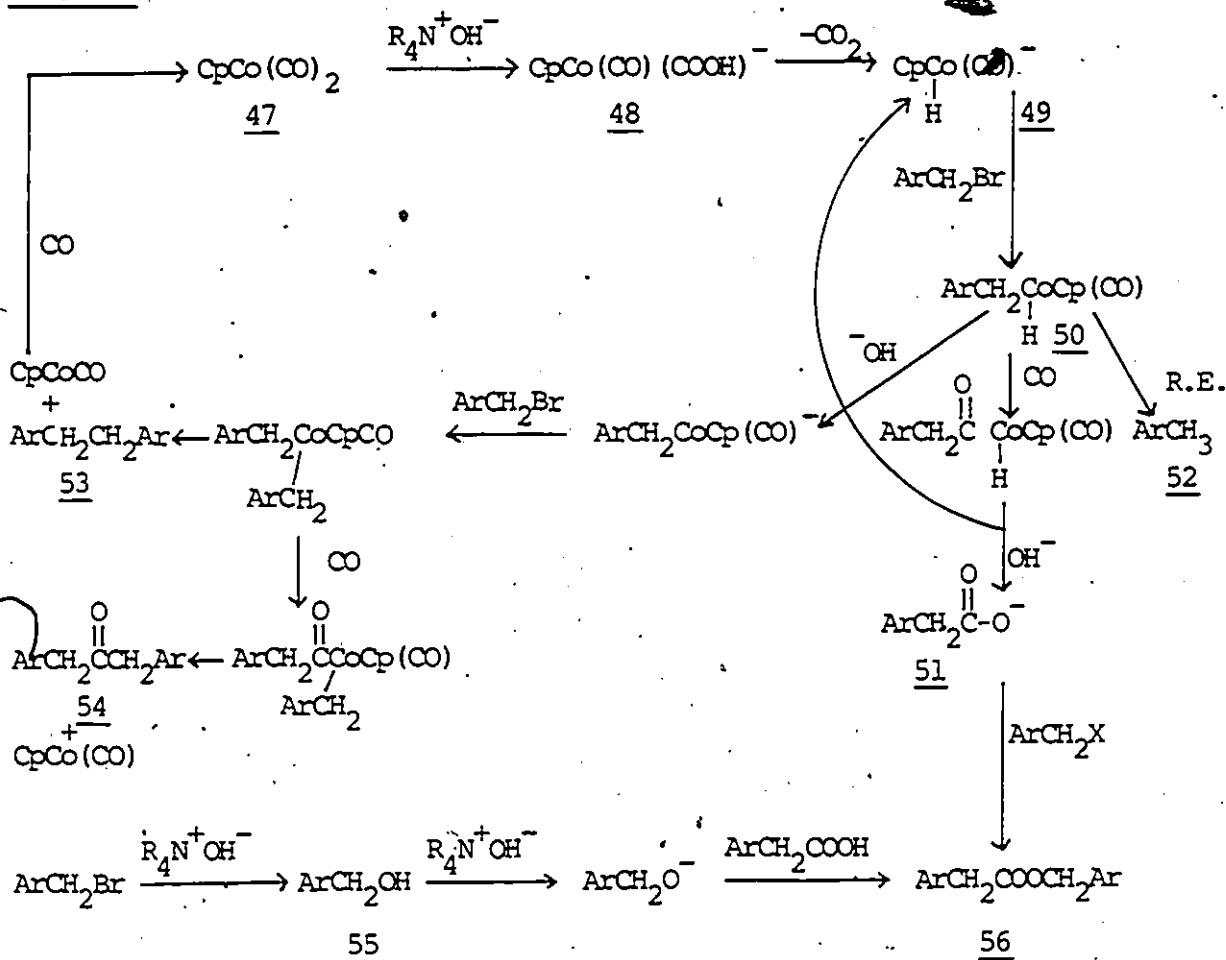
Table 15. (cont'd)

Compound 41-46	^1H NMR (CDCl_3), δ	IR (CHCl_3), cm^{-1}	MS, m/e
$\text{p-FC}_6\text{H}_4\text{CH}_2\text{COOH}$	3.60 (s, 2H, CH_2), 6.76-7.43 (m, 4H, aromatic CH; main peak at δ 7.11), 10.77 (br. s, 1H, COOH)		
$2\text{-C}_{10}\text{H}_7\text{CH}_3$	2.47 (s, 3H, CH_3), 7.17-8.00 (m, 7H, aromatic CH; main peaks at δ 7.39, 7.48 and 7.58)		
$(2\text{-C}_{10}\text{H}_7\text{CH}_2^-)_2$	3.13 (s, 4H, CH_2), 7.17-7.93 (m, 14H, aromatic CH; main peaks at δ 7.43 and δ 7.63)		282 [M] ⁺ , 141 [M- $\text{CH}_2\text{C}_9\text{H}_7$] ⁺
$(2\text{-C}_{10}\text{H}_7\text{CH}_2^-)_2\text{C=O}$	3.76 (s, 4H, CH_2), 7.08-7.96 (m, 14H, aromatic CH)		
$\text{C}_{10}\text{H}_7\text{CH}_2\text{C=O}$ $\text{C}_{10}\text{H}_7\text{CH}_2\text{-O}$	3.15 (s, 2H, CH_2CO), 5.15 (s, 2H, $\text{CH}_2\text{OC=O}$), 7.08-7.98 (m, 7H, aromatic CH; main peak at δ 7.42)		326 [M] ⁺ , 141 [M- $(\beta\text{-C}_9\text{H}_7\text{CH}_2\text{COO})$] ⁺ \equiv [M- $(\beta\text{-C}_{10}\text{H}_7\text{CH}_2)$] ⁺ , 127 [M- $(\beta\text{-C}_{10}\text{H}_7\text{CH}_2\text{COOCH}_2)$] ⁺ \equiv [C ₁₀ H ₇] ⁺
$2\text{-C}_{10}\text{H}_7\text{CH}_2\text{OH}$	2.17 (s, 1H, OH), 4.77 (s, 2H, CH_2), 7.17-8.00 (m, 7H, aromatic CH; main peaks at δ 7.47 and 7.70)		
$2\text{-C}_{10}\text{H}_7\text{CH}_2\text{COOH}$	3.72 (s, 2H, CH_2), 7.10-7.90 (m, 7H, aromatic CH; main peaks at δ 7.46 and 7.69), 11.8 (s, 1H, COOH), [in DMSO- d_6 + CDCl_3]		

Table 15. (cont'd)

Compound	$^1\text{H NMR}(\text{CDCl}_3), \delta$	IR(CHCl_3), cm^{-1}	MS, m/e
$(\text{C}_6\text{H}_5\text{CH}_2)_2$	2.89 (s, 4H, CH_2); 7.15 (s, 10H, aromatic CH)		
$(\text{C}_6\text{H}_5\text{CH}_2)_2\text{C=O}$	3.55 (s, 4H, CH_2); 7.12 (s, 10H, aromatic CH)	ν_{CO} 1711 (vs)	210 [M] ⁺ , 119 [M-C ₆ H ₅ CH ₂] ⁺ , 91 [M-C ₆ H ₅ CH ₂ O] ⁺ , 77 [M-C ₆ H ₅ CH ₂ COOCH ₂] ⁺ * = [C ₆ H ₅] ⁺
$\text{C}_6\text{H}_5\text{CH}_2\text{C=O}$ $\text{C}_6\text{H}_5\text{CH}_2\text{-O}$	3.73 (s, 2H, CH_2CO), 5.13 (s, 2H, CH_2OC), 6.67-7.27 (m, 10H, aromatic CH; main peak at δ 7.07)		226 [M] ⁺ , 119 [M-C ₆ H ₅ CH ₂] ⁺ , [C ₆ H ₅ CH ₂ CO] ⁺ , 108 [C ₆ H ₅ CH ₂ OH] ⁺
$\text{C}_6\text{H}_5\text{CH}_2\text{OH}$	1.82 (s, 1H, OH), 4.67 (s, 2H, CH_2), 7.32 (s, 5H, aromatic CH)	ν_{OH} 3400 (br., s) $\nu_{\text{C-O}}$ 1115 (m)	
$\text{C}_6\text{H}_5\text{CH}_2\text{COOH}$	3.57 (s, 2H, CH_2), 7.27 (s, 5H, aromatic CH), 10.61 (br. s, 1H, COOH)	ν_{OH} 3400 (w) and 3100 (br., m), ν_{CO} 1710 (vs)	

Scheme 8



The pathway outlined in Scheme 8 can account for the reaction products obtained from this reaction. Addition of hydroxide ion to a carbonyl carbon of the catalyst, CpCo(CO)_2 would give the anion 48, which on loss of carbon dioxide would afford the hydride 49. Reaction of the latter with benzyl halide (40) would then lead to the alkyl-metal hydride. (As an alternate possibility, 40 may react with 48.)

Reductive elimination of 50 would give the hydrocarbon 52. This (52) is not formed with CpCo(CO)_2 showing that cyclopentadienyl ligand stabilizes the species and reductive elimination does not occur (except

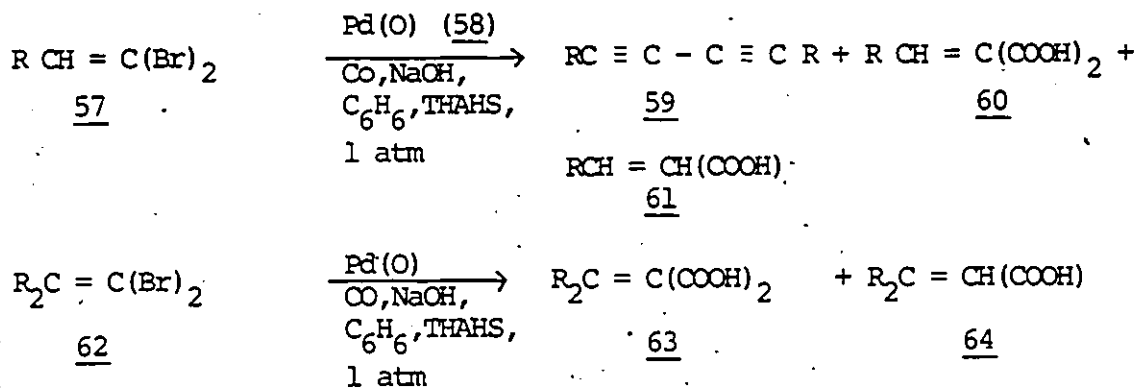
in the case of 2-naphthyl methyl bromide). The reaction of 50 with carbon monoxide, followed by base cleavage, would generate the acid 51 and regenerate 49. The formation of dibenzyl 53 and ketone 54 by-products from 50 is also depicted in the scheme.

Benzyl alcohol (55) may be formed by simple hydrolysis of the bromide. After its (55) deprotonation by quaternary ammonium hydroxide in organic phase, it would react with the phenyl acetic acid to afford the dibenzyl ester 56. Alternatively, the acid anion 51 can react with residual halide (at the interface) to form the ester 56.

b) Reaction of Palladium (0) and Palladium (II) with Vinylic Dibromides

Joshi²¹⁷ has reported that triiron dodecacarbonyl forms a cumulene complex in low yield on reaction with vinylic dibromides. It was of interest to learn whether such dibromides would react in an analogous or different manner with triiron dodecacarbonyl or dicobalt octacarbonyl on solid support. Unfortunately, neither triiron dodecacarbonyl on basic alumina nor dicobalt octacarbonyl on alumina reacted with β, β' -dibromostyrene. Even using phase transfer conditions and dicobalt octacarbonyl or with in situ generated acylcobalt tetracarbonyl as catalysts gave recovered starting material.

These results indicate that a more reactive metal complex is required to activate unreactive halides as vinylic dibromides. A palladium (0) complex was considered a suitable candidate for this, and indeed initial experiments with tetrakis(triphenylphosphine) palladium (0) under phase transfer conditions in a carbon monoxide atmosphere gave a white powder in 40% yield. It was identified by melting point and spectral data as 1,4-diphenyl-1,3-butadiyne.



As the main reaction product was not formed by insertion of carbon monoxide, it was thought probable that carrying out the reaction in nitrogen will increase the yield. But when the reaction was performed under nitrogen, the yield of diyne decreased. That the reaction works only under phase transfer catalysis was proved by carrying it out in homogeneous medium. Even after refluxing a tetrahydrofuran solution of tetrakis (triphenylphosphine) palladium (0) and β, β' -dibromostyrene under carbon monoxide for 41 hours, only starting material was recovered. Performing the reaction under phase transfer catalysis, but without the metal catalyst, also gave no reaction.

The effect of ligands on the palladium (0) catalyzed reaction was examined using Bis[bis(1,2-diphenylphosphino)ethane] palladium (0), $\text{Pd}(\text{dpe})_2$ and bis (dibenzylideneacetone) palladium (0), $\text{Pd}(\text{dba})_2$, it was found that $\text{Pd}(\text{dpe})_2$ gives the best yield of diynes. While $\text{Pd}(\text{PPh}_3)_4$ and $\text{Pd}(\text{dba})_2$ are also active catalysts, the product yields are lower and reaction in the case of $\text{Pd}(\text{dba})_2$ is slow. It is worthwhile noting that palladium acetate can also catalyze the conversion of vinylic dibromides to diynes.

The rate of addition of the palladium catalyst and organic substrate is critical to the success of the reaction. It was found convenient to add palladium catalyst dissolved in 15 mL benzene in a 15 minute period and then the vinylic dibromides in 50-60 minutes.

In one case, the palladium catalyst was added in one portion and β,β' -dibromo-*p*-methoxystyrene in one minute to compare with the yield that was obtained by slow addition. The yield in the first case was only 29% and the product was not clean, whereas on slow addition the yield increased to 50% and the product was quite pure at the crude stage.

Changing the solvent from benzene to methylene chloride also lowered the product yield. However, changing the phase transfer catalyst from tetrahexylammonium hydrogensulfate to benzyltriethylammonium chloride had little influence on the yield of products.

The reaction is not very sensitive to steric effects. With electron donating group ($\text{CH}_3, \text{OCH}_3$) on the aromatic ring, the yields of diynes were similar to the parent system. However, para-chlorine substituent gave 1,4-di-*p*-chlorophenyl-1,3-butadiyne in somewhat reduced yield.

The reaction is general and works even with α,β -unsaturated vinylic dibromides (Table 16). The product of the reaction with $\text{C}_6\text{H}_5\text{CH}=\text{C}(\text{CH}_3)\text{CH}=\text{C}(\text{Br})_2$ gave the anticipated compound $\text{C}_6\text{H}_5\text{CH}=\text{C}(\text{CH}_3)\text{C}\equiv\text{C}-\text{C}\equiv\text{C}(\text{CH}_3)=\text{CHC}_6\text{H}_5$. It was identified by analytical and spectral data (Table 17).

For vinylic dibromides derived from 4-*t*-butylcyclohexanone and *n*-heptanal carboxylation occurred in benzene to give monoacid in good

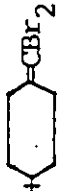


Table 16. Reaction of Vinylic Dibromides with Palladium Catalysts.

Compound	57,62	Catalyst, 58	a	Condition	Temp, °C	Product	Yield, 8
			Time, h	Solvent	(oil bath)		
$C_6H_5CH=CBr_2$		$Pd(PPh_3)_4$	42	C_6H_6	55	$C_6H_5C \equiv C - C \equiv C - C_6H_5$	40
"		$Pd(dpe)_2$	48	C_6H_6	70	$C_6H_5C \equiv C - C \equiv C - C_6H_5$	54
"		$Pd(dpe)_2$	19	t-Ama	50	$C_6H_5CH=C(COOH)_2$	93
4- $CH_3C_6H_4CH=CBr_2$		$Pd(PPh_3)_4$	41	C_6H_6	50	$CH_3C_6H_4C \equiv C - C \equiv C - C_6H_4CH_3$	14 ^b
"		$Pd(PPh_3)_4$	42	C_6H_6	50	"	36
"		$Pd(PPh_3)_4$	41	CH_2Cl_2	50	"	43
"		$Pd(dba)_2$	48	C_6H_6	50	"	42
"		$Pd(dpe)_2$	42	C_6H_6	40	"	56
4- $CH_3OC_6H_4CH=CBr_2$		$Pd(PPh_3)_4$	48	CH_2Cl_2	50	$CH_3OC_6H_4C \equiv C - C \equiv C - C_6H_4$ -OCH ₃	18 ^e
"		$Pd(PPh_3)_4$	43	CH_2Cl_2	50	"	20 ^f
"		$Pd(PPh_3)_4$	25	C_6H_6	105	"	41
"		$Pd(PPh_3)_4$ (fresh)	41	C_6H_6	70	"	49
"		$Pd(dpe)_2$	45	C_6H_6	70	"	61

Table 16. (cont'd)

Compound	57,62	Catalyst, 58	a Time, h	Condition Solvent	Temp, °C (oil bath)	Product	Yield, %
4-CH ₃ OC ₆ H ₄ CH=CBr ₂	Pd(CH ₃ COO) ₂	60	C ₆ H ₆	85	CH ₃ OC ₆ H ₄ C≡C-C≡C-C ₆ H ₄ - OCH ₃	29 ^c	
"	Pd(CH ₃ COO) ₂	48	C ₆ H ₆	82	"	50	
"	Pd(PPh ₃) ₄	41	THF	60	starting material recovered	91 ^d	
4-ClC ₆ H ₄ CH=CBr ₂	Pd(dpe) ₂	32	C ₆ H ₆	75	ClC ₆ H ₄ C≡C-C≡C-OC ₆ H ₄ Cl	41	
"	Pd(CH ₃ COO) ₂	48	C ₆ H ₆	70	"	27	
C ₆ H ₅ CH=C(Me)CH=CBr ₂	Pd(dpe) ₂	68	C ₆ H ₆	70	[C ₆ H ₅ CH=C(Me)C≡C] ₂	41	
1,4-Br ₂ C=CH-C ₆ H ₄ -CH=CBr ₂	Pd(dpe) ₂	48	C ₆ H ₆	75	(C ₆ H ₄ C≡C-C≡C-C ₆ H ₄) _n p-1	0.856 g	
"	Pd(CH ₃ COO) ₂	28	C ₆ H ₆	70	[Br ₂ C=CH-C ₆ H ₄ -C≡C] ₂ p-2	0.768 g	
n-C ₆ H ₁₃ CH=CBr ₂	Pd(PPh ₃) ₄	43	C ₆ H ₆	70	n-C ₆ H ₁₃ CH=CHCOOH	-	
"	Pd(dpe) ₂	70	C ₆ H ₆	70	"	55	

Table 16. (cont'd)

Compound <u>57,62</u>	Catalyst, <u>58</u>	a Time, h	Condition Solvent	Temp, °C (oil bath)	Product	Yield, %
	Pd(dpe) ₂	29	C ₆ H ₆	75		84
"	Pd(dpe) ₂	29	t-AmA	50		80

- a The reactions were run in carbon monoxide atmosphere, unless stated otherwise.
- b Reaction was run in nitrogen atmosphere.
- c Vinylic dibromide was added quickly in one shot instead of slow dropwise addition.
- d The reaction was done under homogeneous condition and not under PIC.
- e Tetra n-hexylammonium hydrogensulfate was used as phase transfer catalyst.
- f Benzyltriethylammonium chloride was used as phase transfer catalyst.

Table 17. Properties of Reaction Products Obtained from the Reaction of Vinylic Dibromides with Palladium Catalysts Under Phase Transfer Catalysis.

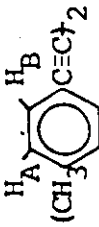

Compound	m.p., °C	^1H NMR (CDCl_3), δ	IR (CHCl_3), cm^{-1}	MS, m/e	^{13}C NMR (CDCl_3), δ
$(\text{C}_6\text{H}_5\text{C}\equiv\text{C})_2$	85-86	7.03-7.73 (m, aromatic CH; main peak at $\delta 7.33$)	ν_{CH} 3055 (s), $\nu_{\text{C}\equiv\text{C}}$ 2224 (w), 2160 (w), $\nu_{\text{C}=\text{C}}$ 1600 (s)	202 [M] ⁺	132.51 (d), 129.21 (d), 128.41 (d), 121.79 (s), 81.57 (s), 73.92 (s)
	162-163	2.33 (s, 6H, CH_3), 7.10 (d, 4H, H_A ortho to CH_3 , J=8Hz), 7.40 (d, 4H, H_B ortho to $\text{C}\equiv\text{C}$, J=8Hz)	ν_{CH} (Ar) 3114, 3100 (w) ν_{CH} (Al) 2962 (m) $\nu_{\text{C}\equiv\text{C}}$ 2257 (vw) $\nu_{\text{C}=\text{C}}$ 1612 (m)	230 [M] ⁺ , 215 [M-CH ₃] ⁺	
	130-131	3.77 (s, 6H, OCH_3), 6.77 (d, 4H, H_A ortho to OCH_3 , aromatic CH, J=8Hz), 7.37 (d, 4H, H_B ortho to $\text{C}\equiv\text{C}$, J=8Hz)	ν_{CH} (Ar) 3012 (m) ν_{CH} (Al) 2947, 2923 (m) 2903, 2838, $\nu_{\text{C}\equiv\text{C}}$ 2150 (w), $\nu_{\text{C}=\text{C}}$ 1605 (m)		160.23 (s), 123.04 (d), 127.41 (s), 114.12 (d), 81.23 (s), 73.00 (s), 55.29 (q)
$(\text{ClC}_6\text{H}_4\text{C}\equiv\text{C})_2$		7.1-7.57 (m, aromatic CH; main peak at $\delta 7.30$)		270 [M] ⁺ , 272 [M+2] ⁺ , 234 [M-Cl] ⁺ , 200 [M-Cl ₂] ⁺	

Table 17. (cont'd)

Compound	m.p., °C	^1H NMR (CDCl_3), δ	IR (CHCl_3), cm^{-1}	MS, m/e	^{13}C NMR (CDCl_3), δ
$[\text{C}_6\text{H}_5\text{CH}=\text{C}(\text{CH}_3)_2]$ CH_2	79-80	2.10 (s, 6H, CH_3), 6.97 (s, 2H, olefinic CH), 7.30 (s, 10H, aromatic)	ν_{CH} (Ar) 3050 (m), 3000 (m), (AlI) 2910 (s), 2924 (w), $\nu_{\text{C}=\text{C}}$ 2200, 2125 (w), $\nu_{\text{C}=\text{C}}$ 1600 (m)	282 [M] ⁺ , 265 [M- CH_3] ⁺	
P-I			ν_{CH} (Ar) 3060-3020, $\nu_{\text{C}=\text{C}}$ 2200, $\nu_{\text{C}=\text{C}}$ 1600, C=C Para substitution 840, [no trans double bond is present. No peak at 990-970 cm^{-1}]. [KBr pellet]		
a			ν_{CH} (Ar) 3035, (AlI) 2952, $\nu_{\text{C}=\text{C}}$ 2363, 2340, ν_{CO} 1699 $\nu_{\text{C}=\text{C}}$ 1597 [KBr pellet]		

Table 17. (cont'd)



Compound	m.p., °C	¹ H NMR (CDCl ₃), δ	IR (CHCl ₃), cm ⁻¹	MS, m/e	¹³ C NMR (CDCl ₃), δ
P-II		7.30 (s, aromatic CH), 7.38 (s, aromatic CH), 7.48 (s, aromatic CH)	ν _{CH} (Ar) 3075, 3060, 3012, (AlI) 2965, 2910, ν _{C=C} 2260, 2210 ν _{C=C} 1600		
n-C ₆ H ₁₃ CH=CHCOOH		0.53-2.97 (br. m, main peaks at δ 0.90, 1.67), 5.60-5.77 (m), 7.50- 7.87 (m, main peak at δ 7.70)	ν _{CH} 2910 (vbr., s) ν _{CO} 1710 (br, vs)	156 [M] ⁺ , 138 [M- H ₂ O] ⁺	
	76-77	0.87 (s, 9H, CH ₃), 1.03- 2.73 (m, 9H, aliphatic ring protons, one peak at δ 1.23); 5.57 (s, 1H, olefinic CH), 9.33 (s, 1H, COOH)	ν _{OH} 3500 (w) 3400-3300 (br., s) ν _{C=C} 1690 (vs), 1645 (s)	196 [M] ⁺ , 181 [M- CH ₃] ⁺ , 57 [CH ₃] ⁺ + 29.82, 29.28, 29.55, 27.56	172.73 (s), 166.82 (s), 112.34 (d), 47.73 (d), 38.15 (t), 32.44 (t),
	178 (d)	0.85 (br. s, 9H, C(CH ₃) ₃), 1.00-3.26 (br. m., 9H, aliphatic protons; main peaks at δ 1.20, 1.93, 2.93 and 3.13) (in DMSO-d ₆)		196 [M- CO ₂] ⁺ , 181 [M-(CO ₂ , CH ₃)] ⁺ , 151 [M-(CO ₂ ⁺ COOH)] ⁺ , 57 [(CH ₃) ₃ C] ⁺	180.95, 173.38, 171.10, 137.46, 60.87, 46.23, 45.56, 42.47, 41.46 (in DMSO-d ₆)

Table 17. (cont'd)

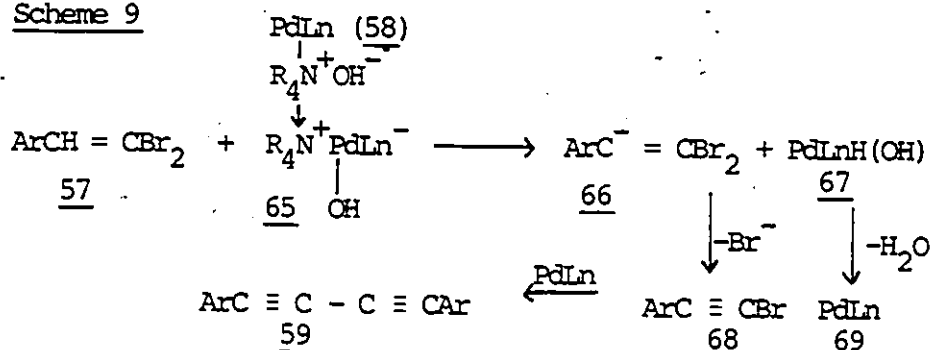
Compound	m.p., °C	¹ H NMR (CDCl ₃), δ	IR (CHCl ₃), cm ⁻¹	MS, m/e	¹³ C NMR (CDCl ₃), δ
<u>C₆H₅CH=C(COOH)₂</u>	194-196 (d)	7.17-8.07 (m, 6H, aromatic and olefinic CH, main peaks at δ 7.37 and 7.83), 8.5 (br. s, 2H, COOH)	ν _{OH} 2932 (vbr., s) ν _{CO} 1682 (vs)	192 [M] ⁺ , 175 [M-OH] ⁺ , 174 [M-H ₂ O] ⁺ , 147 [M-COOH] ⁺ , 102 [M-(COOH) ₂] ⁺	

a After washing and drying in air.

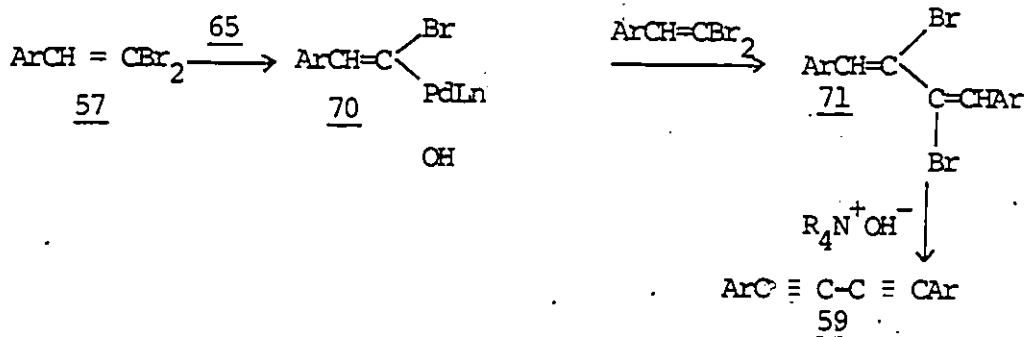
yields. In fact, the reaction proceeds via decarboxylation of a vinylic diacid species. Unpublished results by Dr. V. Galamb in our laboratory have clearly shown that such vinylic dibromides react at lower temperatures to give diacids. The conversion of diacids (60) to monoacids (61) using phase transfer catalysis is well-known²¹⁸.

The results can be rationalized on the basis of the pathways outlined in Schemes 9-11.

Scheme 9



Scheme 10

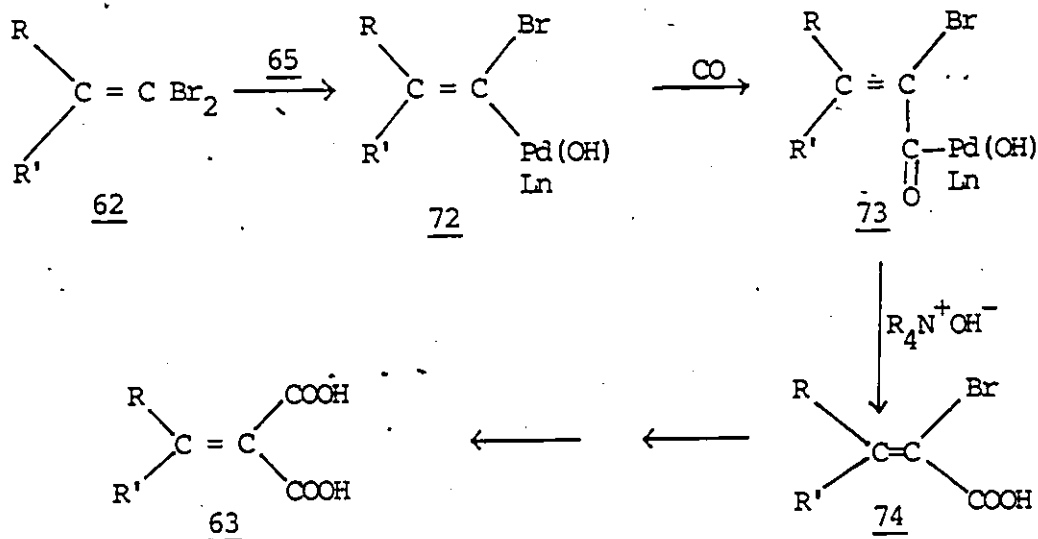


The vinylic hydrogen of a dibromostyrene compound should be sufficiently acidic to be deprotonated under phase transfer conditions to give the vinylic carbanion (66), which on loss of bromide would form the bromoalkyne (68). Palladium mediated coupling of the latter would

form the diyne (Scheme 9). An oxidative addition pathway (Scheme 10) is also conceivable but should occur for the other types of vinylic dibromides studied.

The formation of diacids (Scheme 11) may indeed proceed by sequential oxidative addition, carbonyl insertion and then hydroxide ion cleavage of the palladium-carbon bond. It is, of course, possible that the dicarbonylation reaction occurs at once. Note that when $R'=H$, the vinylic hydrogen is much less acidic than in the aryl analog and consequently deprotonation by base is a less favored process. Therefore, the pathway outlined in Scheme 11 would be preferred to that illustrated in Scheme 9.

Scheme 11



In conclusion, palladium (0) compounds can, by phase transfer techniques, induce the conversion of vinylic dibromides to diynes or acids, subject to the nature of the substrate and solvent.

CHAPTER IV

EXPERIMENTAL SECTION

General Comments

Infrared spectra were recorded using a Unicam SP-1100. A NICOLET MX-1, FT IR spectrometer was used to locate more precisely the positions of the bands of selected products. All IR determinations were calibrated using polystyrene film.

¹H nuclear magnetic resonance (NMR) spectra were determined on a Varian T-60 or Varian 360A NMR spectrometer as solutions in CDCl₃ (unless otherwise stated) with tetramethylsilane (TMS) as the internal standard. ¹³C NMR were recorded at 20 MHz with a Varian FT-20 spectrometer.

Mass spectra were obtained with an AEI MS902-S or VG7070-E mass spectrometers. Gas liquid chromatography was carried out with a GOW-MAC instrument having a thermal conductivity detector and helium carrier gas. High pressure liquid chromatography was performed on Waters Prep LC/System 500A. Melting points (uncorrected) were obtained with a Fischer-Johns hot-stage apparatus. Microanalyses were performed by: Canadian Microanalytical Service Ltd., 5704 University Boulevard, Vancouver, B.C., and by Schwarzkopf Microanalytical Laboratory, Woodside, New York.

The glassware was either dried at 115°C for at least 4h, assembled hot, and allowed to cool under a purge of prepurified nitrogen,

or the reaction flask was degassed and filled with nitrogen three times.

The reactions were carried out under nitrogen, carbon monoxide or CO/H₂ atmosphere in round-bottomed flasks fitted with side arms closed with quick fit joints or capped with rubber septa and were stirred magnetically using oven-dried, teflon-coated stirring bars. All transfers of liquids and solutions of organometallic reagents were done with hypodermic syringes fitted with stainless-steel needles or by a dropping funnel with quick fit joints. Solids were added either in a glove-bag under nitrogen atmosphere or under a fast stream of gas.

Thin layer chromatography (tlc) was routinely employed to monitor reactions and column chromatography separations, and to check the purity of products. It was performed on precoated silica gel plates SIL G-25 UV₂₅₄, whereas preparative tlc was done on glass plates coated with MN-Kieselgel G/UV₂₅₄ (both products manufactured by Macherey-Nagel & Co., West Germany). Spots were made visible by inspection under UV light, by keeping them in an iodine chamber, or by spraying the plates with 5% sulfuric acid in ethanol.

Column chromatography was generally performed with silica gel 60 (E. Merck A.G., West Germany). Florisil and alumina for chromatography were purchased from J.T. Baker Chemical Co. and Bio-Rad Laboratories respectively.

Section I: $\text{Fe}_3(\text{CO})_{12}$ on Alumina

(a) Reaction with Nitrobenzenes

1. Generation of Hydrido Species: Reaction of $\text{Fe}_3(\text{CO})_{12}$ with Basic Alumina.

Basic alumina (Woelm, 20g) was dried by heating overnight at 150°C under reduced pressure (3-6 mmHg). Anhydrous hexane (60-75 mL), and triiron dodecacarbonyl (1.007 g, 2.0 mmol; Pressure Chemical Company) were added to the cooled alumina in the glove-bag. The mixture, which was green due to the color of triiron dodecacarbonyl, was stirred at room temperature (nitrogen atmosphere) for 2 hours or till the color of the solid turned red whereas the liquid became colorless.

The formation of dark red color shows the generation of trinuclear iron hydride, $\text{HFe}_3(\text{CO})_{11}$. This species was used in situ for further reaction.

2. Reaction of $\text{Fe}_3(\text{CO})_{12}$ with Neutral Alumina

Essentially the same conditions as in (1) were employed; the difference being the use of neutral alumina (20g, Biorad AG7, 100-200 mesh) instead of basic alumina. The red color generated was slightly lighter than in (1).

3. Reaction of Nitrobenzenes with Triiron Dodecacarbonyl on Basic Alumina

Nitroarenes were purchased from Aldrich Chemical Co. or Eastman Organic Chemicals and were used as such.

The red colored species was generated as in (1). The nitro compound (2 mmol) was added, either as such or in dry benzene (10 mL),

under a fast flow of nitrogen. The reaction mixture was stirred overnight (20-24h) at room temperature.

The mixture was filtered, and trituration of the solid residue with ether or ethyl acetate was done until the solid was free of organic compound(s) (detected by UV lamp or tlc). The washings were added to the filtrate. The crude product (amine) obtained by rotary evaporation of the filtrate was processed in the following manner for the reactions using different nitro substrates. (Spectral data and melting or boiling points of the products are listed in Tables 5 and 6.)

3.1 p-Nitrotoluene

The crude product was separated from the green iron complex and yellow compound by column chromatography on a silica gel column. Elution with hexane-ether (2:1) gave $\text{Fe}_3(\text{CO})_{12}$ followed by 0.013g (6%) p-azotoluene and 0.143g (64%) of p-toluidine.

3.2 m-Nitrotoluene

Silica gel chromatography using hexane-ether (4:1) as eluant gave m-azotoluene (0.020g, 8%) followed by m-toluidine (0.095g, 40%).

3.3 o-Nitroanisole

The products were isolated from preparative thin layer chromatography [hexane-ether (3:2)] and were identified as o-azoanisole (0.014g, 6%) and o-anisidine (0.127 g, 51%).

3.4 p-Nitroanisole

The crude product was worked-up by silica gel column chromatography with hexane-ether (5:1, 3:1 and 1:1) as eluant to give 0.195g (7%) p-azoanisole followed by 0.198g (73%) p-anisidine.

3.5 p-Chloronitrobenzene

Column chromatography of the crude on a silica gel column [eluant:hexane-ether (4:1 and 1:1) gave p-chloroaniline (0.178g, 70%).

3.6 p-Nitrobenzophenone

The crude product was chromatographed on a silica gel column with hexane-ether (4:1 and 1:1). The major product was identified as p-aminobenzophenone (0.268g, 68%).

3.7 2-Nitrofluorene

Chromatography of the product on silica gel with hexane-ether afforded 0.306g (79%) of 2-aminofluorene.

3.8 p-Nitrobenzoic acid

The products from the reaction of p-nitrobenzoic acid were adsorbed on the alumina and could not be extracted by organic solvents.

3.9 Reaction of Cholest-4-en-3-one with 6

Cholest-4-en-3-one (0.544g, 1.41 mmol) was added to the red species generated by the procedure given in (1). After 18 hours stirring under nitrogen at room temperature, trituration with ethyl acetate and filtration, crude product was obtained. Workup by silica gel column chromatography gave recovered starting material.

3.10 Other Attempted Reactions of Substrates with 6

Similarly starting material was recovered on attempted reaction of 6 with β,β' -dibromostyrene, azobenzene, p,p'-dimethoxybenzophenone, dibenzothiophene and phthalazine.

4. Aliphatic Nitro Compounds

4.1 Preparation of 1-Nitroadamantane from 1-Amino Adamantane²¹⁹

A solution of 1-amino adamantane (3.03g, 20 mmol; Aldrich Chemical Co.) in chloroform (130 mL) was added slowly (30 minutes) to m-chloroperbenzoic acid (24.20g, 140 mmol) in chloroform (100 mL). The mixture was refluxed with stirring under nitrogen for 10 minutes. The solution was cooled, and washed with 10% aq. NaHSO_3 (4x20 mL), saturated sodium bicarbonate (2x200 mL) and then water (200 mL). The chloroform layer was dried and evaporated at room temperature in vacuo to give the crude product. 1-Nitroadamantane was further purified by sublimation at 80°C at 10 mm Hg for 12 h. Yield: 2.75g, 76%.

4.2 1-Nitrooctane was obtained from Dr. B. Despeyroux and 2-nitropropane was purchased from Aldrich Chemical Co.

4.3 Reaction of Aliphatic Nitro Compounds with Triiron Dodecacarbonyl on Alumina

The method followed was essentially that described in (3). The reaction product was distilled in the case of 2-nitropropane. The distillate was analyzed by GLC (10% DEGS on chromosorb ^b) and showed no 2-propyl amine.

On using 1-nitrooctane or 1-nitroadamantane also the corresponding reduced product 1-amino octane or 1-amino adamantane was not formed. The identification of the products was not pursued.

5.1 Reaction of p-Nitrotoluene with Alumina

The blank reaction was run as stated in (3) without using triiron dodecacarbonyl. After the reaction p-nitrotoluene was recovered and no p-toluidine was formed.

5.2 Reaction of Stilbene Epoxide with Alumina

The reaction of trans stilbene epoxide (0.302 g, 1.54 mmol) with alumina in hexane at room temperature for 20 hours did not give any starting material. The products formed were identified as diphenylacetaldehyde and desoxybenzoin.

b) Reaction with Azoxybenzenes and N-Oxides

6. Reaction of Azoxybenzenes and N-oxide with $\text{Fe}_3(\text{CO})_{12}$ on Neutral Alumina

Azoxybenzenes and heterocyclic N-oxides were purchased from Eastman Organic Chemicals or Aldrich Chemical Co., and used as received.

The red trinuclear iron hydride was generated as described in (2). The azoxy compound or N-oxide (2-4 mmol) was added either as a solid or after dissolving in benzene (10 mL). Stirring was continued for 20 hours at room temperature. The mixture was filtered, the solid was treated with ether or methylene chloride, and the washings were added to the filtrate. The crude product was obtained on rotary evaporation. Purification was achieved using Column or thin layer chromatography as described below.

6.1 Azoxybenzene

The residue was chromatographed on Florisil (J.T. Baker Chemical Co., 60-100 mesh) with hexane as eluant to give 0.249 g (61%) of pure azobenzene. (Refer to Table 6 for its characterization.)

6.2 4,4'-Azoxyanisole

Column chromatography on Florisil (eluant-hexane) afforded pure 4,4'-azoanisole (0.232 g, 68%).

6.3 4,4'-Azoxyphenetole

Column chromatography (eluant: hexane) of the crude on Florisil afforded pure azo compound (0.304 g, 59%) and some unreacted 4,4'-azoxyphenetole (0.136 g, 31%).

6.4 Quinoline N-oxide

The liquid obtained was found to be pure quinoline (0.258 g, 79%).

6.5 4-Picoline N-oxide

The crude product was dried under reduced pressure to obtain pure 4-picoline (0.205 g, 86%).

Section II. $\text{Co}_2(\text{CO})_8$ on Alumina

(a) Reaction with Nitrobenzenes

7. Reaction of Nitroarenes with $\text{Co}_2(\text{CO})_8/\text{Al}_2\text{O}_3$

Alumina (20 g, Fischer adsorption, 80-200 mesh) was dried by heating overnight at 150°C under reduced pressure (3-6 mm Hg). Dicobalt octacarbonyl was purchased from Strem Chemicals, Inc.. A mixture of dicobalt octacarbonyl (1.026 g, 3.0 mmol) and cooled alumina in deoxygenated hexane (60-75 mL) was stirred at room temperature for two hours. This resulted in the formation of a deep red mixture. To this mixture was added the nitroarene (2-3 mmol) dissolved in the minimum amount of dry benzene or tetrahydrofuran, and stirring was continued for 20-22 hours. The mixture was filtered, the oxide was treated with ether or ethyl acetate until it was free of product(s), and the washings were added to the filtrate. The crude product, obtained by the rotary

evaporation of the filtrate, was purified by column chromatography on silica gel using hexane-ether as eluant or by recrystallization. See Tables 5,6 for characterization data.

The procedure adopted for working-up the reaction of individual nitroarenes with $\text{Co}_2(\text{CO})_8/\text{Al}_2\text{O}_3$ (19) is described below.

7.1 p-Nitrotoluene

The reaction mixture was chromatographed on silica gel with hexane-ether (4:1 and the polarity was increased by using more ether). The first fraction obtained was 4,4'-azotoluene (0.023 g, 6%) and the second fraction was p-toluidine (0.216 g, 60%).

7.2 p-Nitroanisole

The reaction mixture was purified by silica gel chromatography using hexane-ether (3:1 to 1:1). A yellow solid, eluted first, was 4,4'-azoanisole (0.013 g, 5%). Further elution gave recovered p-nitrotoluene (0.011 g, 0.07 mmol; 3%) and then 0.170 g (62%) of p-anisidine.

7.3 p-Chloronitrobenzene

p-Chloroaniline (0.310 g, 62%) was obtained by silica gel chromatography using hexane-ether (2:1) as eluant.

7.4 p-Nitrobenzophenone

Column chromatography [silica gel, hexane-ether (2:1)] was performed to give 0.227 g (71%) of pure 4-aminobenzophenone.

7.5 m-Nitrotoluene

Workup by silica gel column chromatography with hexane-ether (2:1) gave 0.224g (70%) m-toluidine.

7.6 2-Nitrofluorene

The crude amine was purified by column chromatography [silica gel; using hexane-ether (2:1, v/v)] to give 0.272 g (77%) of 2-aminofluorene.

8. Reaction of $\text{Co}_2(\text{CO})_8$ with Partially Dehydroxylated Alumina

Alumina was heated overnight in a furnace at 550°C. After cooling in a desiccator, it was transferred under a nitrogen atmosphere, to a 100 mL round bottom flask. It was then further heated overnight at 150°C under reduced pressure (2 mm Hg).

Dicobalt octacarbonyl (1.026 g, 3 mmol) and hexane were stirred with the alumina for 2 hours to obtain the red colored species (19A). The nitroarene was added to it and the reaction was run for 20 hours. Filtration, followed by trituration of the solid with ethyl acetate and flash evaporation of hexane-ethyl acetate solvent gave the crude product. Workup was effected in the following manner for the various nitro reactions.

8.1 4-Nitrotoluene

p-Nitrotoluene (0.41 g, 2.72 mmol) afforded the crude (0.288 g) product, which on silica gel chromatography [hexane-ether (2:1 and then 1:1)] gave 0.050 g (14%) p-azotoluene and 0.122 g (38%) of p-toluidine.

8.2 4-Nitroanisole

p-Nitroanisole (0.408 g, 2.67 mmol) afforded 0.358 g of crude product. Silica gel chromatography of the crude on elution with hexane-ether (3:1 to 1:1) gave 0.073 g (23%) 4,4'-azoanisole and 0.129 g (39%) of p-anisidine.

9. Reaction of p-Nitrotoluene with 19 in Carbon Monoxide Atmosphere

The procedure adopted was essentially the same as given in (8), the difference being the use of carbon monoxide instead of nitrogen.

Workup involved chromatography on silica gel with hexane-ether (2:1 to 1:1) and then pure ether. The products were 4,4'-azotoluene (0.051 g, 15%), p-toluidine (0.105 g, 35%), and an unidentified product (0.029 g).

10.1 Reaction of p-Nitrotoluene with Dicobalt Octacarbonyl and Silica Gel

Use of silica gel instead of alumina as the refractory oxide, and following the procedure reported in (7), also afforded a red species. Subsequent reaction with p-nitrotoluene and workup (as in 7.1) gave 0.120 g (40%) of p-toluidine.

10.2 Reaction of p-Nitrotoluene with $\text{Co}_2(\text{CO})_8$ /Florisil

Use of florisil instead of alumina (in 7) in reaction with p-nitrotoluene (as in 7.1) gave 0.120 g (35%) of p-toluidine.

11. Reaction of p-Nitrotoluene with $\text{Co}_4(\text{CO})_{12}$ on Alumina

Tetracobalt dodecacarbonyl was purchased from Strem Chemicals, Inc. and was used as such under nitrogen atmosphere.

Following the procedure given in (7) but using tetracobalt dodecacarbonyl (0.673 g, 1.18 mmol) instead of dicobalt octacarbonyl also generated the red colour. Its reaction with p-nitrotoluene (0.4035 g, 2.7 mmol) afforded 0.143 g (45%) of p-toluidine.

12. Reaction of p-Nitrotoluene with $[\text{Co}_2(\text{CO})_6(\text{PBu}_3)_2]$ on Alumina

Bis (tri n-butylphosphine) dicobalt hexacarbonyl was supplied by Dr. M. Salisova.

The same procedure as reported in (7) was adopted with bis (tri n-butylphosphine) dicobalt hexacarbonyl (0.485 g, 0.69 mmol) being used instead of dicobalt octacarbonyl. The color of the liquid layer turned light orange and the solid became lemon colored after 4 hours of stirring at room temperature. Addition of p-nitrotoluene (0.153 g, 1.00 mmol), stirring for 20 hours under nitrogen, followed by the usual workup (see 7.1) gave 0.009 g (7%) of p-toluidine and 0.090 g (59%) of p-nitrotoluene.

13. Other Attempted Reactions of Substrates with $\text{Co}_2(\text{CO})_8/\text{Al}_2\text{O}_3$

Reaction of the red species (19) with cholest-4-en-3-one (0.546 g, 1.42 mmol), β,β' -dibromo p-methoxystyrene (0.743 g, 2.55 mmol), phthalazine (0.402, 3.09 mmol), p-MeOC₆H₄C=NC₆H₅ (0.412 g, 2.12 mmol), or ethyl phenyl sulfoxide (0.505 g, 3.40 mmol) gave back almost all of the starting material on workup.

(b) Reaction with α -Halosulfoxides

14. Reaction of α -Halosulfoxide with $\text{Co}_2(\text{CO})_8/\text{Al}_2\text{O}_3$

Alumina (20 g, Fischer adsorption, 80-200 mesh) was dried overnight at 150°C under reduced pressure (3-6 mm Hg). Cooled alumina, hexane (60-75 mL) and dicobalt octacarbonyl (3 mmol) were transferred to a 3 necked flask inside a glove bag under a nitrogen atmosphere. The mixture was stirred at room temperature for 2 hours until the adsorbent turned red. (Actually the red color appears within 5 minutes.)

The α -halosulfoxide (2-3 mmol) was then added under a fast flow of nitrogen and the mixture was allowed to stir overnight (ca. 20 hours). The workup involved filtration, and trituration of the solid with ether and ethyl acetate. The filtrate was concentrated using a rotary evaporator.

The crude product was further purified in the following manner for the different α -halosulfoxides.

14.1 α -Chloromethyl phenyl sulfoxide

Column chromatography (silica gel, hexane-ether) gave 0.055 g (13%) of methyl phenyl sulfoxide and 0.473 g (84%) starting material (28) was recovered.

14.2 α -Bromomethyl phenyl sulfoxide

The crude product was dissolved in ethylacetate and methanol and filtered through a short pad of celite. The compound was further purified by preparative thin layer chromatography using hexane-ethyl acetate (1:4). The fast moving compound was identified to be $C_6H_5S(O)CH_2CH_2S(O)C_6H_5$ (0.042 g, 7%). The major product (0.386 g, 80%) was methyl phenyl sulfoxide.

14.3 α -Bromomethyl 4-chlorophenyl sulfoxide

The crude product was allowed to stand overnight. It was then filtered through a small pad of celite after dissolving in a mixture of ethyl acetate and methanol. The filtrate on rotary evaporation gave 0.370 g (100%) pure p-chlorophenyl methyl sulfoxide.

14.4 α -Bromoethyl phenyl sulfoxide

The crude product was dissolved in ethyl acetate and methanol and then passed through celite. Rotary evaporation of the filtrate followed by purification of the resulting oil by preparative thin layer chromatography gave 0.196 g (50%) ethyl phenyl sulfoxide and 0.133 g of an unidentified product: $^1\text{H NMR}$ (CDCl_3), δ 1.86 (dd, 3H, $J=6.5\text{Hz}$; $J=2.0\text{Hz}$), 4.70 (qt, 1H, $J=6.5\text{Hz}$), 7.33-7.93 (m, 5H, aromatic CH; main peak at δ 7.60), IR (CHCl_3), $\nu_{\text{S(O)}}$ 1090 (s), 1076 (sh), 1055 (s), 1033 (sh) cm^{-1} .

14.5 α -Bromomethyl benzyl sulfoxide

Filtration through a short column of celite gave pure benzyl methyl sulfoxide (0.321 g, 1.38 mmol) in quantitative yield.

14.6 α -Bromomethyl naphthyl sulfoxide

The crude product was allowed to stand in air and then filtered through a pad of celite after dissolving in ethyl acetate and chloroform. The filtrate on rotary evaporation gave methyl naphthyl sulfoxide (0.380 g, 2.00 mmol) in quantitative yield.

15. Reaction of α -Chloromethyl phenyl sulfoxide with 19 under ultrasound

The same procedure as given in (14) was followed but the reaction was agitated for 2 hours in the water bath of an ultrasonic laboratory cleaner along with mechanical stirring. Workup afforded 0.105 g (23%) methyl phenyl sulfoxide and rest of the starting material was recovered.

16.1 Preparation of 2-Naphthyl methyl sulfide from 2-naphthalene thiol

Potassium hydroxide (14 g, 0.25 mole) and methyl iodide (14.2 g, 0.1 mole) dissolved in 50 mL methanol were added dropwise to a solution of 2-naphthalene thiol (16 g, 0.1 mole) in methanol (400 mL). The

reaction was stirred overnight under a nitrogen atmosphere. The precipitate was filtered and the filtrate was diluted with water (200 mL). The mixture was extracted with five equal portions of methylene chloride (250 mL). The combined organic extract was washed with 10% potassium hydroxide (4x25 mL), water (3x25 mL) and then dried over magnesium sulfate. Filtration through a short pad of glass wool and evaporation of solvent gave crude sulfide in 82.5% yield.

16.2 Preparation of 2-Naphthyl methyl sulfoxide from 2-naphthalene methyl sulfide

A solution of t-butanol (10 mL) and glacial acetic acid (7 mL) was added in a single portion to a rapidly stirred bleach (Javex) solution (135 mL) at 0°C, and stirring was continued for 3 minutes. The entire reaction mixture was poured into a separatory funnel. The lower aqueous organic layer was washed first with a 30 mL portion of 10% aqueous sodium carbonate and then with 25 mL of water. The product was dried over 0.5 g of calcium chloride and filtered.

The resulting t-butyl hypochlorite²²⁰ was added dropwise to a well stirred solution of the crude sulfide (0.045 mole) in a 500 mL methylene chloride - methanol (4:1, v/v) maintained at -78°C. The resulting solution was warmed to room temperature; at -40°C, sodium carbonate (1 g) was added to it. The solution was stirred at room temperature for 1 hour and then filtered. The filtrate was rotary evaporated and the concentrate was dissolved in water and then extracted with methylene chloride. The extracts were dried over magnesium sulfate and the solvent evaporated to give crude sulfoxide in 100% yield. The solid was recrystallized from ether-hexane affording 2-naphthyl methyl sulfoxide in 67% yield.

16.3 Preparation of α -bromo 2-naphthyl methyl sulfoxide from 2-naphthyl methyl sulfoxide

A solution of bromine (6.4 g, 0.04 mol) in anhydrous acetonitrile (40 mL), cooled to -20°C , was added dropwise to a stirred solution of the sulfoxide (3.8 g, 0.02 mol) and anhydrous pyridine-acetonitrile (50 mL, 1:4 v/v) at -40°C . After 1 hour at -40°C , the mixture was stirred at room temperature for 20 hours. Acetonitrile was removed under reduced pressure, the residue was dissolved in chloroform (100 mL), washed with an aqueous solution of sodium thiosulfate, and then with aqueous sulfuric acid. Evaporation gave the crude α -bromosulfoxide in 96% yield. Purification by column chromatography [silica gel, ether-hexane (1:1)] afforded 70% of the pure α -bromosulfoxide.

16.4 Preparation of α -Bromosulfoxide from Sulfoxides

Sulfoxides were purchased from Parish Chemical Co.. Bromination was carried out either as detailed in (16.3) or by the use of N-bromosuccinimide. Benzyl methyl sulfoxide was brominated by the first procedure²²¹ and 4-chlorophenyl methyl sulfoxide, methyl phenyl sulfoxide and ethyl phenyl sulfoxide were brominated by using the N-bromosuccinimide procedure²²².

17. Reaction of α -Bromo p-methoxyacetophenone with 19

Dicobalt octacarbonyl was reacted with alumina as given in (14). α -Bromo p-methoxyacetophenone was added instead of α -halosulfoxide. Workup, which involved filtration and column chromatography [silica gel, hexane-ethyl acetate (3:1)] gave 0.328 g (75%) p-methoxyacetophenone.

Section III. $\text{Mo}(\text{CO})_6$ on Alumina

(a) Reaction with Azoxybenzenes and N-Oxides

18. Reaction of Azoxybenzenes or N-oxides with $\text{Mo}(\text{CO})_6/\text{Al}_2\text{O}_3$

Alumina (30 g, Fischer A-540, 80-200 mesh) was dried overnight at 350°C. After cooling to room temperature in a desiccator, it was suspended in dry hexane (150 mL) containing molybdenum hexacarbonyl (2.64 g, 10.0 mmol, Pressure Chemical Company) under a nitrogen atmosphere. The hexane was removed by use of a rotary evaporator. Solid $\text{Mo}(\text{CO})_6/\text{Al}_2\text{O}_3$ was heated for 1 hour at 105°C. The N-oxide or azoxy compound (3.0 mmol) was added to the cooled solid, along with 1,2-dimethoxyethane (60-75 mL), and the reaction mixture was stirred at reflux overnight (ca. 20 hours). The mixture was cooled and filtered, the solid residue was treated with ether or methylene chloride, and then washing was added to the filtrate. Concentration of the filtrate gave the crude product, which was purified by chromatographic techniques (florisil, silica gel) for the various reactions, as follows.

18.1 Azoxybenzene

Column chromatography [florisil, hexane and hexane-ether (5:1)] gave 0.172 g (31%) of azobenzene.

18.2 4,4'-Azoxyanisole

The crude product was purified by column chromatography on florisil with hexane-methylene chloride (9:1) to give 0.247 g (34%) of 4,4'-azoanisole and 0.225 g (29%) starting material.

18.3 4,4'-Azophenetole

Chromatography on florisil using hexane as the eluant afforded 0.123 g (15%) of 4,4'-azophenetole along with 84% azoxybenzene (0.729 g, 2.54 mmol).

18.4 Quinoline N-oxide

Column chromatography [silica gel; hexane-ether (1:1)] and subsequent preparative thin layer chromatography gave a yellow oil. This was identified to be quinoline (0.159 g, 41%).

18.5 4-Picoline N-oxide

The crude product was purified by column chromatography on a silica gel column. Elution with ether-hexane (1:2) afforded 0.125 g (32%) of 4-picoline.

In another experiment, 4-picoline N-oxide (0.477 g, 4.4 mmol) was added to the subcarbonyl molybdenum species (generated by the procedure given in 18). The crude obtained after distillation was analyzed by gas chromatography (20% versamid 900 on chromosorb W). The yield of 4-picoline was 45%.

18.6 Nicotinamide N-oxide

Purification by preparative thin layer chromatography [ethanol-hexane (1:1)] gave 0.260 g (71%) nicotinamide.

(b) Desulfurization by Molybdenum Hexacarbonyl on Solid Support

19. Reaction of Sulfur Containing Compounds with $\text{Mo}(\text{CO})_6/\text{Al}_2\text{O}_3$

After being dried overnight at 350-400°C, alumina (30 g, different types) was suspended in hexane (150 mL) containing molybdenum hexacarbonyl (1 to 15 mmol). The hexane was removed by rotary evaporation,

and the $\text{Mo}(\text{CO})_6/\text{Al}_2\text{O}_3$ was heated for 1 hour at 110°C (oil-bath temperature). The sulfur-containing compound (2-3 mmol) was added either as such or along with a solvent (dimethoxyethane, toluene or xylene). The reaction mixture was stirred at $25-130^\circ$ overnight (20 hours). Workup, after filtration, involved with different compounds are given below. Details of the experimental conditions are given in Table 11.

19.1 Reaction of 2-Naphthalene thiol with metal carbonyls on inorganic oxide

Column chromatography [silica gel, hexane-benzene (3:1)] was used to separate the disulfides (0.187 g, 38%) from other products.

19.2 Reaction of triphenylmethyl mercaptan with $\text{Mo}(\text{CO})_6$ on inorganic oxide

The crude product was purified by column chromatography [silica gel, hexane-ether (5:1)]. The second fraction was found to be triphenylmethane (0.338 g, 69%).

19.3 Reaction of Dibenzothiophene with metal carbonyls on inorganic supports

Silica gel chromatography with 4:1 hexane-ether gave back the starting material as the major product.

19.4 Reaction of Thioketone with metal carbonyls on inorganic support

The corresponding ketone (0.244 g, 41%) was isolated after silica gel column chromatography [methylene chloride-ether (1:1)].

19.5 Reaction of thiobenzanilide with metal carbonyls on alumina

Column chromatography [silica gel, hexane-methylene chloride (1:1) to increasing polarity with ether and methanol] gave benzanilide (0.093 g, 16%) as one of the products.

20. Reaction of crude oil with $\text{Mo}(\text{CO})_6/\text{Al}_2\text{O}_3$

Alumina (20-30 g, different types), dried overnight at 350-400°C was cooled to room temperature. Molybdenum hexacarbonyl (1/10 or 15 mmol) in hexane (150 mL) was added to it in a glove bag maintained in a nitrogen atmosphere. The solvent was removed by flash evaporation and the white solid was activated by heating for 1 to 2 hours at 110°C (oil bath). After cooling the solid, crude oil (1 mL to 50 mL) was added as such or in hexane (10-50 mL) under the fast flow of gas (nitrogen or CO/H_2). The mixture was stirred overnight (18-24 hours) at 60-70°C. The solution was allowed to stand for 30 minutes and the liquid was collected and then sent for analysis.

21. Reaction of crude oil with $\text{Mo}(\text{CO})_6$ on inorganic supports

Essentially the same procedure as in (20) above was adopted except that silica gel, magnesium oxide or florisil was used as adsorbent instead of alumina.

22. Preparation of different types (activity grade) of alumina

i) Alumina (30 g, Woelm acid) was taken in a conical flask and the necessary amount of water was added. The solid was shaken with a glass rod to break up the lumps. The resulting deactivated alumina was allowed to stand for 2 or 20 hours in a stoppered vessel.

Activity grade of alumina	I	II	III	IV	V
Water (% w/w) addition	0	3	6	10	15

ii) Freshly distilled $\text{BF}_3(\text{Et}_2\text{O})_2$ (2 mL) and hexane (5 or 10 mL) were added to 20 g alumina (Woelm acid, activity grade I) in a glove bag.

The lumps were broken and the solid was allowed to stand in a stoppered flask for 2 hours. It was used as such or after the resulting alumina was further activated by heating to 400°C overnight.

23. Modification of silica gel

Dilute hydrochloric acid (5 N, 3 mL) was added to silica gel (30 g, Baker Analyzed Reagent, 60-200 mesh). It was allowed to stand for 2 hours and then heated overnight (ca. 16 hours) at 400°C.

Section IV. Phase Transfer Catalysis

(a) Reaction of $\text{CpCo}(\text{CO})_2$ with Benzyl Bromides

24. Reaction of cyclopentadienyl cobalt carbonyl with benzyl bromide under phase transfer conditions

An aqueous solution of 5N sodium hydroxide (20 mL), tetra n-hexylammonium bromide (0.1 g, 0.2 mmol), and benzene (20 mL) were stirred under a nitrogen atmosphere. The gas was then switched to carbon monoxide. Cyclopentadienyl cobalt dicarbonyl (3.5 mmol, Strem Chemicals, Inc.) was added through the septum by syringe. The solution was stirred overnight (18-20 hours) at 45°C under carbon monoxide. After cooling to room temperature benzyl bromide (3.0-5.5 mmol) and benzene (2 mL) were added by syringe. The reaction mixture was stirred under carbon monoxide at 40-45°C for 45-48 hours and then exposed to air.

The two phases were separated, and the organic layer was dried over magnesium sulfate and concentrated at reduced pressure. The organic extract was further purified by filtration through celite followed by column chromatography on silica gel. The compounds having similar R_f values were further purified by preparative thin layer chromatography.

The aqueous layer was neutralized with 5N hydrochloric acid (ca. 20 mL) and the resulting organic acid was extracted with ether (3x50 mL), dried (MgSO_4), and then isolated by rotary evaporation of the ether.

The workup with individual experiments are described below.

24.1 α -Bromo-O-xylene (40, $\text{Ar}=\text{O}-\text{CH}_3\text{C}_6\text{H}_4$).

The crude product (0.793 g) was separated into different fractions by column chromatography [silica gel, hexane-methylene chloride (6:1), methylene chloride-ethyl acetate (1:5) and ethyl acetate]. Fraction I was 42 (0.077 g, 8%) and fraction III 45 (0.055 g, 9%). Fraction II was further purified by preparative thin layer chromatography [silica gel, hexane-methylene chloride (1:1)]. The top fraction from preparative tlc was identified as 44 (0.108 g, 17%) and the lower fraction was the ketone 43 (0.149 g, 26%). The aqueous phase afforded ArCH_2COOH 46 (0.190 g, 26%).

The data for the characterization of the reaction products are given in Table 15.

24.2 40 ($\text{Ar}=\text{p}-\text{CH}_3\text{C}_6\text{H}_4$)

Column chromatography on silica gel with hexane-methylene chloride (7:1) to ether-methylene chloride (1:1) gave three main fractions. Fractions 1 and 2 were further purified by preparative thin layer chromatography. They were found to be 42 (0.135 g, 24%) and 43 (0.247 g, 38%) respectively.

The acid 46 (0.219 g, 27%) was obtained from the aqueous phase.

24.3 40 (Ar=p-FC₆H₄)

The crude mixture was separated by column chromatography [silica gel, hexane-ethyl acetate (25:1 to increasing polarity)].

Fraction I was 42 (0.052 g, 17%). Fraction II was further purified by preparative thin layer chromatography to give 43 (0.108 g, 31%) and 44 (0.038 g, 10%). Alcohol 45 (0.010 g, 3%) was obtained by purification of fraction IV of the column chromatography.

The acid 46 (0.063 g, 15%) was obtained from the aqueous phase.

24.4 40 (Ar=2-C₁₀H₇)

The reaction mixture from the organic layer was divided into different portions by column chromatography [silica gel, hexane-ethyl acetate (30:1 to increasing polarity)]. Further purification of each fraction was carried out by preparative thin layer chromatography affording 41 (0.027 g, 4%), 42 (0.076 g, 11%), 43 (0.024 g, 3%), 44 (0.132 g, 17%) and 45 (0.112 g, 15%).

The aqueous phase afforded the acid 46 (0.292 g, 33%).

24.5 40 (Ar=C₆H₅)

The crude product from the organic layer was chromatographed on silica gel with hexane-ethyl acetate (30:1 to increasing polarity) used as the eluant. Different fractions from column chromatography were further purified by preparative thin layer chromatography. The following compounds were isolated: 42 (0.107 g, 24%), 43 (0.132 g, 26%), 44 (0.118 g, 21%), and 45 (0.069 g, 13%).

Acid 46 (0.088 g, 13%) was obtained from the aqueous phase.

(b) Reaction of Palladium (0) and Palladium (II) with Vinylic Dibromides

25. Preparation of 1,1-dibromoolefins from aldehydes²²³

To carbon tetrabromide (16.5 g, 0.05 mole) in dry methylene chloride (250 mL - distilled from P_2O_5) was added triphenylphosphine (26.2 g, 0.1 mole) giving an orange-red solution. Within 2-3 minutes, the aldehyde (0.05 mole) was added in portions to the stirred solution, which caused the fading of the color. After 5 minutes, an aliquot showed no carbonyl band in the infra-red spectrum.

After 15 minutes of stirring, the solution was washed with water, dried and methylene chloride was removed using a rotary evaporator. The residue obtained was triturated with hexane. Triphenylphosphine oxide (ca. 0.1 mole) was filtered off and the hexane extract was concentrated to give crude 1,1-dibromoalkene. The compound was further purified by column chromatography (silica or alumina, hexane eluant) or distillation under reduced pressure.

In one case, $C_6H_5CH=C(CH_3)CH=C(Br)_2$ was purified by high pressure liquid chromatography with 90:1 (hexane:ethyl acetate) as eluant. The compounds were characterized by spectroscopic techniques. Details are given in Table 18.

25.1 Preparation of 1,1-dibromoolefin from ketone²²⁴

A mixture of carbon tetrabromide (7.43 g, 22.4 mmol), dry benzene (700 mL), triphenylphosphine (11.74 g, 44.8 mmol) and 4-t-butylcyclohexanone (1.357 g, 8.8 mmol) was stirred at reflux, under nitrogen, for 18 hours. After allowing the mixture to cool to room temperature, solid material was removed by vacuum filtration, and the solvent was then removed under

reduced pressure.

The residue was extracted with 2L hexane, filtered, and solvent was again removed in vacuo. The resulting solid was chromatographed on alumina giving 2.565 g (8.3 mmol) of the pure dibromoethylene derivative (62) in 94% yield. (Refer to Table 18 for characterization.)

25.2 Preparation of tetrakis(triphenylphosphine)-palladium (0) from palladium dichloride

The complex was prepared according to the procedure of Coulson²²⁵.

Bis[bis(1,2-diphenylphosphino)ethane]-palladium was purchased from Aldrich Chemical Company, and Bis (dibenzylideneacetone)-palladium was donated by Dr. T. Izumi.

26. Reaction of 1,1-dibromoolefins with palladium (0) catalysts under phase transfer catalysis

In a flask maintained under nitrogen atmosphere, sodium hydroxide (3 g), water (15 mL) and the phase transfer catalyst (0.2 to 0.4 mmol) were stirred. The gas was changed to carbon monoxide and palladium (0) catalyst (0.08-0.1 mmol) in benzene (15 mL) was added dropwise (ca. 15 minutes). In the case of Pd(dpe)₂, 1 mL of methylene chloride was added to dissolve the catalyst before adding 15 mL of benzene. The solution was stirred vigorously for 3-4 hours at room temperature. α,α' -Dibromoolefin (3-5 mmol) was dissolved in 3-4 mL of benzene and added slowly by dropping funnel (ca. 1 h). The reaction mixture was stirred for 2 hours at room temperature and then warmed to 50-70° (oil bath) and it was kept stirring till the starting material was used up. The reaction was followed by tlc (hexane). The usual reaction time was

around 40 hours. Different reaction conditions are listed in Table 16 (Chapter III).

The layers were separated, and the organic phase was washed with 25 mL of water. The aqueous phase was treated with ether (25 mL). The combined organic portions were dried over magnesium sulfate and then chromatographed on silica gel or alumina to give the pure product. The product was characterized by spectroscopic techniques (Table 17).

The aqueous layer was neutralized with dilute hydrochloric acid (5N) and then extracted with ether (3x50 mL). The ether extract was dried over magnesium sulfate and rotary evaporated to yield the product.

The workup performed in individual experiments are listed below.

26.1 Reaction of β, β' -dibromostyrene with catalytic amount of $[\text{Pd}(\text{PPh}_3)_4]$

The crude product from the organic layer was chromatographed (silica gel with hexane) to give 1,4-diphenyl-1,3-butadiyne (0.166 g, 40%), when tetrakis(triphenylphosphine) palladium (0.108 g, 0.09 mmol) catalyst was used against 1.083 g (4.1 mmol) of vinylic dibromide (57, $\text{R}=\text{C}_6\text{H}_5$).

26.2 Reaction of β, β' -dibromostyrene 57 ($\text{R}=\text{p-MeC}_6\text{H}_4$ -) with $\text{Pd}(\text{dpe})_2$

The crude product was purified by column chromatography (silica gel, hexane eluant) to obtain the corresponding diyne (0.194 g, 1.01 mmol) in 56% yield.

26.3 Reaction of β, β' -dibromostyrene 57 ($\text{R}=\text{p-MeOC}_6\text{H}_4$ -) with $\text{Pd}(\text{dpe})_2$

Column chromatography [silica gel, hexane-ether (30:1)] gave the diyne (0.28 g, 1.07 mmol) showing the yield to be 61%.

26.4 Reaction of 57 ($R=p\text{-ClC}_6\text{H}_4\text{-}$) with $\text{Pd}(\text{dpe})_2$

Column chromatography (alumina-hexane) of the crude from the organic layer gave the diyne (0.187 g, 41%).

26.5 Reaction of 57 [$R=\text{C}_6\text{H}_5\text{CH}=\text{C}(\text{CH}_3)\text{-}$] with $\text{Pd}(\text{dpe})_2$

The diyne (0.194 g, 41%) was obtained by column chromatography (silica gel-hexane) of the crude product.

26.6 Reaction of bifunctionalized vinylic dibromides with $\text{Pd}(\text{dpe})_2$

The mixture was filtered and washed with water and ether. The dark brown solid was dried under vacuum to obtain a compound (P-1).

The compound was further washed with ammonium hydroxide, water and ether and then dried in air.

26.7 Reaction of bifunctionalized vinylic dibromides with palladium acetate

The organic phase was filtered and the black residue was washed with water and ether. The filtrate was rotary evaporated to obtain the product referred as P-2.

27.1 Reaction of 62 with $\text{Pd}(\text{dpe})_2$

The procedure given in (26) was followed. $\text{Pd}(\text{dpe})_2$ (0.119 g, 0.15 mmol) and 62 vinylic dibromide (0.868 g, 2.80 mmol) were reacted at 70°C for 23 hours under carbon monoxide.

The aqueous phase was neutralized with dilute hydrochloric acid and then the organic product was extracted with ether (3x50 mL). The compound after removal of the solvent was found to be 4 tert-butyl-cyclohexylidene acetic acid 64 (0.463 g, 84%).

27.2 Reaction of $C_6H_{13}CH=C(Br)_2$ 57 ($R=C_6H_{13}$ -) with $Pd(dpe)_2$

The catalyst $Pd(dpe)_2$ (0.105 g, 0.13 mmol) and the vinylic dibromide (0.981 g, 3.6 mmol) were reacted for 70 hours at 70°C under a carbon monoxide atmosphere. The aqueous phase afforded 2-nonenic acid 61 (0.312 g, 55%).

28. Reaction of vinylic dibromides with palladium acetate under phase transfer conditions

The procedure is similar to the one given in (26), except that palladium acetate was weighed in air and dissolved in 1 mL of methylene chloride.

29. Reaction of 1,1-dibromoolefins with $Pd(dpe)_2$ in tertiary amyl alcohol

The procedure is essentially the same as (26), with tert-amyl alcohol used as the solvent instead of benzene and the reaction time was less.

Bis [bis(1,2-diphenylphosphino)-ethane]palladium (0.119 g, 0.15 mmol) was dissolved in 1 mL of methylene chloride and then added along with tert-amyl alcohol (15 mL) to a mixture of 30% aqueous sodium hydroxide and benzyltriethylammonium chloride (0.11 g, 0.5 mmol). After 4 hours of stirring under carbon monoxide, 1,1-dibromoolefin 57 ($R=C_6H_5$) (0.441 g, 1.70 mmol) in 2 mL of t-amyl alcohol was added drop-by-drop over a period of one hour. The reaction was run for 19 hours at 50°C.

Workup involved acidification of the aqueous phase with dilute hydrochloric acid and extraction of the product by ether (3x50 mL).

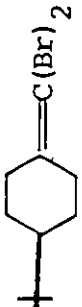
The product was dried over magnesium sulfate, filtered and rotary evaporated. The final compound, isolated in 93% yield, was benzylidenemalonic acid (0.303 g, 1.58 mmol).

Similarly using an aliphatic vinylic dibromide 62 (0.856 g, 2.7 mmol) also gave the corresponding dicarboxylic acid 63 (0.455 g, 1.90 mmol) in 80% yield.

Table 18. Properties of Vinylic Dibromides.

Vinylic Dibromide 57, 62	b.p., °C	¹ H NMR (CDCl ₃), δ	IR (neat), cm ⁻¹	¹³ C NMR (CDCl ₃), δ
C ₆ H ₅ CH=C(Br) ₂	60 (.02mm)	6.96-7.56 (m, aromatic and olefinic CH; main peak at δ7.36)	ν _{CH} 3026 (m), 2984 (m) ν _{C=C} 1594 (s)	
p-CH ₃ -C ₆ H ₄ CH=C(Br) ₂	b	2.30 (s, 3H, CH ₃), 7.10 (d, 2H, aromatic CH, J=8Hz), 7.40 (d, 3H, aromatic CH, J=8Hz); at δ7.37 (s, olefinic CH)	ν _{CH} (Ar) 3008 (m) ν _{CH} (AlI) 2907 (m), ν _{CH} 1612 (m), ν _{C=C} 1600 (sh)	138.54 (s), 136.73 (d), 132.39 (s), 129.05 (d), 128.28 (d), 88.54 (s), 21.36 (q)
p-CH ₃ O-C ₆ H ₄ CH=C(Br) ₂	84-87 (.047mm)	3.74 (s, 3H, CH ₃ O), 6.83 (d, 2H, aromatic CH, J=8.5Hz), 7.23-7.67 (m, 3H, aromatic and olefinic CH)	ν _{CH} 3040 (m), 2995 (s), 2944 (s), ν _{C=C} 1610 (vs)	
p-ClC ₆ H ₄ CH=C(Br) ₂	a	7.0-7.53 (m, aromatic and olefinic CH; 2 doublets with J=9Hz at δ7.19 and 7.38; main peak at δ7.30)	ν _{CH} 3172 (m), 3117 (w), 3089 (w), para substitution 1970 (m), ν _{C=C} 1596 (s)	135.62 (d), 134.35 (d), 133.67 (s), 129.62 (d), 128.64 (d), 90.461 (s)

Table 18. (cont'd)

Vinyllic Dibromide 57,62	b.p., °C	¹ H NMR (CDCl ₃), δ	IR (neat), cm ⁻¹	¹³ C NMR (CDCl ₃), δ
C ₆ H ₅ CH=C(Me)CH=C(Br) ₂	a	2.10 (s, 3H, CH ₃), 6.61 (br. s, 1H, olefinic proton), 7.07 (s, 1H, olefinic proton), 7.23 (s, 5H, aromatic CH)	ν _{CH} (Ar) 3040 (w), 3005 (m), ν _{CH} (Alk) 2950 (m), 2905 (m), ν _{C=C} 1599 (m)	141.10 (d), 136.66 (s), 133.89 (d), 133.40 (s), 129.08 (d), 128.23 (d), 127.20 (d), 87.56 (s), 17.14 (q)
1,4-Br ₂ C=CHC ₆ H ₄ CH=C(Br) ₂	a	7.45 (s, 2H, olefinic protons), 7.53 (s, 4H, aromatic protons)		136.14 (d), 135.22 (s), 128.36 (d), 90.33 (s)
CH ₃ (CH ₂) ₄ CH ₂ CH=C(Br) ₂	63 (.025mm)	0.5-2.47 (br. m, 13H; main peaks at 0.87, 1.3, 2.00 and 2.10), 6.33 (t, 1H, CH ₂ CH=C, J=8Hz)	ν _{CH} (Alk) 2840 (s), 2920 (vs), ν _{C=C} (Br) ₂ 1623 (m)	138.85 (d), 88.51 (s), 33.04 (t), 31.58 (t), 28.75 (t), 27.81 (t), 22.58 (t), 14.06 (q)
	a	0.87 (s, 9H, CH ₃), 1.03-2.33 (m, 7H, aliphatic ring protons), 2.87 (br. s, 1H), 3.07 (br. s, 1H)	ν _{CH} (Alk) 2900-2860 (vs), ν _{C=C} (Br) ₂ 1710 (s), 1628 (w) (in CHCl ₃)	144.90 (s), 81.48 (s), 47.45 (t), 34.61 (t), 32.31 (s), 27.54 (q+d)

a Column chromatography was used to purify it.

b MS, m/e 230 [M]⁺, 215 [M-CH₃]⁺

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CLAIMS TO ORIGINAL RESEARCH

1. The reductive potential of hydride species generated by immobilizing triiron dodecacarbonyl on alumina has not been studied before. The present work is a first application for utilizing this species.
2. The generation of a red hydride of cobalt carbonyl on alumina, to my knowledge, has not been reported before. The application of this in situ generated species for the selective dehalogenation of α -halosulfoxides and the reduction of nitroarenes is also new.
3. The use of molybdenum hexacarbonyl on florasil for desulfurization of oil constitutes a new combination and the results clearly indicate the potential of this promising method.
4. The mechanism of carbonylation of benzyl bromides with dicobalt octacarbonyl under phase transfer catalysis requires the intermediacy of tetracarbonylcobaltate anion. There was a need to study the effect of a stabilizing cyclopentadienyl ligand on a mononuclear cobalt carbonyl for understanding this important reaction.
5. The coupling of vinylic dibromides to form diynes in one step using a palladium (0) catalyst under PIT has not been previously achieved.
6. The dicarbonylation of vinylic dibromides under phase transfer catalysis is original and useful.

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The following articles have been published by the author.

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