Title

HOMOGENEOUS HYDROGENATION OF MODEL-COAL COMPOUNDS

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Publication Date

1982-05-01

LBL-14216

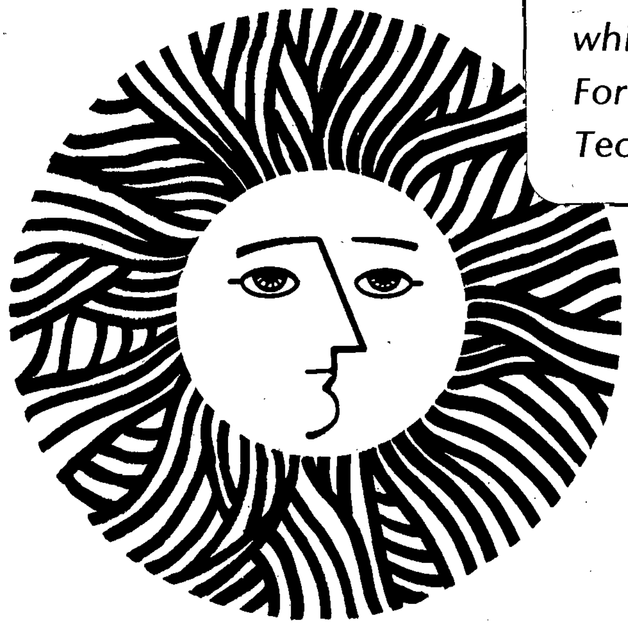
Lawrence Berkeley Laboratory
UNIVERSITY OF CALIFORNIA

ENERGY & ENVIRONMENT DIVISION

HOMOGENEOUS HYDROGENATION OF MODEL-COAL COMPOUNDS

Gregg A. Cremer*, Theodore Vermeulen,
and Richard H. Fish
(*Ph.D. thesis, in part)

May 1982



Prepared for the U.S. Department of Energy under Contract DE-AC03-76SF00098

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LBL-14216

HOMOGENEOUS HYDROGENATION OF MODEL-COAL COMPOUNDS

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*Ph.D. thesis in part. See LBL-14491 for section entitled, "Oxydesulfurization of Coal".

This study was jointly supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division and the Assistant Secretary of Fossil Energy, Office of Coal Research, Liquefaction Division of the U.S. Department of Energy under Contract DE-AC03-76SF00098, through the Pittsburgh Energy Tech. Center.

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Homogeneous Hydrogenation of Model-Coal Compounds

I. INTRODUCTION

Many synthetic fuel processes, such as coal liquefaction and oil shale retorting, lead to hydrogen-deficient liquids which contain a broad distribution of polynuclear aromatic and polynuclear heteroaromatic constituents. Additional hydroprocessing is necessary, primarily to remove sulfur and nitrogen. While it is desirable to hydrogenate only the heterocyclic ring prior to bond rupture, concomitant hydrogenation of other rings and other components may also occur. The ease with which a given molecule is reduced and the position of preferential attack can sometimes be predicted from first principles alone. It is possible, however, to substantially alter the product distribution with the proper selection of catalyst and reaction conditions. Homogeneous catalysts offer the prospect for greater selectivity as well as milder operating conditions when compared to their heterogeneous counterparts. They also afford an opportunity to study the chemistry of hydroprocessing at relatively low temperatures and pressures.

A. Chemical Nature of Coal

Coal is a sedimentary rock primarily composed of carbon, hydrogen, and oxygen, and to a lesser extent sulfur, nitrogen, and mineral matter. Coal formation began when large masses of plant material were transformed into peat under the action of microorganisms and then buried underground by large-scale geological movement. This material was subjected to extreme temperatures and pressures and thus became coalified. Increased severity of these conditions led to increasing coal rank, characterized by higher carbon content and lower hydrogen and oxygen content. Coals are ranked in the following order: peat, lignite (or brown coal), sub-bituminous coal, bituminous coal, and anthracite.

Coal is generally considered to consist of clusters of aromatic centers, connected by ether or alkyl bridges to form a high molecular weight material. Several models for coal structure have been developed (H1, W1, G1, S1). The Shinn model (S1), shown in Figure 1-1, suggests that coal can be converted into liquid products by breaking and capping of both aliphatic and ether linkages. The resulting product contains a broad distribution of aromatic, polyaromatic, and heterocyclic aromatic components.

Most coal-liquefaction processes operate at high hydrogen pressures (>1500 psi) and at pyrolysis temperatures (~450°C). Under these conditions, it is desirable to minimize residence time in order to avoid excessive production of char and gas. This produces a highly aromatic, hydrogen-deficient liquid which requires further upgrading under milder conditions. The types of molecules likely to be present in a coal-derived liquid and their relative abundance is shown in Table 1-1, based on the characterization of lignite, bituminous coal, and anthracite by Hayatsu et al. (H2,H3).

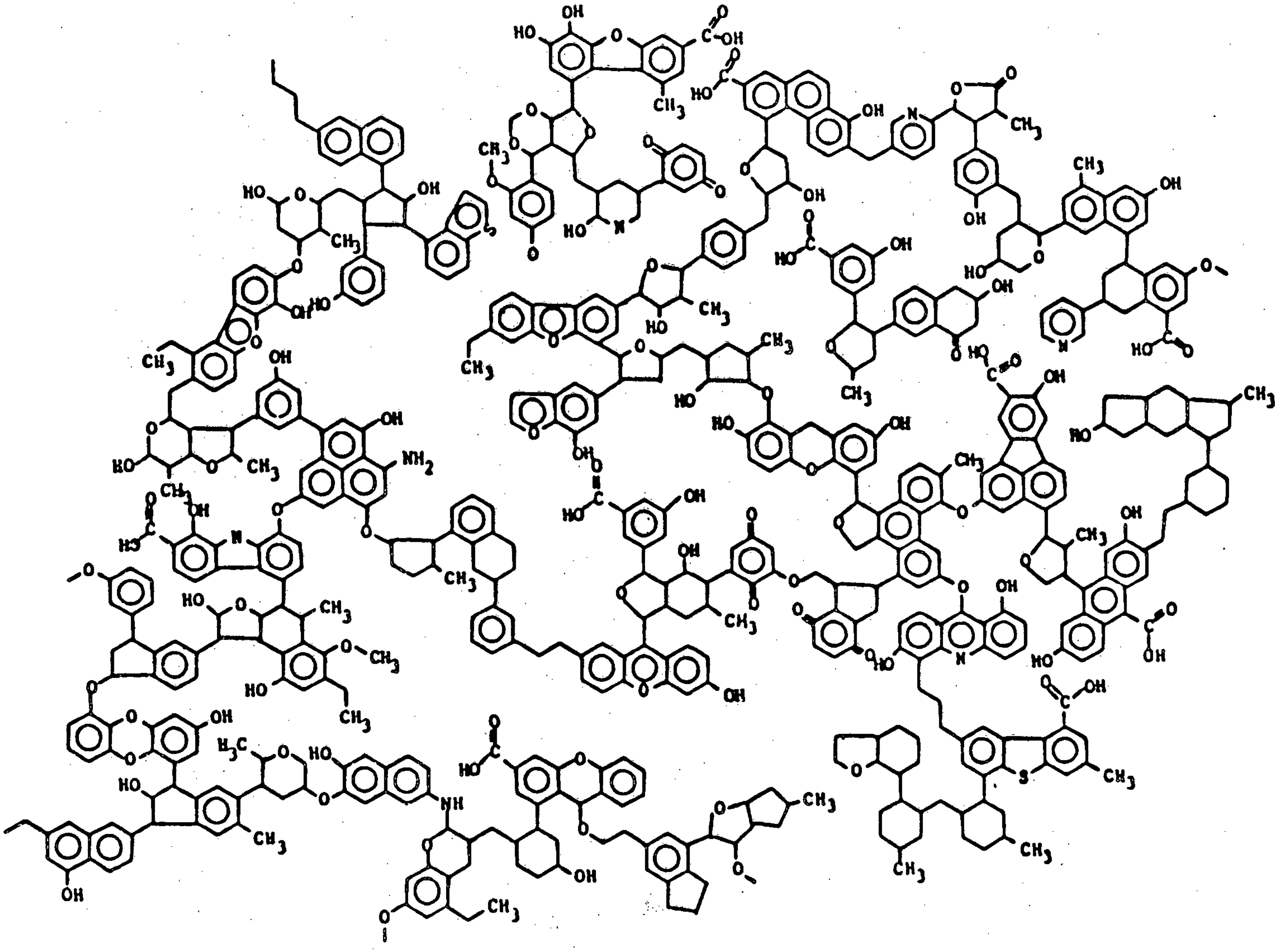

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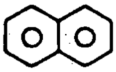
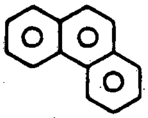
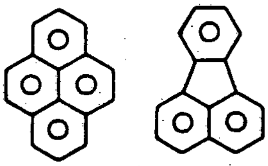
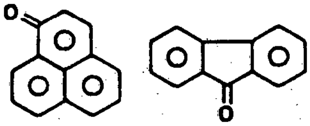
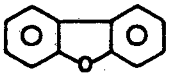
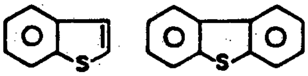
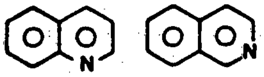
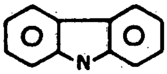
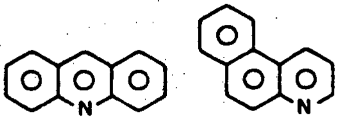
Figure 1-1. A Model of Sub-bituminous Coal Structure (after Shinn, based on work done by Mobil Research Co.)

Table 1-1. Type and abundance of various coal constituents (after Hayatsu et al., references H2, H3).

Structural Unit	Relative Abundance		
	Lignite	Bituminous	Anthracite
	100	100	12
	11	25	8
	0	21	100
	0	5	10
	5	7	80
	3	20	6
	0	10	10
	0	2	3
	0	2	2
	0	5	2
	0	2	18

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The model compounds chosen for this investigation are given in Figure 1-2. A great deal of attention is focused on nitrogen-containing heterocyclic aromatics, because of a pressing need to gain additional understanding of hydrodenitrogenation processes. Anthracene and substituted anthracenes have been used primarily in mechanistic studies of the homogeneous hydrogenation of polynuclear aromatics (PNA's).

B. Metal Carbonyl Chemistry

The chemistry of metal carbonyls, metal carbonyl hydrides, and transition metal complexes in general, has been extensively reviewed (C1,A1,C2,B1,K1,M1,H4). Only a brief summary of their properties, including hydrogenation activity, is presented here.

1. Properties

Transition metals are those elements having partially filled d or f shells. The simplest metal carbonyls are mononuclear of the type $M(CO)_y$ where M is the metal and y is the number of carbon monoxide ligands within the coordination sphere of the metal. Polynuclear carbonyls of the type $M_x(CO)_y$ are also common; with x, the number of metal atoms in the cluster, between 2 and 6. The metal carbonyls used in this study are given in Table 1-2.

It is characteristic of d group transition metals to complex with a variety of neutral molecules including substituted phosphines, arsines, stibines or sulfides, nitric

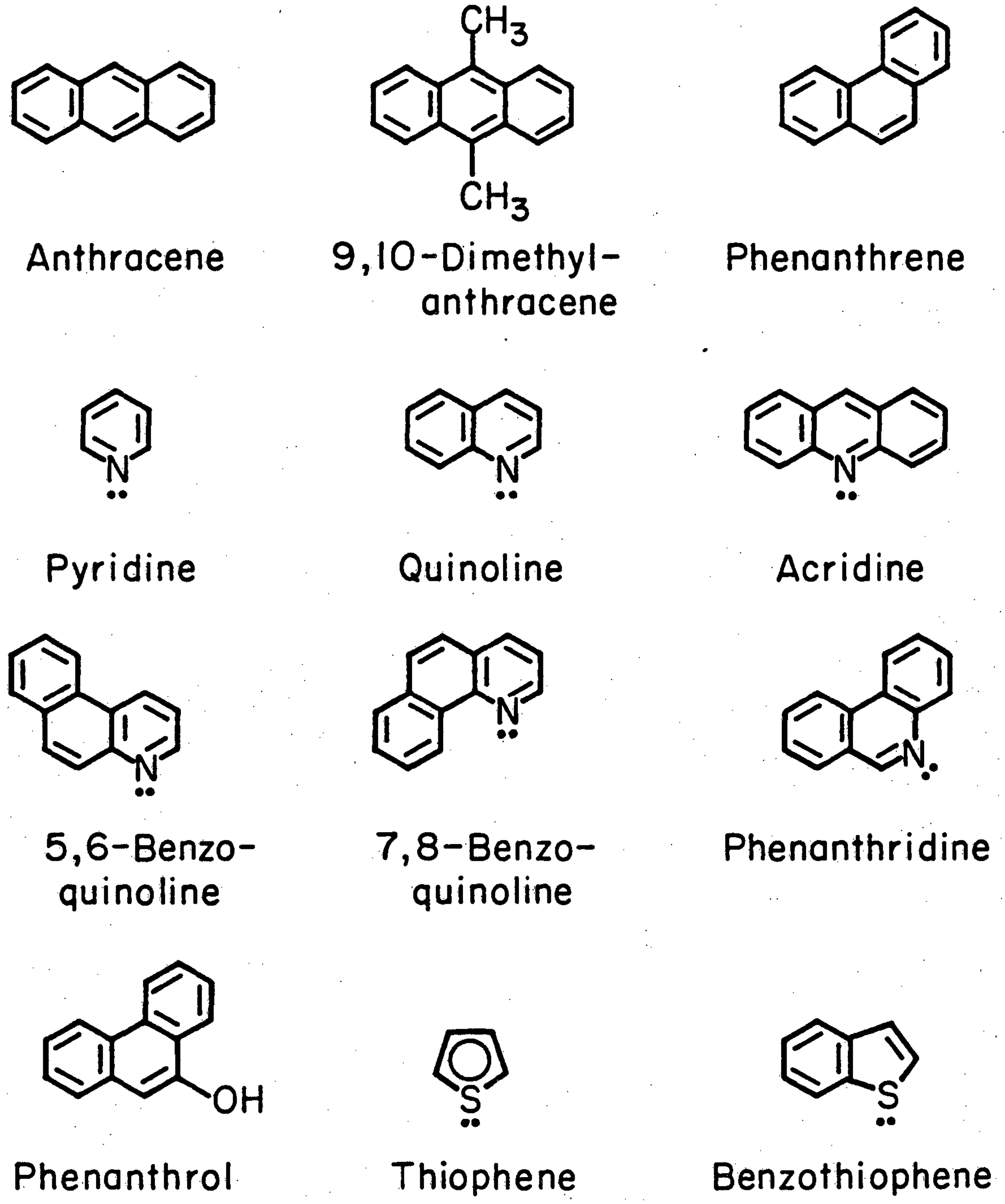

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Figure 1-2. Model coal compounds.

Table 1-2. Metal carbonyls used in this study.

Mononuclear

$Cr(CO)_6$ $Fe(CO)_5$

$Mo(CO)_6$

$W(CO)_6$

Dinuclear

$Mn_2(CO)_{10}$ $Co_2(CO)_8$

$Re_2(CO)_{10}$

Polynuclear

$Ru_3(CO)_{12}$ $Rh_6(CO)_{16}$

$Os_3(CO)_{12}$

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oxide, isocyanides, and pyridine, as well as carbon monoxide. In many of these complexes, the metal atoms are in low oxidation states, stabilized by ligands with vacant π orbitals in addition to lone electron pairs. These vacant orbitals accept electron density from filled metal orbitals to form a type of π bonding that supplements the σ bonding arising from lone pair donation. The high electron density on the metal atom can thus be delocalized on the ligands. The ability of ligands to accept electron density in empty orbitals is termed π- acidity, in the Lewis-acid sense.

Carbon monoxide is a strong π acid but a very weak σ donor. At elevated temperatures, carbonyls tend to dissociate to metal and CO unless they are under a carbon monoxide atmosphere. $Fe(CO)_5$ and $Co_2(CO)_8$ are particularly susceptible, decomposing readily at room temperature and requiring very high carbon monoxide pressures to remain in solution above 100^oC. Replacement of one or more carbon monoxide ligands by strong σ donors, such as substitued phosphines, can substantially increase the stability of the resulting complex. The increased electron density on the metal atom strengthens the back-acceptance by the remaining CO ligands, binding them more tightly. In this investigation, triphenylphosphine (PPh_3) and n-tributylphosphine (PBu_3) were used as stabilizing ligands.

The number of ligands surrounding a metal center can often be calculated by the 18-electron rule, which simply requires that the metal contain 18 electrons in its valence shell (C3). In order to test this rule, one simply takes the number of electrons in the valence shell of the uncomplexed metal, adds or subtracts electrons according to the total charge of the metal complex, and then adds the number of electrons formally contributed to the metal by the ligands. Carbon monoxide and phosphines contribute two electrons each while atomic hydrogen contributes one. Thus, $Fe(CO)_5$, $Fe(CO)_4(PBu_3)$, and $HFe(CO)_4^-$ all satisfy the 18-electron rule. In those compounds where metal-metal bonds are present, each metal is regarded as acting as a one electron ligand to the other. So each ruthenium atom in $Ru_3(CO)_{12}$ also has 18 electrons in its valence shell.

2. Hydride Formation and Hydrogenation

The activation of molecular hydrogen in homogeneous systems by metal complexes and the resulting catalytic activity has received considerable attention (L1,J1,K1,M2,H4). In order that a particular transition metal complex act as a catalyst in the activation of molecular hydrogen, it should form a hydrido complex which has reasonable thermodynamic stability but is also labile enough to react rapidly in solution. Metal-hydrogen bonds may be formed in any of the following three ways:

(1) oxidative addition of H_2 to the metal center; e.g.,

$$2\ Co^{II}(CN)_5^{3-} + H_2 \longrightarrow 2\ Co^{III}H(CN)_5^{3-}$$

or, if preceded by a ligand dissociation step,

$$H_2Ru_4(CO)_{13} \xrightarrow{-CO} H_2Ru_4(CO)_{12} \xrightarrow{+H_2} H_4Ru_4(CO)_{12}$$

(2) heterolytic cleavage of hydrogen and removal of a proton; e.g.,

$$Ru^{III}Cl_6{}^{3-} + H_2 \longrightarrow Ru^{III}HCl_5{}^{3-} + H^+ + Cl^-$$

(3) nucleophilic attack on coordinated CO followed by protonation and loss of CO_2, e.g.

$$Fe(CO)_5 + OH^- \xrightarrow{-CO_2} HFe(CO)_4{}^- \xrightarrow{H_2O \quad OH^-} H_2Fe(CO)_4$$

The electronic effects of ligands on stability and lability of the hydrido-metal intermediate are difficult to predict. Hydrides of transition metals in low valence states are known to be stabilized by acceptors such as carbon monoxide and phosphines. Formation of dihydrides, which are stabilized by more basic phosphine ligands, may be pictured as the interaction of a Lewis base metal center and a Lewis acid hydrogen molecule. Increasing the π acceptor properties of the ligands, therefore, decreases the ease of hydride formation. James (J1) points out that reactivity trends for hydrogenation of organic substrates with dihydride systems have demonstrated increased activity with both increasing and decreasing basicity of phosphines. Phosphite ligands, stronger π acids than corresponding phosphines, generally produce poorer catalysts. In monohydride complexes, introduction of stronger σ donors and weaker π acceptors reduces the acidity of the metal hydride. This has given rise to increased activity of cobalt carbonyl phosphine systems in the homogeneous hydrogenation of polyunsaturated compounds (M3,01).

Many transition metal complexes have been discovered during the last 10-15 years which homogeneously catalyze the hydroformylation and hydrogenation of olefins. All the possible mechanisms for this catalysis appear to have certain common features. Figure 1-3 depicts a simplified mechanism for the homogeneous hydrogenation of an olefin by Wilkinson's catalyst, $RhCl(PPh_3)_3$ (J2,Y1). The initial step involves formation of the dihydride by oxidative addition to the metal center. This is followed by ligand dissociation and binding of olefin to the vacant site. In some instances, the complexation of olefin to the metal center may precede hydride formation. Both routes lead to an organometallic hydride which undergoes stepwise transfer of hydrogen from the metal to the coordinated olefin, forming a metal alkyl. Hydrogenolysis of the metal alkyl produces and alkane and a coordinately unsaturated metal complex which undergoes ligand association to regenerate the original catalyst. Homogeneous hydrogenation of polynuclear aromatics and polynuclear heterocyclic aromatics may proceed in an analogous fashion, but other mechanisms not requiring coordination of the substrate are also possible.

C. Water-Gas Shift Reaction

The reaction of coke, coal, petroleum fractions or

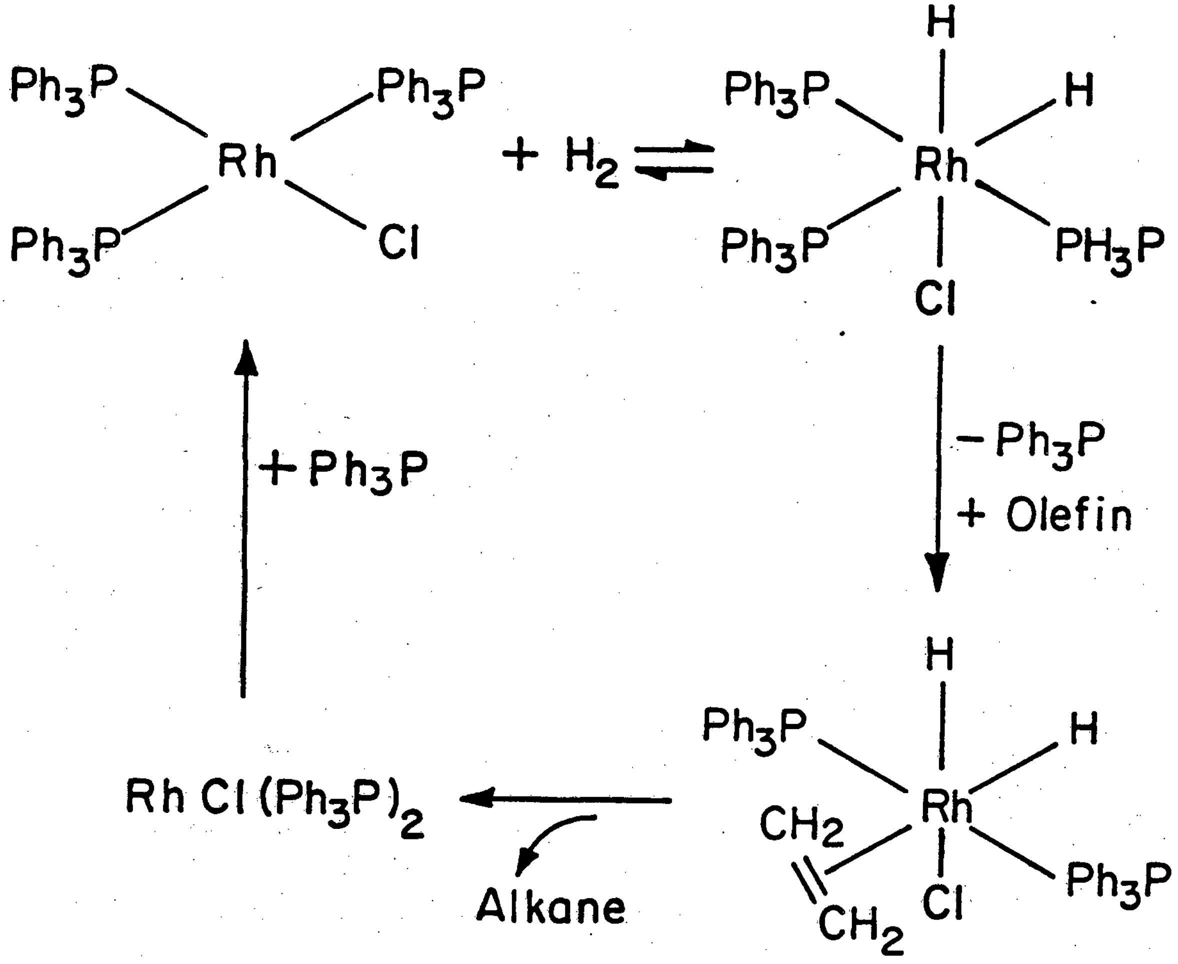

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Figure 1-3. Simplified mechanism for olefin hydrogenation by $RHCl(PPh_3)_3$.

natural gas with water at elevated temperatures produces a mixture of hydrogen and carbon monoxide (with some carbon dioxide) known as water gas. The water-gas shift reaction

$$H_2O + CO \rightleftharpoons H_2 + CO_2$$

used to adjust the H_2/CO ratio of water gas, has found large-scale application in methanation and Fischer-Tropsch synthesis (S2) and in supplying of hydrogen for ammonia synthesis (I1). The production of gaseous liquid hydrocarbon fuels from nonpetroleum sources such as coal requires copious amounts of hydrogen and the shift reaction is an important pathway for the formation of hydrogen from water using the reducing capacity of carbon monoxide.

Commercially, the shift reaction is carried out over solid metal oxide catalysts, the most common being iron oxide promoted by chromium oxide and operating at 350°C. A more active catalyst, however, is based on copper with zinc oxide. When the water is present as steam the thermodynamic equilibrium constant is 385 at 150°C, 51.2 and 250°C, and 12.7 at 350°C. Recent interest has centered around conducting this reaction at much lower temperatures (<200°C) with water present as a liquid and using homogeneous catalysts to accelerate the reaction. Under these conditions the equilibrium constant is 4552 atm at 150°C, 5233 atm at 250°C, and 5762 atm at 350°C. With the water present in a condensed state, the shift reaction is highly favored from a free energy standpoint because of the large positive entropy change, even though the reaction is mildly endothermic.

Definite demonstrations of homogeneous catalysis of the water-gas shift reaction by identifiable metal complexes were first reported in 1977. Laine et al. (L2) found catalysis by triruthenium dodecacarbonyl in alkaline aqueous ethoxyethanol; Eisenberg and co-workers (C4) used $(Rh(CO)_2Cl)_2$ in acetic acid/HCl/NaI medium, and Pettit and co-workers (K2) described catalysis by several metal carbonyls in 25% aqueous trimethylamine. Additional shift catalysis based on metal carbonyls in alkaline solution (F1,K3,U1,K4,D1,F3), in amine solutions (F1), and in acid solutions (F2,F3) has since been reported. In addition, catalysis by mixed metal complexes (F1,C5), a platinum phosphine complex (Y2), and $(Ir(diene)L_2)^+$ complexes (K5) has been described.

Figure 1-4 illustrates a mechanistic sequence proposed by Pettit et al. (K2) for the metal-carbonyl-catalyzed shift reaction in the presence of 25 wt-% aqueous trimethylamine. The cycle consists of the following key steps: (1) nucleophilic attack of hydroxide (or water) on coordinated CO to give the hydroxycarbonyl intermediate, (2) decarboxylation to give the metal hydride anion, (3) proton abstraction to form the dihydride, (4) reductive elimination of H_2, and (5) coordination of another CO. Studies of $Fe(CO)_5$ in alkaline aqueous methanol (K3) suggest that this is indeed a plausible mechanism. In situ infrared studies indicated the pres-

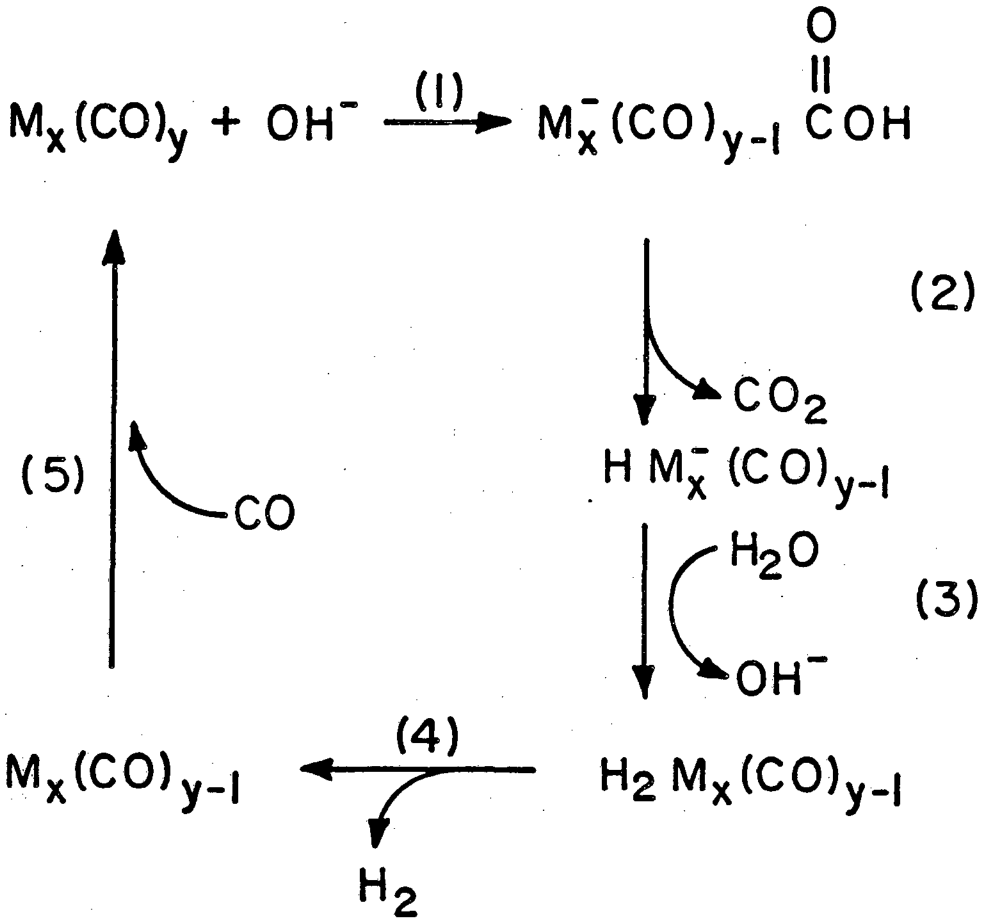

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Figure 1-4. Mechanism for the metal carbonyl-catalyzed water gas shift (after Pettit et al., reference K2) ence of only the mononuclear species $Fe(CO)_5$ and $HFe(CO)_4^-$, and rate studies showed H_2 production to be independent of CO partial pressure. Given the tendency of the system to be less active at low pH, the rate-limiting step was presumed to be the activation of coordinated CO by nucleophilic attack.

$Ru_3(CO)_{12}$ has been found by Ford and co-workers (F2,U1) to behave in a more complicated manner. A number of intermediate cluster complexes have been identified, including $HRu_3(CO)_{11}^-$, $H_3Ru_4(CO)_{12}^-$, $Ru_3(CO)_{12}$, and $HRu_4(CO)_{12}^-$. The first two forms constitute most of the ruthenium in solution, with $H_3Ru_4(CO)_{12}^-$ predominating as the H_2/CO ratio increases. The composition of the reacting solution is independent of whether the ruthenium source is $Ru_3(CO)_{12}$, $H_2Ru_4(CO)_{13}$, or $H_4Ru_4(CO)_{12}$, demonstrating that these clusters interconvert under the reaction conditions. The observed first-order dependence of reaction rate on CO partial pressure points to distinct mechanistic differences between the ruthenium and iron systems. Ford (F3) has interpreted this to mean that the CO must be directly participating in the reductive elimination of H_2 since coordination of CO to a coordinately unsaturated metal (step (5) of Figure 1-4) is unlikely to be rate-limiting. In the ruthenium system steps (4) and (5) of Figure 1-4 would be combined into a single reaction:

$$H_2M_x(CO)_{y-1} + CO \longrightarrow M_x(CO)_y + H_2$$

Work on mixed iron/ruthenium carbonyl systems by Ford and co-workers (F2) shows that these catalysts are considerably more active in basic solutions than either of the individual carbonyls. The principal catalytic species is believed to be $H_2FeRu_3(CO)_{12}$. The synergistic behavior of the mixed-metal system may lie in the stability of the hydridocarbonyl cluster, $H_4FeRu_3(CO)_{12}$ (K6). Greater activities of the Fe/Ru carbonyls and a variety of individual carbonyls have been observed in aqueous amine solutions, compared with alkali (K2,F2). It is possible that the amines are participating in direct attack on coordinated carbonyl as previously reported for $Fe(CO)_5$ (E1).

Homogeneous catalysis of the shift reaction by Group 6B carbonyls, $Cr(CO)_6$, $Mo(CO)_6$, and $W(CO)_6$ has been independently investigated by two research groups (K4,D1). King and co-workers (K4) suggest the following mechanism:

$$CO + OH^- \xrightarrow{\text{fast}} HCO_2^- \qquad \text{(a)}$$

$$M(CO)_6 \rightleftharpoons M(CO)_5 + CO \qquad \text{(b)}$$

$$M(CO)_5 + HCO_2^- \longrightarrow M(CO)_5HCO_2^- \qquad \text{(c)}$$

$$M(CO)_5 + HCO_2^- \longrightarrow HM(CO)_5^- + CO_2 \qquad \text{(d)}$$

$$HM(CO)_5^- + H_2O \longrightarrow H_2M(CO)_5 + OH^- \qquad \text{(e)}$$

$$H_2M(CO)_5 \longrightarrow M(CO)_5 + H_2 \qquad \text{(f)}$$

$$M = Cr, Mo, W$$

This scheme differs from the one presented in Figure 1-4 in several ways. First, it involves a CO dissociation step needed to explain the observed inhibition by carbon monoxide. Then the metal pentacarbonyl reacts with formate ion in step (c) to give a metal formate anion rather than a hydroxycarbonyl. Loss of CO_2, however, results in the same metal hydride anion predicted in Figure 1-4. While production of formate ion according to step (a) unquestionably occurs in basic medium, Darensbourg et al. (D1) claim that its reaction with a coordinately unsaturated metal carbonyl is not an important step; they propose a shift mechanism identical with Figure 1-4, and conclude that formation of a metal formate anion only occurs by reaction of the metal hydride anion with CO_2, i.e. the reverse of step (d). For the Group 6B carbonyls, the ordering of shift activity is $Cr(CO)_6 > Mo(CO)_6 > W(CO)_6$ (K4).

Pettit's work (K2) with a variety of metal carbonyls in trimethylamine suggests the following ordering of catalytic activity for the shift reaction: $Ru_3(CO)_{12} \gg Rh_6(CO)_{16} > Ir_4(CO)_{12} > Os_3(CO)_{12} > Fe(CO)_5$. Laine (L3) observes a slightly different ordering with consistently reduced activities in aqueous KOH: $Rh_6(CO)_{12} > Ru_3(CO)_{12} > Fe_3(CO)_{12} > Ir_4(CO)_{12} > Os_3(CO)_{12}$.

D. Hydrogenation Under Water Gas Shift Conditions

The use of carbon monoxide and water to perform reactions normally requiring an independent hydrogen source dates back to the work of Walter Reppe and co-workers in Germany during the 1930's and early 1940's. Typically Reppe used iron, cobalt, and nickel carbonyl complexes to convert an olefin to the next higher aldehyde or alcohol (hydroformylation) through reaction with CO and H_2O (R1). Interestingly, $Fe(CO)_5$ is a very poor catalyst for the hydroformylation reaction when hydrogen is used, whereas under Reppe's conditions it is an active catalyst at relatively mild temperatures and pressures (B2). Recently, several research groups have investigated the possibility of using other Group 8 carbonyl complexes as catalysts for Reppe reactions. Pettit and co-workers have used iron, rhodium, ruthenium, osmium, and iridium to hydroformylate ethylene (K2) and also to reduce aromatic nitro compounds to amines (C6). Laine (L3) also has reported hydroformylation and hydroxymethylation using essentially the same catalysts. In one instance he begins with $Fe_3(CO)_{12}$, but finds that it is immediately converted to $Fe(CO)_5$ under the reaction conditions. Whereas Laine uses aqueous alcoholic potassium hydroxide, Pettit uses trimethylamine, which apparently results in a slightly different ordering of the hydroformylation activity. A qualitative ordering of Pettit's observed hydroformylation activities is: $Rh_6(CO)_{16} > Ir_4(CO)_{12} > Ru_3(CO)_{12} > Fe(CO)_5 > Os_3(CO)_{12}$. In contrast, Laine reports the following ordering: $Rh_6(CO)_{16} > Ru_3(CO)_{12} > Fe(CO)_{12} > Ir_4(CO)_{12} > Os_3(CO)_{12}$.

Pettit et al. (K2) report that when $Fe(CO)_5$ is heated to 100°C in aqueous KOH, IR analysis indicates that $HFe(CO)_4^-$ is the only metal carbonyl species present in solution. The pH is initially 12.0 but decreases as CO reacts with hydroxide ion to give formate ion. The formation of propanol from ethylene is observed only when the pH drops to around 10.7. However, acetaldehyde is immediately reduced to ethanol at pH 12.0. These results lead Pettit and co-workers to propose the following reaction sequence:

$$Fe(CO)_5 + OH^- \xrightarrow{-CO_2} HFe(CO)_4^- \xrightarrow{H_2O} H_2Fe(CO)_4$$

The investigators concluded that the anion $HFe(CO)_4^-$ is capable of reducing aldehydes, but that the conjugate acid $H_2Fe(CO)_4$ is required to initiate reaction with the olefin. they further conclude that CO and H_2O provide a reducing system superior to molecular hydrogen, considering it easier to form $H_2Fe(CO)_4$ by reaction of $Fe(CO)_5$ and water than from $Fe(CO)_5$ and H_2. This is consistent with previous reports that $Fe(CO)_5$ is an effective catalyst for reduction of polyunsaturated fats only at very high hydrogen partial pressures (02,F3). Under hydrogenation conditions, then, activation of substrate occurs before activation of molecular hydrogen which is the rate-determining step (F4).

Pettit's group has also investigated the reduction of nitrobenzene to aniline in the presence of CO, base, and H_2 (C7). Under these conditions, hydrogen may come from either water or dihydrogen. The reaction pathways are shown in Figure 1-5. The reduction of nitrobenzene to aniline is considered an electron-transfer type reaction in which the anionic metal hydride is the principal electron donor. The

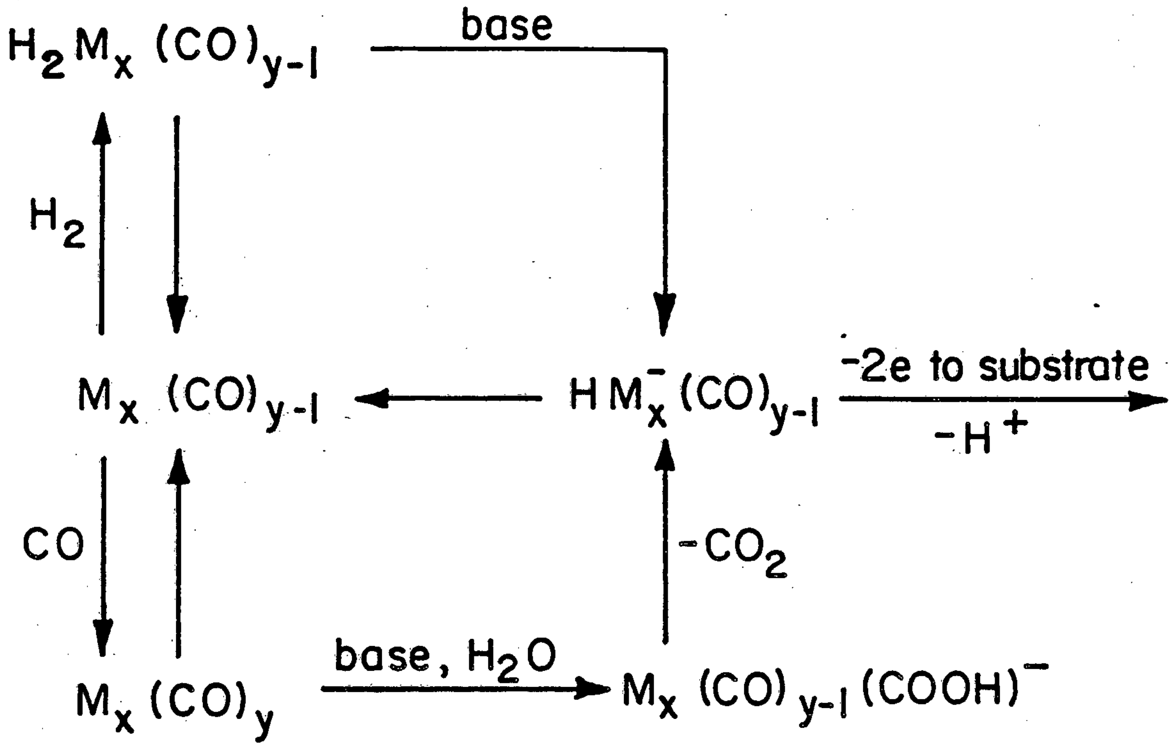

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Figure 1-5. Pathways for reduction with H_2 and CO (after Pettit et al., reference C7).

catalysts shown to be effective in the presence of CO and H_2O (C6) display widely divergent behavior when H_2 is used (C7). As with hydroformylation, $Fe(CO)_5$ is very active with CO and base, but inactive when H_2 is employed. Interestingly, $Os_3(CO)_{12}$ utilizes H_2 when no CO is present but when CO is added only the CO component is used for the reduction. It is therefore reasoned that $Os_3(CO)_{11}$ ($M_x(CO)_{y-1}$ in Figure 1-5) prefers to undergo coordination with CO rather than oxidative addition to H_2. $Ir(CO)_4$ and $Rh_6(CO)_6$ reportedly utilize both the CO and H_2 components in the reduction of nitrobenzene to aniline. At lower temperatures there is a preference for utilization of CO; but as the temperature is increased, so is the relative consumption of hydrogen, suggesting that oxidative addition of H_2 to the metal has a higher activation energy.

Olefin hydrogenation by carbon monoxide and water using a platinum chloride-tin chloride catalyst has been recently reported by Eisenberg and co-workers (C8). Ethylene and propylene are reduced to ethane and propane, but no hydroformylation occurs. When hydrogen is added, reaction proceeds at the same rate as in the absence of H_2 which again illustrates that reaction with CO and H_2O is a more facile path for forming the intermediate hydride than reaction with molecular hydrogen.

E. Homogeneous Hydrogenation of Polynuclear Aromatics

The use of homogeneous catalysts to hydrogenate polynuclear aromatics dates back to the 1950's with the observation by Friedman et al. (F5) that such compounds are reduced with high selectivity in the presence of $Co_2(CO)_8$ and synthesis gas at 3000 psi or more. Anthracene is reduced quantitatively to 9,10-dihydroanthrace at 135°C, while other aromatic compounds are more difficult to hydrogenate. After 5 hours at 200°C, pyrene yields 69% 4,5-dihydropyrene; naphthalene gives 16% tetralin, 2-methylnaphthalene gives 43% methyltetralins; and phenanthrene, which is more refractory, gives only 8% di-and tetrahydrophenanthrene. Subsequently Taylor and Orchin (T1) demonstrated that anthracene is reduced to nearly equal amounts of cis and trans dihydro products in the presence of $Co_2(CO)_8$. Feder and Halpern (F6) have interpreted these results as evidence for a free-radical mechanism illustrated in Figure 1-6. They point out that a conventional mechanism involving an intermediate organocobalt complex should lead to concerted cis addition and hence, to only one isomer. On the basis of Colson's work (C9), the relative reactivities of the different compounds can be explained in terms of radical localization energies. The reduced localization energy of anthracene at the 9-position therefore accounts for the pronounced reactivity of the center ring and leads to the prediction that substituted rings should be more reactive than unsubstituted ones. Recently Derencsenyi (D2) found that $Mn_2(CO)_{10}$ catalyzes the hydrogenation of anthracene to 9,10-dihydroanthracene; Halpern and co-workers (S3) have

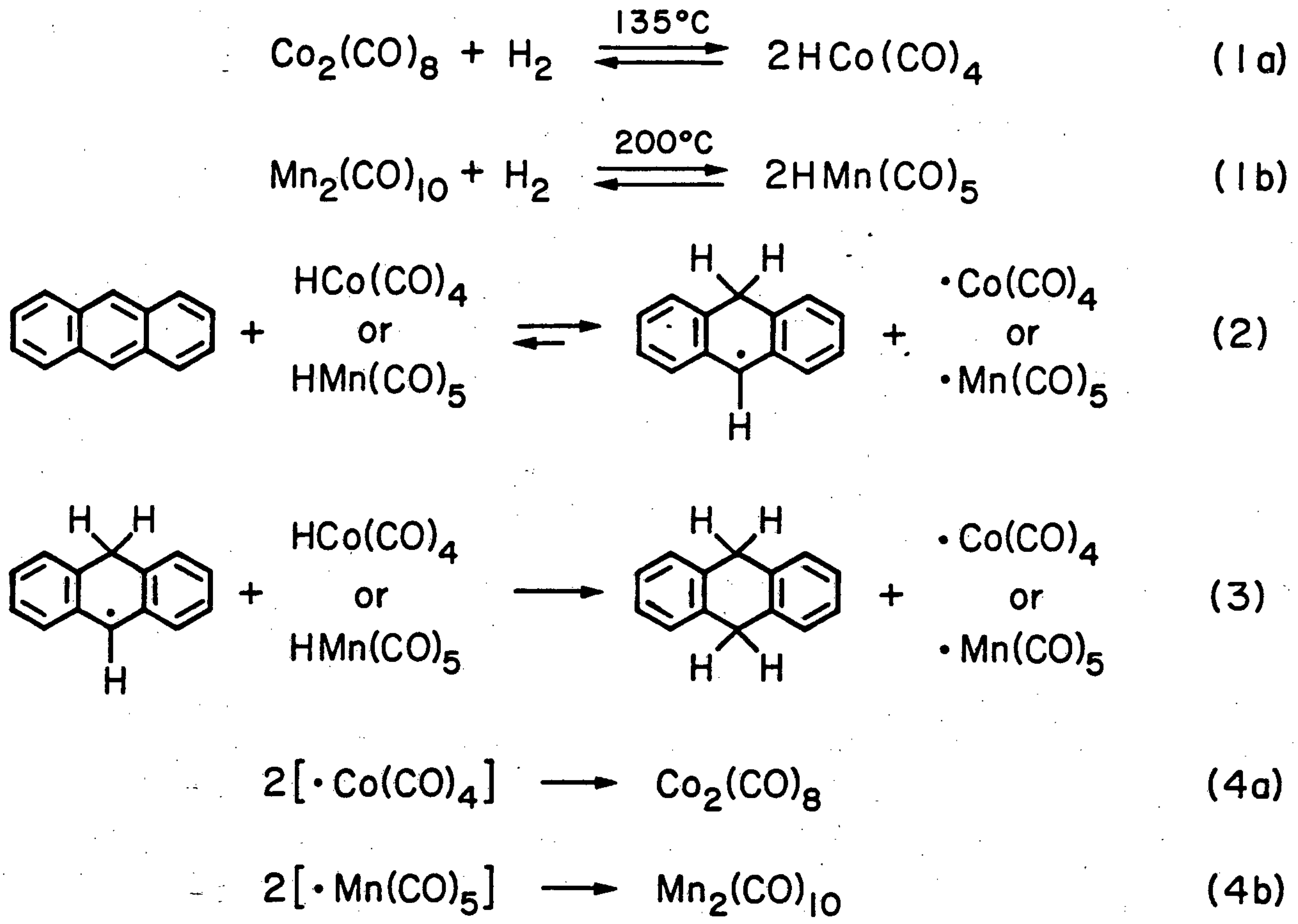

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Figure 1-6. Free-radical mechanism for hydrogenation of anthracene to 9,10-dihydroanthracene (after Feder and Halpern, reference F6).

since proposed that $HMn(CO)_5$ operates in a manner analagous to $HCo(CO)_4$.

In more than 20 years since the first work with $Co_2(CO)_8$, only a handful of catalysts have been reported which will promote homogeneous hydrogenation of aromatics. Apparently, unlike $Co_2(CO)_8$, many catalysts form an organometallic complex, and, as Bennett suggests (B3), aromatics may not bind sufficiently well to the metal atom in the crowded environment provided by the other ligands.

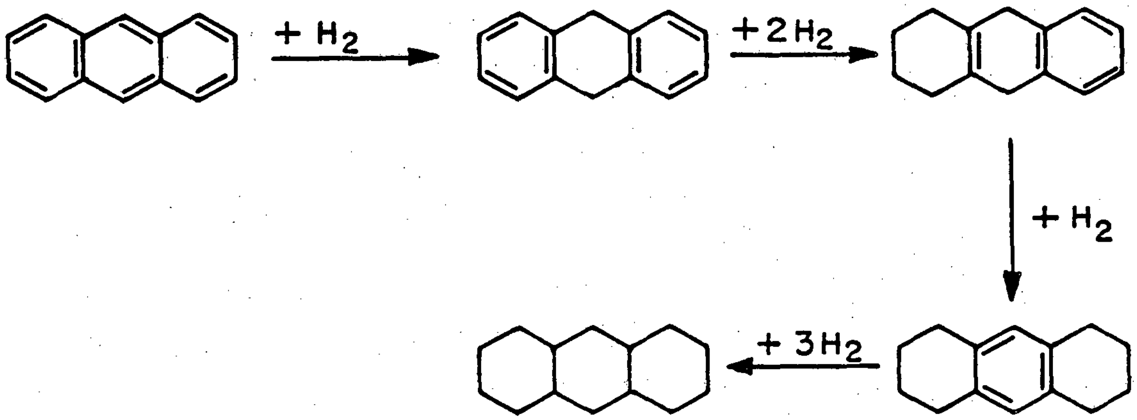
Efimov et al. (E2) have observed that several aromatic compounds are hydrogenated in the presence of a rhodium complex of N-phenylanthranilic acid, and they report the following sequence of reactivities: anthracene > phenanthrene > naphthalene > pyrene > benzene; anthracene is reduced exclusively to 1,2,3,4-tetrahydroanthracene. Similarly, Russell et al. (R2) have reported hydrogenation of benzene to cyclohexene and anthracene to tetrahydroanthracene; with another rhodium complex, $[RhCl_2(\eta^5\text{-}C_5Me_5)]_2$. Base is required as a co-catalyst. They claim that heterolytic cleavage of hydrogen occurs, and that the role of the base is to tie up the HCl generated and promote the formation of rhodium-hydrido species. Bennett (B2) has investigated an isoelectronic ruthenium (II) complex, $[RhCl_2(\eta^6\text{-}C_6Me_6)]_2$, and found it to be extremely active for benzene hydrogenation. He has yet to characterize its activity towards polycyclic aromatics.

Muetterties and co-workers (M4,M5,R3,S4) have shown that η^3-allyl cobalt phosphite complexes such as η^3-$C_3H_5Co(P(OCH_3)_3)_3$ will catalyze homogeneous hydrogenation of aromatics and PNA's at room temperature and 1 atm hydrogen pressure. Anthracene may be hydrogenated all the way to perhydroanthracene (S4), and, interestingly, hydrogen is transferred to benzene with exclusive cis stereochemistry (M5). An unfortunate feature of this catalyst is that it is readily deactivated above 25°C, due to irreversible hydrogenolysis of the η^3-allyl ligand forming propene. Grey et al. (G2,G3) have recently synthesized an anionic ruthenium hydride complex, $(Ph_3P)_2(Ph_2P\overline{C_6H_4)Ru}H_2^-K^+ \cdot C_{10}H_8 \cdot (Et_2O)$, which hydrogenates anthracene to 1,2,3,4-tetrahydroanthracene with 98% selectivity at 100°C. The relative ease with which other polynuclear substrates are hydrogenated is as follows: anthracene > naphthalene > 2-methylnaphthalene > phenanthrene. They report that the rate of hydrogenation of PNA's appears to be unrelated to the anionic character of the catalyst, and suggest that hydrogenation probably proceeds via a conventional π-coordination mechanism. It is interesting to note that for this system naphthalene is more reactive than its substituted derivative.

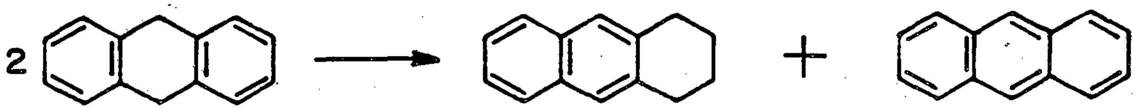
Homogeneous hydrogenation of polynuclear heteroaromatics has been less thoroughly investigated. Jardine and McQuillin (J3) have used N,N'-dimethylformamide (DMF) solutions of a rhodium (II) complex, $py_2(DMF)RhCL_2(BH_4)$, to catalytically hydrogenate quinoline. Derencsenyi (D2) has also reported the reduction of quinoline in the presence of $Mn_2(CO)_8(PBu_3)_2$ at 200°C. In both instances, only the heterocyclic ring was hydrogenated to yield 1,2,3,4-tetrahydroquinoline. Of the previously described aromatic hydrogenation catalysts, only $Co_2(CO)_8$ has been thoroughly studied with compounds containing a heteroatom. Greedfield et al. (G4) found that thiophene could be partially reduced to thiolane in the presence of $Co_2(CO)_8$ at elevated temperatures (180°-190°C) and pressures (5800-6700 psi, $2H_2$:1CO); reaction times on the order of several hours were required although substituted thiophenes were observed to be significantly more reactive. Pino and Ercoli (P1) have used $Co_2(CO)_8$ for catalytic conversion of pyridine to N-formyl and N-methyl piperidine; no piperidine was detected in the final products, and it appears that hydroformylation was followed by reduction of the aldehyde group to hydroxymethyl and then to methyl, and finally complete reduction of the ring.

F. Heterogeneous Hydrogenation of Polynuclear Aromatics

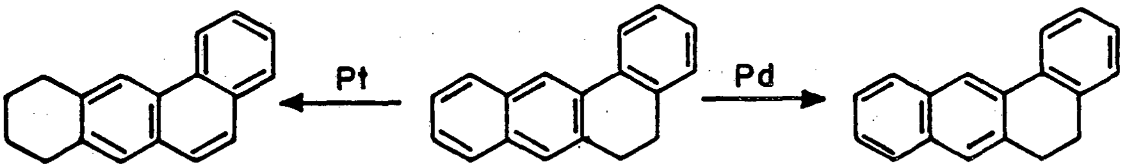
Hydrogenation of PNA's and PNHA's by heterogeneous catalysts has been studied extensively. Structures containing two or more fused benzene rings may undergo hydrogenation to form a variety of products. Selectivity in the partial saturation of fused ring systems depends on both the substrate structure and the catalyst. Rylander (R4) reports that the descending order of selectivity for conversion of naphthalene to tetralin for noble metals is Pd > Pt > Rh > Ir > Ru. Naphthalene is reduced to tetralin over molybdenum oxide or sulfide or tungsten oxide, at temperatures of 400° - $450^{\circ}C$ and hydrogen pressures of about 100 atmospheres (E2). With nickel catalysts, the hydrogenation of naphthalene may proceed only as far as tetralin, or the tetralin may be further hydrogenated depending on the pressure, temperature, and activity of the nickel (L4,W2,M6). Fisher (F7) found that when 2-methylnaphthalene was hydrogenated over nickel only the non-substituted ring was reduced, forming 6-methyltetralin instead of 2-methyltetralin. Naphthols have been hydrogenated over nickel and copper chromite to yield both tetrahydronaphthol and decahydronaphthol, with the hydroxy-substituted ring being the most readily reduced (M6). Stork (S5), however, found that the non-substitued ring could be preferentially reduced in the presence of acid, while a basic medium favored reduction of the substituted ring. Sugino and Outi (S6), after thorough study of anthracene hydrogenation over cupric oxide, propose the following reaction sequence:



Similar studies have been made with platinum, nickel, molybdenum sulfide, molybdenum oxide, and copper chromite catalysts but do not note formation of the hexahydro intermediate (E3). Cowen (C10) reports that palladium tends toward selective hydrogenation of a terminal ring of anthracene while platinum and rhodium produce almost exclusively 9,10-dihydroanthracene. Eisenbraun (E4) proposes that the formation of 1,2,3,4-tetrahydroanthracene may result from disproportionation of 9,10-dihydroanthracene, i.e.

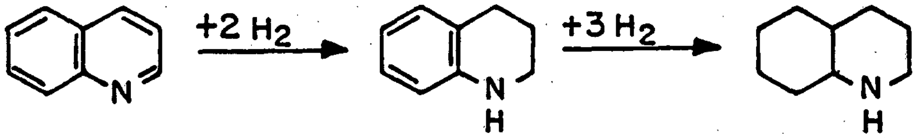


Fu and Harvey (F8) have examined the hydrogenation of various polycyclic aromatic hydrocarbons, and have found that while palladium regiospecifically reduces the electron-rich K-region bond, the region of minimal bond delocalization energy, platinum attacks elsewhere. Hydrogenation of benz(a)anthracene over 10% palladium on carbon yields 97% 5,6-dihydrobenzanthracene, whereas over platinum catalysts 8,9,10,11-tetrahydrobenzanthracene, is obtained in 95% yield.



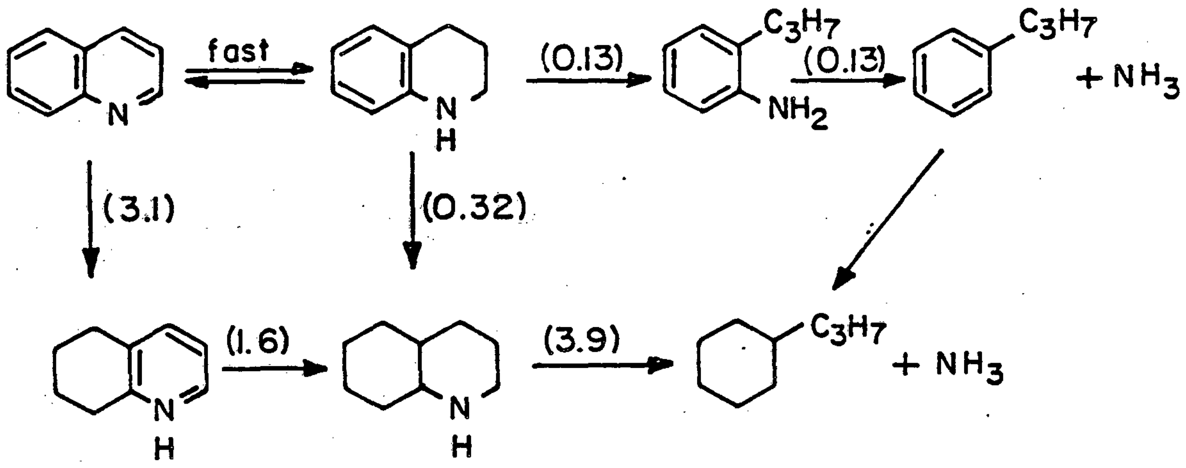
Rylander (R4) claims that hydrogenation becomes more difficult as substitution on an aromatic ring increases. Lozovoy and Senyavin (L5) have studied the relative rates of hydrogenation of naphthalene, anthracene, and chrysene over tungsten sulfide, molybdenum sulfide and nickel-alumina. In all three cases they found that the rate of reduction of naphthalene decreases as cyclohexane rings are fused to it, while the rate of reduction of the benzene ring itself is increased under similar circumstances. Hence naphthalene is much more reactive than tetrahydroanthracene, but octahydroanthracene is more reactive than tetralin, which in turn is more reactive than benzene. Interestingly, octahydrochrysene is even less reactive than benzene.

Heterogeneous hydrogenation of polynuclear heteroaromatics generally results in preferential reduction of the heterocyclic ring regardless of the catalyst. At 110 atmospheres of hydrogen, the reduction of quinoline over nickel at 240°C was observed to proceed through 1,2,3,4-tetrahydroquinoline to decahydroquinoline (A2).



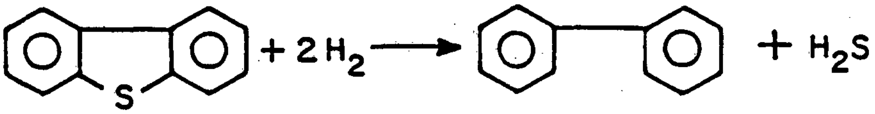
Similar results were obtained at reduced temperatures (25° to 50°C) in acidic media (H5). Von Braun and co-workers (V1,V2), studying the influence of methyl substitution on the formation of tetrahydroquinolines, found that increased methyl substitution on either ring makes its reduction more difficult.

Katzer and co-workers (K7,S7,B4) have investigated the hydrodenitrogenation of quinoline and acridine over nickel-tungsten, nickel-molybdenum, and cobalt-molybdenum on alumina. They present the following reaction network for quinoline with the pseudo first-order rate constants on nickel-molybdenum at 350°C and 34 atm given in parentheses.



Hydrogenation of the heteroaromatic ring occurs rapidly, and the proportions of quinoline and 1,2,3,4-tetrahydroquinoline therefore conform to the thermodynamic equilibrium. The other ring hydrogenation steps are much slower. Conversion of o-propylaniline, in most cases, appears to involve partial hydrogenation of the benzene ring prior to C-N bond scission (N1). Conversion of 1,2,3,4-tetrahydroquinoline to o-propylaniline, or of decahydroquinoline to n-propylcyclohexane and NH_3, clearly involves C-N bond scission. While most nitrogen removal occurs via decahydroquinoline, the pseudo first-order rate constants show that all reactions are kinetically important and no one reaction is rate limiting. Cocchetto and Satterfield (C11) point out that hydrogenation of the heterocyclic ring is thermodynamically the most difficult step. An increase in temperature increases the kinetic rate constants but decreases the equilibrium constant for the first step and reduces the partial pressure of 1,2,3,4-tetrahydroquinoline. A thermodynamic limitation therefore exists on the degree of C-N bond scission that can occur without complete saturation of both rings. Addition of H_2S enhances the rate of nitrogen removal by facilitating the conversion of 1,2,3,4-tetrahydroquinoline to o-propylaniline (N1).

The acridine reaction network is more complex and less thoroughly understood than quinoline hydrodenitrogenation. Nevertheless, Katzer and co-workers (B4) claim that saturation of all three aromatic rings necessarily precedes C-N bond scission. By contrast, desulfurization of dibenzothiophene proceeds via selective hydrogenolysis of the carbon-sulfur bonds. Katzer et al. (K7) report that over a cobalt-molybdenum catalyst at 300° - 350°C, the primary reaction products are biphenyl and H_2S.



G. Ruthenium Carbonyl Hydrides

Some hydrido-metal-carbonyl cluster complexes can be prepared by direct reaction with molecular hydrogen under relatively mild conditions. $H_3Re_3(CO)_{12}$ and $H_4Re_4(CO)_{12}$, $H_2Os_3(CO)_{10}$ and $H_4Os_4(CO)_{12}$, $H_4Ru_4(CO)_{12}$ are derived in high yields and high purity form $Re_2(CO)_{10}$, $Os_3(CO)_{12}$, and

$Ru_3(CO)_{12}$ respectively (K8). These transformations are mechanistically complex, generally requiring the buildup of tetranuclear clusters starting from the trinuclear species. They also involve substitution of coordinated CO by coordinated H_2. The reactions have been found to be reversible, although the pertinent thermodynamic parameters have not been established; for triruthenium dodecacarbonyl,

$$4Ru_3(CO)_{12} + 6H_2 \rightleftharpoons 3H_4Ru_4(CO)_{12} + 12CO$$

Preparation and identification of $H_4Ru_4(CO)_{12}$ date back to the work of Piacenti and co-workers (P2) in 1970. They found that $Ru_3(CO)_{12}$ remains unaltered after 24 hours at temperatures below 80°C, in the presence of 120 atm hydrogen. At 100° - 110°C with hydrogen pressures greater than 50 atm, the IR spectrum showed a weakening of the $Ru_3(CO)_{12}$ bands and the appearance of new bands characteristic of $H_4Ru_4(CO)_{12}$. If the reactor was purged several times and recharged with pure hydrogen, $Ru_3(CO)_{12}$ was quantitatively converted to $H_4Ru_4(CO)_{12}$. Addition of carbon monoxide showed the appearance of a new species, $Ru(CO)_5$, along with $Ru_3(CO)_{12}$ and $H_4Ru_4(CO)_{12}$. The mononuclear ruthenium complex forms according to the reaction

$$Ru_3(CO)_{12} + 3CO \rightleftharpoons 3Ru(CO)_5$$

These same investigators reacted $H_4Ru_4(CO)_{12}$ with triphenylphospine (PPh_3), and found products deriving from the substitution of one, two, three, or four carbon monoxide groups. The degree of substitution depended primarily on reaction temperature and carbon monoxide partial pressure. Kaesz and co-workers (K9) have since reported the formation of $H_4Ru_4(CO)_{12}$ under much milder conditions than those used by Piacenti et al. (P2). They obtained $H_4Ru_4(CO)_{12}$ in higher yield by reaction of H_2 at atmospheric pressure with $Ru_3(CO)_{12}$ in refluxing octane.

Tetraruthenium dodedecacarbonyl tetrahydride and some of its phosphine-substituted derivatives have recently been used by Fediani et al. (F9) as homogeneous catalysts in the hydrogenation of cyclohexanone to cyclohexanol at 100°C and 100 atm H_2. They report that $H_4Ru_4(CO)_{12}$ is a more active hydrogenation catalyst than any of its phosphine-substituted derivatives. Progressive replacement of carbonyl ligands by phospine, however, resulted in increasing activity, with triphenylphosphine substitution giving a more active catalyst than n-tributylphosphine. In contrast, $HCo(CO)_4$ has been observed to be a much less active catalyst for aldehyde and ketone hydrogenation than its phosphine-substituted derivatives (P3). In 1980 Bianchi and co-workers (B5) reported homogeneous hydrogenation of carboxylic acids in the presence of cluster type ruthenium carbonyl hydrides, but found that $H_4Ru_4(CO)_{12}$ could not reduce acetic acid. Below 135°C an insoluble material identified as $[Ru(CO)_2(CH_3COO)]_n$ was formed, and above 150°C, this carbonyl decomposed to a catalytically inactive black solid, believed to be ruthenium metal. The PPh_3 and PBu_3 substituted derivatives remained in solution up to 200°C under a pressure of 100-200 atm H_2, with $H_4Ru_4(CO)_8(PBu_3)_4$ displaying the greatest catalytic activity.

A number of mononuclear ruthenium complexes have been reported as catalysts for the homogeneous hydrogenation of aldehydes to alcohols. Wilkinson and co-workers (S8) used a well-known hydroformylation catalyst, $Ru(CO)_3(PPh_3)_2$, to reduce propionaldehyde. Tsugi and Susuki (T2) have reported reduction of several aldehydes with $RuCl_2(PPH_3)_3$. Strohmeier and Wiegelt (S9) have observed hydrogenation of aliphatic and aromatic aldehydes in the presence of $RuCl_2(CO)_2(PPh_3)_3$ between 160° and 200°C and 15 atm H_2. A similar complex, $RuHCl(CO)(PPh_3)_3$, has been found by Sanchez-Delgado et al. (S10) to be an extremely active catalyst for aldehyde hydrogenation at 80°C and 30 atm H_2. Bradley et al. (B6) have recently reported catalytic hydrogenation of carbon monoxide to methanol in the presence of soluble ruthenium complexes observing that $H_4Ru_4(CO)_{12}$, $H_3Ru_4(CO)_{12}$, and $Ru_3(CO)_{12}$ were all converted to $Ru(CO)_5$ under their reaction conditions (1300 atm, 225° - 275°C). They also noted that Fischer-Tropsch reactions previously reported (M7) were not homogeneous but were catalyzed by ruthenium metal formed by decomposition of $Ru(CO)_5$.

H. Statement of Purpose

The objectives of this study were twofold: 1) to assess the effectiveness of metal carbonyls (and related complexes) as homogeneous hydrogenation catalysts for model coal compounds, and 2) to gain fundamental information about low-temperature, low-pressure coal liquefaction. Since a catalytically active transition metal hydride may form in a number of ways, reaction conditions included various combinations of hydrogen, carbon monoxide, and water (or aqueous base). The effect of the different conditions on catalyst activity and relative reaction rates was investigated and mechanistic interpretations were formulated.

The effective use of carbon monoxide and water as a reducing agent could greatly improve existing synfuels processes by eliminating the need for large quantities of hydrogen. Consequently, an attempt to use the water-gas shift reaction as an in situ source of hydrogen in the metal-carbonyl-catalyzed reduction of polynuclear aromatic and polynuclear heteroaromatic components was undertaken. A thorough examination was conducted to determine if a metal carbonyl hydride formed under shift conditions can directly transfer its hydrogen to an aromatic acceptor molecule. Included in this study were the Group 6B metal carbonyls, $Cr(CO)_6$, $Mo(CO)_6$, and $W(CO)_6$, $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$ of Group 7B, and five carbonyls of the Group 8 metals - $Fe(CO)_5$, $Ru_3(CO)_{12}$, $Os_3(CO)_{12}$, $Co_2(CO)_8$, and $Rh_6(CO)_{16}$. The effects of base, temperature, and n-tributylphosphine (PBu_3) and triphenylphosphine (PPh_3) substitution were also investigated in many cases.

Steam reforming of coal and other carbonaceous material leads to a mixture of carbon monoxide and hydrogen sometimes referred to as synthesis gas or, simply, syngas. Since hydrogen purification is an economically unattractive step, it is important to understand the effect of carbon monoxide on the hydrogenation activity of selected catalysts. $Co_2(CO)_8$ and $Mn_2(CO)_{10}$ have previously been demonstrated to promote PNA hydrogenation under syngas conditions (F1, D1). An expanded investigation into the activity of dicobalt carbonyl complexes was undertaken using $Co_2(CO)_6(PPh_3)_2$ and equimolar quantities of CO and H_2. In addition, screening experiments were performed to evaluate the activity of other metal carbonyls under similar conditions.

The total utilization of syngas, however, would employ both molecular hydrogen and carbon monoxide and water as reducing agents. Reactions performed under these conditions could provide insight into the differences between metal carbonyl hydrides formed under shift conditions and those formed under syngas conditions. $Mn_2(CO)_8(PBu_3)_2$ appeared to be particularly well-suited to this approach, and deuterium-labeling experiments were carried out to determine whether water or diatomic hydrogen was the preferred hydrogen source.

The role of carbon monoxide was further elucidated by a series of reactions in which no CO was present. Two ruthenium complexes, $Ru_3(CO)_{12}$ and $RuCl_2(CO)_2(PPh_3)_2$, were chosen for their thermal stability. These catalysts displayed highly selective hydrogenation activity towards anthracene and aromatic nitrogen heterocycles. Mechanisms were developed to explain these results and to illustrate the important features of a homogeneous aromatic hydrogenation catalyst.

II. EXPERIMENTAL APPARATUS AND PROCEDURE

A. Materials

The materials used in this study are listed in Table 2-1. All materials were used as received except tetrahydrofuran (THF) which was distilled from lithium aluminum hydride. Water was supplied by an on-site distillation system.

B. Apparatus

Reactions were conducted in a 45 ml Parr general purpose bomb constructed of T316 stainless steel and equipped with a 2000 psi pressure gauge, 2000 psi rupture disc assembly, magnetic stirring bar, and needle valve for controlling pressurization. The reactor was suspended in a constant temperature bath, which consisted of a 600 ml pyrex glass beaker containing 500 ml of Dow Corning 550 silicon heat transfer fluid. The bath was placed on a stirrer hot plate and agitated via a magnetic stirring bar (which rotates synchronously with the one in the reactor). Temperature was maintained within $\pm$ 1°C of the set-point using a proportional controller activated by an iron-constantan thermocouple suspended in the bath. A mercury-filled thermometer was used to calibrate the thermocouple.

C. Procedure

Initially, the reactor was charged with substrate,

Table 2-1. Sources and purities of chemicals used

Material	Source	Grade	Minimum Purity (%)
Acridine	Aldrich	--	--
Anthracene	Aldrich	--	98
Benzene	Mallinckrodt	Reagent	98
5,6-Benzoquinoline	Aldrich	--	99
7,8-Benzoquinoline	Aldrich	--	97
Benzothiophene	Aldrich	--	97
Carbon Monoxide	Matheson	Ultra High Purity	99.8
Chromium Hexacarbonyl	Strem	--	--
Cyclohexane	Aldrich	Spectrophotometric	99
Deuterium	LBL	--	99
Deuterium Oxide	Bio-Rad Lab	--	99.75
Dichlorodicarbonyl bis (triphenylphosphine) ruthenium (II)	Strem	--	--
9,10-Dihydroanthracene	Aldrich	--	98
Dimanganese decacarbonyl	Strem	--	--
9,10-Dimethylanthracene	Aldrich	--	99
Dirhenium decacarbonyl	Strem	--	--
Hexarhodium hexadecacarbonyl	Strem	--	--

Table 2-1. Sources and purities of chemicals used

Material	Source	Grade	Minimum Purity (%)
Hydrochloric Acid (37%)	Mallinckrodt	Reagent	99.9
Hydrogen	Matheson	Ultra High Purity	99.999
Iron pentacarbonyl	Strem	--	99.5
2-Methylnaphthalene	Aldrich	--	98
Molybdenum hexacarbonyl	Strem	--	--
Naphthalene	Aldrich	--	98
Phenanthrene	Aldrich	--	98
Phenanthridine	Aldrich	--	98
9-Phenanthrol	Aldrich	--	--
Potassium Bicarbonate	Mallinckrodt	Reagent	98
Potassium Carbonate	MCB	Reagent	80
Potassium Hydroxide	Mallinckrodt	Reagent	85
Pyrene	Aldrich	--	99
Quinoline	Aldrich	--	96
Tetrahydrofuran	Mallinckrodt	Reagent	--
1,2,3,4-Tetrahydroquinoline	Aldrich	--	97
5,6,7,8-Tetrahydroquinoline	Aldrich	--	--
Tetralin	Eastman	Practical	--

Table 2-1. Sources and purities of chemicals used

Material	Source	Grade	Minimum Purity (%)
Tetramethyl ammonium hydroxide (10%)	Eastman	--	99
Trimethylamine (25%)	Eastman	--	99
Tri-n-butlylphosphine	Aldrich	--	95
Triosmium dodecacarbonyl	Strem	--	--
Triphenylphosphine	Aldrich	--	99
Triphenylphosphine cobalt tricarbonyl dimer	Strem	--	--
Triruthenium dodecacarbonyl	Strem	--	--
Tungsten hexacarbonyl	Strem	--	--

catalyst, organic solvent, and sometimes water or aqueous base. Unless otherwise stated, 1 mmole of substrate was dissolved in 15 ml total liquid and a 10 to 1 substrate to metal ratio was maintained. The reactor was then closed, immersed in the constant temperature bath, and purged under ambient conditions by sequentially pressurizing and depressurizing. Carbon monoxide or hydrogen was added and the reactor was heated to the desired temperature. Attainment of the reaction temperature (between 150° and 200°C) required about 30 minutes and a run was considered to begin once the set-point temperature was reached. If both CO and H_2 were being used, H_2 was added to the hot reactor at the beginning of the run. At the end of a run, the temperature was reduced by immersing the reactor body in water. Base, if present, was neutralized with 10 wt-% HCl; benzene was added and the organic layer was recovered.

D. Analyses

1. Gas Analysis

Gas samples were taken from several reactions conducted under water gas shift conditions. The gas was analyzed for carbon monoxide, carbon dioxide, and hydrogen using a CEC Model 21103 Mass Spectrometer. From these results the water gas shift activity of a particular catalyst could be estimated.

2. Liquid Analysis

Liquid-phase products were routinely analyzed by gas chromatography on a 0.1 mm by 12 meter OV 101 capillary column using a Hewlett Packard 5880A gas chromatograph with a flame ionization detector and digital integrator. The column was used in a temperature programmed mode (60°C to 200°C at 10°C/min) to enhance separation. Under these conditions, good resolution was obtained and the reaction products could be easily distinguished from the parent compound.

The identity of the individual chromatographic peaks was determined by comparison with standards of known composition. When standards were unavailable, the products were analyzed by combined gas chromatography/mass spectrometry (GC/MS) using a Finnigan 4000 GC/MS with INCOS data system. The mass spectra of two such compounds, 9,10-dideuteroanthracene and 1,2,3,4-tetrahydroanthracene, are shown in Figures 2-2 and 2-3, respectively.

3. Solid Analysis

Tetraruthenium dodecarbonyl tetrahydride, formed by 1 hour reaction of triruthenium dodecacarbonyl and hydrogen at 150°C and 350 psi, was identified by both mass spectrometry and infrared spectroscopy. The mass spectra of $Ru_3(CO)_{12}$ and $H_4Ru_4(CO)_{12}$ are shown in Figures 2-4 and 2-5, respectively. The IR spectra of $Ru_3(CO)_{12}$ and $H_4Ru_4(CO)_{12}$, shown

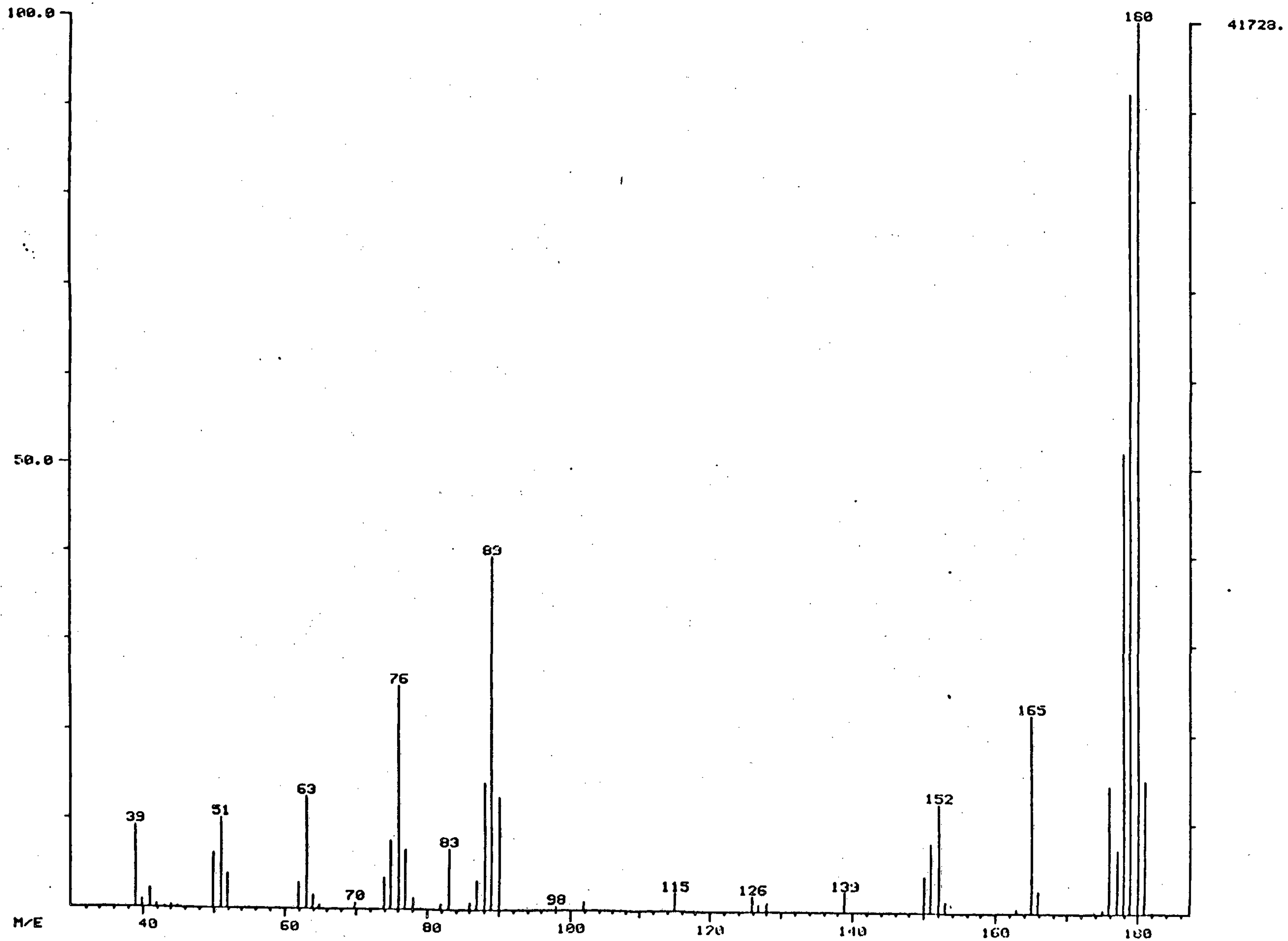


Figure 2-1. Mass spectrum of 9,10-dihydroanthracene.

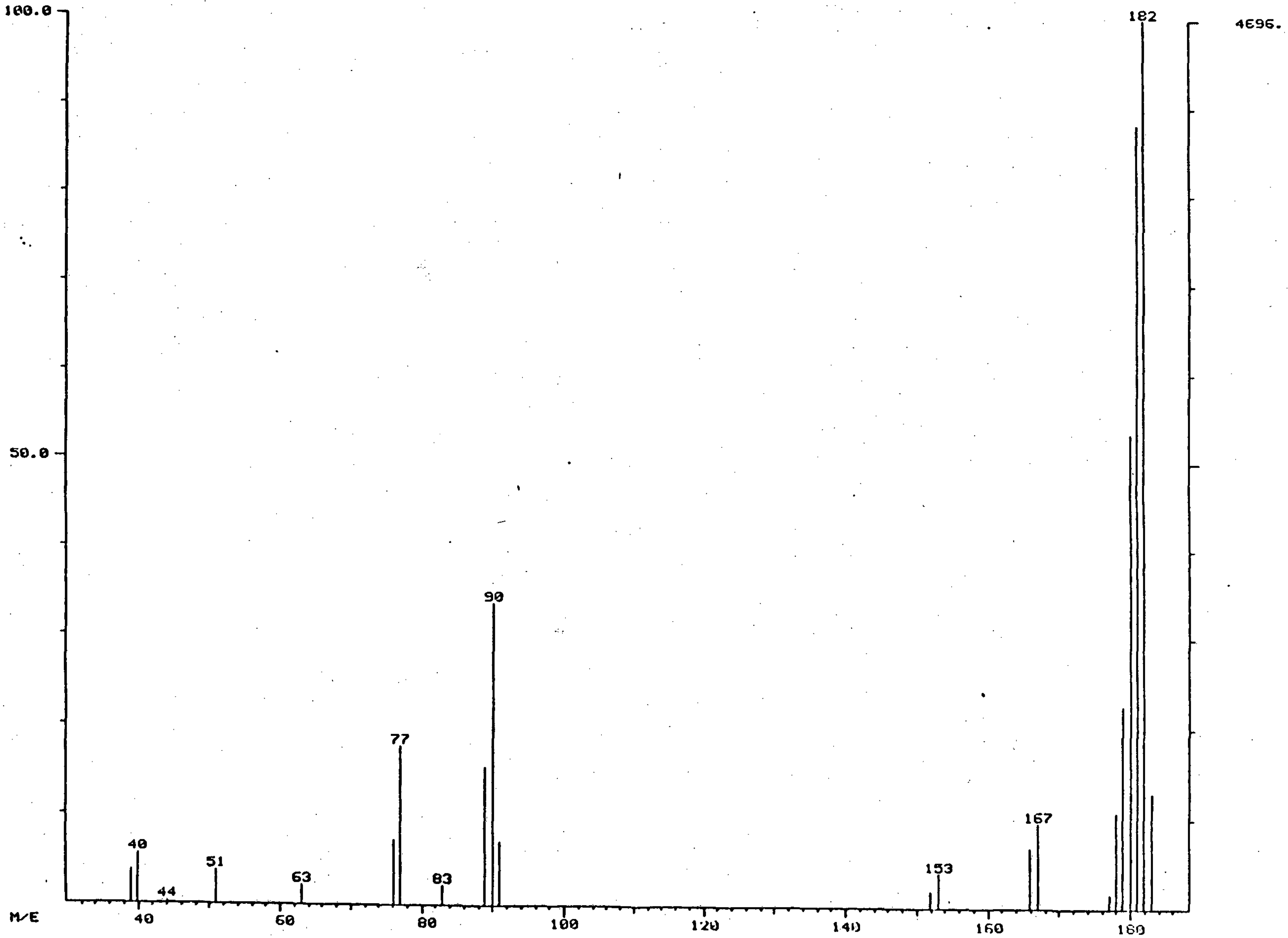


Figure 2-2. Mass spectrum of 9,10-dideuteroanthracene.

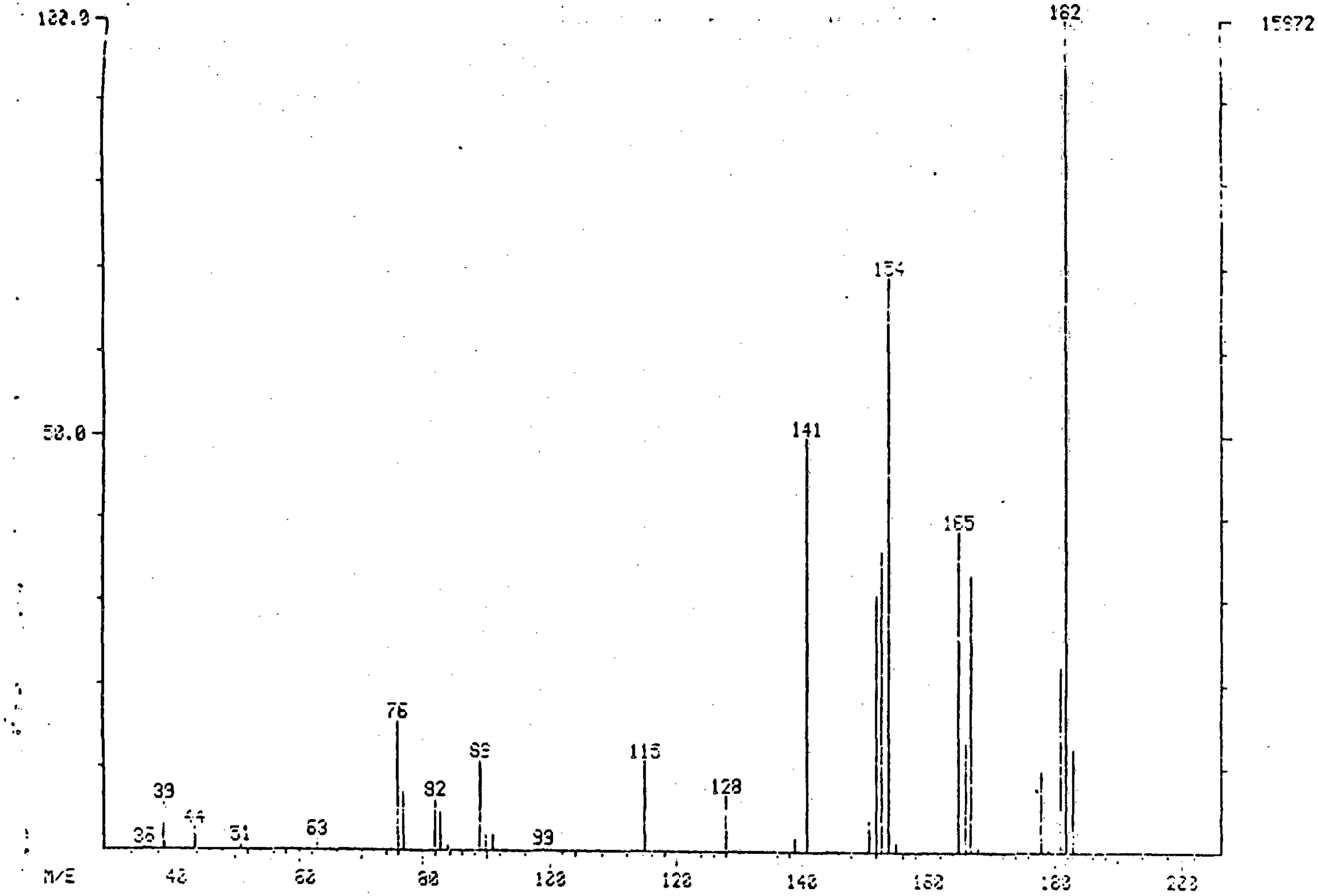


Figure 2-3. Mass spectrum of 1,2,3,4-tetrahydroanthracene.

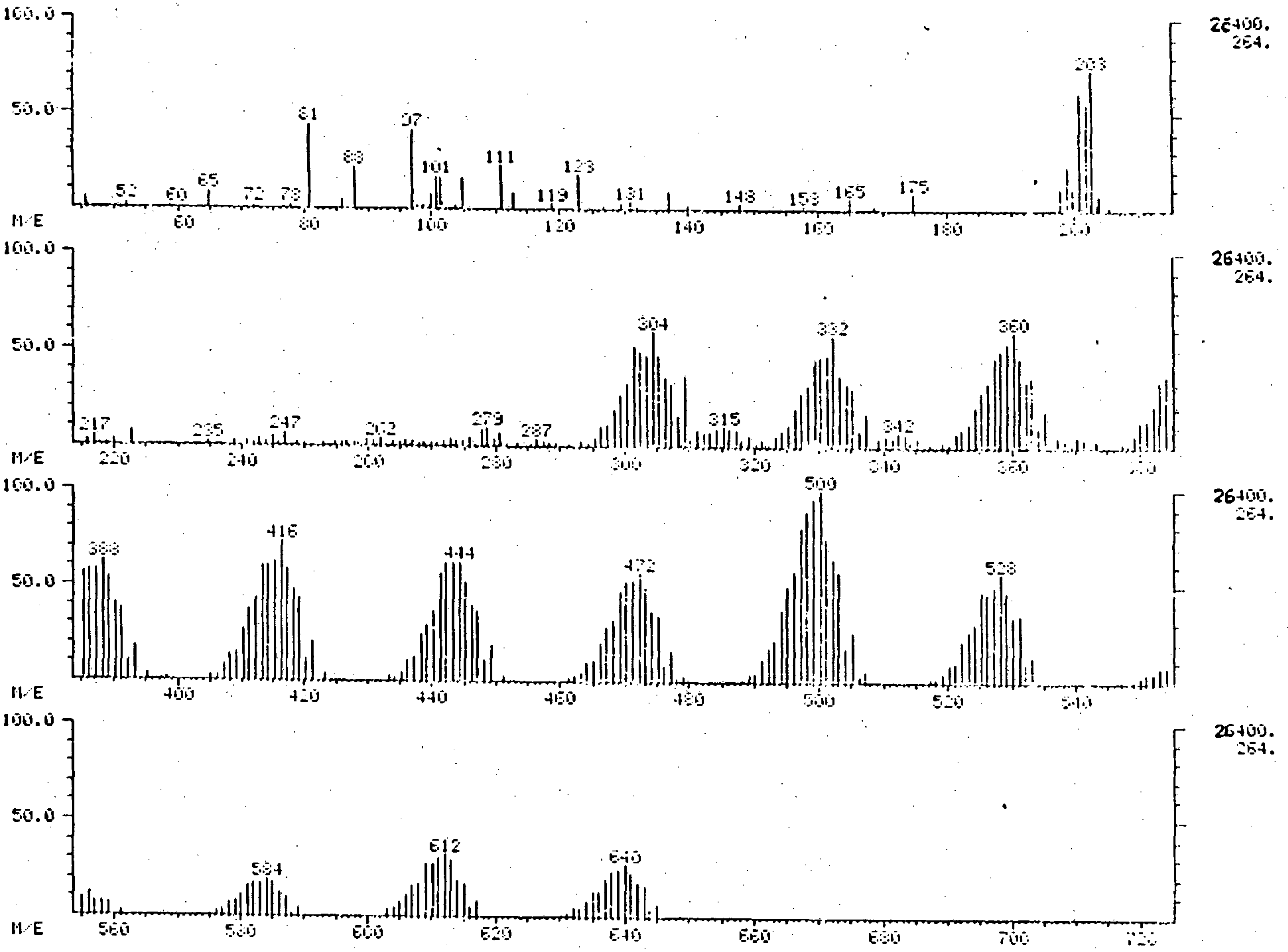


Figure 2-4. Mass spectrum of $Ru_3(CO)_{12}$.

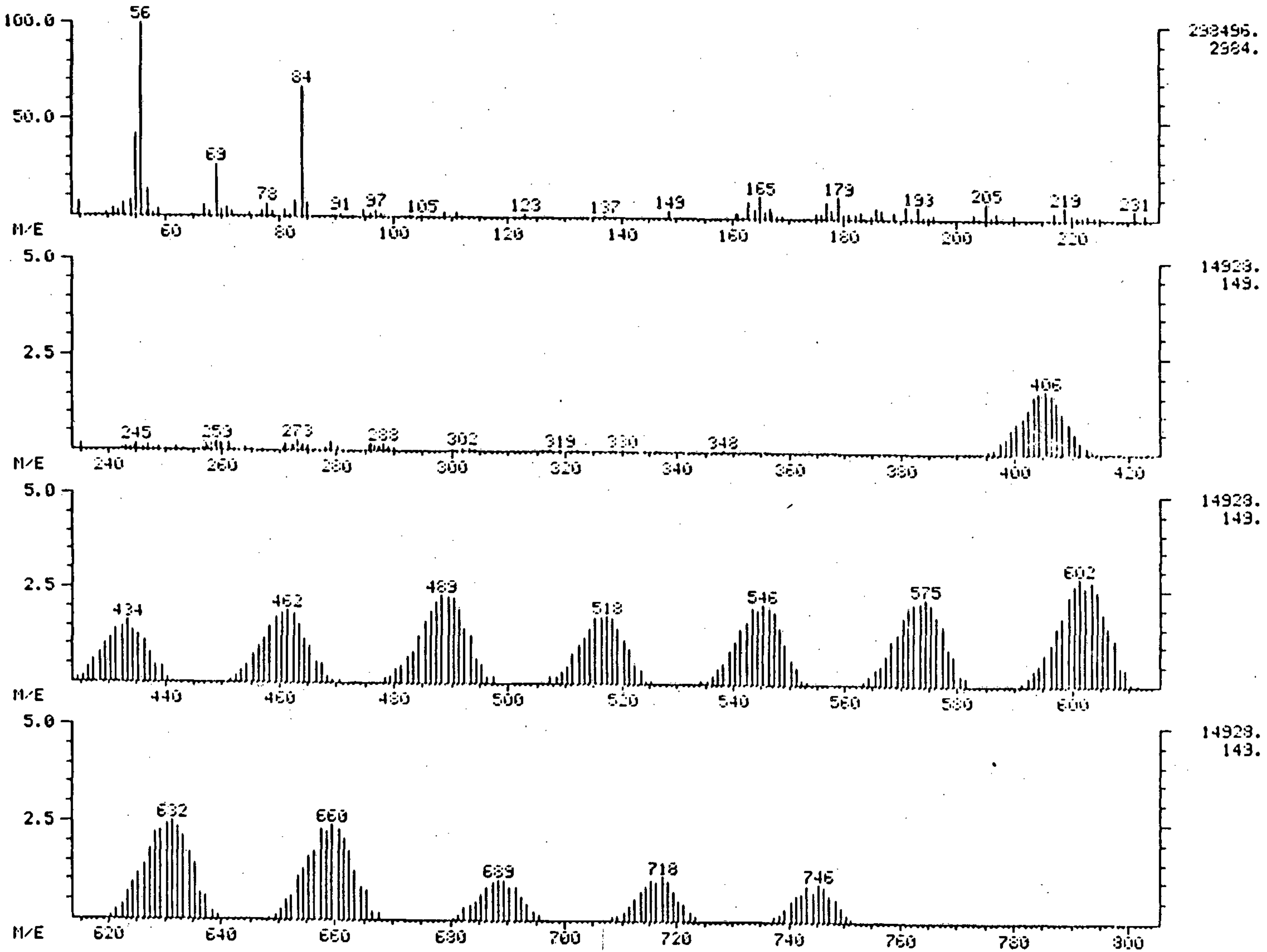


Figure 2-5. Mass spectrum of $H_4Ru_4(CO)_{12}$.

in Figures 2-6 and 2-7, were measured using a Perkin-Elmer 1330 Infrared Spectrophotometer. Piacenti and co-workers (P2) obtained a similar IR spectrum for $H_4Ru_4(CO)_{12}$ at 150°C and 1500 psi H_2.

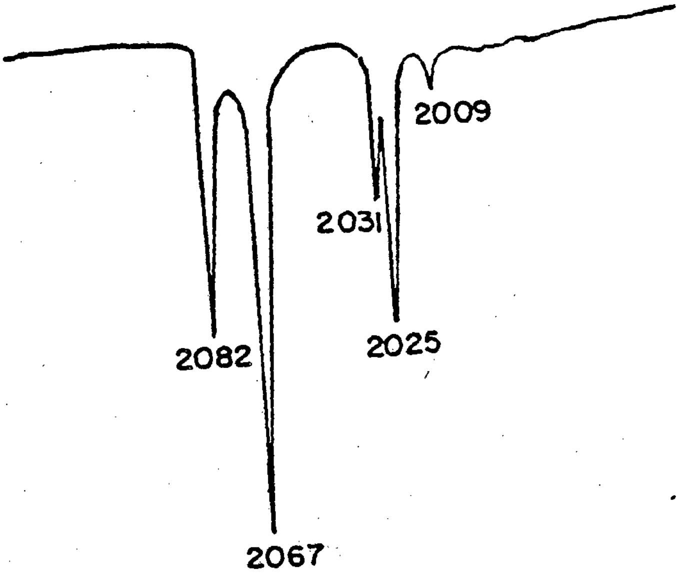


Figure 2-6. Infrared spectrum of $Ru_3(CO)_{12}$.

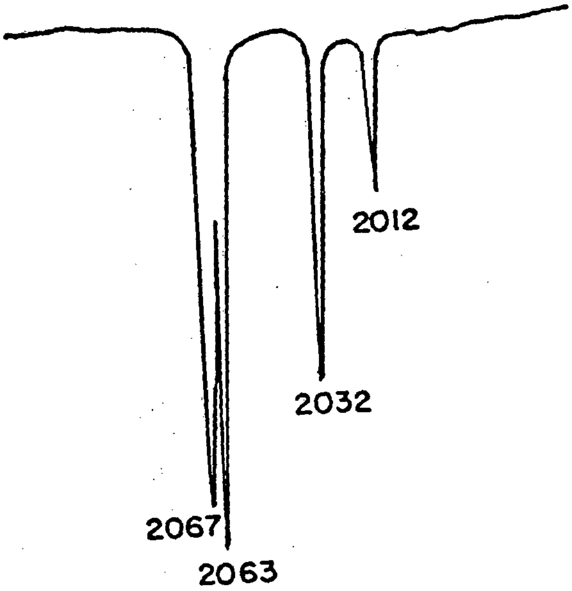


Figure 2-7. Infrared spectrum of $H_4Ru_4(CO)_{12}$.

III. RESULTS AND DISCUSSION

A. Hydrogenation with Metal Carbonyls Under Water-Gas Shift Conditions

1. Anthracene Hydrogenation

A thorough examination of the metal-carbonyl-catalyzed hydrogenation of anthracene under water-gas shift conditions was conducted. The results of these experiments are given in Table 3-1. Reduction of anthracene occurs to a small extent in the presence of manganese, iron or cobalt carbonyls and only 9,10-dihydroanthracene is found as a reaction product. No conversion was observed when other carbonyls were used. Similar runs with phenanthrene and pyrene showed no reaction, using $Mn_2(CO)_8(PBu_3)_2$ as the catalyst, even under optimum conditions for anthracene hydrogenation.

Interestingly, hydrogenation activity in the presence of carbon monoxide and aqueous base was observed only for those carbonyls which proved to be the poorest water-gas shift catalysts. Since the water-gas shift produces 2 moles of gas for each 1 mole of CO consumed under homogeneous conditions, the water-gas shift activity of a particular catalyst can be approximated by monitoring the pressure increase over time. Selected gas analysis were taken to verify this approach, yielding a qualitative ordering as follows: $Rh_6(CO)_{16} > Ru_3(CO)_{12} > Cr(CO)_6 > Mo(CO)_6 > W(CO)_6 > Fe(CO)_5 > Mn_2(CO)_{10} > Co_2(CO)_8$.

Table 3-1. Hydrogenation of polynuclear aromatics under shift conditions

Catalyst	Temp (°C)	Substrate	Product
$Rh_6(CO)_{16}$	180	Anthracene	None
$Ru_3(CO)_{12}$	180	Anthracene	None
$Os_3(CO)_{12}$, $Cr(CO)_6$, $Mo(CO)_6$, $W(CO)_6$, $Re_2(CO)_{10}$	200	Anthracene	None
$Co_2(CO)_6(PPh_3)_2$	160	Anthracene	3% 9,10-Dihydroanthracene
$Fe(CO)_4(PBu_3)$	200	Anthracene	8% 9,10-Dihydroanthracene
$Mn_2(CO)_8(PBu_3)_2$	160	Anthracene	4% 9,10-Dihydroanthracene
$Mn_2(CO)_8(PBu_3)_2$	180	Anthracene	8% 9,10-Dihydroanthracene
$Mn_2(CO)_8(PBu_3)_2$	200	Anthracene	13% 9,10-Dihydroanthracene
$Mn_2(CO)_8(PBu_3)_2$	200	Phenanthrene	None
$Mn_2(CO)_8(PBu_3)_2$	200	Pyrene	None
$Mn_2(CO)_{10}$	180	Anthracene	6% 9,10-Dihydroanthracene
$Mn_2(CO)_6(PBu_3)_4$	180	Anthracene	7% 9,10-Dihydroanthracene
$Mn_2(CO)_4(PBu_3)_6$	180	Anthracene	9% 9,10-Dihydroanthracene
$Mn_2(CO)_2(PBu_3)_8$	180	Anthracene	7% 9,10-Dihydroanthracene

P_{CO} = 350 psi; 12 ml THF; 3 ml 0.2M KOH

2. Effect of Phosphine Substitution

The homogeneous hydrogenation activity under shift conditions was examined for $Mn_2(CO)_{10}$ with partial phosphine substitution, using anthracene as a substrate. The results of this investigation, given in Table 3-1, indicate that of the two phosphine ligands that were evaluated, n-tributylphosphine (PBu_3) is superior. Addition of triphenylphosphine (PPh_3) had no effect on the activity of $Mn_2(CO)_{10}$.

Derencsenyi (D2) performed a similar study under syngas conditions (CO/H_2 1:1) using a variety of substituted phosphines. He also concluded that n-tributylphosphine was a very good ligand and that $Mn_2(CO)_8(PBu_3)_2$ was the most active form of the catalyst. The data of Table 3-1 are presented graphically in Figure 3-1 to suggest that PBu_3 substitution has a mildly beneficial effect under shift conditions as well. A phosphine to metal ratio greater than one, however, has little effect. In contrast, Derencsenyi (D2) reported a deleterious effect of additional phosphine with CO and H_2.

The fact that excess n-tributylphosphine does not inhibit anthracene hydrogenation under shift conditions indicates that its dissociation is not a kinetically important step in the reaction sequence. Phosphine inhibition as reported by Derencsenyi (D2), however, does not necessarily implicate a ligand dissociation mechanism. Additional

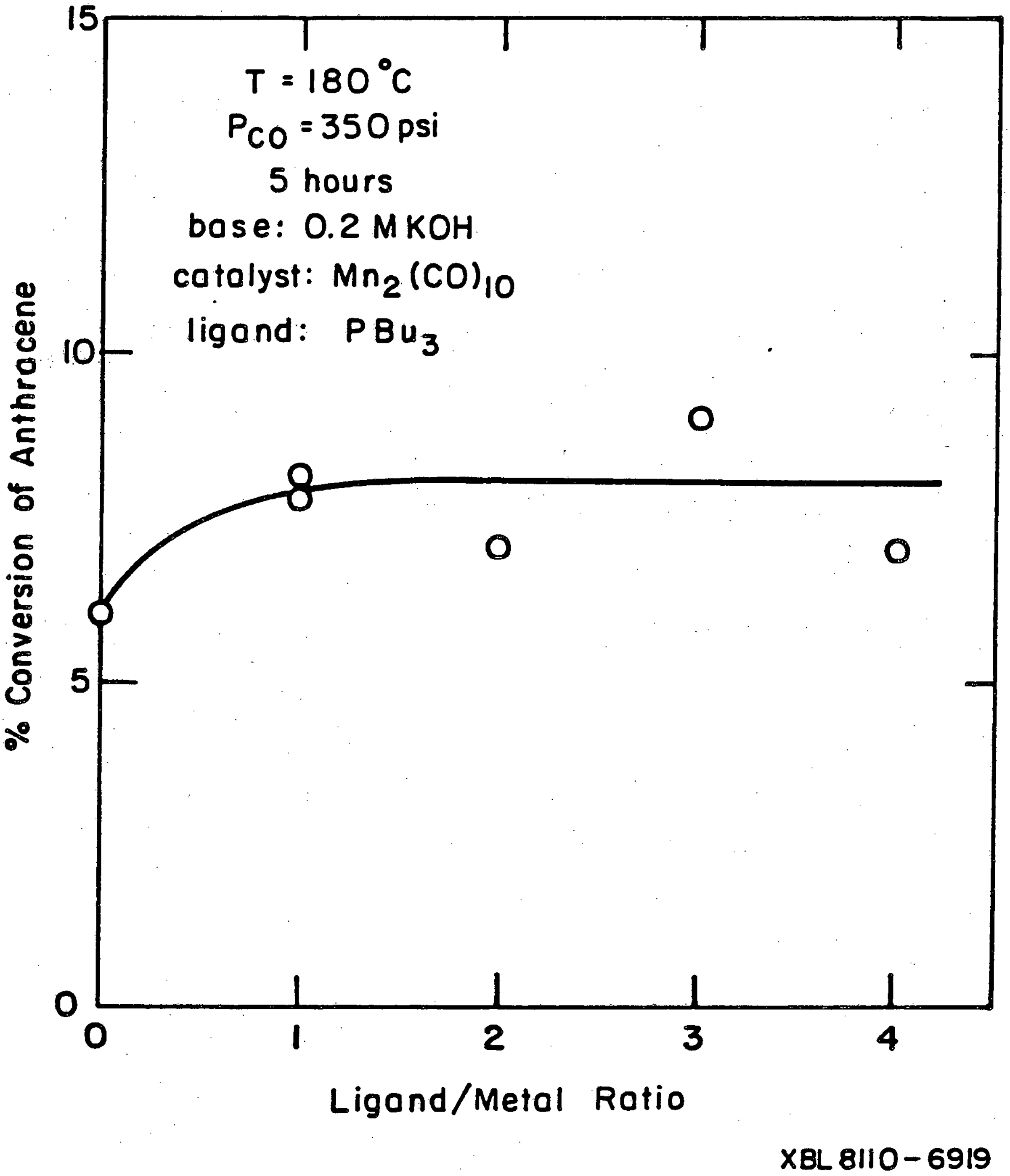


Figure 3-1. Effect of phosphine addition on conversion of anthracene to 9,10-dihydroanthracene.

phosphine may simply result in a less active catalytic species. It is nevertheless important to realize that addition of two or three moles of phosphine per mole of metal atom does not always produce a di- or trisubstituted carbonyl. Each carbon monoxide ligand becomes increasingly difficult to displace as the σ- donating phosphines increase the back bonding between CO and metal. In the presence of excess CO and phosphine, a number of different metal complexes might be present and the true form of the catalyst difficult to identify.

3. Effect of Base

Base facilitates the metal-carbonyl-catalyzed water-gas shift reaction (by promoting nucleophilic attack on coordinated CO), and thus has the potential of influencing hydrogenation reactions. The results of Table 3-2, however, suggest that it has little effect in the case of anthracene. Reaction at 180°C for 5 hours with $Mn_2(CO)_8(PBu_3)_2$ yields 8% of product, whether 0.2M KOH or only water is present. With $Mn_2(CO)_{10}$ at 160°C, reaction in water gives 4% of product, essentially the same conversion as reaction in a two-phase system employing a phase-transfer catalyst ($Me_4N^+OH^-$). These results suggest that attack on coordinated CO by OH^- to give the hydroxycarbonyl (step 1 of Figure 1-4) is not rate-limiting. When a weak base (Me_3N) is used at 25 wt-%, no reduction of anthracene occurs with either $Fe(CO)_5$ or $Mn_2(CO)_{10}$. The amine might directly attack the CO, so as to

Table 3-2. Effect of base on conversion of anthracene to 9,10-dihydroanthracene

Catalyst	Temp (°C)	Base (3 ml)	% Conversion
$Fe(CO)_5$	160	25% aq. Me_3N	None
$Fe(CO)_5$	160	0.2M KOH	4%
$Fe(CO)_4(PBu_3)$*	200	1.25M NaOH	4%
$Fe(CO)_4(PBu_3)$	200	0.2M KOH	8%
$Mn_2(CO)_{10}$	160	25% aq. Me_3N	None
$Mn_2(CO)_{10}$**	160	0.1M $KHCO_3$	3%
$Mn_2(CO)_{10}$	180	H_2O	4%
$Mn_2(CO)_8(PBu_3)_2$	180	0.2M KOH	8%
$Mn_2(CO)_8(PBu_3)_2$	180	H_2O	8%

1 mmole Antracene; 10:1 Anthracene to Metal Ratio; 5 hr; P_{CO} = 350 psi; Solvent: THF (12 ml)

* Solvent: Ethanol

** Solvent: Tetralin; 1 mmole tetramethylammonium hydroxide added.

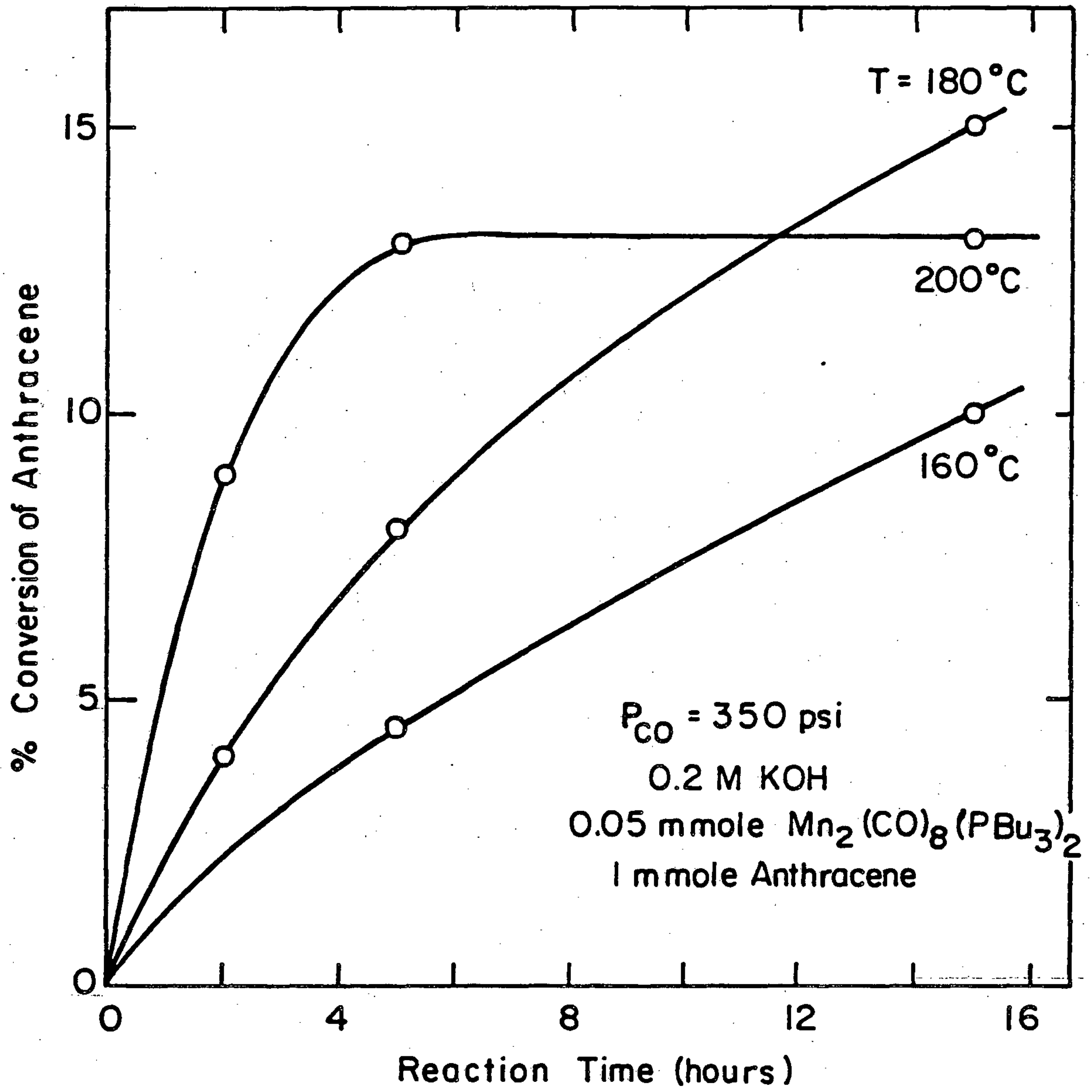
change the nature of the catalyst. A catalyst change is suspected because we observe water-gas shift activity in 25% aqueous trimethylamine than in aqueous KOH for a variety of metal carbonyls. Also, Pettit's (K2) shift activities in amine solutions are much greater than those reported by investigators using other bases (F1,U1,L3).

Reaction with $Fe(CO)_4(PBu_3)$ in ethanolic NaOH (1.25M) gives 4% conversion of anthracene, whereas reaction in THF with aqueous KOH (0.2M) gives 8% conversion. This result may merely reflect partial insolubility of anthracene in the ethanol/NaOH medium at 200°C, which was evident in the experiment.

4. Effect of Temperature

The effect of temperature on the reduction of anthracene under shift conditions, in the presence of $Mn_2(CO)_8(PBu_3)_2$ is displayed graphically in Figure 3-2. Increasing temperature is clearly beneficial at reaction times of a few hours. After 5 hours, conversions of 4%, 8%, and 13% were observed at 160°, 180°, and 200°C, respectively. The hydrogenation rates suggest first-order behavior. After 15 hours total, the conversions were 10%, 15%, and 13%.

At 200°C, the lack of further reduction after 5 hours is due to catalyst decomposition. This is shown by loss of the bright yellow color characteristics of soluble



XBL 8110-6918

Figure 3-2. Effect of temperature on conversion of anthracene to 9,10-dihydroanthracene.

$Mn_2(CO)_8(PBu_3)_2$ and appearance of a black solid material, presumably manganese metal. This change did not occur at 160° or 180°C. An operating temperature of about 180°C therefore appears to be optimum at 350 psi CO in that it allows for maximum reactivity and prolonged catalyst life.

5. Hydrogenation of Nitrogen Heterocycles

Heteroaromatic nitrogen compounds appear to be somewhat more reactive than their hydrocarbon analogs. Table 3-3 shows results obtained in the presence of 350 psi CO and 0.2M KOH. Acridine was reduced after 2 hours of reaction, giving 9,10-dihydroacridine. Hydrogenated products for other nitrogen heterocycles were observed after 5 hours, but in very small yields (Table 3-4). In each case only the nitrogen-containing ring was reduced.

Of all the substrate/catalyst combinations investigated under water-gas shift conditions, the $Fe(CO)_5$-catalyzed hydrogenation of acridine was by far the most successful. A proposed mechanism, given in Figure 3-3, provides a possible explanation. Nucleophilic attack on coordinated CO followed by loss of CO_2 gives $HFe(CO)_4^-$, which is the principal species in solution under these conditions (K10,K2,K3), and shows strong electron-donating ability (W4,S11). The conjugate acid, $H_2Fe(CO)_4$, is not likely to be a reactive intermediate since it is an unstable gas at elevated temperature (C2) and, if formed, would rapidly decompose. In step (2), electron transfer from $HFe(CO)_4^-$ to acridine occurs, forming

Table 3-3. Homogeneous hydrogenation of nitrogen heterocycles under shift conditions

Catalyst	Substrate	Temp (^{o}C)	P_{CO} (psi)	Product
$Mn_2(CO)_8(Bu_3P)_2$	Acridine	200	350	38% 9,10-dihydroacridine
$Mn_2(CO)_8(Bu_3P)_2$	Quinoline	200	350	None
$Fe(CO)_5$	Acridine	180	800	100% 9,10-dihydroacridine
$Fe(CO)_5$	Quinoline 5,6-Benzoquinoline	180	800	None
$Cr(CO)_6$	Acridine	200	200	12% 9,10-dihydroacridine

Solvent: THF; Base: 0.2M KOH; 2 hr

Table 3-4. Homogeneous hydrogenation of nitrogen heterocycles under shift conditions

Catalyst	Substrate	Temp (°C)	Product
$Fe(CO)_4(Bu_3P)$	5,6-Benzoquinoline	180	1% Tetrahydrobenzoquinoline
$Mn_2(CO)_8(Bu_3P)_2$	Quinoline	200	4% Tetrahydroquinoline
$Mn_2(CO)_8(Bu_3P)_2$	5,6-Benzoquinoline	200	4% Tetrahydrobenzoquinoline
$Mn_2(CO)_8(Bu_3P)_2$	7,8-Benzoquinoline	200	None
$Mn_2(CO)_8(Bu_3P)_2$	Phenathridine	200	1% Dihydrophenanthridine

Solvent: THF (12 ml; base: 0.2M KOH (3 ml); P_{CO} = 350 psi;
5 hr; 10:1 Substrate to Metal Ratio

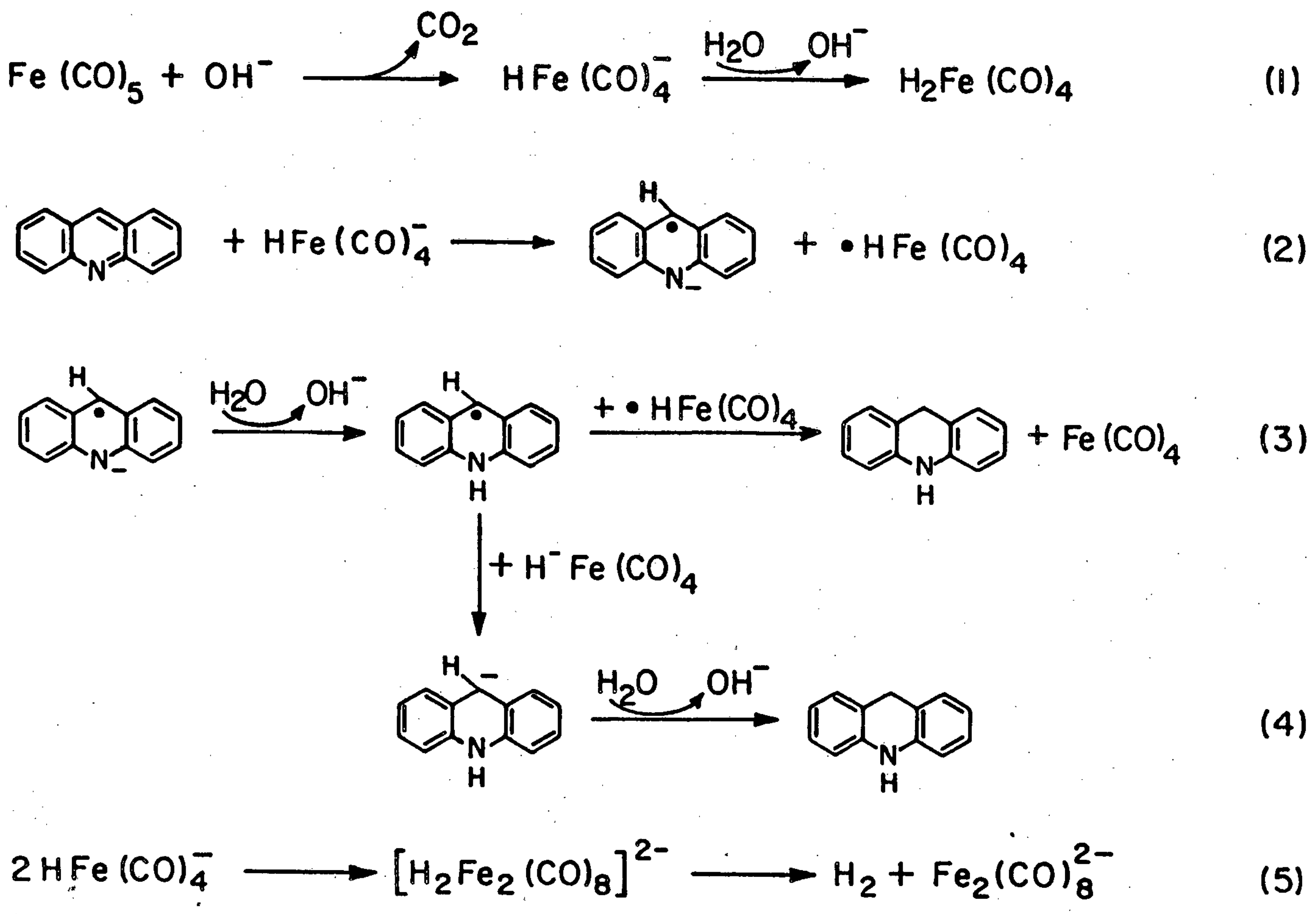


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Figure 3-3. Proposed mechanism for $Fe(CO)_5$-catalyzed reduction of anthracene.

the radical anion.

Protonation in step (3) leads to a neutral radical which may react with the iron tetracarbonyl formed in step (2) or may repeat the sequence of electron transfer and proton addition (step (4)). The ease with which acridine is reduced under shift conditions probably derives from the combination of several properties: electronegativity of the nitrogen atom, reduced aromaticity of the heterocyclic ring, greater radical-delocalization energy of the center ring, and possibly even the ability of the nitrogen to coordinate with the metal via its lone electron pair.

Pettit (K2) proposes protonation of $HFe(CO)_4^-$ followed by reductive elimination of $H_2Fe(CO)_4$ as the mechanism for hydrogen production. However, $H_2Fe(CO)_4$ formation is virtually impossible under basic conditions and reductive elimination of $H_2Fe_2(CO)_8^{2-}$ could account more easily for the hydrogen produced in the water gas shift reaction. The binuclear anion has been isolated (H6), and step (5) of Figure 3-3 has been postulated to account for its presence (S12). In addition to electron transfer via $HFe(CO)_4^-$, reduction of aromatic rings might be achieved by hydrogen transfer from the dihydride intermediate, $H_2Fe_2(CO)_8^{2-}$.

6. Effect of Molecular Hydrogen

The consistently low yields obtained under shift conditions led to an investigation of homogeneous hydrogenation in the presence of molecular hydrogen. In some instances H_2 was used in conjunction with carbon monoxide and aqueous base; in others base was removed and reaction was conducted in a water-free organic solvent. The effect of hydrogen in several systems is shown in Figure 3-4.

For iron pentacarbonyl, base evidently provides a more facile means of forming a metal hydride than oxidative addition of H_2 to a coordinatively unsaturated Fe species. Simply adding hydrogen and conducting the reaction in the presence of CO, base and H_2 has no effect, while removal of base results in no reaction. With the $Fe(CO)_5$-catalyzed reduction of acridine to 9,10-dihydroacridine, quantitative conversion was obtained under shift conditions; no acridine hydrogenation was detected under syngas conditions. With anthracene as the substrate, $Fe(CO)_4(PBu_3)$ gives the same conversion to 9,10-dihydroanthracene (8%) whether or not hydrogen is present; also, no reaction occurs when base is absent. These results are consistent with the observation of Pettit and co-workers (K2) that $Fe(CO)_5$ is a better hydroformylation catalyst when CO and H_2O rather than CO and H_2 are used.

When $Mn_2(CO)_8(PBu_3)_2$ or $Co_2(CO)_6(PPh_3)_2$ is substituted for $Fe(CO)_5$, different reactivity is observed. With $Mn_2(CO)_8(PBu_3)_2$ as the catalyst, 38% reduction of acridine to 9,10-dihydroacridine occurs after 2 hours at 200°C in the presence of CO and base. If hydrogen is substituted for

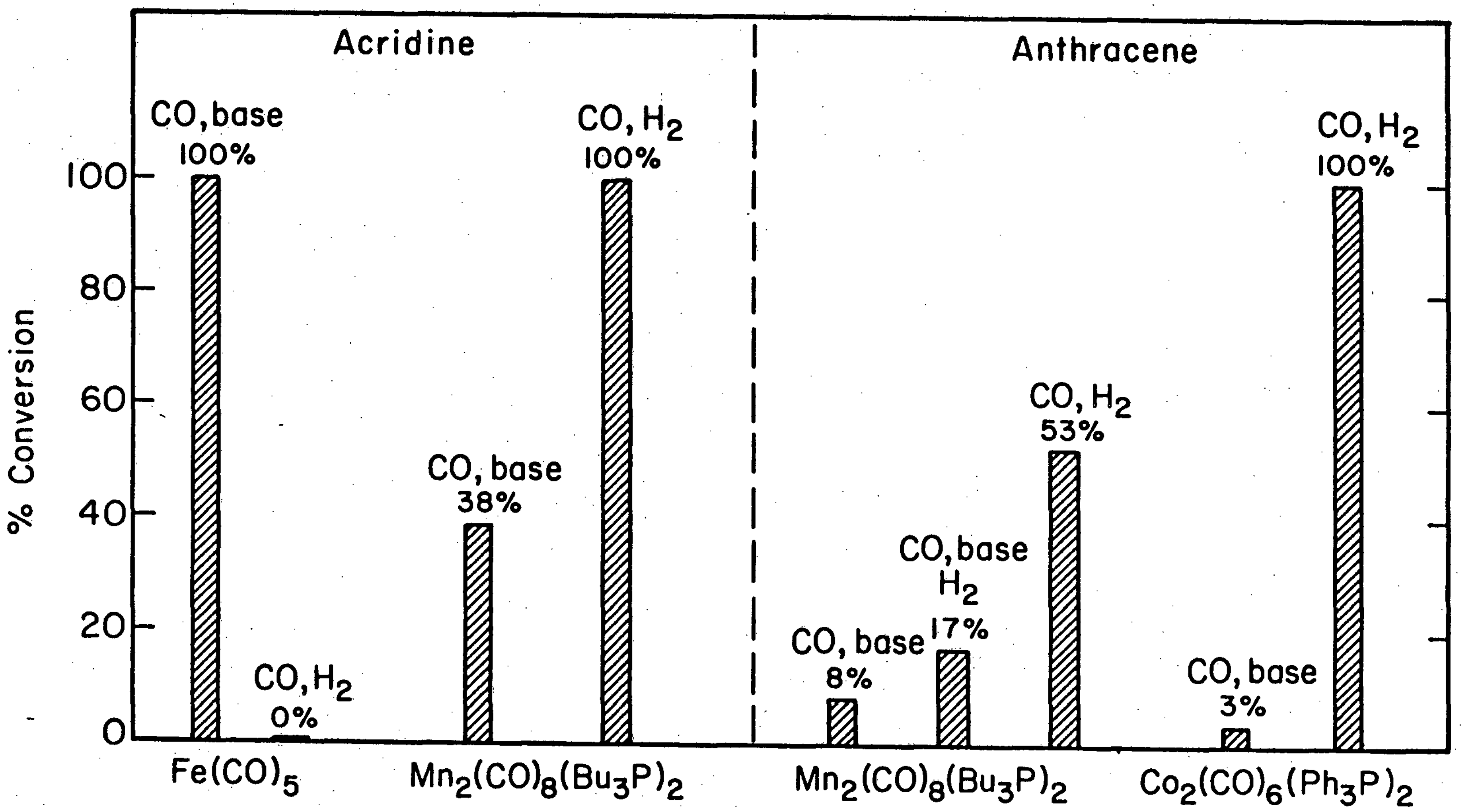

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Figure 3-4. Effect of molecular hydrogen.

base, quantitative conversion of acridine results. Similarly, only 8% conversion of anthracene to 9,10-dihydroanthracene occurs after 5 hours at 180°C when CO and base ared used as reducing agent. If hydrogen is added, the yield increases to 17%. If base is eliminated, and only CO and H_2 are present, 53% of the anthracene is hydrogenated. $Co_2(CO)_6(PPh_3)_2$ behaves in an analogous but even more pronounced fashion.

These results indicate that the dimanganese and dicobalt complexes, unlike $Fe(CO)_5$, are capable of direct reaction with molecular hydrogen under the experimental conditions; base promotes the water-gas shift, an undesirable side reaction. Figure 3-5 illustrates a possible mechanism for the $Mn_2(CO)_{10}$ catalyzed hydrogenation of anthracene in the presence of CO, H_2 and aqueous base. Two different reaction pathways leading to the reduction of anthracene are presented. Hydrogen may add homolytically across the manganese-manganese bond giving manganese pentacarbonyl monohydride. According to Halpern (S3), $HMn(CO)_5$, like $HCo(CO)_4$, catalyzes the hydrogenation of anthracene via a free-radical mechanism (Figure 1-6).

An alternative sequence involves activation of coordinated CO by OH^-, followed by loss of CO_2 to give the dimanganese hydride anion. Conceivably, $HMn_2(CO)_9^-$ could interact with anthracene or could abstract a proton from water giving $H_2Mn_2(CO)_9$. The dihydridodimanganese nonacar-

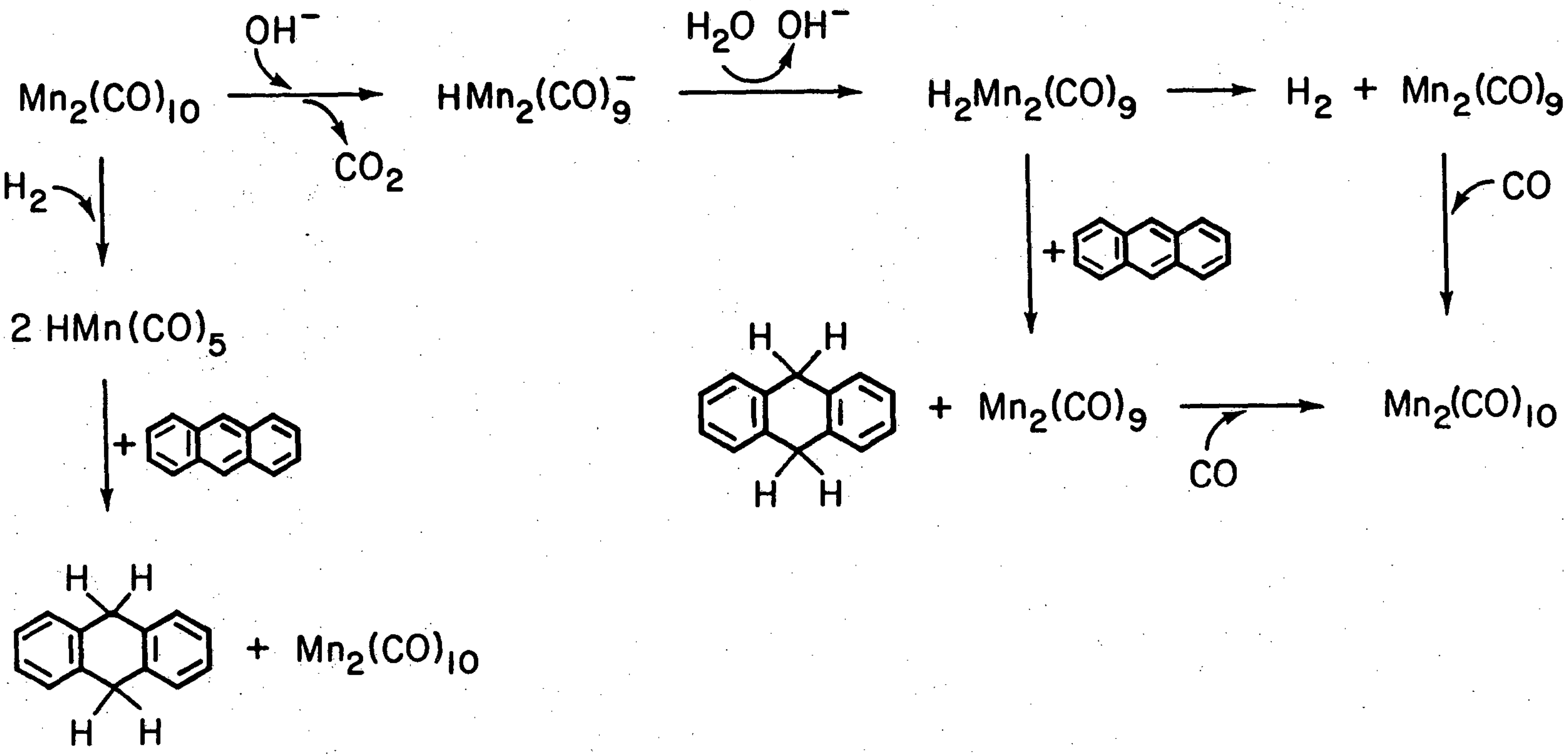

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Figure 3-5. Proposed mechanism for $Mn_2(CO)_{10}$-catalyzed hydrogenation of anthracene under combination syngas and shift conditions.

bonyl (or a similar manganese hydride formed under shift conditions) can either reduce anthracene to 9,10-dihydroanthracene, or undergo reductive elimination of H_2 (the water gas shift reaction) and recoordination of another CO. The inhibitory effect of base and the low conversions under shift conditions can thus be explained in the following manner. Nucleophilic attack by hydroxide ion on coordinated CO has a much lower activation energy than homolytic addition of hydrogen to the manganese (or cobalt) dimer; however, the resulting manganese hydride is much less active towards anthracene hydrogenation than $HMn(CO)_5$. For $H_2Mn_2(CO)_9$ (or $H_2M_x(CO)_{y-1}$ in general) reductive elimination of H_2 occurs more readily than hydrogen transfer to an aromatic center. Thus the metal-carbonyl-catalyzed hydrogenation of aromatics using carbon monoxide and water (or base), without hydrogen, does not appear promising.

In the presence of carbon monoxide and aqueous base, $Mn_2(CO)_{10}$ (or $Mn_2(CO)_8(PBu_3)_2$) catalyzes the water-gas shift. Since some molecular hydrogen is always present, the somewhat unique tendency of the dimanganese carbonyl to reduce anthracene under shift conditions may derive from its ability to react with H_2. The amount of hydrogen produced in the presence of manganese carbonyl, however, is very small. Gas analysis indicates that no more than 10 psi H_2 is produced after 5 hours at 200°C and 350 psi CO in the presence of 0.2M KOH and $Mn_2(CO)_8(PBu_3)_2$. If reaction is conducted under 10 psi H_2 in a nonaqueous solvent, only 6%

anthracene reduction is observed as compared with 13% under shift conditions. In order to further verify that a hydridomanganese complex formed by water-gas shift is capable of reducing anthracene, a series of deuterium-labeling experiments was performed. These results are presented in Table 3-5.

In the presence of 350 psi H_2 and 0.13M K_2CO_3 in D_2O, 17% reduction of anthracene occurs after 5 hours at 180°C - 52% of the product is 9,10-dideuteroanthranene, 36% is 9-monodeutero 10-monohydroanthracene, and 12% is 9,10-dihydroanthracene. If 350 psi D_2 and 0.2M KOH are used, 17% reduction is again observed but with no deuterium incorporation, suggesting that the hydrogen of 9,10-dihydroanthracene comes strictly from water. The presence of mono and dihydroanthracenes in $H_2/K_2CO_3/D_2O$ system might be due to small amounts of water not removed from K_2CO_3 on drying. This conclusion is substantiated by the observation of exclusively dihydroanthracene in 28% yield when the reaction is conducted at 200°C with 0.13M K_2CO_3 and 350 psi D_2.

Two additional runs were made to establish that exchange at the 9,10 positions of dihydroanthracene was not responsible for the lack of deuterated product in the presence of D_2 gas. In one case 9,10-dihydroanthracene was treated with 0.13M K_2CO_3 in D_2O and 350 psi H_2 for 5 hours at 200°C. No deuterium incorporation was detected. In the absence of aqueous base a small amount of deuterium was

Table 3-5. $Mn_2(CO)_8(PBu_3)_2$ - catalyzed deuterium-labeling experiments

Substrate	Temp (°C)	Base (3 ml)	H_2/D_2 (350 psi)	Product
Anthracene	160	D_2O	None	5% dideuteroanthracene
Anthracene*	180	0.13M K_2CO_3 D_2O	H_2	17% reduced anthracene (~52% D_2, 36% D_1, 12% H_2
Anthracene	180	0.2M KOH	D_2	17% dihydroanthracene
Anthracene	200	0.13M K_2CO_3	D_2	28% dihydroanthracene
9,10-Dihydroanthracene	200	0.13M K_2CO_3 D_2O	H_2	100% dihydroanthracene
9,10-Dihydroanthracene	200	None	D_2	100% reduced anthracene (~83% H_2, 15% D_1, 2% D_2)

1 mmole substrate; 0.05 mmole $Mn_2(CO)_8(Bu_3P)_2$; 5 hr; P_{CO} = 350 psi; solvent: THF (12 ml)

* 0.05 mmole $Mn_2(CO)_{10}$

incorporated after 5 hours at 200°C and 350 psi D_2. This result indicates that hydrogen-deuterium exchange may occur due to the reversibility of step (2) in Figure 1-6 but only with high conversion to dihydroanthracene. Weil et al. (W3) report a similar observation when $Co_2(CO)_8$ is used as a catalyst.

The beneficial effect of H_2 in the presence of CO and base (Figure 3-4) remains an anomaly, since it does not appear to be directly participating in the hydrogenation of anthracene. One possible explanation is that $DMn(CO)_5$, formed by reaction of $Mn_2(CO)_{10}$ and D_2, undergoes rapid hydrogen-deuterium exchange with water or base to give $HMn(CO)_5$. This would account for both the increased yields of dihydroanthracene and the absence of deuterated product when aqueous base and deuterium gas are used.

B. Hydrogenation with Metal Carbonyls Under Syngas Conditions

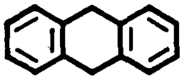
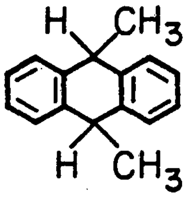
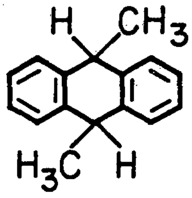
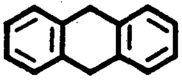
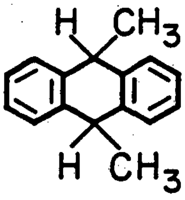
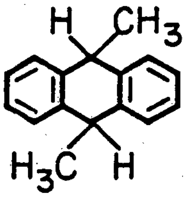
1. Hydrogenation of Polynuclear Aromatics

Both $Mn_2(CO)_8(PBu_3)_2$ and $Co_2(CO)_6(PPh_3)_2$ were observed to display greater catalytic activity for anthracene hydrogenation when aqueous base was replaced with molecular hydrogen. This led to an investigation of the hydrogenation activity of these catalysts towards other model-coal compounds in the presence of carbon monoxide and hydrogen (syngas). Also, the hydrogenation activity of other metal carbonyls was evaluated under similar conditions, using anthracene as substrate.

Results for the catalytic hydrogenation of anthracene under 700 psi 1:1 CO/H_2 and in nonaqueous THF are given in Table 3-6. Of the carbonyls tested, only the dinuclear complexes of cobalt and manganese catalyze the reduction of anthracene under syngas conditions, giving exclusively 9,10-dihydroanthracene. The hexacarbonyls of Group 7B metals - chromium, molybdenum, and tungsten - are ineffective as catalysts of anthracene hydrogenation; probably, like iron pentacarbonyl, they do not undergo ligand dissociation and oxidative addition of hydrogen to form metal carbonyl hydrides, except at very high hydrogen partial pressures. In contrast, both $Re_2(CO)_{10}$ and $Ru_3(CO)_{12}$ readily form hydrido-metal-carbonyl cluster complexes by reaction with molecular hydrogen (K8), but they are catalytically inactive for hydrogenation of anthracene under the experimental conditions. A plausible explanation is that for these complexes, ligand dissociation and binding of the substrate to the vacant coordination site is prerequisite for reduction but totally inhibited by excess carbon monoxide.

The unique ability of the dinuclear cobalt and manganese carbonyls to catalyze the hydrogenation of anthracene is illustrated in Figure 1-6. First, hydrogen is added homolytically across the metal-metal bond under relatively mild conditions, to give the mononuclear monohydride deriva-

Table 3-6. Homogeneous hydrogenation under syngas conditions (700 psi 1:1 CO/H_2).

Catalyst	Substrate	Product
$Co_2(CO)_6(Ph_3P)_2$	anthracene	 100%
$Co_2(CO)_6(Ph_3P)_2$	9,10-dimethyl-anthracene	 ,  (51%) (49%) 100 %
$Mn_2(CO)_8(Bu_3P)_2$	anthracene	 30%
$Mn_2(CO)_8(Bu_3P)_2$	9,10-dimethyl-anthracene	 ,  (50%) (50%) 28 %
$Fe(CO)_4$ Bu_3P, $Cr(CO)_6$, $Mo(CO)_6$, $W(CO)_6$, $Re_2(CO)_{10}$, $Ru_3(CO)_{12}$	anthracene	none

Solvent: THF; 200°C; 2 hr

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tive. Second, according to Halpern and co-workers (F6,S3), these carbonyls promote hydrogenation via a free-radical mechanism. Since formation of an aryl-metal complex is not necessary for reaction, CO inhibition is not a factor. The free-radical mechanism predicts center-ring hydrogenation due to its lowered radical-localization energy and also explains the equal distribution of cis and trans isomers observed in hydrogenation of 9,10-dimethylanthracene (Table 3-6). Concerted cis addition would of course lead to only one isomer. Interestingly, we observed a similar result under shift conditions with $Mn_2(CO)_8(PBu_3)_2$. Using equimolar quantities of 9,10-dimethylanthracene and manganese, 30% conversion (1.1:1 cis:trans) was obtained after 5 hours at 180°C.

Other polycyclic aromatic hydrocarbons proved to be essentially unreactive under the experimental conditions, as illustrated in Table 3-7. Phenanthrene remained unconverted after 5 hours at 200°C and 700 psi (1:1) Co/H_2, with either $Co_2(CO)_6(PPh_3)_2$ or $Mn_2(CO)_8(PBu_3)_2$ as the catalyst. Similarly, naphthalene was not reduced to tetralin. A 10% conversion of 2-methylnaphthalene to 2-methyltetralin was, however, detected after 5 hours in the presence of $Co_2(CO)_6(PPh_3)_2$. Pyrene was also hydrogenated to 4,5-dihydropyrene in very small yield (3%) after 2 hours of reaction with $Mn_2(CO)_8(PBu_3)_2$.

Comparison of $Co_2(CO)_6(PPh_3)_2$ with the unsubstituted

Table 3-7. Homogenous hydrogenation of polynuclear aromatics under syngas conditions

Catalyst	Substrate	Time (hr)	Product
$Co_2(CO)_6(PPh_3)_2$	phenanthrene	5	None
$Mn_2(CO)_8(PBu_3)_2$	phenanthrene	5	None
$Co_2(CO)_6(PPh_3)_2$	naphthalene	5	None
$Mn_2(CO)_8(PBu_3)_2$	naphthalene	5	None
$Co_2(CO)_6(PPh_3)_2$	2-methylnaphthalene	5	10% 2-methyltetralin
$Mn_2(CO)_8(PBu_3)_2$	pyrene	2	3% 4,5-dihydropyrene
$Co_2(CO)_6(PPh_3)_2$	9-phenanthrol	5	None

P_{H_2} = 350 psi; P_{CO} = 350 psi; T = 200°C;
1 mmole Substrate; 0.05 mmole catalyst;

Solvent: THF (15 ml)

carbonyl, $Co_2(CO)_8$, is difficult because of the difference in reaction conditions. The results of Friedman et al. (F5) show greater conversion of the same compounds with $Co_2(CO)_8$ than we observed with $Co_2(CO)_6(PPh_3)_2$. While temperature, residence time, and catalyst concentration were very similar in the two instances, Friedman and co-workers operated at extremely high pressures, generally in excess of 5000 psi CO/H_2 (1:1). If a first-order dependence on hydrogen partial pressure is assumed, a 5 to 10% conversion of naphthalene to tetralin should occur at 350 psi H_2; on this basis $Co_2(CO)_8$ appears to be the more active catalyst. $Co_2(CO)_8$ nevertheless requires much greater CO pressures to remain stable. Decomposition of cobalt carbonyl produces cobalt metal which is catalytically inactive for fused-ring hydrogenation at 200°C.

2. Regioselective Hydrogenation of Heterocyclic Aromatics

The regioselective hydrogenation of polynuclear heteroaromatic nitrogen compounds proceeds at a much greater rate in the presence of synthesis gas than it does under water gas shift conditions. As with the aromatic hydrocarbons, cobalt and manganese complexes display the greatest catalytic activity. Figure 3-6 illustrates the relative reactivities of several nitrogen heterocycles when $Co_2(CO)_6(PPh_3)_2$ is used as the catalyst. Acridine is quantitatively converted to 9,10-dihydroacridine after 1 hour at

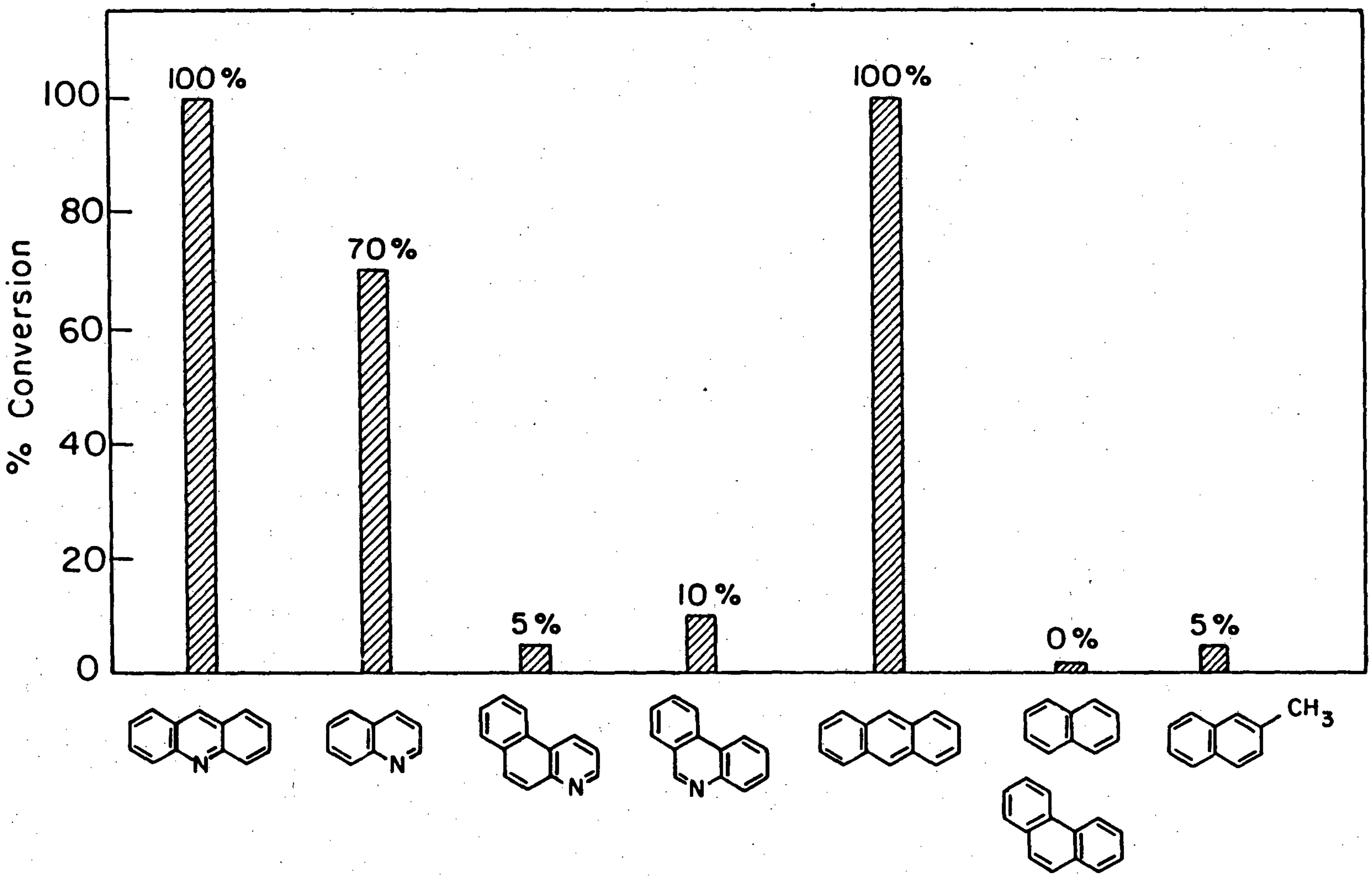

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Figure 3-6. Homogeneous hydrogenation with $Co_2(CO)_6(PPh_3)_2$; 200°C; 1 hr.

200°C, and quinoline gives 70% 1,2,3,4-tetrahydroquinoline. Phenanthridine and 5,6-benzoquinoline are reduced in much lower yields with only the nitrogen-containing ring being hydrogenated.

Figure 3-6 also compares the reactivities of these compounds to their hydrocarbon analogs. The lowered aromaticity of the nitrogen-containing ring greatly enhances its ease of reduction and accounts for the higher product yields with the heteroaromatic compounds. Benzene, for example, has a resonance energy of 36 kcal/mole and is much more difficult to hydrogenate than pyridine which has a resonance energy of 23 kcal/mole (C2). A similar explanation could account for the ease with which anthracene is hydrogenated as compared to phenanthrene. Anthracene has a resonance energy of 92 kcal/mole. Attack at the 9- and 10-positions leaves two benzene rings intact; thus there is a sacrifice of only 12 kcal of resonance energy for anthracene and 20 kcal for phenanthrene.

The effect of carbon monoxide partial pressure on the $Co_2(CO)_6(PPh_3)_2$-catalyzed conversion of quinoline to 1,2,3,4-tetrahydroquinoline is illustrated in Figure 3-7. Below about 300 psi CO, the complex is unstable and slowly decomposes to an inactive, heterogeneous material. At higher pressures, however, $Co_2(CO)_6(PPh_3)_2$ remains homogeneous, and the reaction proceeds at a rate essentially independent of CO partial pressure. In contrast, carbon

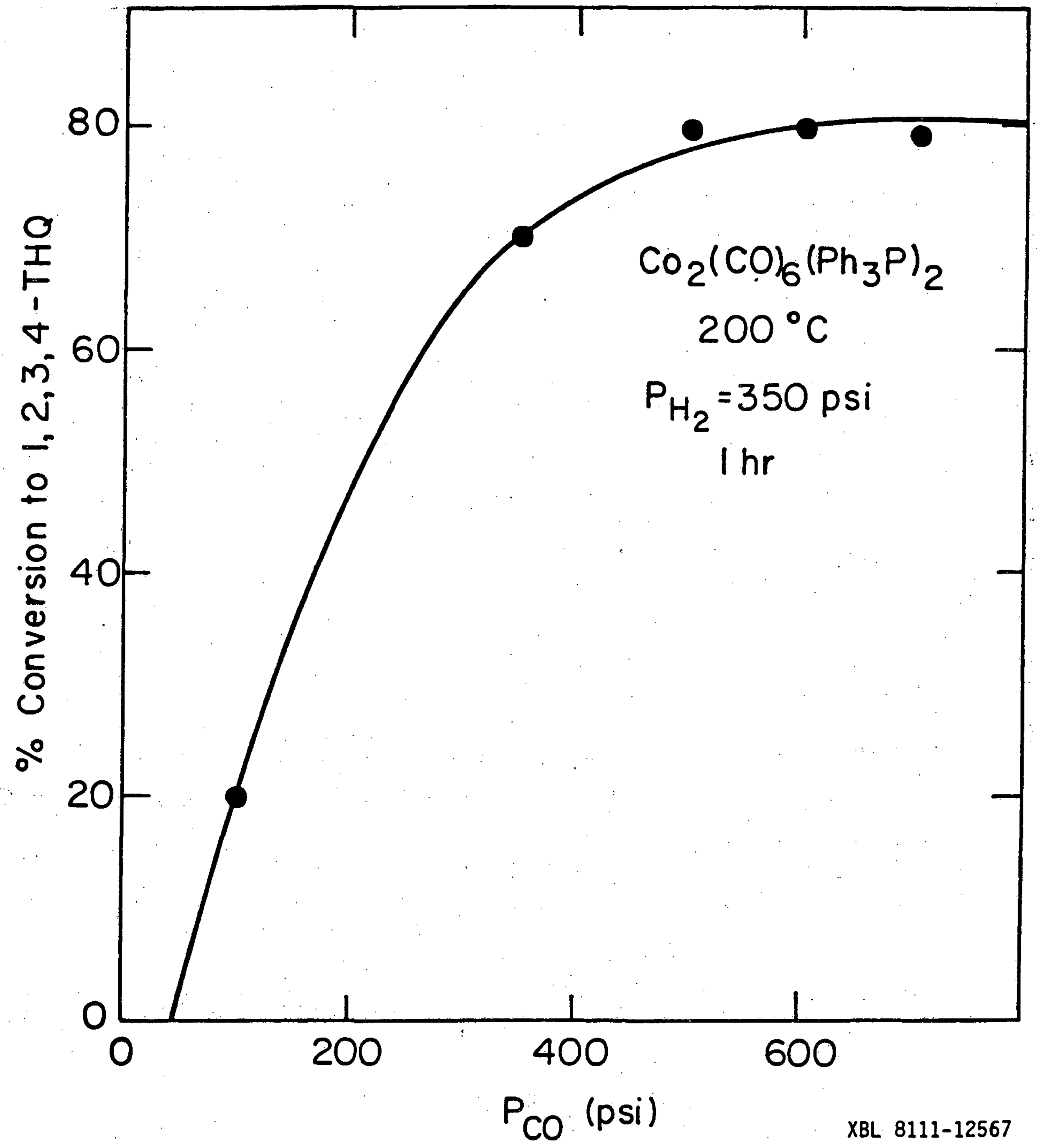
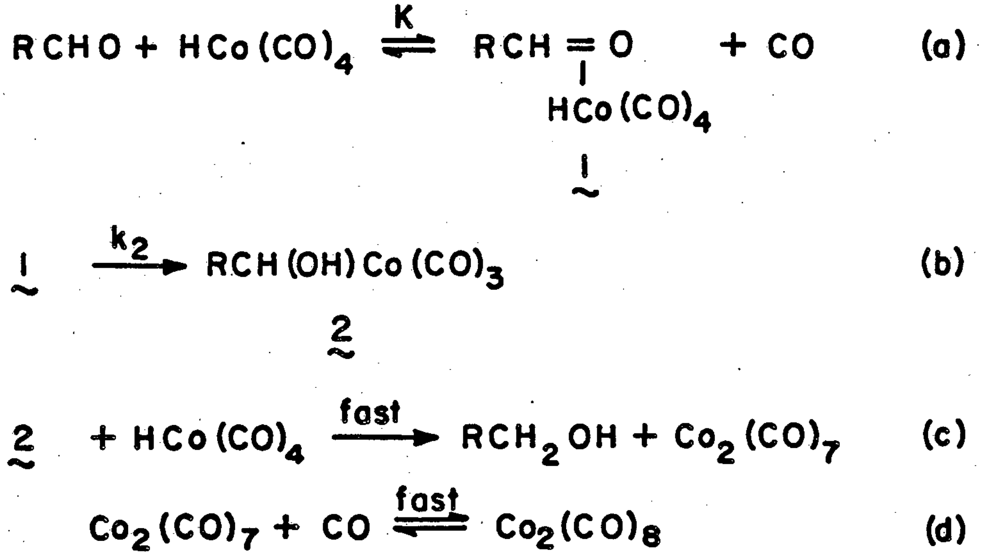


Figure 3-7. Effect of CO partial pressure on $Co_2(CO)_6(PPh_3)_2$-catalyzed hydrogenation of quinoline.

monoxide was found to inhibit $Co_2(CO)_8$ catalysis both for hydrogenation of propionaldehyde (M8) and for hydroformylation of olefins (C12). Aldridge and Johassen (A3) also studied $Co_2(CO)_8$ activity for aldehyde reduction under syngas conditions; they found an inverse first-order dependence on carbon monoxide pressure in the range of 300 to 1000 psi, and interpreted this as evidence for a mechanism requiring CO dissociation with formation of an organocobalt intermediate.



$$RCHO + HCo(CO)_4 \overset{K}{\rightleftharpoons} \underset{\underset{\underset{\sim}{1}}{HCo(CO)_4}}{RCH{=}O} + CO \qquad (a)$$

$$\underset{\sim}{1} \xrightarrow{k_2} \underset{\underset{\sim}{2}}{RCH(OH)Co(CO)_3} \qquad (b)$$

$$\underset{\sim}{2} + HCo(CO)_4 \xrightarrow{fast} RCH_2OH + Co_2(CO)_7 \qquad (c)$$

$$Co_2(CO)_7 + CO \overset{fast}{\rightleftharpoons} Co_2(CO)_8 \qquad (d)$$

The independence of the quinoline hydrogenation rate from CO partial pressure suggests that the mechanism does not involve coordination to the metal center. Figure 3-8 details a plausible mechanism for the hydrogenation of quinoline to 1,2,3,4-tetrahydroquinoline in the presence of $Co_2(CO)_6(PPh_3)_2$. In step (1), the cobalt dimer reacts with H_2 to give 2 moles of the mononuclear monohydride, $HCo(CO)_3(PPh_3)$. While not as strong an acid as the unsubstituted tetracarbonyl cobalt hydride, $HCo(CO)_3(PPh_3)$ is still very acidic with a pK_a of 2.7. Quinoline, itself a

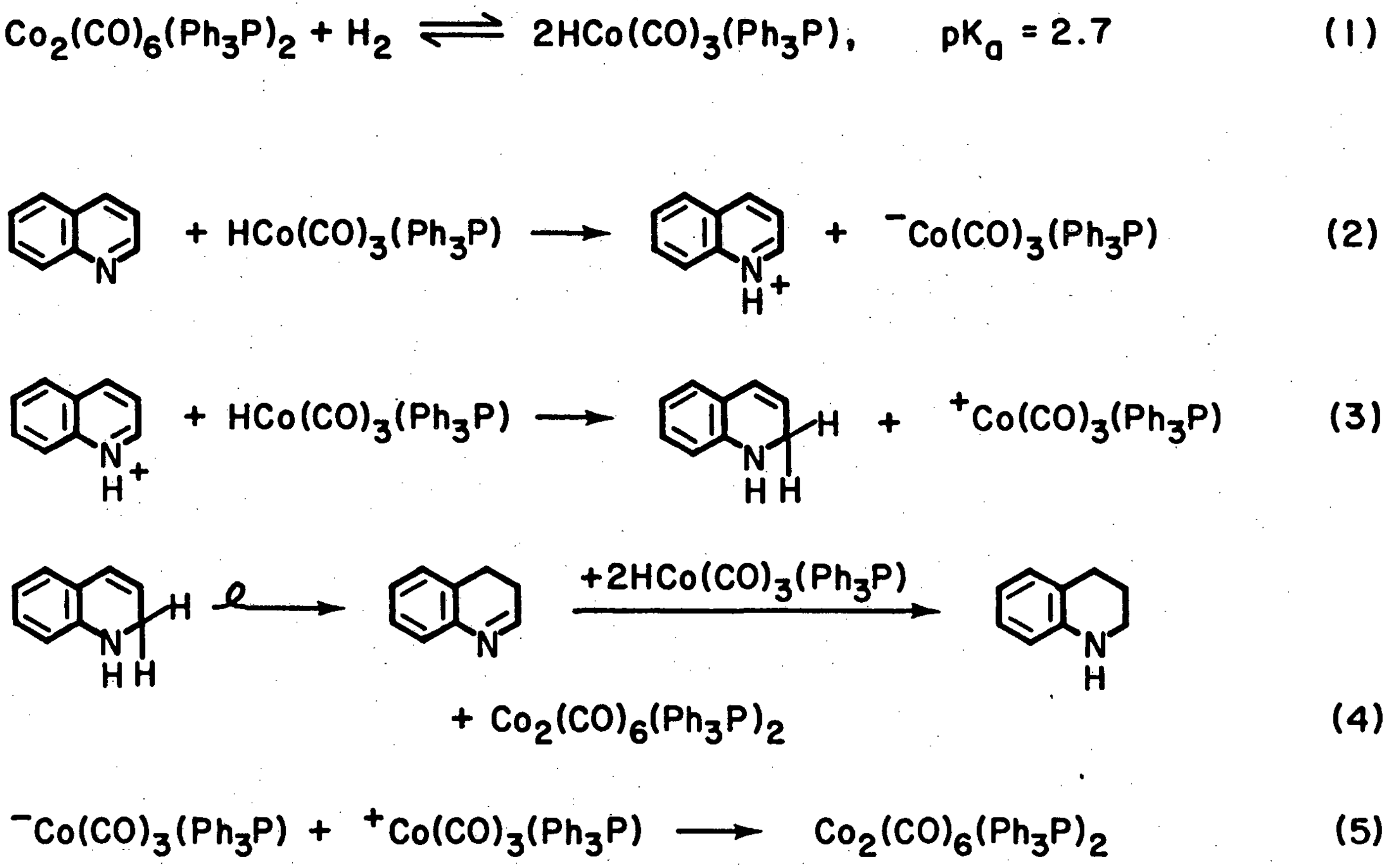


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Figure 3-8. Proposed mechanism for $Co_2(CO)_6(PPh_3)_2$-catalyzed hydrogenation of quinoline.

weak base (pK_b=9.5), could easily be protonated by $HCo(CO)_3(PPh_3)$ which behaves as a superacid in a nonaqueous solvent. Step (3) shows that $HCo(CO)_3(PPh_3)$ may also act as a hydride donor to the protonated quinoline, yielding 1,2-dihydroquinoline. Superacid media are known to induce hydride abstraction (03), and H_2 might even act as hydride donor.

Rapid rearrangement leads to the 3,4-dihydroquinoline which reacts with 2 moles of $HCo(CO)_3(PPh_3)$ to give 1,2,3,4-tetrahydroquinoline. The absence of any dihydroquinolines in the reaction product suggests that partial hydrogenation of the heterocyclic ring produces an intermediate which is rapidly converted to the tetrahydro derivative. The cobalt carbonyl anion generated in step (2) and the cobalt carbonyl cation generated in step (3) combine in step (5) to regenerate the original catalyst.

The results of Table 3-8 offer support for this mechanism. $Co_2(CO)_6(PPh_3)_2$ provides only 50% conversion in cyclohexane as compared with 70% conversion in THF. This is one of the few instances where a solvent effect was observed; it would be expected that reaction involving protonation and hydride abstraction should proceed faster in a polar solvent such as THF than in a non-polar one such as cyclohexane. Furthermore, the reaction is greatly accelerated by addition of a small amount of 5 wt-% sulfuric acid, giving 100% conversion after 1 hour; this suggests

Table 3-8. $Co_2(CO)_6(PPh_3)_2$ - catalyzed hydrogenation of nitrogen heterocycles

Substrate	Solvent	Time (hr)	Product
Quinoline	Cyclohexane	1	50% 1,2,3,4-Tetrahydroquinoline
Quinoline	THF	1	70% 1,2,3,4-Tetrahydroquinoline
Quinoline*	THF	1	100% 1,2,3,4-Tetrahydroquinoline
Phenanthridine	THF	2	21% 9,10-Dihydrophenanthridine
5,6-Benzoquinoline	THF	2	8% 1,2,3,4-Tetrahydro-5,6-benzoquinoline
7,8-Benzoquinoline	THF	2	8% 1,2,3,4-Tetrahydro-7,8-benzoquinoline

P_{H_2} = 350 psi; P_{CO} = 350 psi; T = 200°C;

1 mmole Substrate; 0.05 mmole $Co_2(CO)_6(PPh_3)_2$

* 2 ml 5 wt-% H_2SO_4 added.

that protonation of the nitrogen-containing ring (step (2)) is the rate-limiting step. The mechanism of Figure 3-8 could also account for the greater reactivity of quinoline relative to benzoquinoline or phenanthridine in terms of its greater basicity. In addition, the identical results obtained with both 5,6- and 7,8-benzoquinoline are explained by a mechanism which does not involve a coordination of the substrate to the catalyst.

The $Mn_2(CO)_8(PBu_3)_2$-catalyzed hydrogenation of polynuclear heteroaromatic nitrogen compounds displays an ordering of reactivities very similar to that obtained for $Co_2(CO)_6(PPh_3)_2$. As illustrated in Figure 3-9, the order is acridine > quinoline >> phenanthridine > 5,6-benzoquinoline > 7,8-benzoquinoline. The manganese complex, however, is much less active than the corresponding cobalt complex. This could be due to the lower acidity of $HMn(CO)_4(PBu_3)$ relative to $HCo(CO)_3(PPh_3)$.

C. Hydrogenation with Soluble Ruthenium Complexes

1. Anthracene Hydrogenation

With the dinuclear cobalt and manganese complexes under syngas conditions, hydrogenation of anthracene produces exclusively 9,10-dihydroanthracene, the thermodynamically preferred product. In the absence of carbon monoxide, other investigators (E2,R2,G3) have observed outer ring hydrogenation, generally with ruthenium or rhodium complexes. These

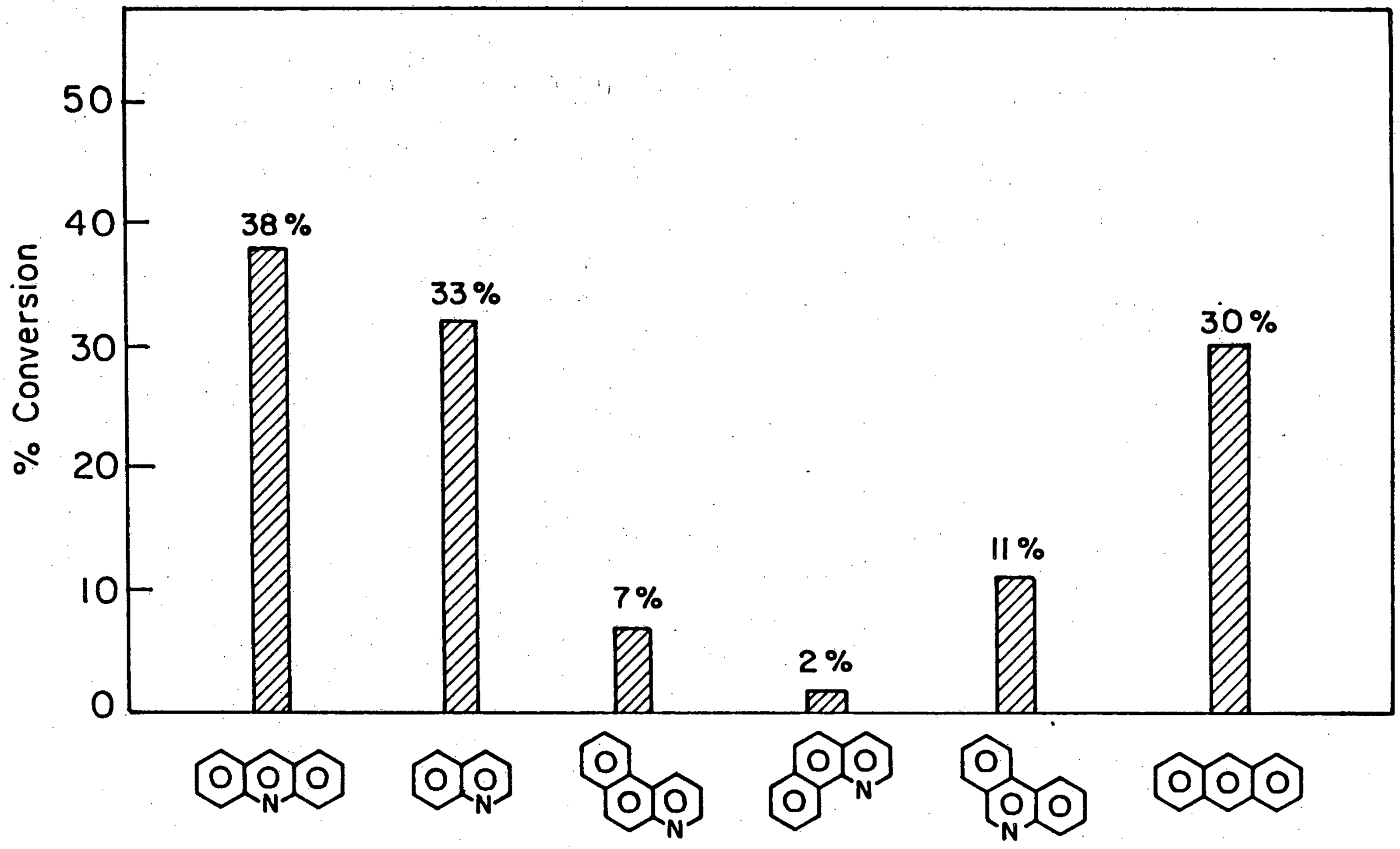

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Figure 3-9. Homogeneous hydrogenation with $Mn_2(CO)_8(PBu_3)_2$; 200°C; 1 hr.

reports prompted a study of ruthenium complexes which do not require carbon monoxide to remain in solution at elevated temperatures. Two catalysts were chosen - $RuCl_2(CO)_2(PPh_3)_2$ and $Ru_3(CO)_6(PPh_3)_6$ - and a series of experiments was performed with each one using various combinations of carbon monoxide, hydrogen, and base.

Results are summarized in Table 3-9. For these two catalysts both base and hydrogen are needed for anthracene reduction, and only 1,2,3,4-tetrahydroanthracene is produced. If base is not present or if carbon monoxide is added, no reaction occurs. In order to verify that 1,2,3,4-tetrahydroanthracene was not formed by disproportionation of 9,10-dihydroanthracene, the latter compound was added to the $RuCl_2(CO)_2(PPh_3)_2/H_2/0.2M$ KOH system; it remained unchanged after 5 hours at 180°C.

When unsubstituted $Ru_3(CO)_{12}$ is heated to 180°C in the absence of carbon monoxide, it rapidly decomposes to ruthenium metal, which is an extremely active aromatic hydrogenation catalyst. Under these conditions anthracene was converted to a variety of hydrogenated anthracenes, including 1,2,3,4,5,6,7,8-octahydroanthracene and the totally saturated compound, perhydroanthracene.

A generalized mechanism for the hydrogenation of anthracene in the presence of both the monuclear and trinuclear ruthenium complexes is presented in Figure 3-10, where "Ru" represents a ruthenium complex with two vacant

Table 3-9. Ruthenium-catalyzed hydrogenation of anthracene

Catalyst	P_{H_2} (psi)	P_{CO} (psi)	Base	Product
$RuCl_2(CO)_2(Ph_3P)_2$	350	0	None	None
"	0	350	0.2M KOH	None
"	350	0	0.2M KOH	30% 1,2,3,4-tetrahydroanthracene
"	350	350	0.2M KOH	None
$Ru_3(CO)_6(Ph_3P)_6$	350	0	0.2M KOH	25% 1,2,3,4-tetrahydroanthracene
$Ru_3(CO)_{12}$ [decomposed to Ru metal]	350	0	None	100% - variety of hydrogenated anthracenes

Solvent: THF; 5 hr; T = 180°C

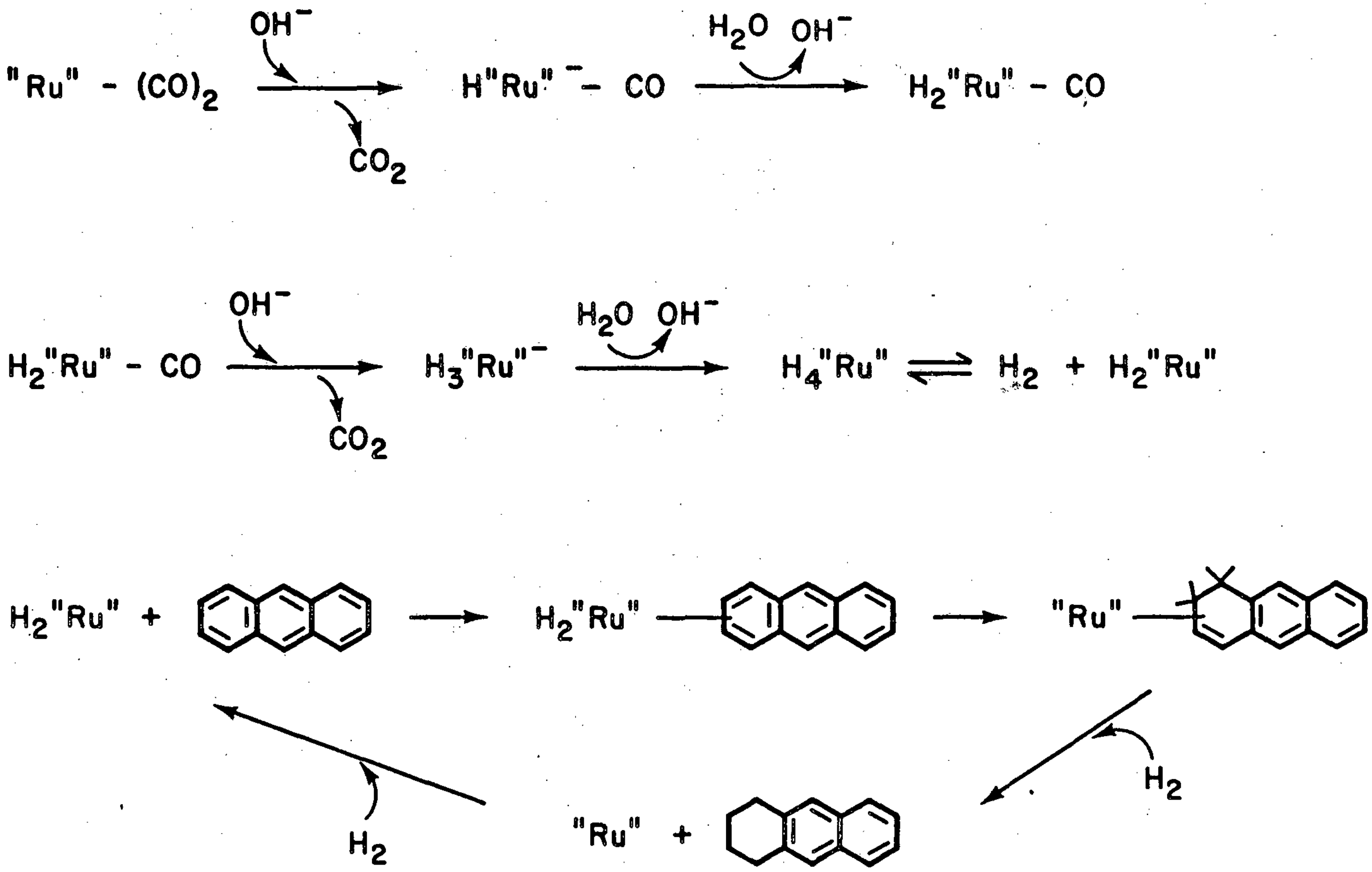

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Figure 3-10. Generalized mechanism for the catalytic hydrogenation of anthracene by a soluble ruthenium complex.

coordination sites - $RuCl_2(PPh_3)_2$ for example. The two carbon monoxide ligands per ruthenium atom are susceptible to nucleophilic attack by OH^- and loss as CO_2. This allows for the formation of a coordinatively unsaturated ruthenium hydride which can bind anthracene to a vacant coordination site. Figure 3-10 shows a 16 electron dihydridoruthenium species which complexes with the outer ring of anthracene in a dihapto manner (Using two π-electrons). Coordination to the center ring may be sterically hindered since 9,10-dihydroanthracene is not a reaction product.

Base may also facilitate heterolytic cleavage of hydrogen with $RuCl_2(CO)_2(PPh_3)_2$:

$$RuCl_2(CO)_2(PPh_3)_2 + H_2 \text{ ---> } HRuCl(CO)_2(PPh_3)_2 + H^+ + Cl^-$$

This provides a means by which a 14 electron ruthenium hydride, $HRuCl(PPh_3)_2$, can be formed. Anthracene could then bind to the metal in a tetrahapto manner (using four π-electrons). The primary role of base, however, is not to promote hydride formation, but to produce a coordinatively unsaturated ruthenium complex by eliminating carbon monoxide, which thus competes with the substrate for coordination sites. Phosphine-substituted triruthenium carbonyls readily form tetranuclear hydrides by direct reaction with molecular hydrogen in nonaqueous solvents (P2), yet will not hydrogenate anthracene unless base is present. Similarly, Sanchez-Delgado et al. (S10) report that $RuCl_2(CO)_2(PPh_3)_2$, is an excellent aldehyde hydrogenation catalyst in the presence of

400 psi hydrogen and toluene (conditions which give no reduction of anthracene).

2. Regioselective Hydrogenation of Nitrogen Heterocycles

Results for $RuCl_2(CO)_2(PPh_3)_2$-catalyzed hydrogenation of aromatic nitrogen heterocycles are presented in Table 3-10. After 5 hours at 180°C, in the presence of 350 psi H_2 and 0.2M KOH, acridine is quantitatively reduced to 9,10-dihydroacridine, 5,6-benzoquinoline gives 10% 1,2,3,4-tetrahydrobenzoquinoline, phenanthridine gives 5% 9,10-dihydrophenanthridine, and 7,8-benzoquinoline remains totally unconverted.

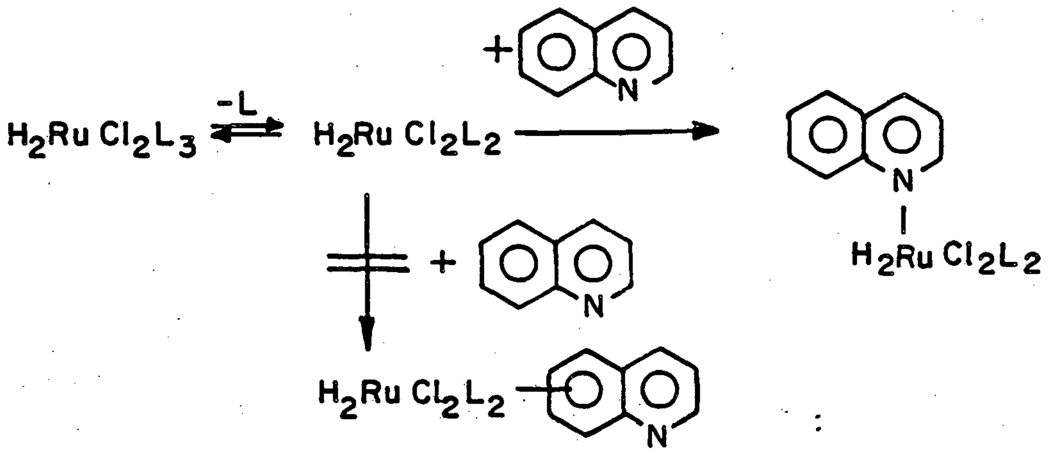
After 2 hours under similar conditions, quinoline is reduced to two products - 1,2,3,4-tetrahydroquinoline (42%) - and 5,6,7,8-tetrahydroquinoline (5%). This is the only instance in which we observed homogeneous hydrogenation of the nonheterocyclic ring of a heteroaromatic compound. If the base is omitted quinoline is quantitatively converted to 1,2,3,4-tetrahydroquinoline with no trace of the 5,6,7,8-isomer. Clearly, base is necessary to provide for proper coordination of the aromatic ring but not the nitrogen-containing ring. In the absence of base, a reversible lingand dissociation step is necessary to produce a coordinately unsaturated ruthenium complex which can coordinate with the substrate:

Table 3-10. $RuCl_2(CO)_2(PPh_3)_2$ - catalyzed hydrogenation of nitrogen heterocycles

Substrate	Base	Time (hr)	Product
Quinoline	0.2 M KOH	2	42% 1,2,3,4-tetrahydroquinoline 5% 5,6,7,8-tetrahydroquinoline
Quinoline	None	2	100% 1,2,3,4-tetrahydroquinoline
Acridine	0.2 M KOH	5	100% 9,10-dihydroacridine
5,6-Benzoquinoline	0.2 M KOH	5	10% 1,2,3,4-tetrahydrobenzoquinoline
7,8-Benzoquinoline	0.2 M KOH	5	None
Phenanthridine	0.2 M KOH	5	5% 9,10-Phenanthridine

P_{H_2} = 350 psi; T = 180°; THF (12 ml)

0.1 mmole $RuCl_2(CO)_2(PPh_3)_2$; 1 mmole Substrate



Apparently the lone electron pair on nitrogen allows it to compete successfully with ligand for the vacant coordination site. However, the aromatic portion of the ring can only coordinate if there is no excess ligand present. Hence, oxidation of CO to CO_2 in the presence of base is an irreversible means of providing a coordinatively unsaturated metal complex.

The production of 5,6,7,8-tetrahydroquinoline in the presence of 0.2M KOH, 350 psi H_2, and $RuCl_2(CO)_2(PPh_3)_2$ offers insight into the mechanism of anthracene hydrogenation under these conditions. The scheme presented in Figure 3-10 predicts the formation of a 16 electron species $H_2RuCl_2(PPh_3)_2$, very similar to $H_2RuCl_2L_2$, where L may be either CO or PPh_3. $H_2RuCl_2L_2$ appears unable to interact with the nonheterocyclic ring of quinoline, since only 1,2,3,4-tetrahydroquinoline is produced in the absence of base. Rather, it seems likely that the 14 electron ruthenium hydride, $HRuCl(PPh_3)_2$, necessary to properly coordinate the aromatic ring, can only be formed when base is present. The outer ring of anthracene, therefore, probably coordinates to ruthenium in a tetrahapto rather than dihapto manner.

Triruthenium dodecacarbonyl is also an effective catalyst for the homogeneous hydrogenation of aromatic nitrogen heterocycles. It reacts readily with molecular hydrogen at 150°C to form tetrahydridotetraruthenium dodecacarbonyl. In fact, greater conversions are achieved if $H_4Ru_4(CO)_{12}$ is generated separately and then used as the catalyst. For example, $H_4Ru_4(CO)_{12}$ gives 75% conversion of 5,6-benzoquinoline to 1,2,3,4-tetrahydrobenzoquinoline after 2 hours of reaction at 150°C and 350 psi H_2 while $Ru_3(CO)_{12}$ gives only 7% conversion under the same conditions. Figure 3-11 illustrates the relative reactivities of several aromatic nitrogen compounds in the presence of $H_4Ru_4(CO)_{12}$.

Acridine is reduced to 9,10-dihydroacridine in 75% yield after 1 hour of reaction at 150°C and 350 psi H_2. Under identical conditions, quinoline proves to be almost as reactive as acridine, giving 70% 1,2,3,4-tetrahydroquinoline, while 5,6-benzoquinoline gives 45% 1,2,3,4-tetrahydrobenzoquinoline. 7,8-benzoquinoline is much less reactive than the 5,6-isomer, probably due to steric hinderance, and is converted to reduced product in only 5% yield. This is in contrast to the results obtained

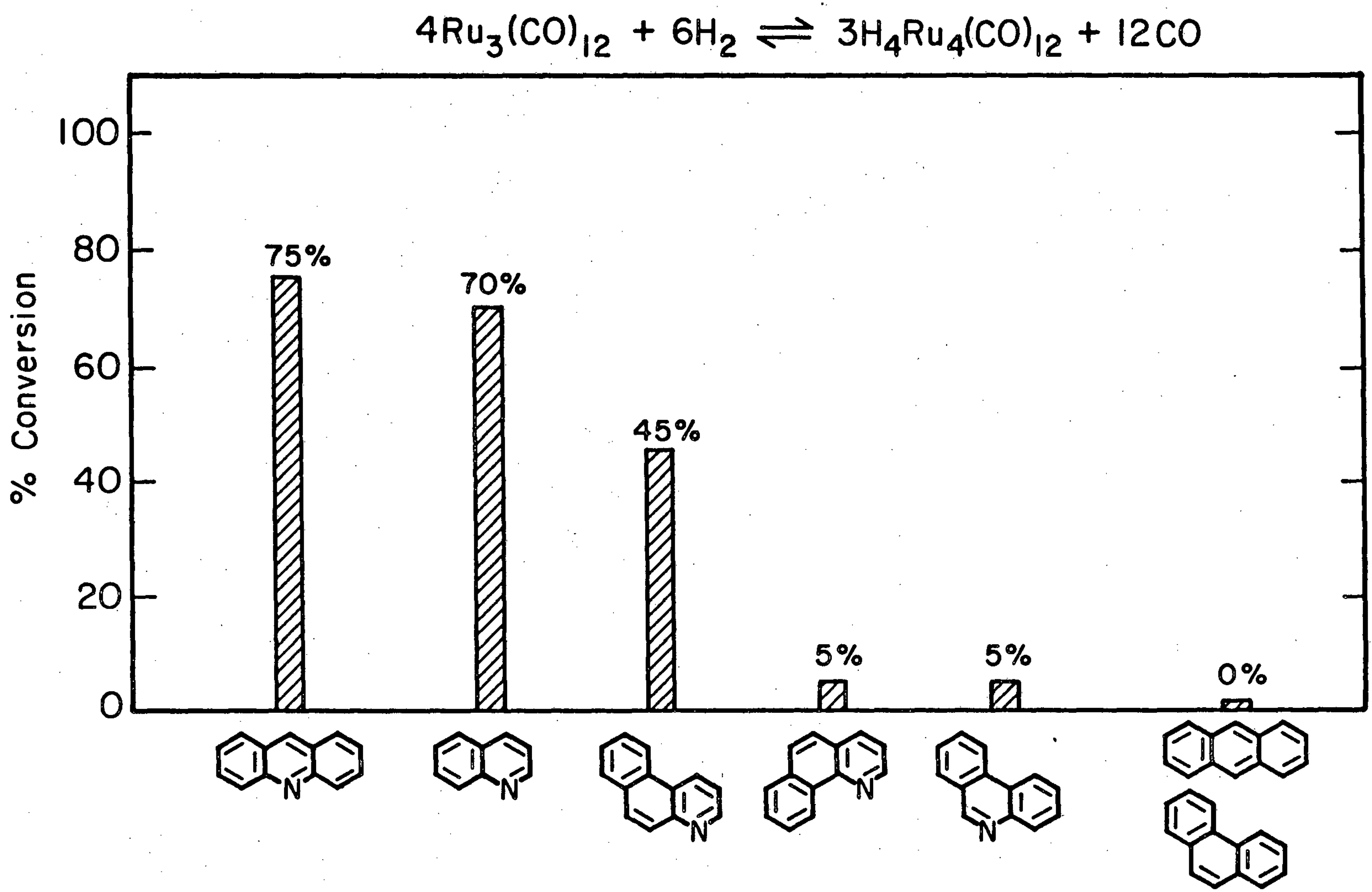


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Figure 3-11. Homogeneous hydrogenation with $H_4Ru_4(CO)_{12}$; 150°C; 1 hr.

with $Co_2(CO)_6(PPh_3)_2$ in which 5,6-benzoquinoline and 7,8-benzoquinoline were equally reactive. Similarly, only 5% 9,10-dihydrophenanthridine is produced by reaction of phenanthridine. There should, however, be no steric limitation to proper coordination of the nitrogen of phenanthridine which possesses an electron pair orthogonal to the pi cloud. The low reactivity is probably due to an electronic effect; the complex may be formed but not undergo hydrogen transfer or, conversely, the complex may not possess sufficient thermodynamic stability to be formed at all.

The ordering of reactivities is essentially the same with $H_4Ru_4(CO)_{12}$ as with $Co_2(CO)_6(PPh_3)_2$, although the relative magnitudes are different: acridine > quinoline > 5,6-benzoquinoline >> 7,8-benzoquinoline ~ phenanthridine. Unlike $Co_2(CO)_6(PPh_3)_2$, $H_4Ru_4(CO)_{12}$ is incapable of reducing aromatics. The effect of carbon monoxide partial pressure on the homogeneous hydrogenation activity of $H_4Ru_4(CO)_{12}$ suggests distinct mechanistic differences. Figure 3-12 illustrates the dependence on CO partial pressure of quinoline hydrogenation with $H_4Ru_4(CO)_{12}$. A mere 20 psi CO reduces the conversion of quinoline from 70% to 50% while 100 psi CO totally quenches the reaction. This is in direct contrast to $Co_2(CO)_6(PPh_3)_2$, which promotes quinoline hydrogenation at a rate independent of carbon monoxide partial pressure provided it is sufficiently great to prevent catalyst decomposition (Figure 3-7).

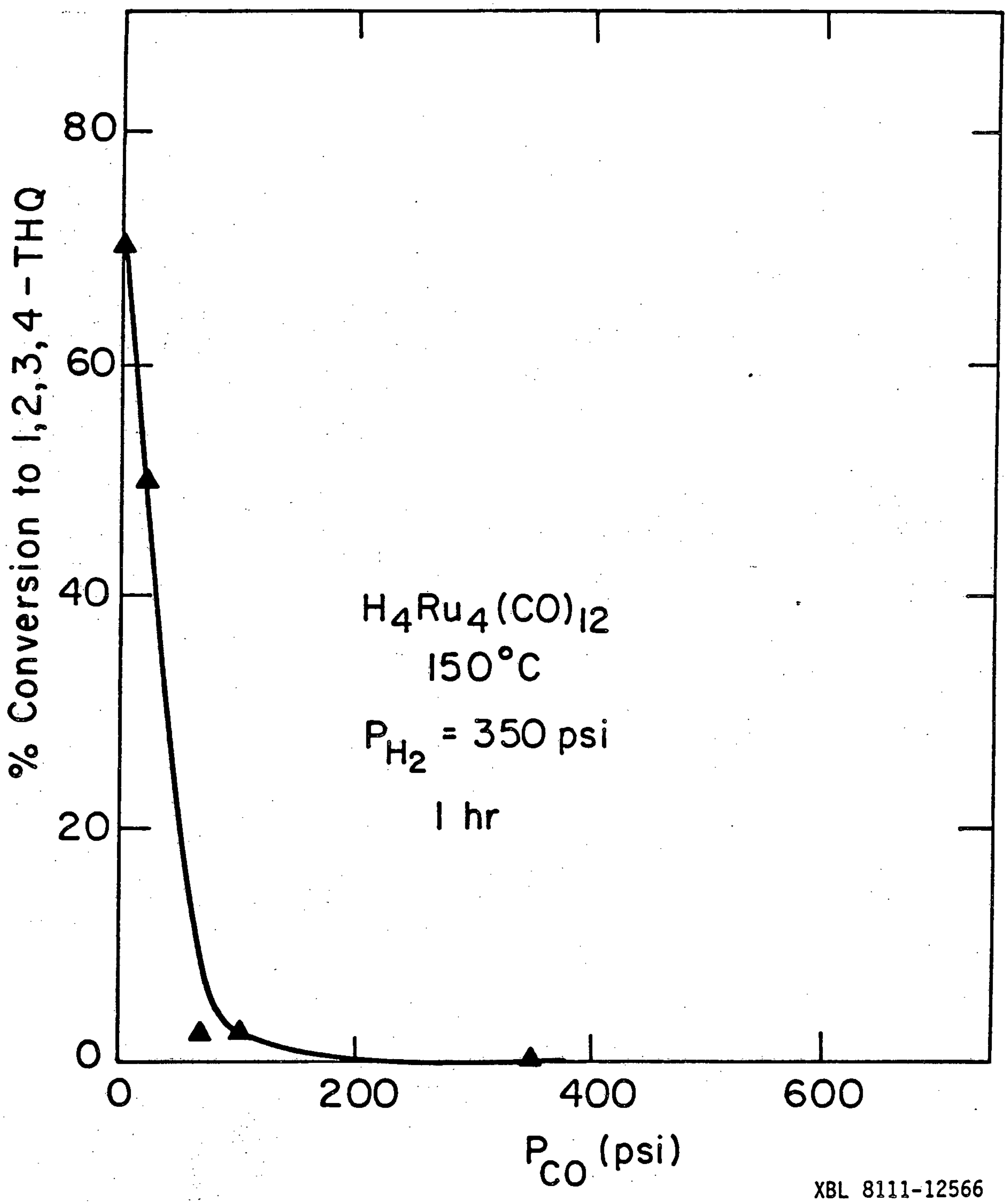

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Figure 3-12. Effect of CO partial pressure on $H_4Ru_4(CO)_{12}$-catalyzed hydrogenation of quinoline.

Figure 3-13 presents a mechanism which explains the inhibitory role of carbon monoxide. As long as the CO pressure is kept below 100 psi, $H_4Ru_4(CO)_{12}$ remains the primary form of ruthenium in solution with a small amount of $Ru_3(CO)_{12}$ present at higher pressures. The mononuclear species $Ru(CO)_5$ only begins to form at CO pressures in excess of 350 psi. The catalytically active complex, $H_4Ru_4(CO)_{12}$, is therefore present in high concentration under all reaction conditions. In order to complex with the substrate, $H_4Ru_4(CO)_{12}$ must first undergo CO dissociation to provide a vacant coordination site. As long as the CO pressure is sufficiently low (<20psi), the nitrogen heterocycle can effectively compete with carbon monoxide and bind to the metal center. At higher carbon monoxide pressures (>100 psi), $H_4Ru_4(CO)_{11}$ will recoordinate CO rather than complex with the substrate. Once an organometallic species is formed, intramolecular hydrogen transfer occurs very rapidly giving the reduced compound, in this case, 1,2,3,4-tetrahydroquinoline. Polynuclear aromatics, which probably require two vacant sites to properly coordinate, are not sufficiently good ligands to complex with $H_4Ru_4(CO)_{10}$ even if it is formed. The pronounced carbon monoxide inhibition thus provides strong evidence for a mechanism in which binding of the substrate to a coordinatively unsaturated metal complex is the rate-limiting step.

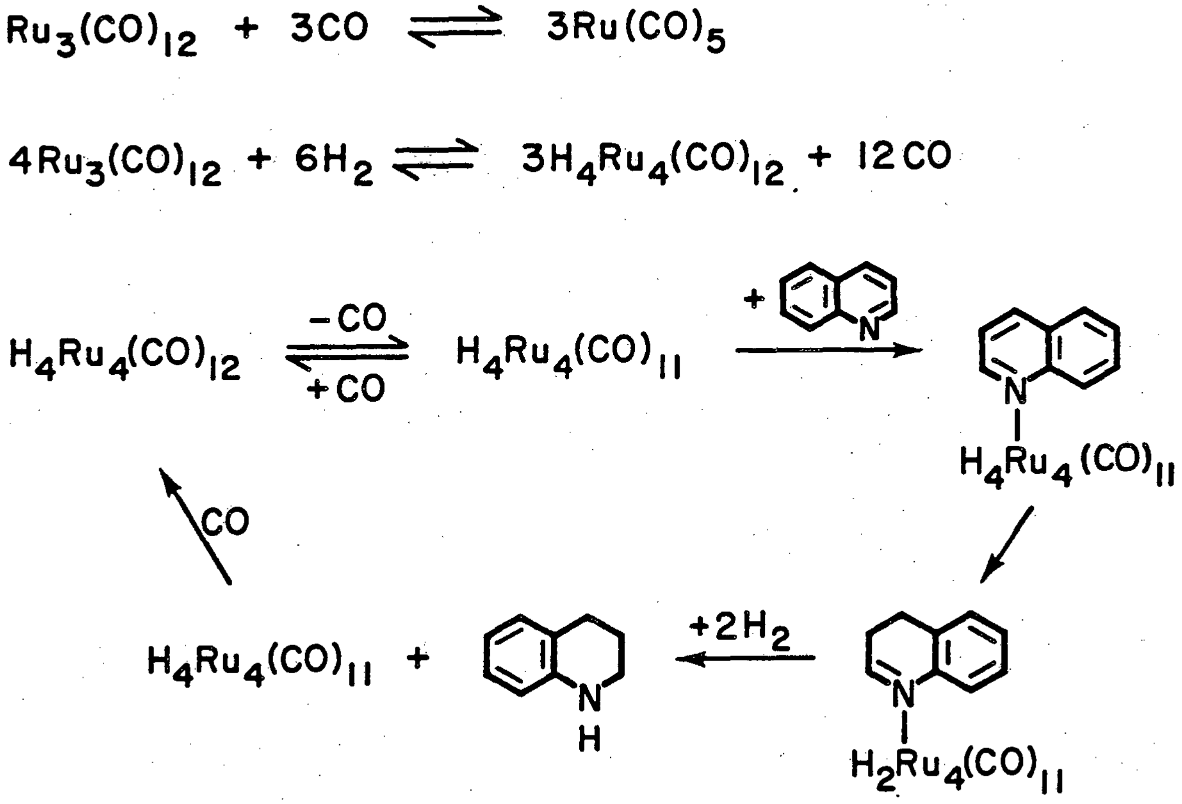

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Figure 3-13. Proposed mechanism for the $H_4Ru_4(CO)_{12}$-catalyzed hydrogenation of quinoline.

IV. CONCLUSIONS

The metal-carbonyl-catalyzed reduction of polynuclear aromatics and polynuclear heteroaromatics under shift conditions does not appear promising. Deuterium-labeling experiments indicate that reductive elimination of H_2 from the metal carbonyl hydride occurs at a much greater rate than transfer of hydrogen to an aromatic substrate. In addition, many homogeneous catalysts require coordination of the substrate prior to hydrogen transfer - a step that is totally inhibited by excess carbon monoxide. The exceptional ability of $Fe(CO)_5$ to reduce acridine in the presence of CO and aqueous base is probably the result of an electron-transfer reaction in which $HFe(CO)_4^-$ is the principal electron-donating species. The reduced aromaticity and the increased radical-delocalization energy of the center, nitrogen-containing ring make acridine particularly reactive.

Under syngas conditions (1:1 CO/H_2) only the dinuclear cobalt and manganese carbonyls promote fused-ring hydrogenation. Their unique activity derives from two features: 1) they readily form hydrides by homolytic addition of H_2 across the metal-metal bond; and 2) their mode of action does not require formation of an aryl-metal complex so CO inhibition is not a factor. Since there are no steric limitations attack occurs at the position of highest free valence, favoring inner rings, substituted rings, and rings containing heteroatoms.

Two ruthenium complexes, $Ru_3(CO)_{12}$ and $RuCl_2(CO)_2(PPh_3)_2$, were evaluated under strictly hydrogenation conditions (only H_2 and a water-free organic solvent). Both display high selectivity towards reduction of aromatic nitrogen-containing rings, with $H_4Ru_4(CO)_{12}$ being the most active form of ruthenium in solution. Carbon monoxide was observed to be extremely inhibitory, suggesting a mechanism that involves coordination of the substrate to the metal center.

If both aqueous base and molecular hydrogen are used, anthracene is reduced exclusively to 1,2,3,4-tetrahydroanthracene in the presence of $RuCl_2(CO)_2(PPh_3)_2$. No reaction occurs in the absence of base. Furthermore, quinoline is quantitatively reduced to 1,2,3,4-tetrahydroquinoline with $RuCl_2(CO)_2(PPh_3)_2$ under strictly hydrogenation conditions, but if base is added, approximately 10% of the product is 5,6,7,8-tetrahydroquinoline. In the absence of base, a reversible ligand dissociation step gives a 16 electron ruthenium complex which can coordinate with nitrogen via its lone pair of electrons orthogonal to pi cloud. The role of base is to promote nucleophilic attack on coordinated CO and loss as CO_2. This potentially produces a 14 electron ruthenium complex, which must be necessary to properly coordinate the hydrocarbon ring. Thus the aromatic ring coordinates in a tetrahapto rather than a dihapto manner.

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ACKNOWLEDGEMENTS

We wish to thank Drs. H. Heinemann, K.P.C. Vollhardt, and R.G. Bergman for helpful comments concerning this study.

This study was jointly supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division and the Assistant Secretary of Fossil Energy, Office of Coal Research, Liquefaction Division of the U.S. Department of Energy under Contract DE-AC03-76SF00098, through the Pittsburgh Energy Technology Center.

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