Title

REGIOSELECTIVE REDUCTION OF POLYNUCLEAR HETEROAROMATICS CATALYZED BY TRANSITION METAL COMPLEXES AND HYDRODENITROGENATION CHEMISTRY

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DISCLAIMER

REGIOSELECTIVE REDUCTION OF POLYNUCLEAR HETEROAROMATICS CATALYZED BY TRANSITION METAL COMPLEXES AND HYDRODENITROGENATION CHEMISTRY

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ARNE DALE THORMODSEN

ABSTRACT

The use of transition metal complexes as catalysts for the reduction of the heteroatom containing ring in polynuclear heteroaromatic compounds has been investigated. Additionally, a study has been made of the heterogeneously catalyzed cleavage of carbon-nitrogen bonds in the regioselectively reduced compound, 1,2,3,4-tetrahydroquinoline.

Chlorotris(triphenylphosphine)rhodium(I) (both homogeneous and polymer-supported), dichlorotris-(triphenylphosphine)ruthenium(II) and dicarbonyldichlorobis(triphenylphosphine)ruthenium(II) have been used as catalysts for the selective reductions of a variety of compounds, including: quinoline, 5,6-benzoquinoline, 7,8-benzoquinoline, acridine, phenanthridine, indole and benzothiophene. Both molecular hydrogen and easily dehydrogenated saturated nitrogen aromatics have been used as hydrogen sources.

The rates of reduction of single compounds and various mixtures of compounds have been determined. The ability of a substrate to bind to the catalyst has been found to be a

primary factor in determining reduction rates.

Deuterium gas has been substituted for hydrogen gas in the reduction of quinoline and phenanthridine. The deuterium incorporation into the products was examined by ^{1}H NMR and mass spectroscopy. These results indicate that the reduction of quinoline is a two step process, a reversible hydrogenation of the 1-2 carbon-nitrogen bond followed by an irreversible reduction of the 3-4 carbon-carbon bond.

Mixtures of quinoline and chlorotris(triphenylphosphine)rhodium(I), in the presence and absence of hydrogen, have been examined by ^{31}P NMR. Several quinoline rhodium complexes have been identified in these mixtures.

Various heterogeneous catalysts have been investigated for the cleavage of the carbon-nitrogen bonds in 1,2,3,4-tetrahydroquinoline. Two highly loaded nickel on silica catalysts have proven to be active for this reaction. Preliminary surface studies on one of these, a 30wt% Ni/SiO_2 catalyst, indicates a bimodal distribution of nickel crystallites, and the presence of some nickel(II) as well as metallic nickel.

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Arne D. Thormodsen

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SECTION I

GENERAL INTRODUCTION

As supplies of petroleum become scarcer serious attention has been given to the use of shale oil and coal derived liquid fuels as refinery feedstocks. These materials present many novel processing problems, since they are hydrogen poor as compared to crude oil, and contain a much higher proportion of heteroatoms: sulfur, oxygen and nitrogen.

In particular, nitrogen presents a unique problem. It is a poison for many of the catalysts used in refinery processing, and is an undesired component in the fuels produced by this processing[1]. While petroleum contains typically less than 0.3% nitrogen, by weight, coal derived liquids can contain up to 0.8% nitrogen[2] and shale oils can have up to a 2.2% nitrogen content[3]. Methods exist for the removal of nitrogen, by catalytically reducing the nitrogen contained within various organic structures to ammonia, this process is called hydrodenitrogenation (HDN). The processing conditions are quite severe, 300 to 400°C, under approximately 1000 psi of hydrogen, using supported catalysts such as $NiMo/Al_2O_3$ or $CoMo/Al_2O_3$.

The general mechanism of HDN involves first the full reduction of any multiple carbon-nitrogen bonds in the substrate, followed by cleavage of the resulting single bonds to remove the nitrogen. Most typically the nitrogen is found contained in a six membered (pyridine) or five

membered (pyrrole) ring, fused into a larger aromatic structure. The processing conditions necessary to reduce the nitrogen containing portion of these compounds are unfortunately so severe that reduction of other aromatic rings, not containing nitrogen, occurs as well. This leads to excessive and uneconomical consumption of hydrogen.

The object of this research has been directed towards two areas of the HDN process. The first area, which forms the major portion of this thesis, has been an investigation of mild and selective means for the reduction of nitrogen containing rings (as well as some sulfur containing rings) in larger fused aromatic compounds. The second area, which is still in the preliminary stages, has been research into catalysts which can selectively remove nitrogen from such regioselectively reduced compounds. Together these two processes form a conceptual basis for the proposal and investigation of more efficient methods of hydrodenitrogenation.

Regioselective Reduction of Polynuclear Heteroaromatics Catalyzed by Transition Metal Complexes:

The investigation of transition metal complexes as catalysts for the selective reduction of polynuclear heteroaromatics constitutes the major portion of this study. Several transition metal complex catalysts which promote the mild and regioselective reductions of the heterocyclic ring in nitrogen (and sulfur) containing

heterocycles, such as quinoline, have been identified. These include $RhCl(PPh_3)_3$ (both homogeneous and polymer-supported), $RuClH(PPh_3)_3$, and $Ru(CO)_2Cl_2(PPh_3)_2$. Both hydrogen gas and easily dehydrogenated reduced nitrogen aromatics have been used as a source of hydrogen. Reductions have been carried out on substrates alone, and on mixtures of substrates and potential inhibitors/enhancers, in order to define the reactivity of these catalysts better in the complex mixtures typical of actual HDN feeds.

More detailed studies of the reduction of quinoline in particular have been carried out. The substitution of deuterium gas for hydrogen gas in the reduction of this compound, as well as other deuterium experiments, has indicated several plausible mechanistic steps necessary to account for the pattern of deuterium incorporation found in the products and unreduced quinoline. The binding of quinoline to a particular catalyst ($RhCl(PPh_3)_3$) in the presence and absence of hydrogen and in the presence and absence of a reduction promoter (p-cresol) has been investigated by ^{31}P and ^{1}H NMR.

Hydrodenitrogenation Chemistry:

An initial study has been carried out investigating the reactions of 1,2,3,4-tetrahydroquinoline, which is produced by the selective reduction of quinoline as described above, over a variety of heterogeneous catalysts.

Pure metals, supported metals and some oxides have been investigated, and two highly loaded nickel on silica catalysts (30% and 50% Ni) have been singled out as deserving further investigation.

These highly loaded nickel catalysts have been found to promote the selective cleavage of the carbon-nitrogen bonds in 1,2,3,4-tetrahydroquinoline to form both benzene and aniline derivatives. Importantly, little or no reduction to cyclohexane derivatives (other than some formation of 5,6,7,8-tetrahydroquinoline) was observed in these nickel catalyzed reactions, validating our proposal that separation of the reduction and nitrogen removal steps in hydrodenitrogenation can lead to more efficient utilization of hydrogen.

The reactions of 2-propylaniline and propylbenzene over these two nickel catalysts, under hydrogen, have been investigated. Both of these compounds are possible intermediates in the HDN of 1,2,3,4-tetrahydroquinoline. These results indicate that the cleavage of the 1-2 carbon-nitrogen bond in tetrahydroquinoline to form 2-propyl-aniline is at least partially reversible, and that the poisoning activity of the various nitrogen bases present in a reaction is critical in moderating the catalyst activity.

Additionally, some preliminary structural studies have been carried out with the 30% Ni/SiO_2 catalyst, indicating a bimodal distribution of nickel crystallite sizes on the surface of the silica. XPS data for this same

catalyst indicates the presence of some nickel (II) on the surface, however nickel (Ø) appears to predominate.

SECTION II

REGIOSELECTIVE REDUCTION OF POLYNUCLEAR HETEROAROMATICS CATALYZED BY TRANSITION METAL CATALYSTS

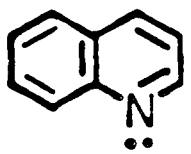
II.A BACKGROUND

We have investigated the selective catalytic reductions of several heteroaromatic nitrogen containing compounds using homogeneous and polymer-supported transition metal complexes and hydrogen. A few sulfur containing aromatics were also examined. The hetero-aromatic compounds, shown in Figure II.1, were chosen as models for the nitrogen containing compounds found especially in coal derived liquids, examples of which are in Figure II.2. The objective of this present study was to reduce only the nitrogen containing ring selectively. Once reduced, the carbon-nitrogen bonds in this ring can conceivably be broken by a separate treatment, and the nitrogen removed, under conditions mild enough to prevent reduction of carbon aromatic rings.

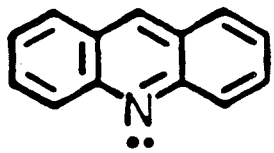
Existing heterogeneous methods of catalytic hydrogenation can result in selective reduction of the heteroatomic ring under suitable conditions, for example quinoline can be reduced to the saturated N-ring product over PtO_2 in methanol[4], but more typically heterogeneous catalysts result in less selective reductions, as in the HDN process described above (a more detailed description of this process appears in section

FIGURE II.1

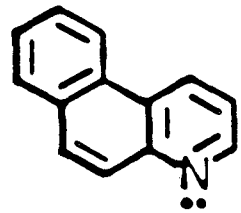
Model Compounds Used as Substrates



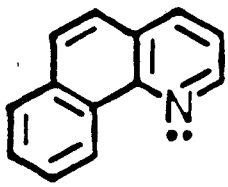
Quinoline



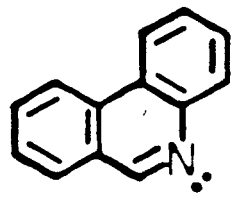
Acridine



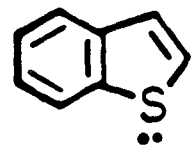
5,6-Benzo-quinoline



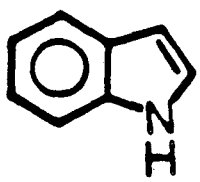
7,8-Benzo-quinoline



Phenanthridine



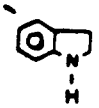
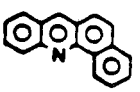
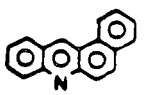
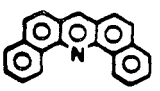
Benzothiophene



Indole

FIGURE II.2

Representative Nitrogen-Containing Compounds Found in Petroleum Crude, Shale Oil, and Coal-Derived Liquids[a]

Compound	Formula	Structure
Nonheterocyclic compounds:		
Aniline	$C_6H_5NH_2$	
Pentylamine	$C_5H_{11}NH_2$	
Nonbasic heterocyclic compounds:		
Pyrrole	C_4H_5N	
Indole	C_8H_7N	
Carbazole	$C_{12}H_9N$	
Basic heterocyclic compounds:		
Pyridine	C_5H_5N	
Quinoline	C_9H_7N	
Indoline	C_8H_9N	
Acridine	$C_{13}H_9N$	
Benz(a)acridine	$C_{17}H_{11}N$	
Benz(c)acridine	$C_{17}H_{11}N$	
Dibenz(c,h)acridine	$C_{21}H_{13}N$	

[a]Coal-derived liquids also contain methyl and alkyl substitution on most of the aromatic compounds.

III.A).

In order to improve the selectivity of this type of reduction, the use of various mononuclear transition metal complexes as catalysts for these reductions was studied. Transition metal complexes, such as the well known homogeneous transition metal hydrogenation catalyst, $RhCl(PPh_3)_3$ (Wilkinson's catalyst), have been proven to be very selective in the reductions they promote. As well, the conditions used for reduction with these catalysts are generally quite mild, as opposed to the severe conditions often used with heterogeneous catalysts, such as described above for the HDN process.

The use of transition metal complexes as catalysts for the reduction of heteroaromatic compounds has not received much attention. The dinuclear cluster, $Co_2(CO)_8$ has been found to reduce thiophene under forcing conditions (180°-190°C, 4000 psi H_2, 2000 psi CO)[5]. This same complex has also been used to reduce pyridine to a mixture of N-methyl and N-formyl piperidine, also under H_2 and CO, the CO is responsible for the formylation and methylation of the nitrogen[6]. Quinoline has been selectively reduced to 1,2,3,4-tetrahydroquinoline (the N-ring reduced product) under hydrogen, using the mononuclear complexes $Mn_2(CO)_8(PBu_3)_2$[7] and $RhCl_2(BH_4)(DMF)py_2$[8] as catalysts.

More recently, Laine et. al. have demonstrated the selective reduction of quinoline to 1,2,3,4-tetrahydro-

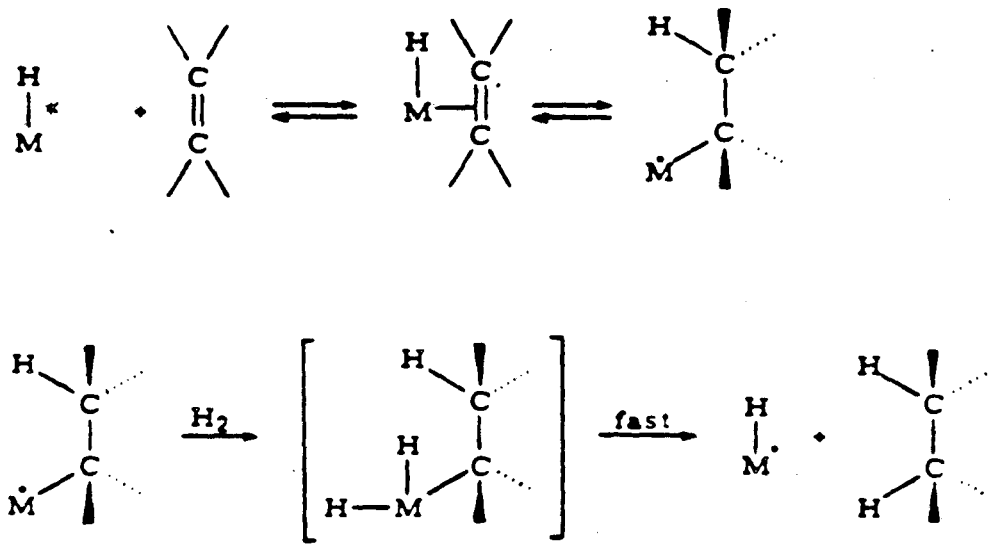
quinoline, using a hexarhodium carbonyl cluster under hydrogen and carbon monoxide[9]. T. J. Lynch et. al. have found that iron pentacarbonyl will selectively reduce quinoline to the 1,2,3,4-tetrahydro product under water gas shift conditions (H_2O and CO), as well as reducing acridine, isoquinoline, and phenanthroline selectively[10,11]. Metallophthalocyanine compounds have been shown by Boucher et. al. to selectively reduce quinoline to 1,2,3,4-tetrahydroquinoline[12]. These compounds were investigated both as homogeneous and as silica or alumina supported catalysts.

Mononuclear transition metal hydrogenation catalysts of the type examined in this study can be classed into two general categories: monohydrides, in which the active catalytic species contains one hydrogen bound to the metal atom, and dihydrides, in which two hydride ligands are present. The general features of reduction mechanisms for olefins (the most studied class of substrates) using both types of catalysts are shown in Figures II.3 and II.4[13].

Certain features are common to both mechanisms. It is necessary that the substrate and hydrogen be simultaneously bound to the metal atom. In general a transition metal complex, metal atom and ligands bound to it, must share 18 electrons or fewer between them, corresponding to full or partial occupation of the outermost s, p and d orbitals of the metal atom (many exceptions to this rule are known however)[13]. Since most metal complex catalysts contain

FIGURE II.3

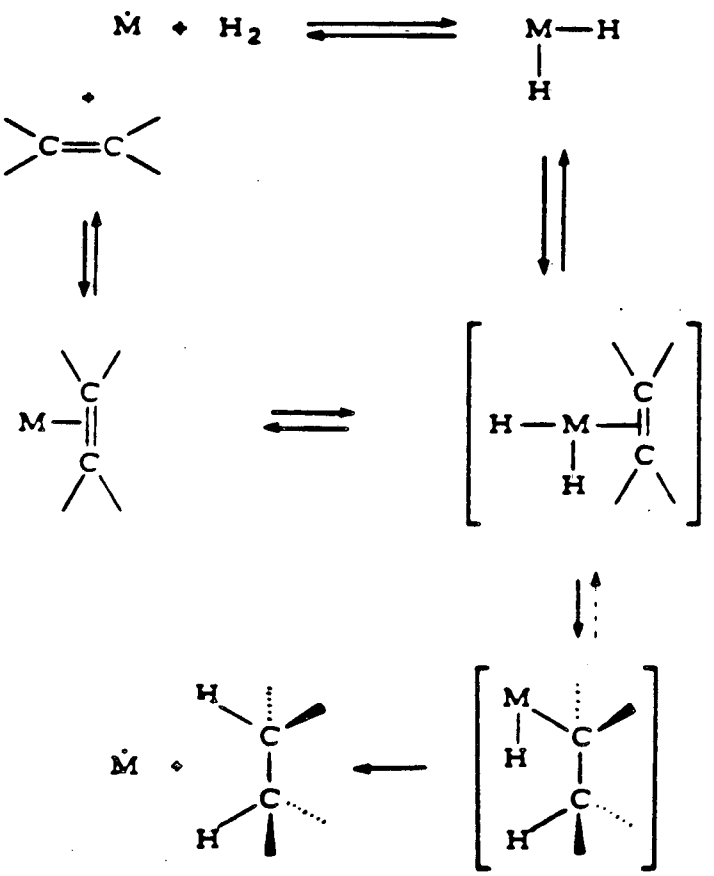
Monohydride Reduction Mechanism



such intermediates have
not been detected

FIGURE II.4

Dihydride Reduction Mechanism



18 outer electrons in their active form (as hydrides), a ligand must be displaced by the substrate molecule, or must be displaced before the substrate binds, in order not to form species containing more than 18 electrons.

Good hydrogenation catalysts thus must typically contain one or more easily removed ligands. All of the catalysts examined in this study contained triphenyl-phosphine groups, which bind to the metal through the phosphorus atom, as ligands. They are easily displaced under suitable conditions by other ligands, such as the heterocycles used as substrates in this study.

In the monohydride reduction mechanism (Fig. II.3), the catalyst initially contains one hydride. It must lose a ligand or otherwise be unsaturated (indicated by the asterix) in order to bind the substrate. After this binding a rapid transfer of the hydride ligand from the metal to the substrate occurs, partially reducing the substrate. In order to fully reduce the substrate a second hydrogen must be added. It is hypothesised that this occurs through the addition of dihydrogen to the metal, followed by rapid transfer of the second hydrogen to the subtrate. The now fully reduced substrate is released from the complex, and the monohydride complex is regenerated, completing the catalytic cycle. It is important to note that no dihydride species such as are proposed here have been observed.

The addition of dihydrogen to the metal is termed an

oxidative addition. This is because this addition is formally regarded as a two electron oxidation of the metal atom, these two electrons are transferred to the dihydrogen, resulting in cleavage of the hydrogen-hydrogen bond. Each hydrogen atom is then regarded at a hydride ligand, with the transferred electrons considered to be localized on the ligands. A more correct treatment of this type of addition is complex, see reference 13.

In the dihydride mechanism (Fig. II.4), two possible pathways exist. The initial complex (which must as described above contain less than its full complement of ligands) may either bind the substrate first, or may oxidatively add hydrogen first, followed in each case by addition of the other component. The resulting complex contains two hydrogen atoms and the substrate. The hydrogens are both rapidly transferred to the substrate, which then leaves the complex and regenerates the catalyst.

As indicated, the transfer of hydrogen to the substrate may be reversible, this proved to be a crucial issue in the reduction of quinoline using the dihydride catalyst $RhClH_2(PPh_3)_3$, in which the reversibility of this step is necessary to explain our results. We also found a similar reversible step in the reduction of quinoline as catalysed by the monohydride catalyst, $RuClH(PPh_3)_3$.

II.B REDUCTIONS CATALYZED BY $RuClH(PPh_3)_3$ and $RhCl(PPh_3)_3$

II.B.1 Introduction:

In order to gain a greater understanding of the effects involved in the reduction of polynuclear heteroaromatic compounds, separate studies were carried out to determine the rates of reduction of various hetero-aromatics, using $RuCl_2(PPh_3)_3$ and $RhCl(PPh_3)_3$ as catalysts. Experiments were performed to determine the individual rates of reduction of several compounds, additionally rates of reduction were measured in mixtures of two reducible compounds and in mixtures of one reducible compound and added compounds that could potentially interact with the catalyst, thereby affecting the rate of reduction.

Experiments were also performed in which deuterium gas was substituted for hydrogen gas in the reduction of quinoline with both catalysts. Additionally the reaction of 1,2,3,4-tetrahydroquinoline with deuterium and each catalyst was examined. The positions and amounts of deuterium incorporation into the products of these reactions were determined using ^1H NMR and GC-MS techniques. The substitution of deuterium gas for hydrogen gas in homogeneous reductions has proven to be an invaluable technique for the elucidation of mechanisms and stereochemistry in other studies[14,15], and in this

present study it has provided extensive evidence supporting several specific mechanistic details of the reduction of quinoline.

The binding of quinoline to $RhCl(PPh_3)_3$ in the presence and absence of hydrogen was examined by ^1H and ^{31}P NMR. This binding was also examined for systems in which p-cresol was present. This compound was found to dramatically increase the rate of reduction of quinoline (see Section II.B.2), and these experiments increased our understanding of this effect. The binding of 1,2,3,4-tetrahydroquinoline to $RuClH(PPh_3)_3$ (the active catalytic species formed from $RuCl_2(PPh_3)_3$, as described below) was also briefly examined to help clarify some of the deuterium results obtained with this catalyst.

Both catalysts were found to promote the regio-selective reduction of only the heteroaromatic ring in virtually all of the compounds studied. The ability of the various substrates to bind to the catalyst has been identified as a primary factor in determining the overall rates of reduction, and as well has been found to determine the relative rates of reduction in mixtures of substrates. Some of the steric and electronic effects surrounding this binding ability have been determined, as well as other factors determining reduction rates.

Several compounds which inhibit the reduction of quinoline by both catalysts have been identified, and the nature of this inhibition examined. Some compounds which

enhance reduction rates were also found, although these effects are not as clearly defined. The relative activities of the two catalysts have been compared, and in general the ruthenium catalyst has been found to provide higher reduction rates than the rhodium catalyst.

The binding and deuterium experiments have provided evidence for the existance of several plausible intermediates in the reduction of quinoline by each catalyst. These proposed intermediates have been combined into mechanistic schemes for both catalysts (section II.B.5). The reduction of quinoline is proposed to occur in two steps, the first is a reversible reduction of the 1-2 carbon-nitrogen bond, the second an irreversible reduction of the 3-4 carbon-carbon bond. Several other possible steps are proposed to account for the deuterium exchange patterns found in the experiments described above.

Both of these catalysts have been extensively investigated by other workers for reductions of various compounds, but little previous work has been found in connection with heteroaromatic substrates. The nature of these two catalysts and previous studies are described below.

$RuCl_2(PPh_3)_3$ is a very active hydrogenation catalyst and has been used to reduce a wide variety of compounds, including olefins, aldehydes, ketones and nitro compounds[16-23]. Dichlorotris(triphenylphosphine)-ruthenium(II) is a precursor to the actual catalytic

species, chlorohydrotris(triphenylphosphine)-ruthenium(II). This species is a monohydride hydrogenation catalyst, as discussed in section II.A.

The monohydride is rapidly formed from the dichloro compound and hydrogen in the presence of base, which reacts with the HCl generated during the formation of the active species[16,22,23]. The base may be quite weak, ethanol for example will promote formation of the chlorohydro complex. In the reductions described in this section it was found that the nitrogen heterocycles were all able to promote the formation of the active species, but benzothiophene would not and a base had to be added along with the substrate in this case.

Chlorotris(triphenylphosphine)rhodium(I), commonly known as Wilkinson's catalyst after one of its first discoverers, is one of the most extensively researched of all the homogeneous transition metal catalysts. It has been used to hydrogenate a wide variety of olefinic compounds and alkynes[24-26,14,15]. The scope of functional groups reduced by this catalyst, though, is not as wide as that found with $RuCl_2(PPh_3)_3$, ketones, aldehydes and nitro compounds are in particular not reduced by this catalyst[13]. The active catalytic species in reductions catalyzed by this complex is the dihydro species, $RhClH_2(PPh_3)_3$, formed by the rapid and reversible oxidative addition of hydrogen to the starting complex[24,33]. This catalyst is one of the best known

examples of a dihydride hydrogenation catalyst, as described in section II.A.

We have found no previous references to the use of either of these complexes for the reduction of polynuclear heteroaromatic compounds. $RhCl(PPh_3)_3$ has, however, been used in the dehydrogenation of both 1,2,3,4-tetrahydroquinoline and 2,3-dihydroindole[27,28], and a carboline compound[29,30], which combines both an indole and pyridine functionality. All of these dehydrogenation reactions took place under much more severe conditions than used in this present work.

II.B.2 RATE STUDIES

These reactions were all carried out in the kinetic reactor system, the construction and use of which is described in the experimental section(IV). The conditions used with both catalysts were the same: 85° C, 310 psi H_2 (measured initially at room temperature), 0.1 millimole of catalyst and 1.0 millimole of each compound present. The solvent was dry, degassed benzene (20ml), stirring was accomplished by a small magnetic stirring bar. The stirring rate was not a crucial parameter, in the absence of stirring the rates were found to be essentially unchanged.

Samples were withdrawn from the reactor at regular intervals and analyzed by capillary gas chromatography, to provide percent conversion versus time data. Such data was typically obtained up to approximately 25% conversion, or until the conversion versus time data were no longer linear (i.e. pseudo-zero-order conditions). A linear least squares analysis of this data provided an initial, pseudo-zero-order rate. In the individual rate reduction tables (to follow) relative rates are also provided. These rates are normalized so that the reduction rate of quinoline, with each catalyst, is 1.0. These provide for an easy basis for comparison of rates.

Although pseudo-zero order kinetics were assumed in fitting the kinetic data, the actual kinetic order of the underlying reactions are not known. Substantial

conversions, up to 50%, well beyond any reasonable zero order regime, were sometimes accompanied by zero order kinetics. This fact does not invalidate the interpretation of the rates discussed below, but limits them to low conversions of substrate, i.e. a region of true 'pseudo-zero order' kinetics.

Samples were inspected for visible signs of decomposition when they were withdrawn from the reactor. For both catalysts the samples were clear, with no signs of heterogeneity or precipitates. With $RhCl(PPh_3)_3$ the sample color was pale yellow, indicative of the formation of $RhClH_2(PPh_3)_3$[24,33], while with $RuCl_2(PPh_3)_3$ the samples were red-violet, indicative of $RuClH(PPh_3)_3$[16,22,23].

For the reductions of phenanthridine and acridine it was found necessary to co-inject pyridine with the sample during GC analysis in order to inhibit the dehydrogenation of the products of reduction. The pyridine presumably poisons the slight catalytic activity of the glass injector port of the gas chromatograph. Despite this precaution reproducible rate data were very difficult to obtain with phenanthridine, and thus the rates of reduction reported for this compound are approximate.

For the reduction of benzothiophene with $RuCl_2(PPh_3)_3$ it was found that this substrate was not able to promote the formation of the catalytically active chlorohydro species, presumably because it is not a strong

base. For this compound, 0.1 millimole of triethylamine was added to the reaction mixture in order to form the active species. The effect that this had on the reduction rate was not examined.

The chlorohydro compound, $RuClH(PPh_3)_3$, was also synthesized using literature methods[22] and used to reduce quinoline, providing essentially the same rate as when this complex was formed in situ. This is somewhat surprising since any HCl formed during the reaction should precipitate out some quinoline (or the product, 1,2,3,4-tetrahydro-quinoline) as insoluble salts and affect the rate. However, since the rates reported here are in terms of percent conversion versus time, the effects of a small variation in substrate concentration tend to be eliminated. Small amounts of precipitate were occasionally found in the reactor when reducing quinoline with the ruthenium catalyst. These were found to contain varying amounts of quinoline and tetrahydroquinoline upon reaction with base, the small amounts of material involved prevented any accurate quantification.

An additional problem that was encountered during the course of this work was the instability of $RhCl(PPh_3)_3$. Despite the precaution of storing this material under nitrogen or argon it was found to have increased in activity by a factor of approximately 1.4 after a five month period between certain experiments. For these particular runs, in which the rate of quinoline reductions

was examined in the presence of various compounds, the rates are normalized by division by the rate of reduction of quinoline alone. The quinoline reduction rate used for normalization was always determined immediately before or after a particular series of runs, compensating for any change in catalyst activity. The actual quinoline rates used for the various normalizations are noted in the tables.

Results With Chlorotris(triphenylphosphine)rhodium:

Table II.5 contains the results for the reduction of a variety of heteroaromatic compounds using $RhCl(PPh_3)_3$ as catalyst. The compounds are arranged in order of decreasing reduction rates.

Phenanthridine, acridine and benzothiophene, in which addition of only two hydrogen atoms is necessary for complete reduction of the heteroatomic ring, were reduced most rapidly. Two products were formed from acridine. In addition to the expected heteroatomic ring reduction product, 9,10 dihydroacridine, the outer ring reduction product, 1,2,3,4-tetrahydroacridine, was also produced. Phenanthridine was reduced much faster than acridine, by a factor of 28, when only the 9,10 dihydro products are considered. Benzothiophene, a sulfur containing heteroaromatic, was reduced at about half the rate of acridine.

Quinoline and its derivatives, in which four hydrogen

TABLE II.5

Rates of Reduction of Heterocyclic Aromatics
Using $RhCl(PPh_3)_3$ as Catalyst

Substrate	Product	Rate (%/min)	Relative Rate[1]
Phenanthridine	9,10-Dihydrophenanthridine	ca. 6	ca. 76[2]
Acridine	9,10-Dihydroacridine[3]	0.21	2.7
Benzothiophene	2,3-Dihydrobenzothiophene	0.12	1.5
Quinoline	1,2,3,4-Tetrahydroquinoline	0.079	1.0
5,6-Benzoquinoline	1,2,3,4-Tetrahydro-5,6-bquin.	0.030	0.39
7,8-Benzoquinoline	1,2,3,4-Tetrahydro-7,8-bquin.	0.013	0.16
Indole	None	0.000	0.00

CONDITIONS: 1.0 mmole of substrate and 0.1 mmole catalyst in 20 ml of dry, degassed benzene. Pressure H_2 (initial) = 310 psi, T = 85° C. Conversion data obtained until ca. 25% conversion or until conversion vs. time data was not linear. Least-squares analysis of this data provides the initial (pseudo-zero order) rates given.

NOTES:

1) Relative rates are obtained by dividing the rate of reduction of a given compound by the rate of reduction of quinoline (0.079%/min).

2) In this case the reaction was too rapid to accurately follow, and the product is thermally unstable, so these values are approximate.

3) Another product, identified as 1,2,3,4-tetrahydroacridine by GC-MS, was formed at the rate of 0.12 %/min (relative rate = 1.5) and represents 36% of the total products.

atoms must be transferred for complete reduction, were all reduced more slowly. Quinoline was reduced faster than either of the two benzoquinoline isomers, with 5,6-benzoquinoline being reduced at approximately 1/3 the rate of quinoline and 7,8-benzoquinoline being reduced at about 1/5 the rate of quinoline. Indole was not reduced by $RhCl(PPh_3)_3$.

Table II.6 contains the rates of reduction of quinoline with the rhodium complex in the presence of an equimolar amount of a second compound. The rates given here are all relative to the reduction rate of quinoline alone. The compounds are arranged in order of decreasing enhancement (or increasing inhibition) of the reduction rate of quinoline.

P-cresol gave the greatest rate enhancement, 2.5, followed by benzothiophene, carbazole and indole, all of which gave enhancements of 1.9. Pyrrole and thiophene both gave rate increases of 1.5.

5,6-Benzoquinoline caused a very slight inhibition in the reduction rate, a factor of 0.92. 7,8-Benzoquinoline gave a larger inhibition of 0.72, followed by 2-methylpyridine, 0.57, and 1,2,3,4-tetrahydroquinoline, 0.49. 3-methylpyridine almost completely inhibited the reduction, affording only 5% of the uninhibited rate. Pyridine and phenanthroline both entirely quenched the reduction.

An additional study was made of the effect of quinoline concentration on the initial rate of quinoline

TABLE II.6

Relative Rates of Reduction of Quinoline in the Presence of Other Added Compounds, Using $RhCl(PPh_3)_3$ as Catalyst

Added Compound	Relative Rate[1]
P-Cresol	2.5
Benzothiophene[2]	1.9
Carbazole	1.9
Indole	1.9
Pyrrole	1.5
Thiophene	1.5
None	1.0
5,6-Benzoquinoline[2]	0.92
7,8-Benzoquinoline[2]	0.72
2-Methylpyridine[3]	0.57
1,2,3,4-Tetrahydroquinoline	0.49
3-Methylpyridine[3]	0.05
Phenanthroline	0.00
Pyridine	0.00

CONDITIONS: 1.0 mmole of quinoline, 1.0 mmole of added compound, and 0.1 mmole catalyst in 20 ml of dry, degassed benzene. Pressure H_2 (initial) = 310 psi, T = 85° C. Conversion data obtained until ca. 25% conversion or until conversion vs. time data was not linear. Least-squares analysis of this data provides the initial (pseudo-zero order) rates given.

NOTES:

1) Relative rates are obtained by dividing the rate of reduction of quinoline in the presence of another compound by the rate of reduction of quinoline alone (0.13 %/min, see also text and note 3).

2) In these cases, the added compound was reduced along with quinoline. (see also table II.11)

3) These rates are normalized using the quinoline reduction rate of 0.079%/min found at the time of these experiments.

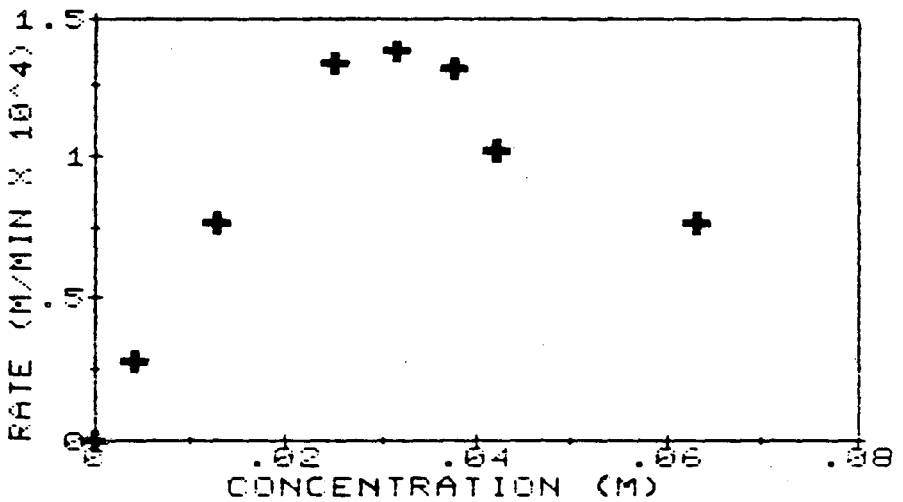
reduction with $RhCl(PPh_3)_3$, using a constant concentration of catalyst. The results of these experiments are presented in Figure II.7. The initial rates are expressed here in moles/liter-min. rather than percent conversion/min. because of the varying quinoline concentrations used here. The latter units are only appropriate for comparing rates all obtained at the same concentrations, as in the previously described experiments. For comparisons sake, the concentration of substrate used in the previous experiments was 0.05 moles/liter, near the high end of the concentrations used in these experiments.

The effect of varying the quinoline concentration is striking. For concentrations of quinoline below 0.025 M the initial rate varies linearly with quinoline concentration, pure first-order behavior. However, above this concentration, the rate stops increasing abruptly, and then decreases with increasing quinoline concentration. This latter region must be the result of kinetically complex phenomena involving inhibition of the catalyst by the substrate.

For the initial, linear region of this graph, a first order rate constant may be defined for the dependence of the rate on the quinoline concentration (the catalyst concentration, being constant, is eliminated from this simple expression of rate). A least squares analysis gives a slope of 0.0053 min^{-1} for the region up to 0.025 M quinoline. It is important to note that this rate

FIGURE II.7

Initial Quinoline Reduction Rate Versus Concentration
Using $RhCl(PPh_3)_3$ as Catalyst



CONDITIONS: 0.1 mmole of catalyst in 20 ml of dry, degassed benzene, quinoline concentration as given (moles/liter). Pressure H_2 (initial) = 310 psi, T = 85° C. Concentrations followed by capillary GC until approximately 25% conversion or until concentration vs. time data was not linear. Least-squares analysis of the data provides the initial (pseudo-zero order) rates given. Rates expressed in moles/liter x min.

constant is unfortunately of limited use, since it is based on initial rates only, in the absence of any appreciable amounts of product. As previously shown, the inhibition of the catalyst by 1,2,3,4-tetrahydroquinoline, the product of quinoline reduction, is severe. Therefore, even in this first order region, a term incorporating this inhibition would have to be added to the rate expression to allow calculation of rates at substantial quinoline conversions. No attempt was made to determine this product inhibition term, the number of experiments needed to do so being large, since for this determination two concentrations (quinoline and tetrahydroquinoline) would have to varied.

The second, non-linear region of the graph, above a quinoline concentration of 0.025 M, is not easily explained. Several attempts were made to fit this region by assuming quinoline and $RhCl(PPh_3)_3$ can react reversibly to form catalytically inactive species, leading to an equilibrium of the form:

Eq. 1 - $K_{eq} = (C_{inactive\ Rh}) / (C_{active\ Rh} \times C_{quin.}^{n})$

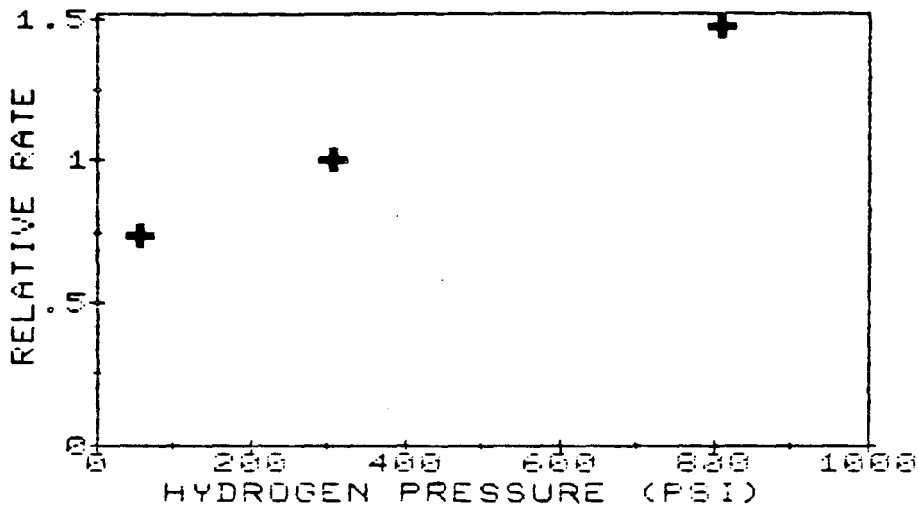
N is determined by the stoichiometry of the reaction forming the inactive species, which is assumed to contain only one rhodium. It is not unreasonable to assume such species are formed, NMR data for quinoline / $RhCl(PPh_3)_3$ solutions under hydrogen (see section II.B.3) indicate

several quinoline-rhodium complexes are formed. Nevertheless, assuming such an equilibrium (with n=1,2 or 3, larger values are unreasonable) did not lead to a satisfactory fit with the data shown, and in particular did not duplicate the rapid decrease of rate found at the higher quinoline concentrations. We are unable to propose a mechanism for this large substrate inhibition, and this fact is not accounted for in the mechanism for quinoline reduction using $RhCl(PPh_3)_3$ presented in the conclusions. More knowledge about the nature of the species formed during the reduction of quinoline is needed in order to gain a better understanding of this phenomenon.

A brief study was also made of the effects of varying hydrogen pressure on the reduction rate of quinoline, the results are presented in Figure II.8. The rates here are relative, with the rate of quinoline reduction at 310 psi H_2 set to 1.0 in keeping with the relative rate data presented in table II.5. The rate is clearly not strongly dependent on the hydrogen pressure in this pressure range, the dependence is approximately one-third, much less than first order. This implies that addition of hydrogen to the catalyst is not a rate limiting factor at the pressures we are using. Other studies, carried out at much lower pressures of hydrogen with olefinic substrates, show orders in hydrogen of zero to one[14].

FIGURE II.8

Initial Quinoline Reduction Rate Versus Hydrogen Pressure
Using $RhCl(PPh_3)_3$ as Catalyst



CONDITIONS: 0.1 mmole of catalyst, 1.0 mmole substrate in 20 ml of degassed benzene. Pressure H_2 (initial) as given, T = 85° C. Concentrations followed by capillary GC until approximately 25% conversion or until concentration vs. time data was not linear. Least-squares analysis of the data provides the initial (pseudo-zero order) rates given.

Results With

Chlorohydrotris(triphenylphosphine)ruthenium(II):

Table II.9 contains the reduction rates of the same compounds as in table II.5, using $RuClH(PPh_3)_3$, formed in situ from the dichloro complex, as catalyst. The compounds are arranged in decreasing order of reduction rates.

As with the rhodium catalyst, phenanthridine and acridine were reduced the fastest, phenanthridine at almost three times the rate of acridine. 1,2,3,4-tetrahydro-acridine was not produced by this catalyst. Quinoline came next in rate, at 10% of the rate for acridine. Indole, 5,6-benzoquinoline, benzothiophene and 7,8-benzoquinoline came after quinoline in decreasing order of rates, with the fastest, indole, being reduced at only 1/5 the rate of quinoline and the slowest, 7,8-benzoquinoline, reduced at 1/30 the rate for quinoline.

Table II.10 contains the reduction rates for quinoline in the presence of a variety of other compounds. Unlike the results for $RhCl(PPh_3)_3$ (Table II.6), no compounds that enhanced the rate of reduction were identified. Benzothiophene had no effect on the rate, and 7,8-benzoquinoline had an effect too small to be of significance. Carbazole slightly lowered the rate of reduction, by a factor of 0.89, 2-methylpyridine gave a similar inhibition of 0.85. 5,6-benzoquinoline gave a larger inhibition, 0.79, followed by indole at 0.66 and

TABLE II.9

Rates of Reduction of Heterocyclic Aromatics
Using $RuCl_2(PPh_3)_3$ as Catalyst

Substrate	Product	Rate (%/min)	Relative Rate[1]
Phenanthridine	9,10-Dihydrophenanthridine	ca. 11	ca. 24[2]
Acridine	9,10-Dihydroacridine	4.3	9.2
Quinoline	1,2,3,4-Tetrahydroquinoline	0.47	1.0
Indole	2,3-Dihydroindole	0.085	0.18
5,6-Benzoquinoline	1,2,3,4-Tetrahydro-5,6-bquin.	0.059	0.12
Benzothiophene	2,3-Dihydrobenzothiophene	0.041	0.09
7,8-Benzoquinoline	1,2,3,4-Tetrahydro-7,8-bquin.	0.014	0.03

CONDITIONS: 1.0 mmole of substrate and 0.1 mmole catalyst in 20 ml of dry, degassed benzene. Pressure H_2 (initial) = 310 psi, T = 85° C. Conversion data obtained until ca. 25% conversion or until conversion vs. time data was not linear. Least-squares analysis of this data provides the initial (pseudo-zero order) rates given.

NOTES:
1) Relative rates are obtained by dividing the rate of reduction of a given compound by the rate of reduction of quinoline (0.47%/min).

2) In this case the reaction was too rapid to accurately follow, and the product is thermally unstable, so these values are approximate.

TABLE II.10

Relative Rates of Reduction of Quinoline in the Presence of Other Added Compounds, Using $RuCl_2(PPh_3)_3$ as Catalyst

Added Compound	Relative Rate[1]
None	1.0
Benzothiophene[2]	1.0
7,8-Benzoquinoline[2]	0.98
Carbazole	0.89
2-Methylpyridine	0.85
5,6-Benzoquinoline[2]	0.79
Indole[2]	0.66
1,2,3,4-Tetrahydroquinoline	0.34
3-Methylpyridine	0.00

CONDITIONS: 1.0 mmole of quinoline, 1.0 mmole added compound, and 0.1 mmole catalyst in 20 ml of dry, degassed benzene. Pressure H_2 (initial) = 310 psi, T = 85° C. Conversion data obtained until ca. 25% conversion or until conversion vs. time data was not linear. Least-squares analysis of this data provides the initial (pseudo-zero order) rates given.

NOTES:

1) Relative rates are obtained by dividing the rate of reduction of quinoline in the presence of another compound by the rate of reduction of quinoline alone (0.47%/min).

2) In these cases, the added compound was reduced along with quinoline. (see also table II.12)

1,2,3,4-tetrahydroquinoline at 0.34. 3-methylpyridine completely inhibited the reduction of quinoline.

Discussion of Rate Results:

An examination of the order of reduction rates for the basic nitrogen heterocycles (phenanthridine, acridine, quinoline and its derivatives) shows that they are reduced with the same ordering of rates by both catalysts. Phenanthridine is reduced the fastest, followed by acridine, quinoline, 5,6-benzoquinoline, and finally 7,8-benzoquinoline. This suggests that a common set of factors are governing the reduction rates of these compounds with both catalysts.

The reduction rates for quinoline and its two benzo derivatives are best explained by consideration of the steric factors governing the binding of these compounds to the catalyst. Quinoline is reduced the fastest by both catalysts, followed by the bulkier benzo derivatives, with 5,6-benzoquinoline being reduced faster than 7,8-benzoquinoline.

This is the ordering that would be expected if the reduction rate was dependent on the ability of each compound to bind to the catalyst through the basic nitrogen atom, a type of binding that has been verified by NMR observations in the case of quinoline and $RhCl(PPh_3)_3$ (see Section II.B.3). An examination of molecular models

of the substrate-catalyst complex (a trans phosphine, cis hydride complex as indicated for the case of quinoline) reveals that the reduction rates for these three compounds decrease in the same order as the increase in steric interaction between the bound substrate and the catalyst. The binding of these three similar compounds to the catalyst would be expected to be strongly dependent on this degree of steric interaction, with this binding being disfavored in cases where the interaction is large, resulting in a lower reduction rate.

7-8-benzoquinoline is reduced the slowest. Complexation of this molecule to the catalyst directs the 7,8-benzo substituent towards the catalyst center, where it can undergo strong interactions with the metal atom and its ligands, making this binding unfavored. 5,6-benzoquinoline is reduced faster than the 7,8-benzo derivative. In this case coordination to the nitrogen results in directing the 5,6-benzo ring away from the catalyst center, where presumably it undergoes less repulsive interactions than in the case of 7,8-benzoquinoline. Finally, quinoline, which contains no bulky benzo substituent, is reduced the fastest.

Such steric effects are quite common in the reductions catalyzed by homogeneous catalysts. A dramatic example is provided by the reduction of cyclohexene and 1-methylcyclohexene using $RhCl(PPh_3)_3$, in which case several workers find that the former compound is reduced 50 to 100 times

faster than its methyl substituted derivative[14].

As an additional test of steric effects on rate, 2-methylquinoline was reduced with the rhodium catalyst (not shown in tables), to provide a rate 29% of that found with quinoline alone. In this case, the partial blocking of the nitrogen atom by the methyl group in the 2-methyl derivative decreases the ability of it to bind to the catalyst, and so leads to a lower rate of reduction.

Phenanthridine and acridine are both reduced faster than quinoline and its derivatives. In light of the steric arguments presented above this is somewhat surprising since both of these molecules are bulkier than quinoline. However, reduction of these molecules requires addition of only two hydrogen atoms, as opposed to four with the quinoline compounds. Furthermore, while this addition takes place at the adjacent 9 and 10(N) positions in phenanthridine, it occurs at opposing sides of the center ring in acridine. Thus it it difficult to directly compare these results with each other or with the quinoline results, since the reduction mechanisms may be different.

Phenanthridine is reduced faster than acridine by both catalysts. This is probably due to the differences between these molecules noted above. In phenanthridine the sites of hydrogen addition are adjacent. This allows for the concerted addition (or rapid separate additions) of two hydrogens without any re-arrangement of the phenanthridine relative to the metal center. With acridine

the two hydrogens must be added to non-adjacent sites on opposing sides of the center ring. This possibly requires some rearrangement of the complex between addition of the two hydrogen atoms, thus leading to a slower overall reduction rate.

When acridine is reduced with $RhCl(PPh_3)_3$ as the catalyst two products are obtained, the heteroatomic ring reduced material, 9,10-dihydroacridine, and the homoatomic ring reduced product, 1,2,3,4-tetrahydroacridine. The latter product is formed at about half the rate of the former. These results seem to indicate that acridine can bind to the rhodium catalyst in two modes. One, through the nitrogen atom, leads to the 9,10 dihydro product, while the other, through the pi orbitals of the outer, homoatomic ring, leads to the 1,2,3,4 tetrahydro product. A search of the literature provides some examples of similar outer ring reductions occuring with anthracene using other homogeneous transition metal catalysts[31,32].

The factors surrounding the reduction of indole and benzothiophene are more complex than those found with the basic nitrogen heterocycles as described above. The two catalysts show quite different behavior towards these substrates. Of the two substrates, $RhCl(PPh_3)_3$ reduces only benzothiophene, at a rate 1.5 times the rate found for quinoline. $RuClH(PPh_3)_3$ reduces both compounds, indole faster than benzothiophene, at rates much less that the rate of quinoline reduction.

These two substrates are sterically very similar, differing only at the heteroatom (NH in indole, S in benzothiophene) and so the rate differences found for the reductions with the ruthenium catalyst must reflect other factors. It is not clear if these substrates coordinate at the heteroatom, which is not a basic site in either of the two, and so would be expected to bind less strongly to the metal than the nitrogen in the basic nitrogen heterocycles. The coordination may instead be through the 2,3 carbon double bond, similar to the coordination of an olefin (see section II.A). In either case, the difference in reduction rates could be reflecting a difference in the ability of these compounds to bind to the ruthenium catalyst.

Benzothiophene is reduced by $RhCl(PPh_3)_3$, at a higher rate than that found for quinoline. Since benzothiophene is not basic it would not be expected to bind to the catalyst as well as quinoline, this higher rate must be due to other factors not evident from these experiments. Similarly, the failure of the rhodium catalyst to reduce indole is not due to any obvious difference between this substrate and benzothiophene.

The ability to bind to the catalysts also appears to be a major factor in determining the ability of several compounds to inhibit the reduction of quinoline. However, many instances of rate enhancement are observed when using $RhCl(PPh_3)_3$ as catalyst. The reason for these

enhancement effects is not as clear.

Examining first the data for the ruthenium catalyst, found in Table II.10, the effects of 7,8-benzoquinoline and 2-methylpyridine, when compared to 5,6-benzoquinoline and 3-methylpyridine, indicate the importance of binding ability in determining if a compound will inhibit the reduction of quinoline. These data also provide additional insight into the steric requirements for binding to the catalyst. 7,8-benzoquinoline and 2-methylpyridine would be expected to bind to the catalyst through nitrogen less effectively than 5,6-benzoquinoline and 3-methylpyridine, due to steric factors as discussed earlier. Consistent with this, 5,6-benzoquinoline and 3-methylpyridine are both much more effective at inhibiting the rate of quinoline reduction than the more sterically hindered isomers. In a similar manner carbazole (2,3-benzoindole) did not inhibit the reduction rate as much as indole.

1,2,3,4-Tetrahydroquinoline, which is a somewhat stronger base than quinoline (Pk_b=9.38 as versus 9.52 for quinoline) has a considerable inhibiting effect. Since in most cases the products formed by the reduction of the compounds studied here are stronger bases than the starting compounds, such product inhibitions would probably be a limiting factor in attempting to carry out a reduction to completion (The reduction of quinoline was carried to completion using $RuClH(PPh_3)_3$, but required approximately three days. Obviously the rate of reduction

becomes very low as the product concentration increases).

Benzothiophene shows no inhibition of the quinoline reduction rate with the ruthenium complex, while indole inhibits this reduction by a factor of 0.66. This indicates that indole can bind more effectively to the catalyst than benzothiophene, and thus compete with quinoline. As discussed above, the fact that indole is reduced more rapidly than benzothiophene by the ruthenium catalyst also indicates that it can bind more effectively than benzothiophene, a conclusion which is strongly supported by these competitive binding experiments.

The results obtained with $RhCl(PPh_3)_3$, Table II.6, are not as easily explained as the results obtained with the ruthenium complex. Some effects are consistent with competitive binding. Thus pyridine totally inhibits quinoline reduction, 3-methylpyridine severly retards the reaction (rel. rate = 0.05) and 2-methylpyridine, in which the nitrogen is partially blocked by the methyl group, inhibits the reduction much less (rel rate=0.57). Phenanthroline entirely inhibits the reduction rate of quinoline, an expected result for this strong, chelating, ligand, and 1,2,3,4-tetrahydroquinoline slows the rate of reduction by half.

However, 5,6-benzoquinoline, which should compete more effectively for catalyst than 7,8-benzoquinoline, based on the steric factors discussed in connection with the reduction rates above, actually inhibits the reduction

less. Additionally, several compounds enhance the rate of quinoline reduction, including benzothiophene, which is reduced at the same time.

The origin of these enhancement effects (including perhaps a mixed enhancement/inhibition with 5,6-benzoquinoline, leading to the anomalous rate effect) are not clear. One possible explanation is that these compounds simply act to increase the solvent polarity, a factor known to increase reduction rates of olefins by $RhCl(PPh_3)_3$[14,15]. Candlin and Oldham[25] find that using phenol as a solvent for $RhCl(PPh_3)_3$ reductions of olefins provides higher reduction rates than less polar solvents, this may be related to the large rate increase induced by p-cresol (p-methylphenol) in the experiments described above.

It is also possible that the rate enhancers are directly interacting with triphenylphosphine so as to enhance the dissociation of this ligand from the complex, leading to greater complexation of quinoline and thus higher rates. In the case of p-cresol, which gives the largest enhancement, it was found by NMR spectroscopy apparently to hydrogen bond to triphenylphosphine, but its effect on the dissociation of catalyst, in the presence and absence of quinoline, was minimal (these results are described in more detail in the next section, II.B.3).

For the cases of indole (with Ru), benzothiophene, 5,6-benzoquinoline and 7,8-benzoquinoline these compounds are reduced along with quinoline in the mixtures, providing

additional insight into binding effects and rates.

Tables II.11 and II.12 contain values derived from the various experiments described above. The first column of rates in each table are derived by dividing the reduction rate of quinoline by the reduction rate of the other substrate, using data taken from the individual reduction rate experiments (Tables II.5 and II.9). The second column of rates are calculated in a similar manner, except that the rates used here are those found in the competitive reductions, with both compounds present (Tables II.6 and II.10). In all cases the relative rate of reduction of quinoline, as versus the other compounds, is greater in the mixtures, indicating a selectivity for the reduction of quinoline in the presence of other reducible substrates.

For example, in the case of the reduction of benzothiophene and quinoline by the ruthenium catalyst, quinoline is reduced 11.5 time faster than quinoline when the reductions are carried out separately, but 43 times faster than quinoline in a mixture of the two. The same experiment with the rhodium catalyst is even more extreme, quinoline is reduced slower than benzothiophene when the reductions are carried out separately, but 3.8 times faster than benzothiophene in a mixture of the two. In both cases the quinoline can compete more effectively for catalyst than the benzothiophene. Additionally, in the case of $RhCl(PPh_3)_3$, the rate enhancement of quinoline

TABLE II.11

Selectivity for the Reduction of Quinoline in Competition with Other Reducible Substrates, Using $RhCl(PPh_3)_3$ as Catalyst

Other Substrate	Selectivity in Separate Reductions[1]	Selectivity in Mixture[2]
7,8-Benzoquinoline	6.1	32
5,6-Benzoquinoline	2.6	7.3
Benzothiophene	0.66	3.1

CONDITIONS: For separate reductions see Table II.5, for mixed reductions see Table II.6.

NOTES:

1) These values are derived from the data in Table II.5 by dividing the rate of reduction of quinoline by the rate of reduction of the other compound.

2) These values are derived from the data in Table II.6 by dividing the rate of reduction of quinoline by the rate of reduction of the other compound.

TABLE II.12

Selectivity for the Reduction of Quinoline in Competition with Other Reducible Substrates, Using $RuCl_2(PPh_3)_3$ as Catalyst

Other Substrate	Selectivity in Separate Reductions[1]	Selectivity in Mixture[2]
7,8-Benzoquinoline	33.6	42
Benzothiophene	11.5	43
5,6-Benzoquinoline	8.0	11
Indole	5.5	8.2

CONDITIONS: For separate reductions see Table II.9, for mixed reductions see Table II.10.

NOTES:

1) These values are derived from the data in Table II.9 by dividing the rate of reduction of quinoline by the rate of reduction of the other compound.

2) These values are derived from the data in Table II.10 by dividing the rate of reduction of quinoline by the rate of reduction of the other compound.

reduction by benzothiophene further contributes to the rate difference in the mixture.

The effect of quinoline concentration on the reduction rate of quinoline, investigated only with $RhCl(PPh_3)_3$ (Fig. II.7), does not have an obvious explanation. As discussed above, the initial rate is first order in quinoline concentration at low concentrations, and is a complex function of concentration at higher concentrations. Furthermore, the behavior at the higher concentrations cannot be explained by assuming that the catalyst is reversibly deactivated at these concentrations of substrates. It is possible that a trace impurity in the quinoline is deactivating the catalyst, but this seems unlikely due to the relatively large amount of catalyst present. The cause of this effect remains unclear.

The effect of hydrogen pressure on the reduction of quinoline (Fig. II.8) is not large. The low order in hydrogen, approximately one third, indicates that hydrogen addition to the catalyst (or possibly to the catalyst/ quinoline complex) is not a rate limiting factor at the pressures of hydrogen we investigated.

Finally, a comparison of the relative activity of the two catalysts shows that the ruthenium catalyst is from 1.1 times more active (for 7,8-benzoquinoline) to 21 times more active (for acridine) than the rhodium catalyst. In addition it does not catalyze the undesired formation of 1,2,3,4-tetrahydroacridine during the reduction of

acridine, and is able to reduce of indole. $RuCl_2(PPh_3)_3$ is thus in general a superior catalyst for the reduction of the hereroaromatic compounds examined, and would be the catalyst of choice except in cases where the particular selectivity between two substrates offered by $RhCl(PPh_3)_3$ is desired.

II.B.3 BINDING OF SUBSTRATES TO CATALYSTS

In view of the importance of competitive binding in determining the rates of reduction of the various substrates investigated (see Section II.B.2) a study was carried out investigating the binding of quinoline to $RhCl(PPh_3)_3$ and $RhClH_2(PPh_3)_3$. Several species were found to be formed in mixtures of quinoline and the rhodium complexes, and these have been identified or tentatively described. Additionally, a brief experiment was carried out investigating the binding of 1,2,3,4-tetrahydroquinoline to $RuClH(PPh_3)_3$. Under the conditions of this experiment (room temperature) no dehydrogenation of tetrahydroquinoline to the imine intermediate proposed in the deuterium exchange section (Sec. II.B.4) was observed.

The effect of p-cresol on the equilibrium between quinoline and $RhClH_2(PPh_3)_3$ was also investigated. We had postulated that cresol acts to increase the rate of reduction of quinoline by enhancing the dissociation of triphenylphosphine from the catalyst. However, the evidence presented below clearly indicates that this is not the case and that cresol must be increasing the rate via another mechanism.

Most of the data presented below are proton decoupled ^{31}P NMR spectra of various mixtures of substrates and complexes. The preparation of these samples is described in detail in the experimental section(IV). Briefly, the

rhodium dihydride was prepared in situ in the NMR tube immediately before addition of any other compounds and before sealing the tube. All other samples were prepared by simply dissolving all the components in the tube. Methylene chloride-d_2 was the solvent of choice, but chloroform-d was used occasionally as well with no changes noted in the spectra. Some spectra were also obtained in benzene-d_6, in this case substantial differences were noted between these spectra and those in the chlorinated solvents when both were taken. All the data presented below are for the chlorinated solvents, except where as noted in the figures.

The U C Berkeley 200 MHz NMR was used for all these experiments, in general the spectra were taken at -20°C to -40°C due to the much improved quality of the spectra over those taken at room temperature. Several peaks which were broad and indistinct at room temperature were noted to sharpen at the lower temperatures due to the slowing of inter and intra-molecular exchange reactions involving the several species found to be present. Temperature effects, where important to the interpretation of the spectra, are discussed.

Binding of Quinoline to Rhodium Complexes and the Effect of p-Cresol on this Binding Equilibrium:

The binding of quinoline to the rhodium catalyst was investigated by ^{31}P NMR as well as ^{1}H NMR and infrared

spectroscopy. Three new species are formed when quinoline is added to a solution of $RhClH_2(PPh_3)_3$ under one atmosphere of hydrogen, one of which is only observable on the NMR timescale at low temperature. Two of these species are apparently rhodium dihydride quinoline complexes, while the third is cis-chlorobis(triphenylphosphine)quinoline-rhodium (I).

The ^{31}P NMR spectrum of $RhClH_2(PPh_3)_3$ at -20°C is shown in Figure II.13, along with the structure of this complex. The doublet of doublets at 40.4 ppm is assigned to the two trans phosphine groups (J_{Rh-P}=114 Hz, J_{P-P}=19.3 Hz), the doublet of triplets at 20.8 ppm (J_{Rh-P}=90.4 Hz) is assigned to the remaining phosphine ligand, trans to one of the hydrides. The signals at 31.9 ppm are from the trans phosphines in $RhCl(PPh_3)_3$, present in residual amounts (J_{Rh-P}=143 Hz, J_{P-P}= 38.3 Hz), the phosphine cis to these ligands gives a weak signal at approximately 49 ppm[33]. A trace amount of free triphenylphosphine is apparent at about -6 ppm. The other signals in this spectrum were not assigned, and are presumably due to impurities.

The hydride ligands for $RhClH_2(PPh_3)_3$ were observed in the ^1H NMR at -9.8 ppm (doublet) and -17.3 ppm (singlet) as shown in Figure II.14, and are assigned respectively to the hydride trans to the chloride and the hydride trans to a phosphine[33].

When a similar sample of the rhodium hydride was

FIGURE II.13

^{31}P NMR of $RhClH_2(PPh_3)_3$

(-20°C, CCl_2D_2)

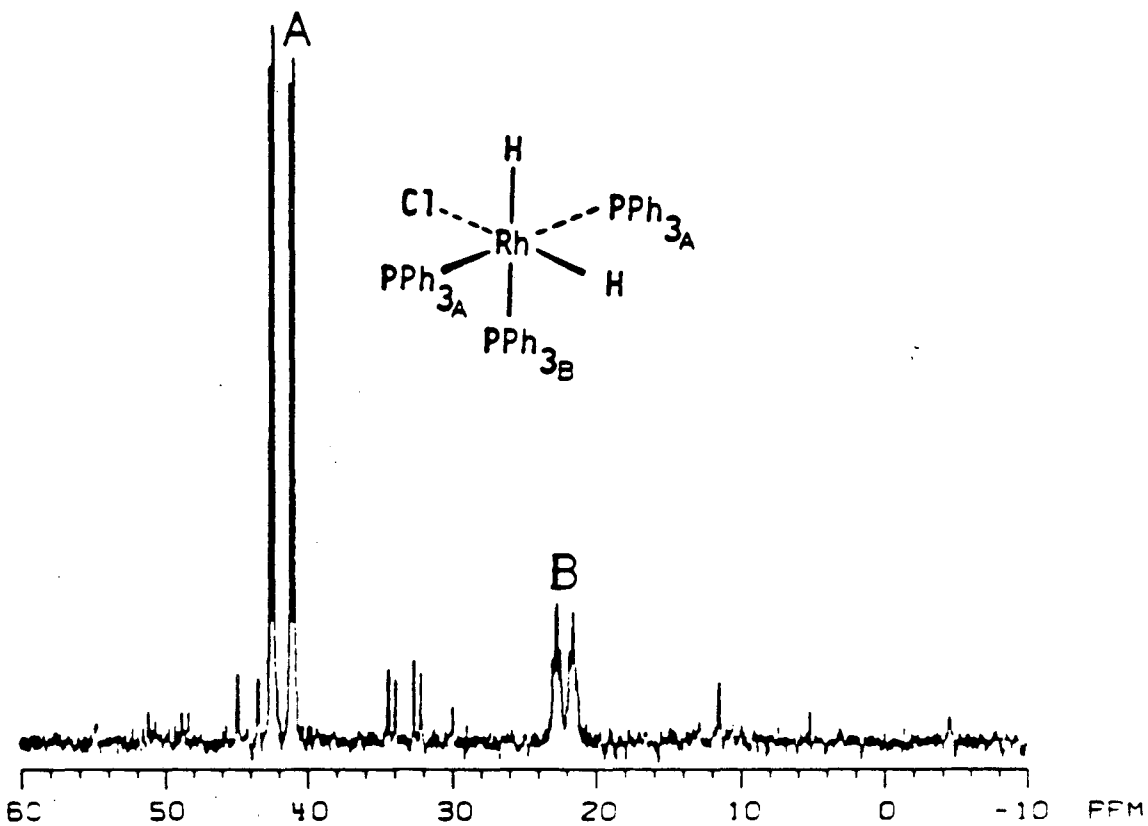
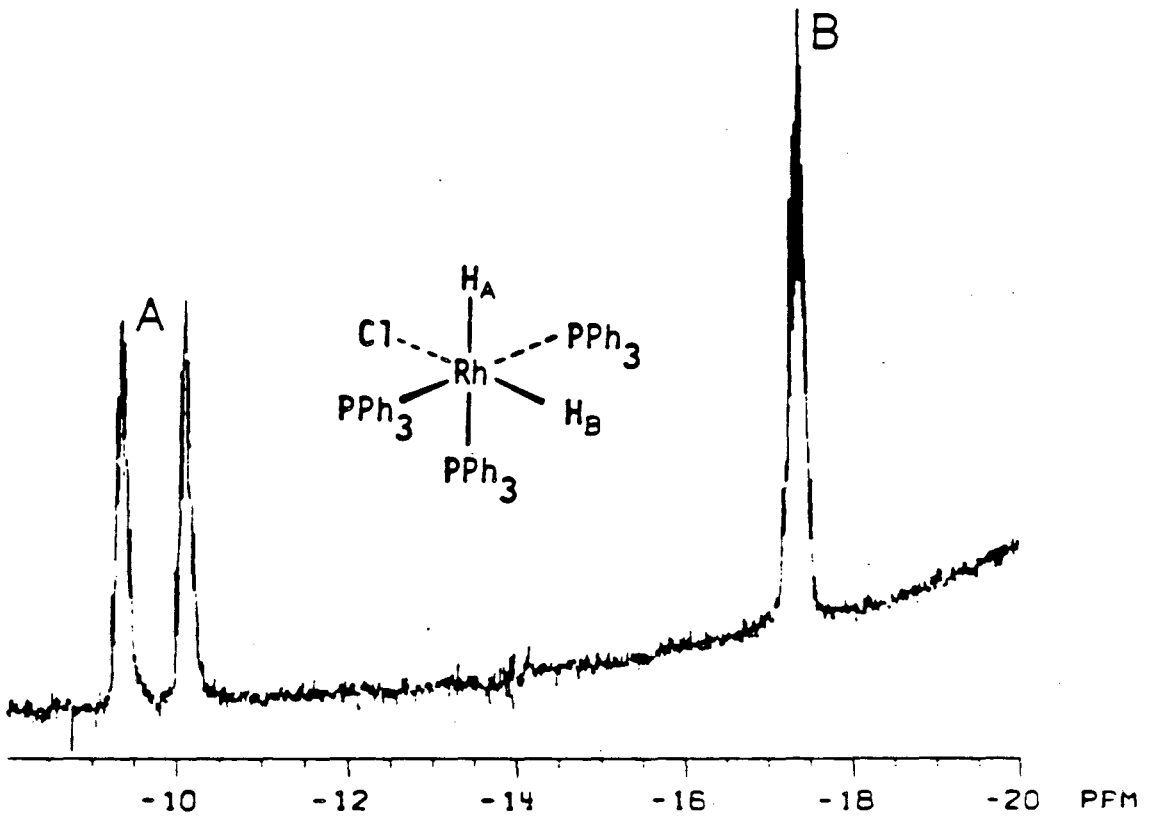


FIGURE II.14

^1H NMR of $RhClH_2(PPh_3)_3$

(-40°C, CCl_2D_2)



prepared in the presence of a 10 fold excess of quinoline the ^{31}P spectrum in Figure II.15 was obtained. In addition to signals for the starting hydride and $RhCl(PPh_3)_3$ several new signals are apparent in the range of 50 ppm to 60 ppm, and the amount of free triphenylphosphine has increased dramatically, indicating that quinoline has partially replaced triphenylphosphine as a ligand, forming several new complexes.

A proton NMR of the hydride region of a 90 fold excess mixture of quinoline and $RhClH_2(PPh_3)_3$ is in Figure II.16. The large excess of quinoline was used in this case to shift the equilibrium towards the quinoline complexes. The original hydride signals are still faintly apparent, but have been almost completely replaced by two new signals at -16.5 and -17.6 ppm. The fine splitting of these two new peaks are different, indicating that they represent two nonequivalent hydrides.

In addition to the above data, it was also found that the proton signals for the 2 and 8 positions of quinoline were slightly broadened in the presence of the rhodium dihydride. An infrared spectrum of the hydride-rhodium stretches in a mixture of the rhodium dihydride and quinoline also showed slight changes when compared with the dihydride alone, with peaks at 2110 (sh) and 2040 cm^{-1} shifting to 2122 and 2065 cm^{-1} upon addition of quinoline. This latter result is consistent with those found for bipyridine-rhodium (I) hydride complexes[34].

FIGURE II.15

^{31}P NMR of 10:1 Quinoline:$RhClH_2(PPh_3)_3$ Mixture

(-40°C, CCl_2D_2)

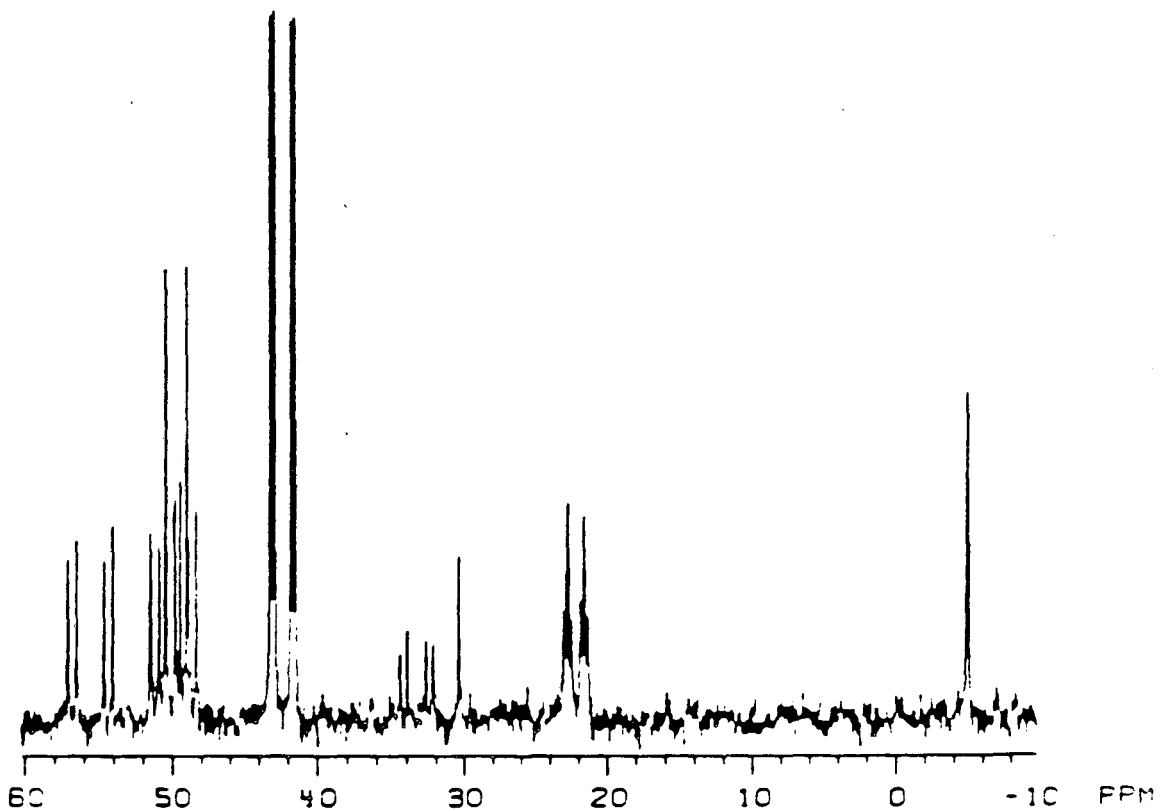
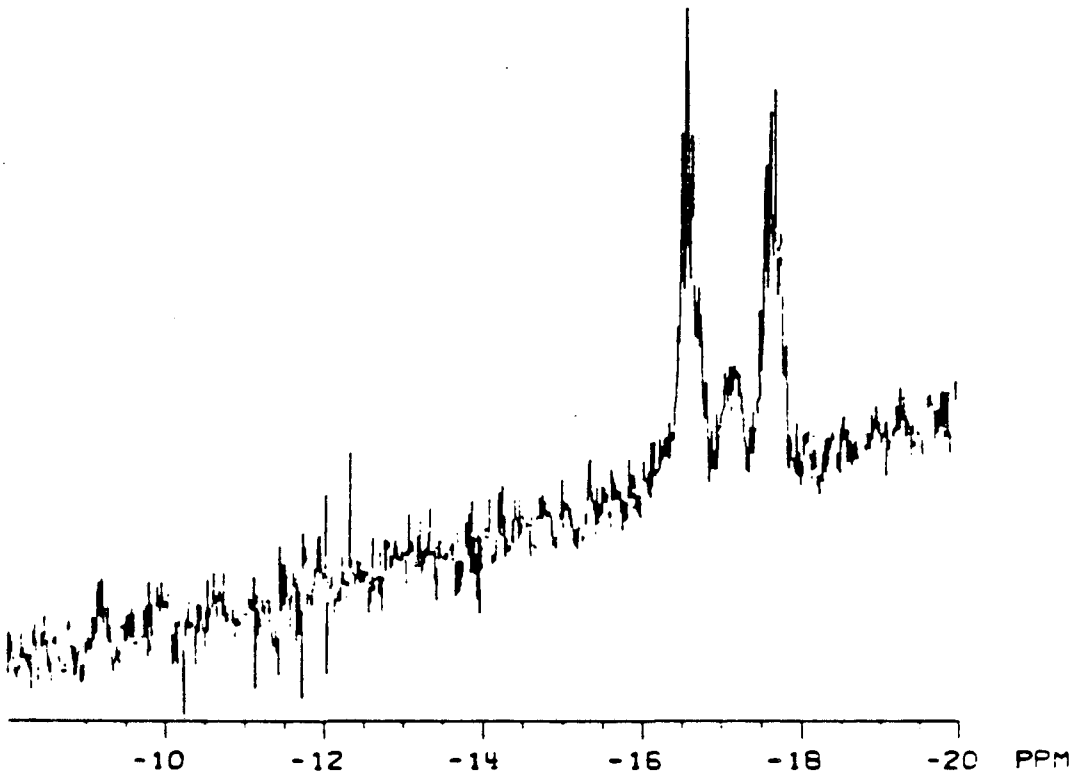


FIGURE II.16

^1H NMR of 90:1 Quinoline:$RhClH_2(PPh_3)_3$ Mixture

(-25°C, CCl_2D_2)



It is clear that the addition of quinoline to $RhClH_2(PPh_3)_3$ has produced new species. The probable identity of these new complexes is best established from the ^{31}P NMR. An expansion of the ^{31}P spectrum, showing just the new signals in the presence of quinoline, is in figure II.17. This spectrum can be resolved into two doublets of doublets (A) and two doublets (B and C) as indicated.

The two doublets of doublets, A, remain sharp at room temperature. The small couplings are the same for both (47.6 Hz), the large couplings are (left to right) 200 Hz and 166 Hz. Based on the similarity between these values and the P-P and Rh-P couplings found in $RhCl(PPh_3)_3$ (see above) a sample was made up of $RhCl(PPh_3)_3$ in 80 fold excess of quinoline. The spectrum of this mixture is in Figure II.18. Cleary this spectrum is identical to the doublets of doublets in the hydride quinoline mixture. It must be the cis diphosphine complex shown (cis-$RhCl(PPh_3)_2$Quin.) because the two phosphine ligands are inequivilant. Similar cis-phosphine complexes have been observed in the reactions of $RhCl(PPh_3)_3$ with other nitrogen compounds, for example: benzo(c)-cinnoline[35], methylbenzylamine[36] and pyrrolidine[37]. Interestingly, ethylene forms a trans complex when reacted with $RhCl(PPh_3)_3$[33], and the results with quinoline illustrate again the special features of nitrogen bases as substrates for this catalyst.

FIGURE II.17

Expanded Region of ^{31}P NMR of Quinoline:$RhClH_2(PPh_3)_3$ Mixture

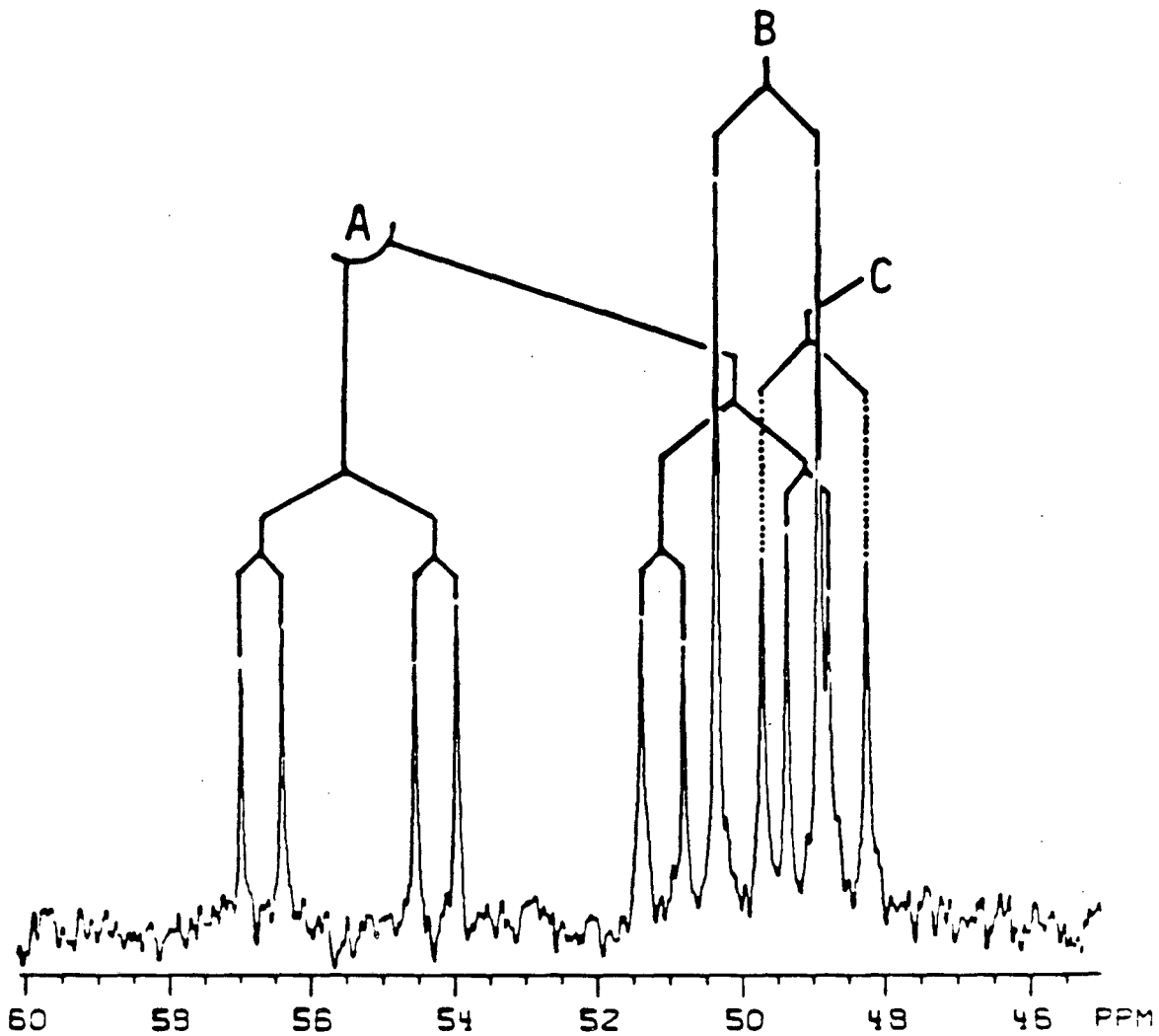
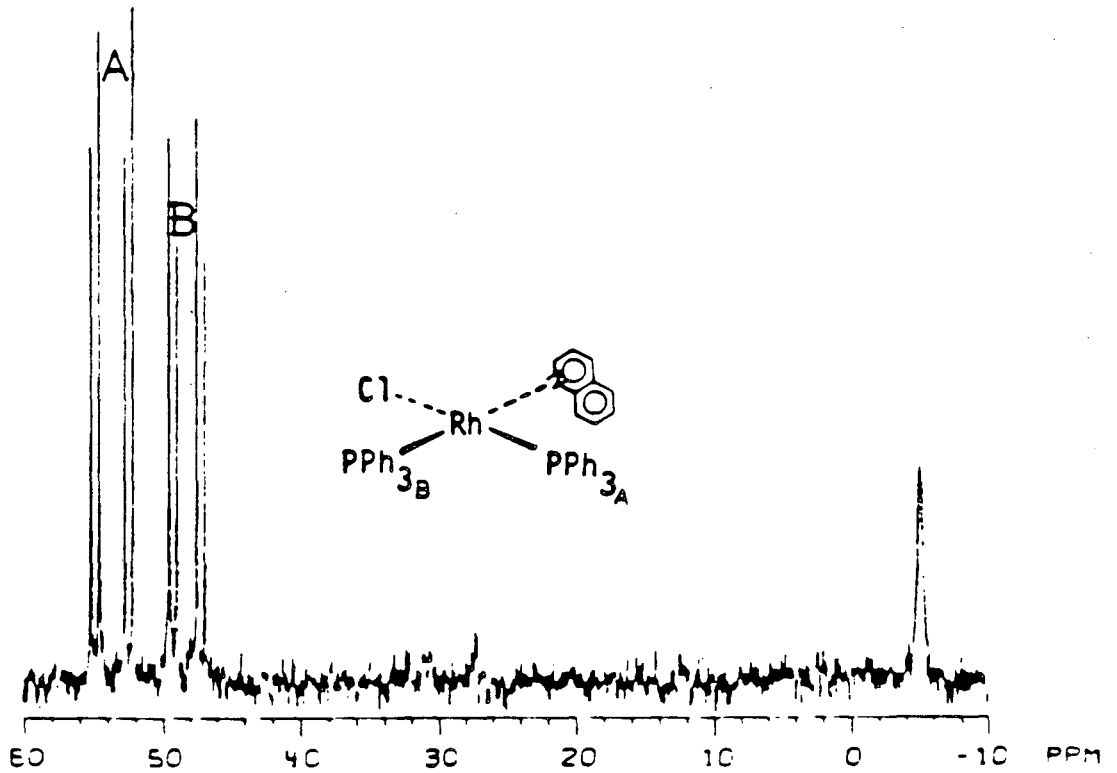


FIGURE II.18

^{31}P NMR of 80:1 Quinoline:$RhCl(PPh_3)_3$ Mixture

(20°C, CCl_2D_2)



The doublets at 49.4 and 48.7 ppm are not sharp at room temperature, the larger pair being somewhat broadened while the smaller pair are virtually unobservable. At 40°C they are broadened and coalesced, and begin to merge with the trans phosphine signal for the unsubstituted dihydride (immediately to the right). The overlap of this region with the quinoline-rhodium complex described above prevents a simple measurement of peak widths, since several peaks overlap, especially at the higher temperatures (e.g. 22°C). The lack of small couplings for either of these doublets indicates that the phosphine ligands must be equivalent in each case. The couplings are the same for both (119 Hz), similar to the value of the Rh-P coupling for the trans phosphines in $RhClH_2(PPh_3)_3$ (114 Hz). This evidence suggests that both of these doublets are due to trans bis(phosphine) quinoline complexes, in which the quinoline is bound symmetrically with respect to the phosphine ligands, making them equivalent.

It is possible that one of these new doublets is due to the formation of trans-$RhCl(PPh_3)_3$Quin., isomeric with the cis complex discussed above. However, no evidence was obtained for the formation of this complex in mixtures of quinoline and $RhCl(PPh_3)_3$. The similarity of the couplings in each doublet to the couplings of the trans phosphines in $RhClH_2(PPh_3)_3$ suggests that both new species are quinoline dihydride complexes.

The complex trans-chlorodihydrobis(triphenylphosphine) pyridine rhodium (III) has been prepared and characterized by Wilkinson et. al.[23]. Since it was expected that this known complex would be similar to the quinoline dihydride species described above it was prepared both in situ in an NMR tube and by the methods described in the aforementioned reference, and examined by NMR. The following results are for the in situ preparation combining 1 equivalent of pyridine with a preformed solution of the rhodium dihydride, the isolated material gave similar but poorer quality spectra.

The ^{31}P spectra of this material appears in Figure II.19. There is a doublet at 48.3 ppm (J_{Rh-P}=119 Hz) and a signal for free triphenylphosphine at -6 ppm. The proton spectra of the hydride region for this sample is shown in Figure II.20. It is virtually identical to the hydride region in the quinoline spectra described above, with signals at -16.8 and -17.9 ppm. The nature of the small baseline distortion at -14.2 and -15.5 ppm is uncertain, this may represent a trace amount of a different hydride species.

Clearly the quinoline complexes are both very similar to this pyridine complex. The hydride region of the quinoline spectrum indicates that both hydride species must be virtually identical, since only one set of hydride absorbances is observed for both species. This rules out isomers in which the relative disposition of the hydride

FIGURE II.19

^{31}P NMR of 25:1 Pyridine:$RhClH_2(PPh_3)_3$ Mixture

(-25°C, CCl_2D_2)

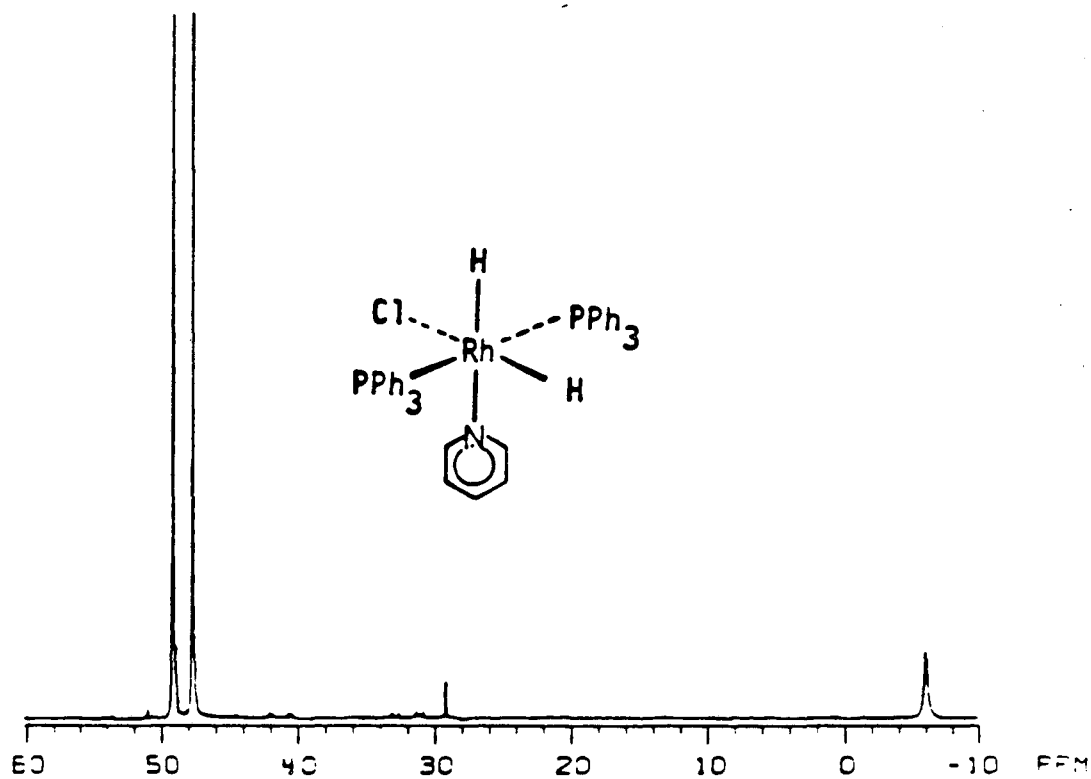
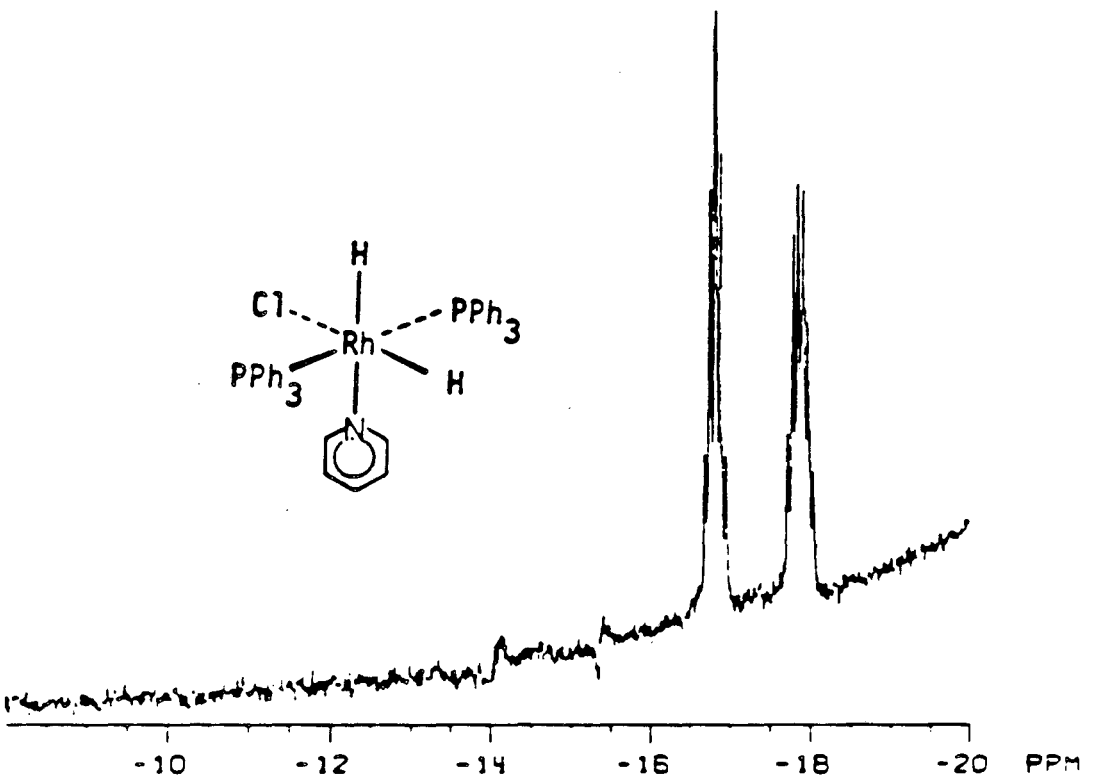


FIGURE II.20

^1H NMR of 25:1 Pyridine:$RhClH_2(PPh_3)_3$ Mixture

(-25°C, CCl_2D_2)



ligands are different with respect to the other ligands. Similarily, the phosphorus spectra indicates that the two complexes are both trans phosphines, eliminating the possibility of cis and trans phosphine isomers.

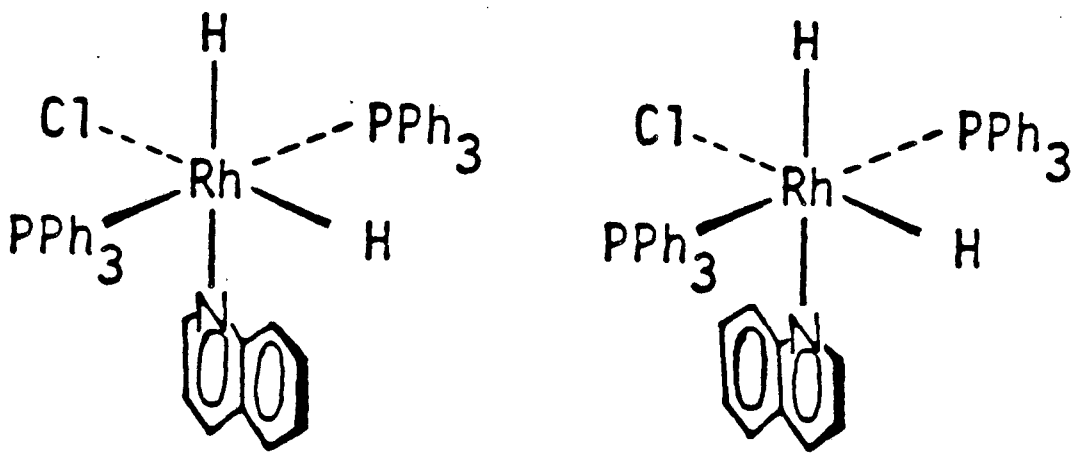
The only possibility that seems to remain is a trans phosphine dihydride quinoline complex in which the quinoline can adopt two conformations, one in which the carbon aromatic ring projects towards a hydride, the other in which it projects towards the chloride. This is illustrated in Figure II.21. It would be expected that the rotation of the quinoline would occur at sufficiently high temperatures, explaining the apparent broadening of the two doublets at room temperature. At higher temperatures the two doublets should merge into one, since the two conformations would be rapidly interconverting. While this was not observed at 40°C, the peaks did begin to coalesce.

Molecular models provide insight into the steric factors surrounding the two conformations, and indicate a substantial interaction between the quinoline and the chloride ligand in conformation B as illustrated in the figure. This should lead to a preference for one conformation, A in the figure, and could at least in part explain the greater sharpness of one of the quinoline hydride doublets as compared with the other, at room temperature.

While this does explain the two similar doublets in

FIGURE II.21

Proposed Quinoline Rhodium Dihydride Complexes



the phosphorus spectrum, it is still difficult to rationalize the fact that the proton spectrum of the hydride region, taken alone, would only indicate one new hydride species. Experiments with other unsymmetrical ligands containing a pyridine ring, such as 2 or 3 substituted pyridines, would be helpful in fully understanding this situation.

Having established the general nature of quinoline/ $RhClH_2(PPh_3)_3$ mixtures, the effects of para-cresol on these mixtures was investigated. As discussed earlier, the presence of p-cresol in quinoline hydrogenations with the rhodium catalyst led to a three-fold increase in rate (table II.6), the largest found with any added compound. One possible cause of this higher rate is an increase in the dissociation of triphenylphosphine from the rhodium complex in the presence of cresol, leading to a more facile binding of quinoline to the catalyst. Therefore the interaction of cresol with the components of the catalytic system, together and separately, was examined by NMR.

Figure II.22 is the room temperature ^1H NMR spectra of p-cresol. The concentration of cresol is 1ul/ml, low enough that cresol/cresol hydrogen bonding is minimized and the hydroxyl signal is sharp. It was important to work at concentrations low enough to allow observation of hydrogen bonding interactions between cresol and any other compound without interfering effects.

Figures II.23 and II.24 show the ^1H NMR of cresol

FIGURE II.22

^1H NMR of P-Cresol

(20°C, C_6D_6)

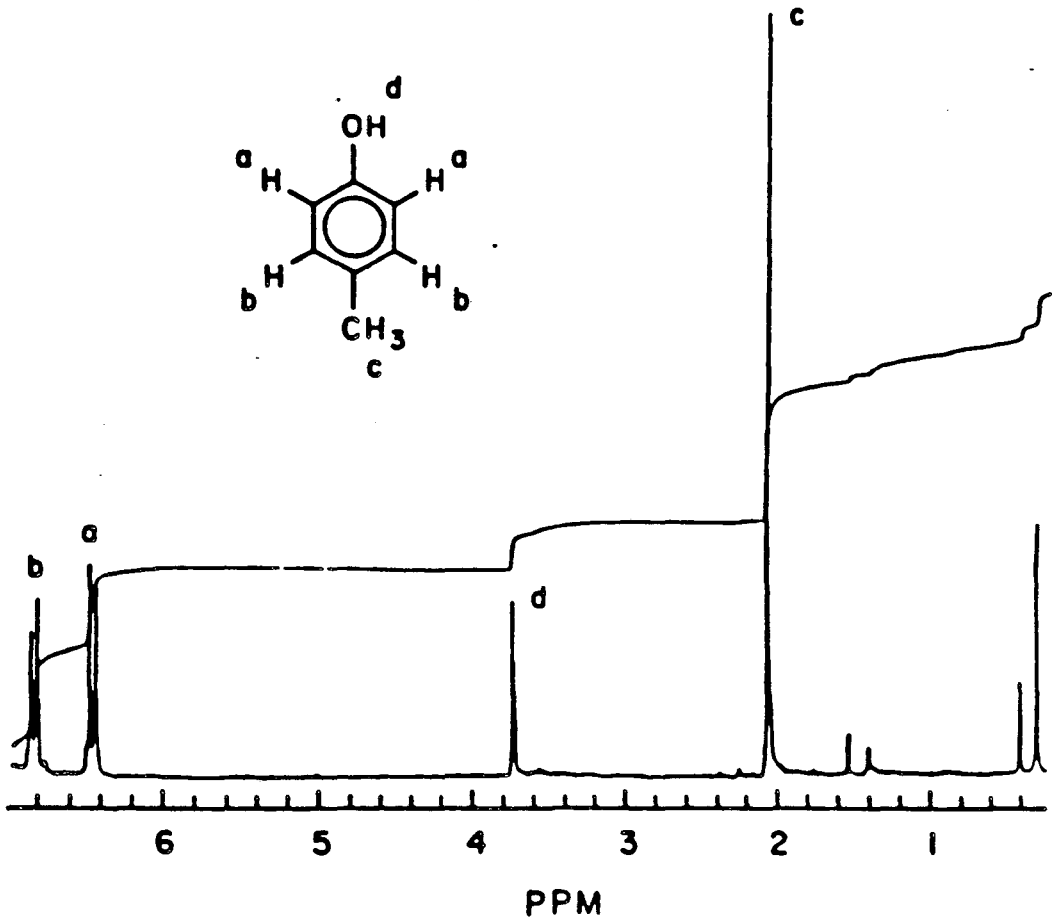


FIGURE II.23

^{1}H NMR of 1:1 p-Cresol:Triphenylphosphine Mixture

(20°C, C_6D_6)

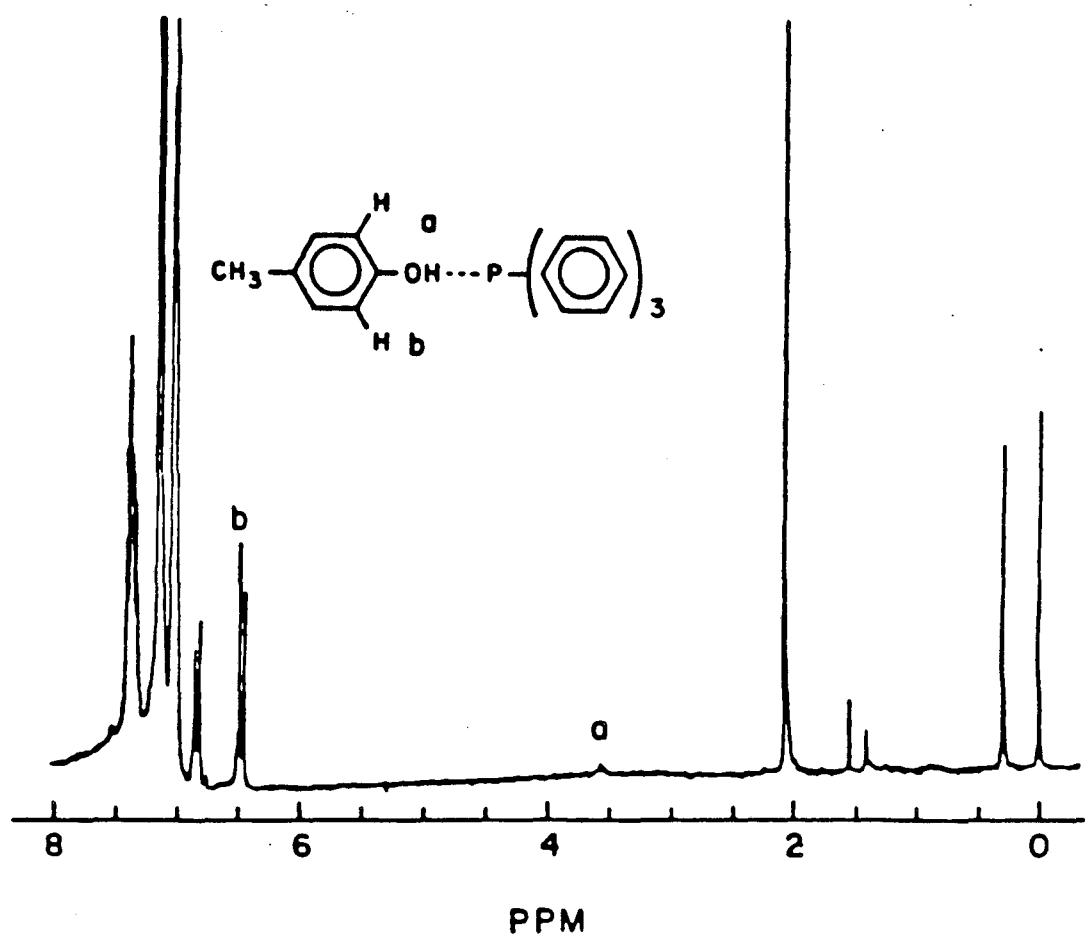
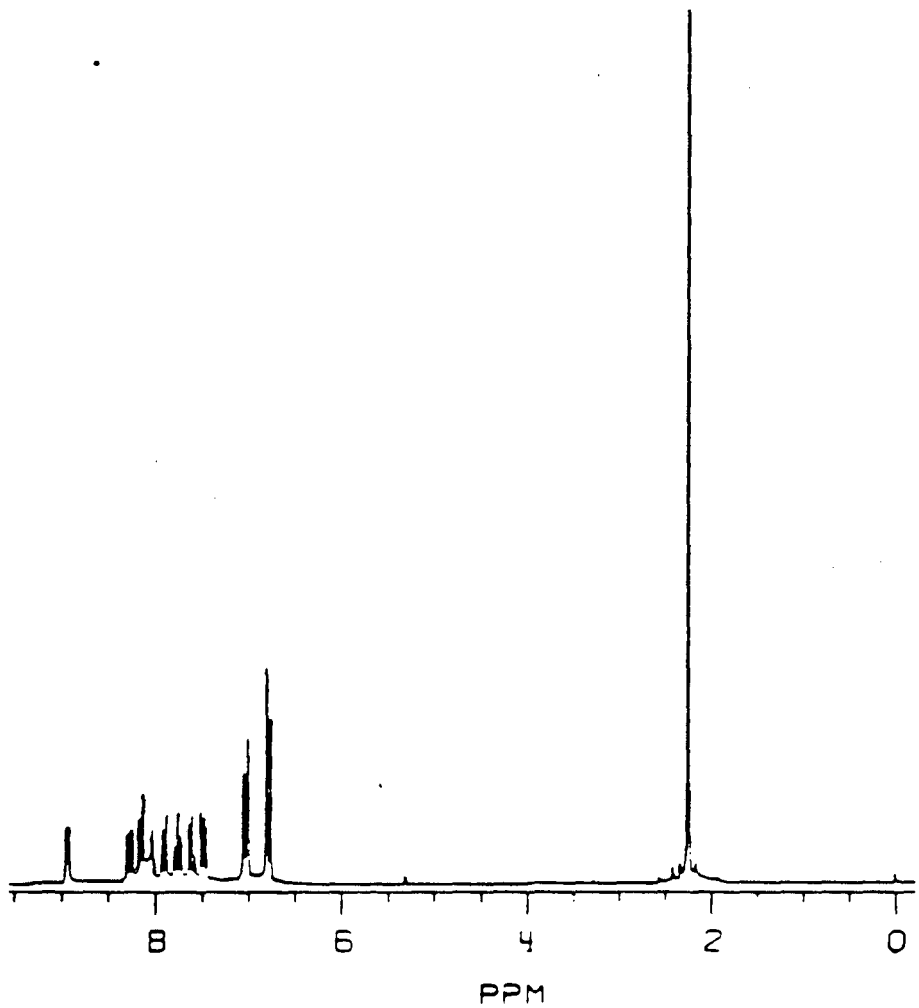


FIGURE II.24

^1H NMR of 1:1 p-Cresol:Quinoline Mixture

(20°C, CCl_2D_2)



in the presence of equimolar amounts of triphenylphosphine and quinoline, respectively. In both cases the cresol hydroxyl signal is absent, indicating that hydrogen bonding, which causes in effect an exchange of the hydroxyl proton between two compounds, has occurred. The alternative proton transfer (acid/base) reaction that could occur with quinoline is ruled out because the quinoline portion of this NMR spectrum is essentially unchanged from the free compound (see appendix VI for quinoline spectrum). There were no changes observed in the phosphorus spectrum of the cresol/triphenylphosphine mixture as versus free triphenylphosphine, with the exception of a tiny perturbation of the phosphorus-phenyl proton coupling constants observed in the undecoupled spectrum in the presence of cresol. Thus it is apparent that cresol hydrogen bonds well with both of the free ligands present in the catalytic system, and so the effect it might have on any equilibria between these ligands and the rhodium catalyst is unclear from these results.

Further experiments were conducted, in which a 10:1 (molar) mixture of cresol and $RhClH_2(PPh_3)_3$ and a similar 10:10:1 mix of cresol, quinoline and the rhodium hydride were made up and examined by ^{31}P NMR. In both cases the spectra were identical to those obtained in the absence of cresol (Figures II.13 and II.14), no evidence of new species or of large changes in the concentration of any species were found (concentration changes less that

10% are below the experimental limit of error and cannot be ruled out, but such small changes could not account for the large reduction rate increase of quinoline induced by cresol).

All of this evidence indicates that the action of cresol is not to change the binding of quinoline to the rhodium complex. Since the rates were measured under pseudo-zero order conditions any interaction of cresol with the product is also ruled out, the concentration of the product being intentionally too low to affect the rate. The nature of the rate enhancement caused by cresol remains uncertain, further experiments are planned in which compounds with the same basic structure and similar dipole moments as p-cresol (such as p-chlorotoluene) will be investigated as rate enhancers. If the effect of cresol is primarily to change the dielectric properties of the solvent then these other compounds should show similar reduction rate enhancements, otherwise some unique property of cresol is involved.

The Binding of 1,2,3,4-Tetrahydroquinoline to Chlorohydrotris(triphenylphosphine)ruthenium:

As discussed in the deuterium experiments section that follows the ruthenium catalyst was found to exchange deuterium for hydrogen at the 2-carbon of 1,2,3,4-tetrahydroquinoline. An imine intermediate is proposed to

explain this result. In order to further investigate this possibility a 1:1 mixture of tetrahydroquinoline and the preformed ruthenium hydride, prepared using standard methods[22], was made up and examined by ^1H NMR at room temperature.

All of the signals for 1,2,3,4-tetrahydroquinoline were found (see appendix for a NMR spectrum of this compound), and were shifted downfield by small amounts from the free compound signals, except for the nitrogen proton (position 1), which was substantially shifted by 2.4 ppm. The next largest shifts were 0.2 ppm (H-2) and 0.25 ppm (H-8). This data indicates that binding of 1,2,3,4-tetrahydroquinoline to the ruthenium complex has occured, but that formation of the imine type intermediate has not.

The formation of this imine intermediate, which still seems likely based on other evidence discussed in the following section, may not occur until higher temperatures are reached. Further NMR experiments at elevated temperatures are planned, as well as an examination of the mixture of tetrahydroquinoline and $RuClD(PPh_3)_3$, in which case exchange of the metal bound deuterium with tetrahydroquinoline may occur.

II.B.4 DEUTERATION STUDIES

The substitution of deuterium gas for hydrogen gas in homogeneous reductions has proven to be an invaluable technique for the elucidation of mechanisms and stereochemistry[14,15]. In order to gain greater insight into the details of the reduction of basic nitrogen heterocycles by both $RuHCl(PPh_3)_3$ and homogeneous and polymer-supported $RhCl(PPh_3)_3$, experiments were carried out in which quinoline and 1,2,3,4-tetrahydroquinoline were reacted with deuterium in the presence of each catalyst. Additionally, phenanthridine was reduced with deuterium using $RhCl(PPh_3)_3$. The results of these studies have lead us to propose several specific mechanistic steps involved in the reduction of quinoline, which are incorporated into overall reduction mechanism schemes presented in the following section (II.B.5).

The reductions were carried out for the most part in the batch reactor system under a variety of conditions detailed in the figures referred to below. The solvent was in every case dry, degassed benzene. The products formed from these reactions were observed by NMR spectroscopy, using several different instruments, and in some cases mass spectra were also obtained. Examples of most of the spectra referred to in this section are found in the appendix (Sec. IV). Generally each of the experiments discussed was repeated once or twice, the spectra in the appendix are typical results.

In order to conserve deuterium gas the pressures used in some reactions are lower than others, reflecting the pressure at the deuterium tank. While this pressure difference may effect the rates of the various processes described below, it would not effect the general patterns of deuterium substitution found.

The positions of deuterium substitution were deduced by comparison of the NMR spectra of the deuterated products with spectra of the undeuterated compounds, locating those proton signals that had been reduced in area in the deuterated compounds. The approximate amounts of deuterium substitution could also be determined from the integrated spectra, however errors inherent in such integrals, mainly determining where a peak is distinct from the baseline, limit the accuracy of this method.

In those cases where the mixture was sufficiently simple the mass spectra provide a more accurate determination of actual amounts of deuterium substitution, by determining the relative abundance of the base ion corresponding to each deuterated product. For complex mixtures, those containing several different deuterated isomers, determining the relative abundance in the mass spectra proved intractable, and the NMR spectra provide the only measure of the degree of substitution.

An additional problem sometimes encountered in the mass spectroscopy work was the differing retention times of the various deuterated analogs of the same compound.

Although the retention times vary only slightly, mass spectra taken at intervals during the emergence of a peak can be different. This was a particular problem in the complex mixtures mentioned above. The MS results described below correspond to spectra taken at the middle of an eluting peak.

The homogeneous catalyst reaction mixtures were prepared for analysis by first passing them through a 10 cm column containing Florosil chromatographic absorbant to remove the catalysts, which were strongly absorbed on this material. As a result of this treatment any deuterium on a nitrogen (in tetrahydroquinoline and dihydrophenanthridine) was fully exchanged for hydrogen by interaction with hydroxyl groups in the Florosil. The only case in which this did not occur was with the polymer supported $RhCl(PPh_3)_3$, which eliminated the necessity of catalyst removal by absorption. The nitrogen was observed to be partially deuterated in this case (the remainder of the results are described fully below), probably some exchange with atmospheric moisture of hydroxyl groups in the glass NMR tubes prevented a fully deuterated nitrogen from being observed in those cases were it was presumably formed using this polymer catalyst.

$\underline{RhCl(PPh_3)_3}$ Results and Discussion:

The results of the various deuteration studies made

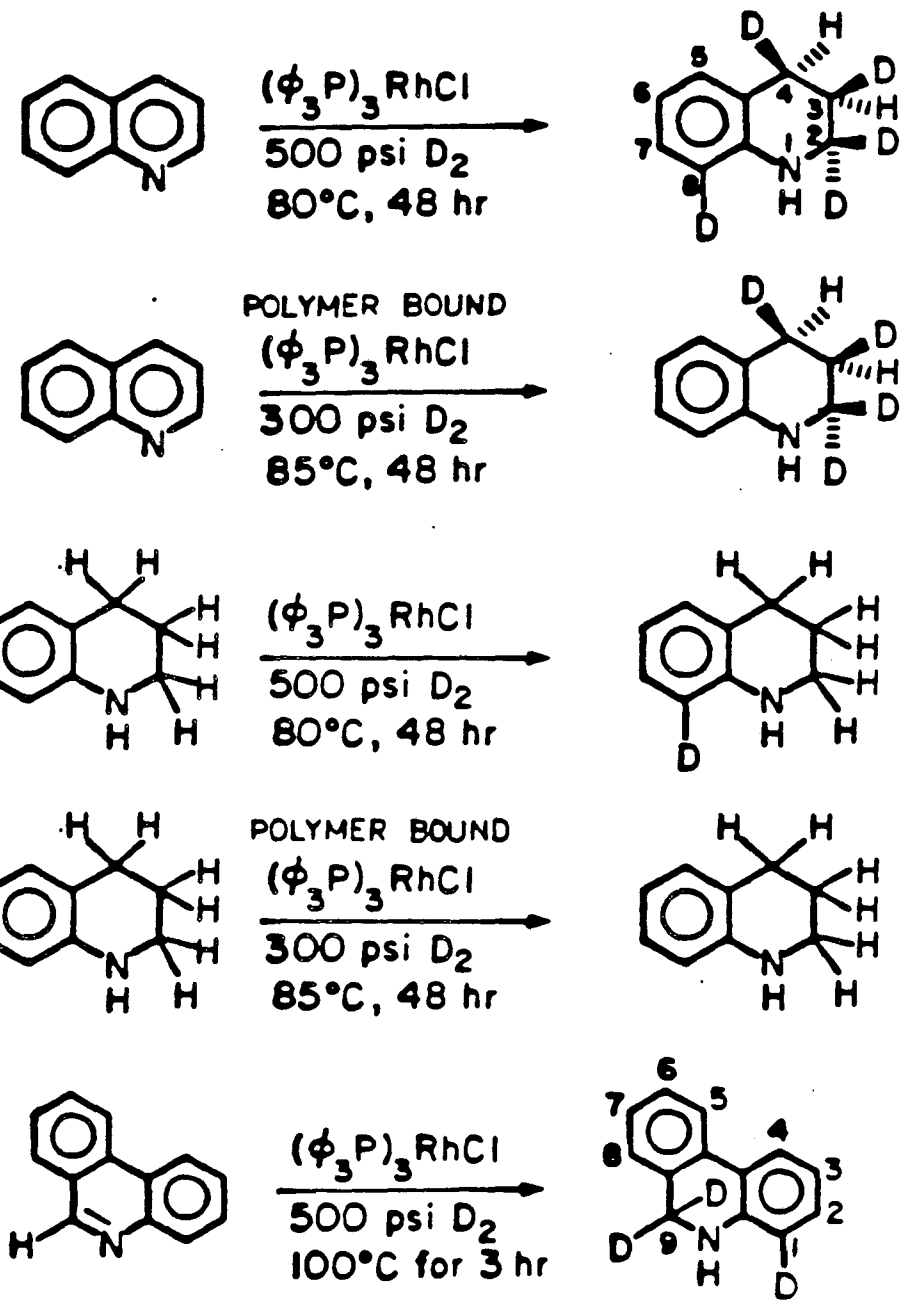
with homogeneous and polymer-supported $RhCl(PPh_3)_3$ are illustrated in Figure II.25. Both of these catalysts were examined for the reduction of quinoline by deuterium, as well as the reaction of 1,2,3,4-tetrahydroquinoline with deuterium. The reduction of phenanthridine was investigated only with the homogeneous catalyst.

The reaction product with quinoline and the homogeneous catalyst was analyzed by GC-MS and 400 MHz NMR. By NMR the deuterium substitution of the product, 1,2,3,4-tetrahydroquinoline, was found to be 1.6 D at position 2, 1.0 D each at positions 3 and 4, and 0.7 D at position 8. The MS revealed d_3,d_4 and d_5 products. Importantly, a small amount (c.a. 2%) of unreduced quinoline remained at the end of the reaction and a mass spectrum of this material showed it to be monodeuterated. The amount of quinoline was too small to obtain an NMR spectrum.

This experiment was repeated more than once, during which it was found that occasionally a slight excess of deuterium was incorporated at the 3 or 4 positions. This excess, when observed, was less than 20% (1.2 D). It is not known if this is an artifact of the NMR spectrum integration or a result of some subtle difference between the various repeat experiments. This result is not accounted for in the discussion of mechanisms below, in which exactly one deuterium is presumed at the 3 and 4 positions.

FIGURE II.25

Deuterium Results Using $RhCl(PPh_3)_3$



In order to determine the position of deuteration on the unreduced quinoline, this same reduction was carried out to 50% conversion. The reduced product was found by GC-MS to be almost entirely 1,2,3,4-tetrahydroquinoline-d_3, while 250 MHz NMR showed one deuterium each at the 2,3 and 4 positions, with a trace of substitution at the aromatic 8 position. The unreduced quinoline was found by 250 MHz NMR to be substituted with deuterium exclusively at the 2 position. By NMR the substitution at this position was 0.3 D, however a GC-MS of the same material indicated only 0.1 D (10% RA of m/e=130). The latter value is probably more accurate than the former due to the inaccuracies inherent in the NMR integration technique.

Very similar results were obtained using the polymer-bound catalyst, with the important difference that no deuterium substitution of the aromatic 8 position was found. For the complete reduction of quinoline, the product was found by 250 MHz NMR to contain 1.6 D at position 2 and 1.0 deuterium each at positions 3 and 4. The amount of quinoline remaining (less than 0.3 %) was too small to examine. A partial reduction was not carried out with this catalyst due to technical problems involving the relatively high initial reduction rate of quinoline.

The fact that more than one deuterium is found incorporated at the 2 position of the product in the complete reductions described above is very significant. If the reduction of quinoline is assumed to be irreversible

then only one deuterium would be incorporated at position 2 during this reduction, and the excess deuterium found here would have to be incorporated by some exchange process involving either the product, in a post-reduction step, or the quinoline, in a pre-reduction step. Alternatively, the reduction of quinoline could be reversible, although this reversibility would have to be confined to the 1-2 carbon-nitrogen positions, since the 3 and 4 positions in the product contained only one deuterium each.

To define more clearly the nature of this exchange, 1,2,3,4-tetrahydroquinoline was reacted with deuterium in the presence of each of the two catalysts. In both cases, no exchange of the 2,3 or 4 positions for deuterium was seen by NMR or mass spectroscopy. In the homogeneous case 0.7 D was found at the 8 position, this position was not substituted with deuterium when the polymer catalyst was used. The lack of any exchange at the nitrogen ring indicates that the deuterium substitution found here when reducing quinoline must all be occuring during the reduction.

Since the reversibility of the reduction step is a possible explaination of the results presented above, phenanthridine, which we had independently found to hydrogenate reversibly under many conditions (see the hydrogen transfer section II.D), was also reduced with deuterium gas, using only the homogeneous catalyst. In this case the product, 9,10-dihydrophenanthridine, was

found by 250 MHz NMR to be almost entirely exchanged with deuterium at the nine position, and exchanged with 0.3 D at position 1 (analogous to position 8 in quinoline). A mass spectrum of this material showed d_1, d_2 and d_3 products. As was the case with quinoline, the mass spectrum shows a somewhat lower deuterium substitution than the NMR results. This result clearly verifies that the reduction of phenanthridine is highly reversible, and has important implications for the reduction of quinoline.

The substitution of the 3-4 bond found in the tetrahydroquinoline produced by quinoline reduction is best explained as an irreversible reduction, otherwise products with more than one deuterium substituted at each position would have been expected (as noted above slight excesses of deuterium were sometimes found at these positions, but not nearly as great as the excess at the 2 position). The large extent of deuterium substitution at the 2 position found in the 1,2,3,4-tetrahydroquinoline produced by reducing quinoline with deuterium indicate a reversible hydrogenation/dehydrogenation step, or an exchange process involving either the product or the reactant. The lack of any exchange when 1,2,3,4-tetrahydroquinoline was reacted with deuterium under the same conditions used to reduce quinoline clearly rules out the last of these three processes, and as well eliminates the possibility of a reversible hydrogenation involving tetrahydroquinoline.

The remaining possibilities are either direct exchange

on quinoline, or a reversible hydrogenation step involving quinoline and an unobserved intermediate. These two possibilities cannot clearly be distinguished based on the evidence at hand, however the phenanthridine result strongly suggests that a reversible hydrogenation step is responsible for the incorporation of excess deuterium at the 2 position of both product and reactant.

The most direct way to explain the above results is to assume that the reduction of quinoline to 1,2,3,4-tetrahydroquinoline is a two step process. The first step is the reversible reduction of the 1-2 carbon-nitrogen bond, with the 3-4 double bond remaining intact. The resulting compound, 1,2-dihydroquinoline, is easily dehydrogenated to form quinoline, this was verified by the synthesis and catalytic dehydrogenation of this substrate (see section II.D). Additionally this compound was virtually impossible to analyze by gas chromatography due to its extreme thermal instability, and so would not be observed during a reduction. The reversible hydrogenation/dehydrogenation of this bond continues until reduction of the 3-4 bond in the 1,2-dihydroquinoline to form 1,2,3,4-tetrahydroquinoline. Once this bond is reduced the 1-2 bond is no longer activated (allylic to 3-4 double bond), and so may no longer be dehydrogenated. Thus 1,2,3,4-tetrahydroquinoline shows no exchange with deuterium at position 2 in the presence of the rhodium catalyst.

This scenario is additionally supported by the exchange results found with phenanthridine. This compound is reduced to 9,10-dihydrphenanthridine, which may be considered analogous to 1,2-dihydroquinoline with a benzene ring substituted for the double bond at the 3-4 position of the latter. Unlike the 3-4 double bond in dihydroquinoline, though, this ring cannot be reduced. As a result dihydrophenanthridine is easily dehydrogenated to reform phenanthridine, leading eventually to the nearly total deuterium exchange found at the nine position of the product when phenanthridine was reduced.

A problem with the above mechanism is that only one deuterium was found at the 2 position of the tetrahydroquinoline produced by the partial reduction of quinoline, while more than this amount would be anticipated. However, the substitution on the unreduced quinoline at this position was only 10% (by MS) and so less than 1.1 D would be anticipated in the product, an excess too small to observe reliably by NMR spectroscopy. This result implies that the forward rate of the reduction is faster than the reverse, since the amount of quinoline-d_1 formed was much less than the total amount of tetrahydroquinoline formed.

It is possible instead that the deuterium exchange at the 2 position of quinoline occurs through an oxidative addition/reductive elimination mechanism, in which a rhodium-carbon bond is formed in the intermediate, dihydroquinoline complex, with the rhodium-nitrogen bond

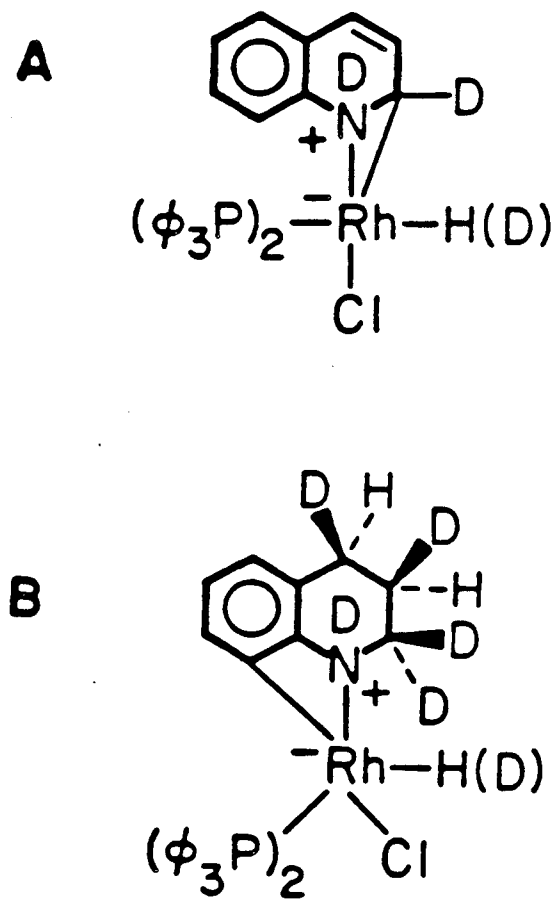
remaining intact. This would provide a 3-membered ring, metalla-azacyclopropane (Fig. II.22A). Such compounds have been reported by Kaesz et. al.[38,39], and have been postulated by Laine et. al.[40] to explain their results with deuterium exchange on tertiary alkyl amine catalyzed by rhodium clusters. Such a complex is highly strained though, and a reversible hydrogenation step remains a more likely explanation.

One final result to be explained is the exchange of the aromatic C-H bond at the 8 position of tetrahydroquinoline and the 1 position of phenanthridine found in the homogeneous reductions. A means for this exchange to occur would be the formation and cleavage of a 4 membered cyclometallated intermediate (Fig. II.26B). This proposed complex is similar to five membered rings formed from the reaction of 7,8-benzoquinoline and osmium and ruthenium clusters by Stone[41,42]. No direct evidence for the formation of this complex was found during this work however.

It is not apparent why the deuterium exchange at position 8 did not occur with the polymer supported catalyst. The intermediate illustrated in Figure II.26B is a bisphosphine complex, with one hydride ligand. If instead this intermediate is a monophosphine, dihydride then the polymer result can be rationalized by the fact that displacement of two phosphines from the rhodium is difficult due to the attachment of at least one to the

FIGURE II.26

Proposed Cyclometallated Intermediates in Deuterium Exchange



polymer backbone. As discussed in the section on polymer supported rhodium reductions, the attachment of the phosphines to the polymer causes entropic effects which can profoundly affect the equilibrium between bound and free phosphines[43]. However, there are also steric effects in the polymer that are absent in the homogeneous system, and these as well may effect the formation of the proposed cyclometallated intermediate.

The mechanistic details described above, along with other results, have been incorporated together in a proposed mechanism for the reduction of quinoline using $RhCl(PPh_3)_3$, which may be found in the following section.

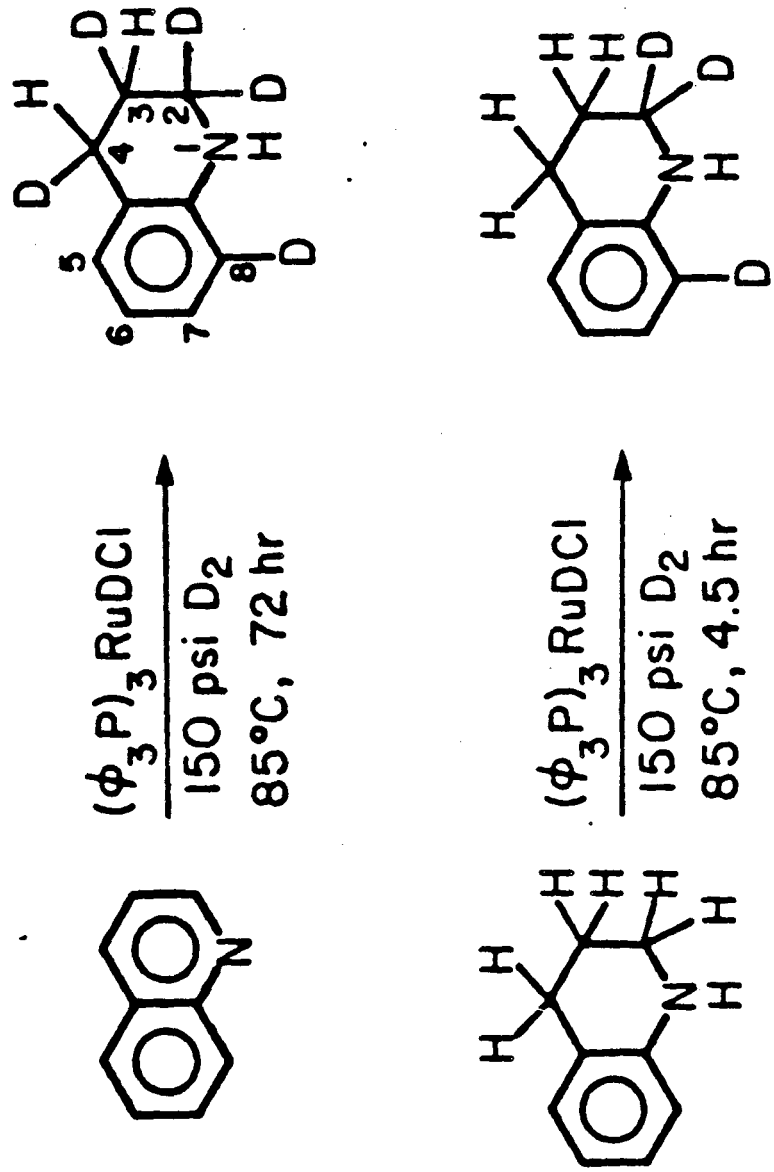
$RuCl_2(PPh_3)_3$ Results and Discussion:

A study similar to the above work, although less extensive, was carried out using $RuClD(PPh_3)_3$ as catalyst, this material being formed in situ from $RuCl_2(PPh_3)_3$ and deuterium (see section II.B.1 for more detail on this reaction). Both quinoline and 1,2,3,4-tetrahydroquinoline were reacted with deuterium and the catalyst, to provide rather different results than were found with the rhodium catalyst, these are shown in Figure II.27.

When quinoline was completely reduced by this catalyst the resulting product was very similar to that found with the rhodium catalyst. A 200 MHz NMR analysis of the

FIGURE II.27

Deuterium Results Using $RuClD(PPh_3)_3$



resulting tetrahydroquinoline showed 1.8 D at position 2 and one deuterium each at positions 3 and 4. Position 8 on the aromatic ring was exchanged with 0.8 deuterium.

When this same reaction was carried out to 50% completion the product was substituted with 1.8 D at the 2 position and 0.2 D at the 8 position. The 3 and 4 positions were substituted as in the total reduction. The unreduced quinoline was observed by 200 MHz NMR to contain 0.5 D at the 2 position.

When 1,2,3,4-tetrahydroquinoline was reacted with deuteriun and the ruthenium catalyst the result was quite different than that found with the rhodium catalyst. Position 2 of the tetrahydroquinoline was again substituted with 1.8 D, as in the quinoline reductions. The 8 position was substituted with 0.1 D. Thus there must be an exchange process involving the 1,2,3,4-tetrahydroquinoline.

It is important to note that $RuHCl(PPh_3)_3$ was not observed to dehydrogenate tetrahydroquinoline either in the reaction described above, nor in a separate reaction carried out under a small pressure of nitrogen. The deuterium incorporation into the 2 position of the unreduced quinoline in the partial reduction experiment, and the deuterium incorporation into tetrahydroquinoline as described, are the results of two separate mechanisms.

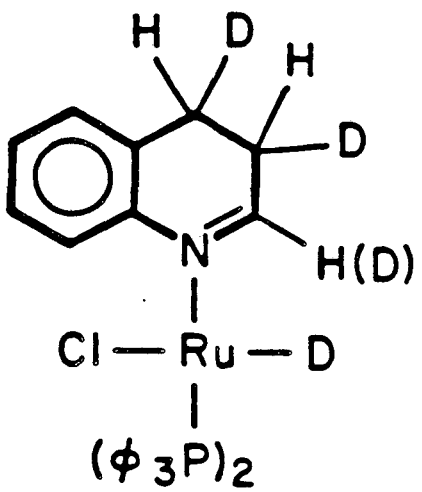
To account for the exchange of deuterium found when starting with tetrahydroquinoline an imine intermediate may

be proposed (Figure II.28). $RuCl_2(PPh_3)_3$ is known to be an active catalyst for alkyl amine chain scrambling and deuterium exchange at carbons adjacent to nitrogen in amines[44-46]. This type of reactivity is generally explained by proposing hydridochlororuthenium-imine complexes formed by the catalytic dehydrogenation of amines. Such an imine intermediate has in fact been directly observed by Garrou et. al.[44]. The reversible formation and reduction of the imine intermediate we propose here would account for the deuterium incorporation found when starting with 1,2,3,4-tetrahydroquinoline, and as well would account for some of the deuterium incorporation in the product formed by reducing quinoline. We were unable to observe such an intermediate in our systems, or the imine itself, 3,4-dihydroquinoline. It is doubtful that the imine would be stable enough to isolate or observe, and we were in fact unable to find any evidence in the literature of this particular compound being synthesised or otherwise observed.

The remainder of the deuterium results found with the ruthenium catalyst can be explained in exactly the same manner as the results obtained with $RhCl(PPh_3)_3$. The incorporation of deuterium found in the quinoline after the partial reduction experiment indicates a reversible hydrogenation/dehydrogenation which must not involve tetrahydroquinoline, as evidenced by the inability of $RuHCl(PPh_3)_3$ to form quinoline from tetrahydro-

FIGURE II.28

Proposed Imine Intermediate in Deuterium Exchange



quinoline. As with the rhodium catalysts, this implies the existence of a 1,2-dihydroquinoline containing intermediate. The somewhat greater degree of substitution of deuterium on quinoline found with the ruthenium complex after 50% reduction implies that the reverse reaction is faster relative to the forward rate in this case. The substitution of deuterium found at the aromatic 8 position of the product indicates the possibility of a cyclometallated intermediate similar to that proposed for $RhCl(PPh_3)_3$.

The results described above, along with other data, have been used to propose a mechanism for the reduction of quinoline using $RuHCl(PPh_3)_3$. This mechanism is described in the following section.

II.B.5 PROPOSED REDUCTION MECHANISMS

Chlorotris(triphenylphosphine)rhodium(I):

The previously discussed results with $RhCl(PPh_3)_3$ can be incorporated together in a proposed reduction mechanism, Figure II.25. The principal pathway is from A to C, leading to the reduction product, 1,2,3,4-tetrahydroquinoline. The intermediate D is proposed to explain the deuterium exchange at position 8 on the tetrahydroquinoline, found with this catalyst.

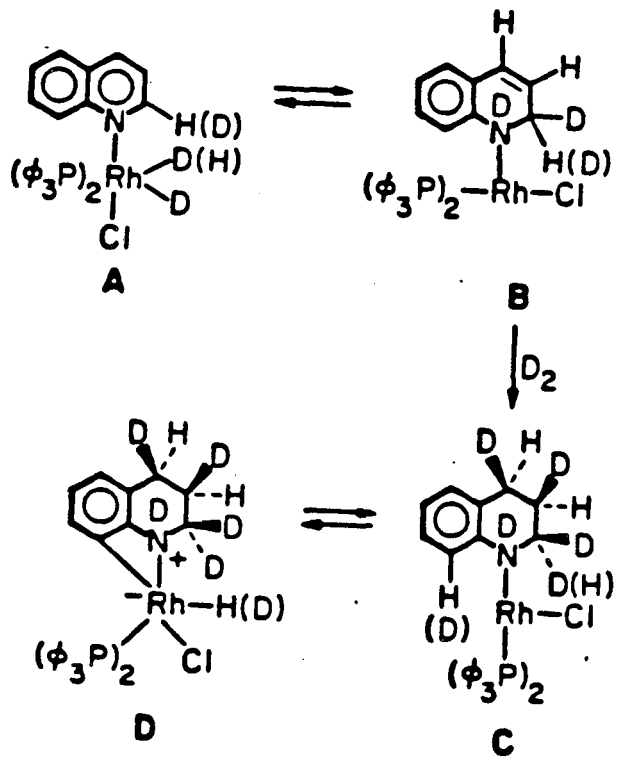
Intermediate A can occur as the result of addition of quinoline to the rhodium dihydride, or can result from the addition of hydrogen to cis-chlorobis(triphenylphosphine)quinoline rhodium(I), a species discussed in section II.B.3. Species B may be formed from A via intramolecular addition of hydrogen (or deuterium as shown) to the carbon-nitrogen double bond. The exchange of deuterium at the 2 position of the product and unreduced reactant, found using deuterium gas as a reductant, can be explained by the reversibility of this first reduction step.

The next step of the reduction, B to C, is irreversible, accounting for the lack of deuterium exchange at the 2 position found when 1,2,3,4-tetrahydroquinoline was reacted with the rhodium catalysts and deuterium. As well, the addition of only one deuterium each to the 3 and 4 positions indicates that this step is irreversible.

However it is not known if the reduction of the 3,4

FIGURE II.29

Proposed Quinoline Reduction Mechanism With $RhCl(PPh_3)_3$



double bond is intermolecular or intramolecular. It could occur by the complexation of the 3,4 bond to another rhodium center (intermolecular), as for olefin reductions[21], but molecular models provide some insight into the plausibility of an intramolecular addition of hydrogen from the rhodium binding to the nitrogen atom.

The extent of deuterium incorporation into the tetrahydroquinoline produced by complete reduction of quinoline(section II.B.5) indicates that the overall forward rate of reduction must be comparable to the reverse of the first step. If the forward step predominated only the product monodeuterated at the 2 position would be anticipated. If the reverse predominated, then a d_2 product would be expected. The actual substitution of 1.6 D indicates that the two rates are comparable.

Finally, the cyclometallated intermediate D, formed by oxidative addition of the position 8 carbon and hydrogen to the metal complex, may be proposed to explain the exchange of deuterium found at the 8 position of the product when reducing quinoline, and as well from the exchange reaction of deuterium with 1,2,3,4-tetrahydroquinoline. The formation and cleavage of this four membered ring cyclometallated complex would lead to deuterium exchange as position 8 due to the metal-carbon bond formed at this position in the complex.

Chlorohydrotris(triphenylphosphine)ruthenium(II):

The reduction mechanism for quinoline proposed for

$RuClH(PPh_3)_3$ is shown in figure II.30. The overall features are very similar to those for the previously discussed system, the difference is the incorporation of intermediate D, to account for the exchange of deuterium at the 2 position of 1,2,3,4-tetrahydroquinoline catalyzed by the ruthenium complex.

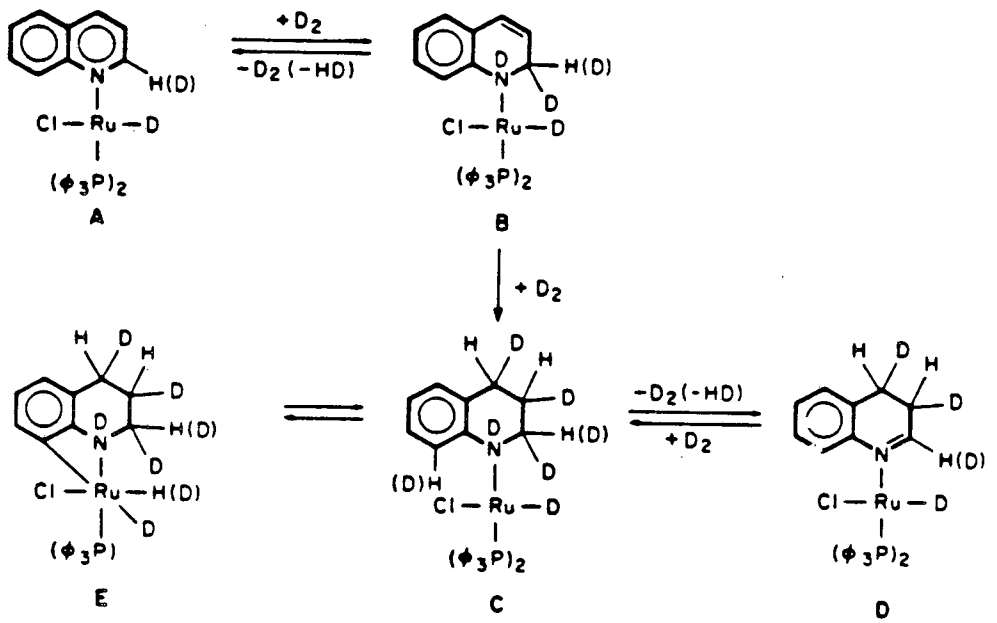
As with the rhodium complex, the pathway for reduction incorporates two steps. The first, A to B, is the reversible reduction of the 1,2 carbon-nitrogen double bond. The second step, which is irreversible, is the reduction of the 3,4 double bond.

The NMR evidence at our disposal was not sufficient to assign the stereochemisty of the addition to the 3-4 bond. Nevertheless, this data did indicate only one deuterium incorporated each at the 3 and 4 positions of the product when quinoline was reduced using deuterium. The lack of excess deuterium exchange at these two positions is strong evidence for the irreversibility of the 3-4 reduction.

Not all of the exchange found at the two position of deutero-1,2,3,4-tetrahydroquinoline, produced by reduction of quinoline with deuterium and the ruthenium catalyst, can be accounted for by the reversible first step of this reduction (A to B in fig. II.26). When the reduction was carried out to 50% completion the unreduced quinoline was substituted with 0.5 D at the 2 position, the product was substituted wit 1.85 D at this position. If all of the exchange had been occuring through the reversible reduction

FIGURE II.30

Proposed Quinoline Reduction Mechanism With $RuClH(PPh_3)_3$



step no more than 1.5 D would have been found at the two position of the product. The extra exchange indicates an additional exchange mechanism, as described below.

Intermediate D is proposed to explain the exchange results obtained with 1,2,3,4-tetrahydroquinoline. The complexed tetrahydroquinoline is bound as an imine, the reversible formation and reduction of this imine intermediate would lead to the exchange of deuterium for hydrogen at the 2 position. As discussed in section II.B.3, this species was not observed in the NMR of a mixture of 1,2,3,4-tetrahydroquinoline and $RuHCl(PPh_3)_3$ taken at room temperature. However, the existence of this intermediate at higher temperatures, such as during a reaction, is not ruled out.

Species E is proposed to account for the exchange of deuterium found at the 8 position of 1,2,3,4-tetrahydroquinoline. This four membered ring cyclometallated complex is similar to that described for the rhodium complex above. In this case as well, the formation and cleavage of the metal-carbon bond at the 8 position of tetrahydroquinoline leads to the deuterium exchange found here.

II.C RATE STUDIES COMPARING HOMOGENEOUS AND POLYMER-SUPPORTED $RhCl(PPh_3)_3$

II.C.1 INTRODUCTION

While homogeneous transition metal catalysts offer many advantages as to selectivity and rate, one disadvantage they share is the difficulty with which they are recovered after a reaction. To circumvent this problem, catalysts have been prepared in which a transition metal complex is immobilized on an insoluble support, most often triphenylphosphine substituted polystyrene-divinylbenzene polymer. In addition to immobilizing the catalyst, such supports often provide other advantages, such as increased selectivity or stability. The preparation, use and properties of such catalyst have been extensively reviewed[43,47-57].

In this study, homogeneous $RhCl(PPh_3)_3$ was compared to the polymer-supported complex, at the same metal/substrate ratio in both cases (1:91). The polymer material (supplied by Strem Chemical Co.) was 2% crosslinked, 30 micron average diameter, polystyrene-divinylbenzene beads, substituted with triphenylphosphine groups. The polymer was substituted with $RhCl(PPh_3)_3$ by ligand exchange between the homogeneous complex and the polymer, to give a composition of 2.19% Rh, 1.9% P (analysis by Strem), corresponding to a ligand to metal ratio of 2.9, slightly lower than the ratio for the

homogeneous catalyst (3).

This material was originally prepared by first reacting butyllithium with brominated polystyrene-divinylbenzene, followed by reaction of the resulting resin with $PBr(Ph)_2$. This causes incorporation of phosphine groups into the polymer, via coupling of the phosphorus to phenyl rings in the polymeric structure. This forms an immobilized triphenylphosphine group, in which one of the phenyl rings is supplied by the polymer. This phosphinated resin was then exchanged with homogeneous $RhCl(PPh_3)_3$, resulting in the incorporation of this complex into the polymer, with a polymer bound phosphine replacing one (or possibly more) of the triphenylphosphine groups of the original complex.

Both the polymer-supported and homogeneously catalyzed hydrogenations were performed in the dip tube kinetic reactor system described in the experimental section. The substrate to catalyst ratio was 91 for both catalysts, corresponding to 10.2 mg of the homogeneous complex and 52 mg of the polymer. Lower catalyst/substrate ratios than in the previously described homogeneous reductions were used in this study to avoid having to use inconveniently large amounts of polymer catalyst. The conditions were 85° C, 310 psi H_2 (measured initially at room temperature), 20 ml of dry degassed benzene was used as the solvent (except for the model coal liquid experiment described below). Data was obtained and analyzed in

exactly the same manner as described in section II.B.2, to provide initial (pseudo-zero-order) rates and rates relative to quinoline.

It was necessary to contain the polymeric material in a small stainless steel mesh basket attached to the end of the dip tube. Otherwise, quantitative recovery of the catalyst was difficult and the internal parts of the reactor became clogged with beads. This was found to present no diffusional problems, as explained in the next section. Significant variation in rates were typical during the first few runs with fresh polymer catalysts. After these runs a period of constant activity lasting for up to twenty runs was observed, followed by a rapid decline in activity. To provide consistent results the same beads were used for all the data in the table below. Between runs the beads were washed with three 20 ml aliquots of hot, degassed benzene and stored under vacuum to minimize decomposition of the catalyst. Several rate runs with quinoline were made during the course of this work to ensure that the activity of the polymeric catalyst remained constant.

II.C.2 RESULTS AND DISCUSSION

The results for the reduction of a variety of heteroaromatic compounds with both polymer supported and homogeneous $RhCl(PPh_3)_3$ are in Table II.31. The polymer results were all obtained using the same polymer catalyst, which was monitored for changing activity by redetermining the rate of quinoline reduction between runs (the activity was constant during the course of these runs). Surprisingly, the polymer catalyst was found to be much more active than the homogeneous catalyst, on an equivalent metal basis. Additionally, the polymer was more selective in the reduction of acridine, providing only the 9,10 dihydro product, unlike the homogeneous catalyst which produced 1,2,3,4-tetrahydroacridine as well.

For the reduction of quinoline, 5,6-benzoquinoline and 7,8-benzoquinoline the homogeneous and polymer-supported catalysts gave virtually the same relative rates, with the polymer supported catalyst having approximatly 20 times the activity of the homogeneous catalyst. The fact that the relative reduction rates are the same for these compounds using both catalysts suggests that similar factors are governing the reduction rates in the two cases. However, the uniformly higher reduction rates found with the polymer clearly indicates that the two catalysts are not equivalent. The differences between the two catalysts are more apparent in the reductions of acridine and benzothiophene.

TABLE II.31

Rates of Reduction of Heterocyclic Aromatics Using Homogeneous and Polymer-Supported $RhCl(PPh_3)_3$ as Catalyst

Substrate	Product	Polymer Rate (%/min)	(rel)[1]	Homogeneous Rate (%/min)	(rel)[2]	Poly/Homo Ratio
Quinoline	1,2,3,4-Tetrahydro	0.29	1.0	0.013	1.0	22
5,6-Benzoquin.	1,2,3,4-Tetrahydro	0.14	0.48	0.0065	0.5	22
7,8-Benzoquin.	1,2,3,4-Tetrahydro	0.024	0.08	0.0012	0.09	20
Acridine	9,10-Dihydro	ca. 0.4	ca. 1.4	ca. 0.04	ca. 3	10
Acridine	1,2,3,4-Tetrahydro	0.0	0.0	0.047	3.6	0
Benzothiophene	2,3-Dihydro	ca. 0.06	ca. 0.2	0.044	3.4	1.4

CONDITIONS: 1.0 mmole substrate, 0.011 mmole catalyst (10.2 mg of $RhCl(PPh_3)_3$ or 52 mg of 2% x-linked polymer, 2.19% Rh by wt.) in 20 ml of dry, degassed benzene. Pressure H_2 (initial) = 310 psi, T = 85° C. Conversion data obtained until ca. 25% conversion or until conversion vs. time data was not linear. Least-squares analysis of this data provides the initial (pseudo-zero order) rates given.

NOTES:

1) Relative rates are obtained by dividing the rate of reduction of a given compound by the polymer reduction rate of quinoline (0.29).

2) Relative rates are obtained as described above, but with homogeneous quinoline reduction rate (0.013).

The high selectivity of the polymer catalyst in the reduction of acridine, producing only the 9,10 dihydro product, may reflect steric constraints within the polymer, making the binding of the acridine through the outer ring (1,2,3,4 positions) unfavorable. The fact that quinoline and the benzoquinolines are reduced with the same relative rates by both forms of the catalyst argues against a difference in steric enviornments though. The relative rate of acridine reduction was lower with the polymer than with the homogeneous catalyst, unlike the similarity found with quinoline and its derivatives.

The lower relative rate found with acridine may be due to an exclusion of this material from the polymer, due to the different environment presented within a polymer bead than outside it. Acridine is less soluble in benzene than any other substrate investigated, the difference in "solvent" environments found inside and outside the beads could be leading to precipitation of solid acridine within the beads, interfering with the accessibility of the catalyst rhodium sites within the matrix.

Adding to this argument, it was found that after an acridine reduction runs the polymer beads contained considerable acridine even after several hot benzene washes, a situation not found with the other substrates investigated. While other workers have not to our knowledge reported the same effect with any other

substrates, many have noted that the interaction between solvent and polymer is a critical factor in determining reduction rates with polymer supported catalysts, and the role of solvent versus polymer polarity has been specifically addressed by Pittman[47].

Similar solvent vs polymer polarity effects might in part also explain the higher rates of reduction found with the polymer catalyst. It is possible that the polymer selectively extracts the substrate molecules from the surrounding solution, resulting in a higher concentration of substrate in the polymer, and thus higher reduction rates. Such an effect is related to the 'enrichment effect' as discussed by Challa[49].

Benzothiophene behaved very differently with the two catalysts, providing a relative rate of 1.4 with the homogeneous catalyst, but only 0.2 with the heterogenized catalyst. The reason for this lower rate is not apparent. It was difficult to get reproducible results for the reduction of benzothiophene with the polymeric catalyst, this may be related to the lower rate.

In order to evaluate the practical application of this catalyst to the upgrading of an actual synthetic fuel product, a mixture was made up consisting of several types of compounds found in coal derived liquids. The mixture, diluted to 25 wt% in benzene, consisted of (by weight) 30% pyrene, 5% tetralin, 38% methylnaphthalene, 17% p-cresol, 7.5% quinoline and 2.5% 2-methylpyridine. This

was hydrogenated using the same conditions as in the table to provide 1,2,3,4-tetrahydroquinoline as the only reaction product (initial rate 0.42%/min). The removal of the 2-methylpyridine from this mixture had no effect on the rate. When quinoline alone was hydrogenated, at the same concentration as in the coal liquid, the initial rate was 0.18%/min, 2.2 times slower than the rate in the mixture.

The rate increase in the mixture is apparently due to the rate enhancement effect of the cresol, as described in section II.B.2. It is interesting that removal of the 2-methylpyridine had no effect on the rate. The inhibitory effect of this component (also discussed in the section II.B.2) is entirely compensated for by the enhancement effect of the larger amount of cresol. This result illustrates the potential usefulness of polymer-supported catalysts for the selective reduction of specific components in the highly complex mixtures produced by synthetic fuel processes.

As discussed in the introduction the activity of the polymer catalyst was not constant. Typically an initial period of increasing rate was followed by a period of constant rate and finally by a decline in activity. An analysis of the beads used in these reductions showed a 12% loss of rhodium from the polymer (2.14% Rh initially, 1.89% Rh after use). This loss of metal is probably the cause of the eventual loss of catalytic activity, but we do not know if it is a steady loss or if it occurs primarily

at the end of the catalyst lifetime. The constant activity found before the decline in activity argues for the latter case. The period of rising activity noted at the beginning of a series of runs may be due to a leaching out of free phosphine or other impurities that would interfere with reductions. A small amount of triphenylphoshine and triphenylphosphine oxide was ocassionally observed in the products during the first few uses of a batch of catalyst polymer. We were unable, however, to obtain a satifactory phosphorus analysis of the catalyst, and so the actual amount of phosphine lost from the catalyst is not known.

Since diffusion into the catalyst beads may be an important factor in the rates of reduction experiments were carried out to determine if diffusion was a limiting factor in these reductions. It was found that wide variation of the stirring rate had no effect on the reduction rate of quinoline (using beads contained within a basket). Additionally, whole (30 micron) and finely ground beads were used for quinoline reduction, without containment in a mesh basket. Again both situations gave the same rate of reduction. These experiments effectively rule out internal and external mass transfer as rate limiting processes, and thus the rates reported here are the true, intrinsic, rates of reduction.

Additionally, 20% crosslinked (0.89% Rh) catalyst beads were compared with the 2% beads used in the study reported above. On a per metal basis the 2% material was

3.1 times as active as the 20% material for the reduction of quinoline. This is consistant with what has been observed by other workers[50] and seems related to the accessability of the catalytic sites, which is lower in rigid, high cross linked, polymers.

The higher rate found with the polymeric catalyst, as compared to the homogeneous system, is extremely relevant for practical applications. In virtually all studies homogeneous catalysts have proven more active than their polymer supported analogues, only a few studies have shown a rate enhancement[51,55-57].

In this particular case it is not clear what effect the polymer immobilization of the rhodium catalyst has had to increase its activity so dramatically. In addition to the polarity effects discussed above, one factor that would increase the rate of reduction is the lower phosphine/rhodium ratio in the polymer. This would lead to greater coordinative unsaturation of the rhodium centers, increasing the ability of the catalyst to bind quinoline.

To test this theory a phosphine deficient homogeneous catalyst was produced by reacting triphenylphosphine with chloronorbornadienerhodium(I) dimer at a phosphine/ rhodium ratio of 2.8/1. This catalyst, prepared in situ with quinoline and hydrogen, gave a rate only 1.3 times faster than the conventional homogeneous catalyst (the mixture was identical in appearance to the conventional

catalyst, with no evidence of decomposition to metal). Thus other factors must be causing the polymer catalyst rates to be so high.

NMR evidence (see Section II.B.3) suggests that several species are in equilibrium during a homogeneous reduction with $RhCl(PPh_3)_3$. By separating and immobilizing the catalyst centers, the polymer catalyst may be acting to prevent the formation of catalytically inactive species, and thus provide a higher rate. This is unfortunately a difficult hypothesis to test, since the polymer matrix prevents simple NMR experiments to observe the catalyst interaction with substrates. Solid state NMR experiments were not attempted in this study, but clearly would be of great use in elucidating the origin of the rate increase in the polymer catalyst.

II.D CATALYTIC HYDROGEN TRANSFER REACTIONS

II.D.1 INTRODUCTION

Catalyzed reductions via hydrogen transfer, in which the source of hydrogen for a reduction is a molecule that can dehydrogenate, have been the subject of several previous studies. This type of reduction is of particular interest because it has been observed to be a factor in the liquefaction of coal[58,59].

Cobalt carbonyls have been used in the hydrogen transfer reaction from 9,10-dihydroanthracene and 9-fluorenol to 1,1-diphenylethane[60]. In these reactions anthracene and fluorenone are formed, respectively. Ketones have been reduced with alcohols as the hydrogen source, using various ruthenium complexes[61], and in particular with the rhodium complex, $RhH(PPh_3)_4$[62]. Ketones have been reduced by hydrogen transfer from formyl compounds in the presence of several Ru, Rh and Ir complexes[63]. Reduction of olefins using 1,4-dioxane as the hydrogen source has been carried out in the presence of the dimeric species, tetra(cyclooctene)di-u-chloro-dirhodium(I)[64].

There are only a few examples of the use of reduced nitrogen heterocycles as the hydrogen source in catalyzed reductions. In a series of papers, Linstead and co-workers demonstrated the use of saturated nitrogen heterocycles as hydrogen donors in the thermal (uncatalyzed) reductions of olefins, nitrogen heterocycles, quinones, etc.[65-67].

Natural iron pyrites have been implicated as catalysts in the liquefation of coal via hydrogen transfer from 1,2,3,4-tetrahydroquinoline[59]. Nishiguchi and co-workers have investigated the use of both 1,2,3,4-tetrahydroquinoline and indoline as hydrogen donors in reductions catalyzed by $RhCl(PPh_3)_3$, the acceptor molecules being olefins or the triphenylphosphine ligands of the catalyst itself (which undergo hydrogenolysis to produce benzene and unidentified products)[60]. The conditions under which these reactions occur are quite extreme, with temperatures as high as 190° C, based on our own experience it is likely that rhodium metal is produced at these high temperatures, and so these may not be homogeneous reactions.

Since we had observed on numerous occasions that both 9,10-dihydrophenanthridine and 9,10-dihydroacridine readily dehydrogenate under quite mild conditions, we were led to an investigation of the use of these molecules as hydrogen donors in the catalytic reduction of nitrogen containing heterocycles. These compounds were produced by reduction of the corresponding aromatics using polymer-supported $RhCl(PPh_3)_3$ (see section II.C.2). 1,2-Dihydroquinoline, which we propose as an intermediate in the catalytic reduction of quinoline (see Section II.B.5), was also investigated as a hydrogen donor. This material was prepared by a lithium aluminum hydride reduction of quinoline. 1,2,3,4-Tetrahydroquinoline was

not investigated as a donor because it was not observed to dehydrogenate under same conditions that led to hydrogen loss from the other compounds described above.

Both $RhCl(PPh_3)_3$ and $RuClH(PPh_3)_3$, the latter formed in situ from the dichloro complex, were investigated as catalysts. These two catalysts had received the most previous attention in this study (see sections II.B.1-5).

All of the reactions discussed below were carried out in the batch or kinetic reactor systems described in the experimental section, at 85° C under an inert atmosphere (N_2 or Ar). As in the various reductions with hydrogen that we investigated, the reduced products were formed by complete reduction of only the nitrogen containing ring. The yields are based on the conversion of the hydrogen acceptor molecule, the thermal instability of the hydrogen donors prevented an accurate determination of the degree of dehydrogenation of the donor. In those cases in which the acceptor was acridine the yields are approximate for the same reason, and so are reported only to the nearest ten percent. To avoid disturbing the headspace gas in the reactor rate data were not obtained, only final conversions. Thus during a run the headspace remained closed and any hydrogen in it could not escape.

II.D.2 RESULTS AND DISCUSSION

Table II.32 contains the results for hydrogen transfer reactions with the hydrogen donors discussed above, using $RuClH(PPh_3)_3$ (formed in-situ from $RuCl_2(PPh_3)_3$, see Section II.B.1) and $RhCl(PPh_3)_3$ as catalysts. In only about half of the systems investigated did any hydrogen transfer occur.

9,10-Dihydrophenantridine proved to be the best hydrogen donor investigated, but nevertheless it was only able to reduce acridine, and, to a lesser extent, quinoline. Neither 5,6-benzoquinoline nor 7,8-benzoquinoline were reduced by this donor. These results are qualitatively similar to those obtained when these various compounds were reduced with molecular hydrogen; as discussed in previous sections, in that acridine is reduced more readily than quinoline, which in turn is reduced more easily than its benzo derivatives.

9,10-Dihydroacridine was less effective in the reduction of quinoline than was dihydrophenanthridine. This may reflect a greater thermodynamic stability for dihydroacridine as versus dihydrophenanthridine. Dihydroacridine was in fact found to be more stable in solution than dihydrophenanthridine. Additionally, though, the two labile hydrogens in dihydrophenanthridine may be more rapidly transferred to the catalyst than those in dihydroacridine, since in dihydroacridine they are on opposite sides of the center ring while in dihydrophen-

TABLE II.32

Hydrogen Transfer Reactions

Donor	Acceptor	Catalyst	Conversion
9,10-Dihydrophenanthridine	Quinoline	$RuCl_2(PPh_3)_3$	9.3%
9,10-Dihydrophenanthridine	Acridine	$RuCl_2(PPh_3)_3$	70.0%
9,10-Dihydrophenanthridine	7,8-Benzoquinoline	$RuCl_2(PPh_3)_3$	0.0%
9,10-Dihydrophenanthridine	Acridine	$RhCl(PPh_3)_3$	30.0%
9,10-Dihydrophenanthridine	5,6-Benzoquinoline	$RhCl(PPh_3)_3$	0.0%
9,10-Dihydrophenanthridine	7,8-Benzoquinoline	$RhCl(PPh_3)_3$	0.0%
9,10-Dihydroacridine	Quinoline	$RuCl_2(PPh_3)_3$	0.0%
9,10-Dihydroacridine	Quinoline	$RhCl(PPh_3)_3$	7.4%
1,2-Dihydroquinoline	Acridine	$RuCl_2(PPh_3)_3$	20.0%
1,2-Dihydroquinoline	Acridine	$RhCl(PPh_3)_3$	10.0%

CONDITIONS: 0.5 mmole hydrogen donor, 0.25 mmole hydrogen acceptor (except 0.5 mmole acridine, due to stoichiometry), 0.025 mmole catalyst, in 20 ml of dry, degassed benzene. Inert gas (Ar or N_2) pressure = 300 psi, T = 85°C. Analysis of products by capillary gas chromatography.

anthridine they are adjacent to each other at the nitrogen coordination site. Attempts to investigate the hydrogen transfer between dihydroacridine and phenanthridine were inconclusive, due to the thermal instability of the product, 9,10-dihydrophenanthridine, which prevented analysis by gas chromatography.

1,2-Dihydroquinoline was not as effective a hydrogen source as phenanthridine for the reduction of acridine, and yet it was found to dehydrogenate as readily as phenanthridine when in contact with the catalysts investigated here. This lower activity is probably due to steric factors affecting the binding of dihydroquinoline and quinoline as versus acridine and dihydroacridine to the catalyst. As was found in several cases with quinoline and its benzo derivatives (see Sect. II.B.2) the more sterically hindered benzo derivatives were unable to effectively compete for catalyst in the presence of quinoline. In the present case it is also quite likely that the presence of dihydroquinoline and quinoline decrease the ability of acridine to bind to the catalyst relative to its binding ability in the presence of dihydrophenanthridine and phenanthridine. This would account for the lower yields of dihydroacridine found when dihydroquinoline was used as the donor.

In those cases in which both of the catalysts were used for the same transfer reactions, the relative activity of the two catalysts varies, with no clear trend apparent.

For the reduction of acridine by 9,10-dihydrophenanthridine and 1,2-dihydroquinoline, $RuCl_2(PPh_3)_3$ was the more active catalyst, providing approximately twice the yield as found with $RhCl(PPh_3)_3$. However in the reduction of quinoline by 9,10-dihydroacridine the hydrogen transfer occured only with $RhCl(PPh_3)_3$, no transfer was observed with $RuCl_2(PPh_3)_3$.

An important question raised in considering these results is whether the hydrogen transfer is direct, involving the simultaneous coordination of both the donor and acceptor species to the catalyst, or indirect, i.e. dehydrogenation of the donor to form a catalytic hydride species, followed by decomplexation of the donor and complexation of the acceptor, which is then reduced. Furthermore, if the indirect route is followed, can the intermediate hydridic species lose hydrogen, followed later by uptake of hydrogen and reduction of the acceptor in the manner of a conventional reduction under hydrogen gas.

When hydrogen transfer reactions like those described above were attempted in open systems, in which any hydrogen evolved from the reaction mixture was allowed to escape, very little or no reduction of the acceptor molecules was seen. This suggests that the indirect route is being followed. In an effort to resolve this point an experiment was carried out in which dihydrophenanthridine and quinoline were placed in a batch reactor with $RhCl(PPh_3)_3$ as catalyst, under the same conditions as in

table II.32. After one hour the head space gas was collected and analyzed for hydrogen by mass spectroscopy, and was found to contain 1.3% hydrogen, representing about 7% of the total hydrogen avaliable in the system. Clearly at least some of the overall hydrogen transfer is occuring by the indirect mechanism as described above, although whether all or a fraction of the total reduction occurs by this means cannot be established by these results.

II.E REDUCTIONS CATALYZED BY $Ru(CO)_2Cl_2(PPh_3)_2$

II.E.1 INTRODUCTION

A brief study was made of reductions catalyzed by dicarbonyldichlorobis(triphenylphosphine)ruthenium(II). This work was conducted before construction of the kinetic reactor system, and so rates could not be determined. This catalyst was examined in the absence and presence of KOH, which can act to modify the ruthenium complex as described below. In general both catalyst systems were found to regioselectively reduce heteroaromatics, although with KOH 5,6,7,8-tetrahydroquinoline (as well as the 1,2,3,4 product) was produced.

$Ru(CO)_2Cl_2(PPh_3)_2$ has been used as a hydrogenation catalyst for aldehydes and ketones, olefins, and nitro compounds[69-74]. To our knowledge it had not been used to hydrogenate polynuclear heteroaromatic compounds prior to this study. This ruthenium complex is a precursor to the active catalytic species, which has been identified in recent work as the chlorohydro complex, $Ru(CO)_2ClH(PPh_3)_2$[74]. This complex is formed from the reaction between hydrogen and the dichloro complex, liberating HCl. A similar process occurs in the formation of $RuClH(PPh_3)_3$ as described in section II.B.1. This reaction is promoted by base, and would be expected to be facile in the presence of most of the substrates investigated here.

The activity of this catalyst in the presence of KOH was also examined. In previous work in this laboratory the addition of aqueous or ethanolic KOH solutions to metal carbonyls was found to promote hydrogenation activity. This promotion is postulated to be the result of one or both of two related reactions, the water gas shift reaction (Eq. 2) and the attack of a hydroxide ion on a metal bound carbonyl to form an anionic hydride complex (Eq. 3).

Eq. 2) $CO + H_2O \rightarrow H_2 + CO_2$

Eq. 3) $M\text{-}CO + OH^- \rightarrow M\text{-}H^- + CO_2$

Both of these reactions have been extensively investigated for a variety of homogeneous systems[33,75-77]. The important aspect of these two reactions is that they both lead to an irreversible loss of carbon monoxide, either from the metal complex itself or from the overall system. This loss of CO can lead to a higher degree of coordinative unsaturation of the metal complex, and as per equation 3 can be accompanied by the formation of hydridic complexes. Both of these factors can lead to higher catalytic activity. The only previous reference found for the use of KOH with $Ru(CO)_2Cl_2(PPh_3)_2$ was in work by Knifton, investigating the reduction of aliphatic nitro compounds to amines[73].

In addition to the above reactions, the KOH may as well promote the formation of hydride species by the

neutralization of HCl as discussed previously. However, this would not be a unique feature of KOH, any base, including the substrates investigated, could promote this reaction.

The reductions were all carried out in the batch reactor system. The conditions used in the presence and absence of KOH were the same: 180°C, 240 psi H_2, 2 hr reduction time, 1.0 mmole substrate, 0.1 mmole catalyst. The solvent was of dry, degassed tetrahydrofurane, distilled from lithium aluminum hydride to remove peroxides. Both aqueous and ethanolic solutions of KOH were used, but lower concentrations of base were necessary with ethanol due to solubility limitations. The total solvent volume, THF and added base solution, if any, was 15 ml.

II.E.2 RESULTS AND DISCUSSION

Table II.33 shows the results for the reaction of a variety of heterocyclic compounds with hydrogen, using $Ru(CO)_2Cl_2(PPh_3)_2$ as catalyst precursor. Quinoline and its two benzo derivatives, as well as the related compounds acridine and phenanthridine, were all reduced. The product was in each case that formed by complete reduction of only the nitrogen containing ring. 5,6,7,8-Tetrahydroquinoline was reduced to a lesser extent, to form the completely saturated product, decahydroquinoline (unidentified isomer). Pyridine was not reduced by this catalyst, nor were the sulfur containing heteroaromatics, thiophene and benzothiophene.

The fact that all of these reductions are exclusively directed to the nitrogen containing ring suggests that coordination to this basic site is an important factor in the overall reduction. This interpretation is supported by a comparison of the conversion data for quinoline, 5,6-benzoquinoline and 7,8-benzoquinoline, which indicates that steric hindrance at the nitrogen is a major factor affecting the conversion. Quinoline, in which the nitrogen atom is the least hindered, is reduced to the greatest extent, followed by the larger 5,6-benzoquinoline and finally by 7,8-benzoquinoline, in which the nitrogen atom is partially blocked by an aromatic ring. These are the same factors that determined the reduction rates found with $RhCl(PPh_3)_3$ and $RuCl_2(PPh_3)_3$, as described in

TABLE II.33

Reductions Catalyzed by $RuCl_2(CO)_2(PPh_3)_2$ in Unmodified System

Substrate	Product	Yield
Quinoline	1,2,3,4-Tetrahydroquinoline	96.7%
5,6,7,8-Tetrahydroquinoline	Decahydroquinoline	12.1%
5,6-Benzoquinoline	1,2,3,4-Tetrahydro-5,6-Bquin.	92.3%
7,8-Benzoquinoline	1,2,3,4-Tetrahydro-7,8-Bquin.	71.6%
Phenanthridine	9,10-Dihydrophenanthridine	17.8%[1]
Acridine	9,10-Dihydroacridine	73.8%
Pyridine	No Reaction	-----
Thiophene	No Reaction	-----
Benzothiophene	No Reaction	-----

CONDITIONS: 1.0 mmole of substrate and 0.1 mmole catalyst in 15 ml of dry, degassed tetrahydrofurane. Pressure H_2 (initial) = 240 psi, T = 180° C, Time = 2 hr. Analysis of products by capillary gas chromatography.

NOTES:
1) Phenanthridine value is an average of three runs.

previous sections.

5,6,7,8-Tetrahydroquinoline was reduced at a slower rate than quinoline. This may be due to the loss of aromatic stabilization for partially hydrogenated intermediates, such as are proposed for some of the other catalytic reductions investigated in this work. Reduction of this substrate was not observed with any of the other catalysts studied. Pyridine was not reduced by this complex, but probably acts as a ligand, displacing one or both phosphine groups. Pyridine complexes have been prepared directly from $RuCl_3$, carbon monoxide, and pyridine[78], but no literature references have been found for mixed ligand pyridine/triphenylphosphine complexes such as proposed here.

Neither phenanthridine nor acridine were reduced to the same extent as was quinoline. This is in contradiction to results with other catalysts, in which rate studies showed that both of these molecules were reduced much more rapidly than quinoline. Both 9,10-dihydroacridine and 9,10-dihydrophenanthridine can easily dehydrogenate, both in the presence and absence of catalyst. This reaction was rapid enough in the case of dihydrophenanthridine to cause complete conversion back to phenanthridine in less than one-half hour after removal of hydrogen pressure from a reaction mixture. These facile dehydrogenations also occur in the gas chromatograph used for product analysis, presenting difficulties in quantifying yields. Together

these observations suggest that the yield of dihydro product in both of these cases was higher under reaction conditions than was found after the reactor was opened. Similar problems were encountered in the rate studies described earlier, although the dip-tube reactor system allowed for a more rapid analysis than the batch system used in this study, an so this problem was less severe.

Neither of the two sulfur containing heteroaromatics, thiophene and benzothiophene, were reduced by this catalyst. This is probably related to the low basisity of these compounds, relative to the nitrogen heteroaromatics. As discussed in the introduction, the presence of base is necessary for the formation of the presumed catalytically active hydride species. With these two substrates, it is likely that this active hydride is not forming. The same problem was encountered in the reduction of benzothiophene by $RuCl_2(PPh_3)_3$, in which case base is also necessary to form the active hydride species. The addition of a base such as triethylamine along with these substrates might have caused reduction to take place, however this was not attempted.

The results of the reactions carried out in the presence of KOH are in Table II.34. Additionally the effects of water alone and of a trace amount of ethanolic KOH were investigated. From the results it is clear that the addition of substantial amounts of KOH radically alters the activity of the catalyst system, possibly due to the

TABLE II.34

Reductions Catalyzed by $RuCl_2(CO)_2(PPh_3)_2$ in Presence of KOH

Substrate	Product(s)	Yield	Amt. KOH Added
Quinoline	1,2,3,4-THQ / 5,6,7,8-THQ	34.8% / 3.6%	3ml 0.2M in H_2O
Quinoline	1,2,3,4-THQ / 5,6,7,8-THQ	20.5% / trace	3ml 0.2M in H_2O[1]
Quinoline	1,2,3,4-THQ / 5,6,7,8-THQ	7.1% / trace	2ml 0.1M in Ethanol
Quinoline	1,2,3,4-Tetrahydroquinoline	97.7%	Drop 0.1M in Ethanol
Quinoline	1,2,3,4-Tetrahydroquinoline	100%	3ml of H_2O alone
5,6,7,8-THQ	No Reaction	----	3ml 0.2M in H_2O[1]
5,6,7,8-THQ	No Reaction	----	2ml 0.1M in Ethanol

CONDITIONS: 1.0 mmole substrate and 0.1 mmole catalyst in 15 ml total volume dry, degassed tetrahydrofurane and added KOH solution. Pressure H_2 (initial) = 240 psi, T = 180° C, Time = 2 hr. Analysis of products by capillary gas chromatography.

NOTES:
1) Catalyst, KOH and hydrogen allowed to react at 150° C for 1 hr. prior to addition of substrate and reaction at conditions listed above.

formation of a new catalytic species.

Quinoline was reduced to a much lesser extent in the presence of KOH than in its absence, and the product selectivity was no longer as exclusive, with both isomers of tetrahydroquinoline being produced (although the N-ring reduction product was predominant). This result was the essentially the same for both aqueous and ethanolic KOH. Additionally it was found that pre-reaction of aqueous KOH and the Ru complex before addition of substrate provided similar results to the addition of all components together. Neither water alone, nor a trace amount of ethanolic KOH, produced results significantly different than found with the unmodified system (see above). 5,6,7,8-Tetrahydroquinoline was not reduced in the presence of KOH.

The production of 5,6,7,8-tetrahydroquinoline is unusual, and was not observed in any of the other catalyst systems investigated. The only time this product was otherwise observed was in cases where decomposition of homogeneous metal complexes led to formation of metallic deposits in the reactor, or when heterogeneous catalysts were used, as in part III. No visible decomposition of the catalyst was observed in this case, the solutions all being a clear yellow when the reactor was opened. The absence of small amounts of colloidial metal, however, cannot be completely ruled out.

In an effort to clarify the nature of the catalytic species in these experiments a solution of

$Ru(CO)_2Cl_2(PPh_3)_2$ in tetrahydrofurane was reacted with ethanolic KOH, under refluxing nitrogen. A IR spectrum of the resulting orange-yellow solution was taken, and compared with the spectrum of the starting complex, as shown in Figure II.35. The starting material (A) has two CO stretches, at 1990 and 2030 cm^{-1}, indicative of a cis-carbonyl complex[79,80]. After reaction with KOH two new bands appear, at 1900 and 1935 cm^{-1}, and the two original bands are still present, but weaker. James et. al.[79], reports the spectra of several monocarbonyl species of the form $Ru(CO)X_2(PPh_3)_2L$, with X = Cl, Br and L a (possible) coordinated solvent molecule. In all cases these complexes show a band in the range from 1925-1940 cm^{-1}. Additionally, in two cases, in which dimethylformamide was coordinated to the complex, a weak band at 1871 cm^{-1} appeared. None of the dicarbonyl complexes investigated in this study, including a chlorohydro ruthenium complex, had any bands below 1965 cm^{-1}.

A proton NMR of a similarily prepared sample was also taken, and showed no hydridic signals in the range from 0 to -23 ppm. This strongly suggests that the new species is not a hydride, although the incomplete conversion as evidenced in the IR spectrum could have lead to a hydride signal so weak as to be unobservable.

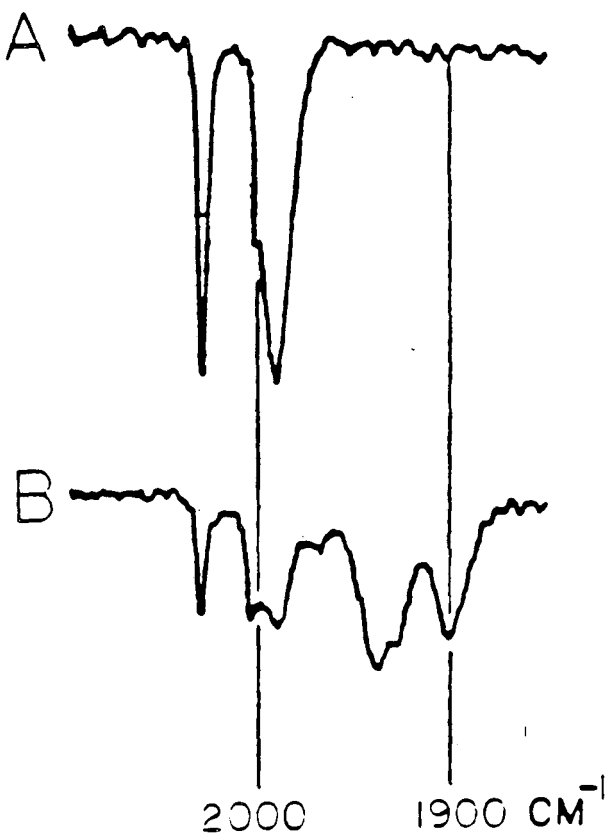
Based on this evidence it seems likely that the active species in these reductions is a mono-carbonyl complex, as

FIGURE II.35

Infrared Spectrum of Ruthenium Carbonyls

A - $Ru(CO)_2Cl_2(PPh_3)_2$

B - $Ru(CO)_2Cl_2(PPh_3)_2$ + KOH



would be anticipated from equations 2 and 3 above. The NMR data indicates that this species is probably not a hydride, which favors the reaction in equation 2 (water is avaliable in the ethanolic KOH systems from the reaction between the base and the alcohol). In any case the active catalytic species in the presence of KOH is clearly different than in its absence. The fact that the homoaromatic ring of quinoline was reduced to a small extent by this catalyst seems to indicate that it is able to bind to the pi orbitals of the aromatic ring, as well as to the nitrogen atom in the heteroaromatic ring, providing that metallic ruthenium is indeed not present. Overall, however, this catalytic system is neither as active nor as selective as that formed in the absence of KOH.

II.F CONCLUSIONS AND PROPOSED FUTURE WORK

The ability of several metal complexes to regioselectively reduce the heteroaromatic ring in polynuclear heteroaromatic compounds has been clearly demonstrated. For the case of quinoline reduction with $RhCl(PPh_3)_3$ and $RuClH(PPh_3)_3$ the reduction has been shown to occur in two steps, a reversible reduction of the 1-2 carbon nitrogen bond followed by an irreversible reduction of the 3-4 carbon-carbon bond.

The regioselective nature of the reductions was a general feature of all the systems investigated, with very few exceptions. The nature of these exceptions, in particular the production of 1,2,3,4-tetrahydroacridine from acridine using $RhCl(PPh_3)_3$, deserve further investigation. NMR techniques may prove useful in this study, as they did in the study of the quinoline/Rh system.

The reduction rates depended strongly on the catalyst used, but for most catalysts the relative order of reduction rates among the substrates investigated was preserved. Two factors seemed to predominate in determining the order of rates, the number of hydrogens necessary to effect complete reduction and steric factors surrounding the binding of the substrate to the catalyst. The results obtained with indole and benzothiophene are not as consistent with this interpretation as those obtained with the basic nitrogen heterocycles, indicating the

importance of other factors as well in determining reduction rates.

Two hydrogen reductions, i.e. for phenanthridine and acridine, proceed faster than four hydrogen reductions, for quinoline and its derivatives. This would be anticipated from our proposed mechanisms for quinoline reduction, which requires two hydrogen transfer steps. These would be expected to be slower than the assumed one step reduction of phenanthridine and acridine. This explanation is somewhat inconsistant with the results for indole and benzothiophene, which also require only two hydrogen atoms for complete reduction, but were in some cases reduced at lower rates than quinoline. Experiments with other substrates, of both types described, could help clarify the importance of this factor in the reductions.

Clearly, steric factors are responsible for the ordering of reduction rates seen with quinoline and its two benzo derivatives. In every case quinoline is reduced the fastest, followed by the bulkier 5,6-benzoquinoline and finally by 7,8-benzoquinoline. This ordering reflects the increasing interactions between the substrate and the catalyst, leading to decreased binding. One experiment was carried out with 2-methylquinoline as a substrate, giving a slower rate than with quinoline, more examination of similarly substituted quinolines as substrates would further clarify steric factors and their effect on reduction rates.

Many compounds have been identified which inhibit the reduction of quinoline by the various catalysts. In most cases this inhibition is due to the ability of the second compound to compete with quinoline for catalyst. Several compounds which enhance the reduction rate of quinoline by $RhCl(PPh_3)_3$ were discovered. The nature of these enhancements is not clear. An NMR investigation of the interaction between one enhancer, p-cresol, quinoline, hydrogen, and $RhCl(PPh_3)_3$, showed no effect by p-cresol on the catalyst-substrate binding equilibrium. More work of this nature, examining other enhancers, could help the understanding of this important phenomenon.

Of all the catalysts investigated the polymer-supported $RhCl(PPh_3)_3$ gave the highest per metal rates. This is of particular practical importance given the reusable nature of this catalyst. Solid magic-angle spinning NMR experiments with the polymer-supported catalyst are planned, in which hopefully the binding between substrate and catalyst can be observed as it was for the homogeneous catalyst.

Finally, the NMR has proven to be one of the most powerful tools at our disposal for investigating the nature of the complexes formed from substrates and catalysts. The results with $RhCl(PPh_3)_3$ and quinoline indicate the formation of three principal species under one atmosphere of hydrogen. One of these is cis-chlorobis(triphenyl-phosphine)quinoline rhodium(I), which is not a direct

intermediate in the reduction of quinoline. Two quinoline-rhodium-dihydride species are also formed, both possible reduction intermediates. The species are apparently different conformers of the same complex, and exchange rapidly on the NMR timescale at room temperature. The relation between two conformations and the hydrogen transfer step of the reduction needs to be further explored. Additionally, a similar NMR study with $RuClH(PPh_3)_3$ and quinoline should be carried out for comparative purposes.

SECTION III

HYDRODENITROGENATION CHEMISTRY

III.A BACKGROUND

The HDN reaction has been investigated by several workers [1,9,81-93]. Katzer et. al.[81], in work with the reduced compound, decahydroquinoline, have found that acidic catalysts or thermolysis alone were not sufficient to remove the nitrogen. He proposes that a metal site and an acidic support site on a HDN catalyst act in conjunction to reduce and remove the nitrogen. Somewhat contradictory to this, Maier et. al.[82] haves found that very high loading of platinum on silica (eg. 40%) is very effective as a HDN catalyst under relatively mild conditions (1 atm. H_2, 150-200°C), and that this high loading is critical to the catalyst's activity.

Sonnemans et. al.[84-86] and Satterfield et. al.[87-92] have both demonstrated through the analysis of byproducts that the removal of nitrogen via HDN is not a direct process. Transalkylation, in which a C-N bond is replaced by a different C-N bond, forming a new compound, may in fact be the predominant reaction during HDN, with reduction of nitrogen to ammonia occuring only after several such steps. Related to this, Laine et. al.[9,93] have demonstrated that the homogeneous transition metal cluster Rh_6CO_{16} can catalyze reduction and C-N bond cleavage of pyridine to form N-pentyl piperidine derivatives, under

mixtures of either water or hydrogen, and carbon monoxide. No ammonia was produced in this reaction.

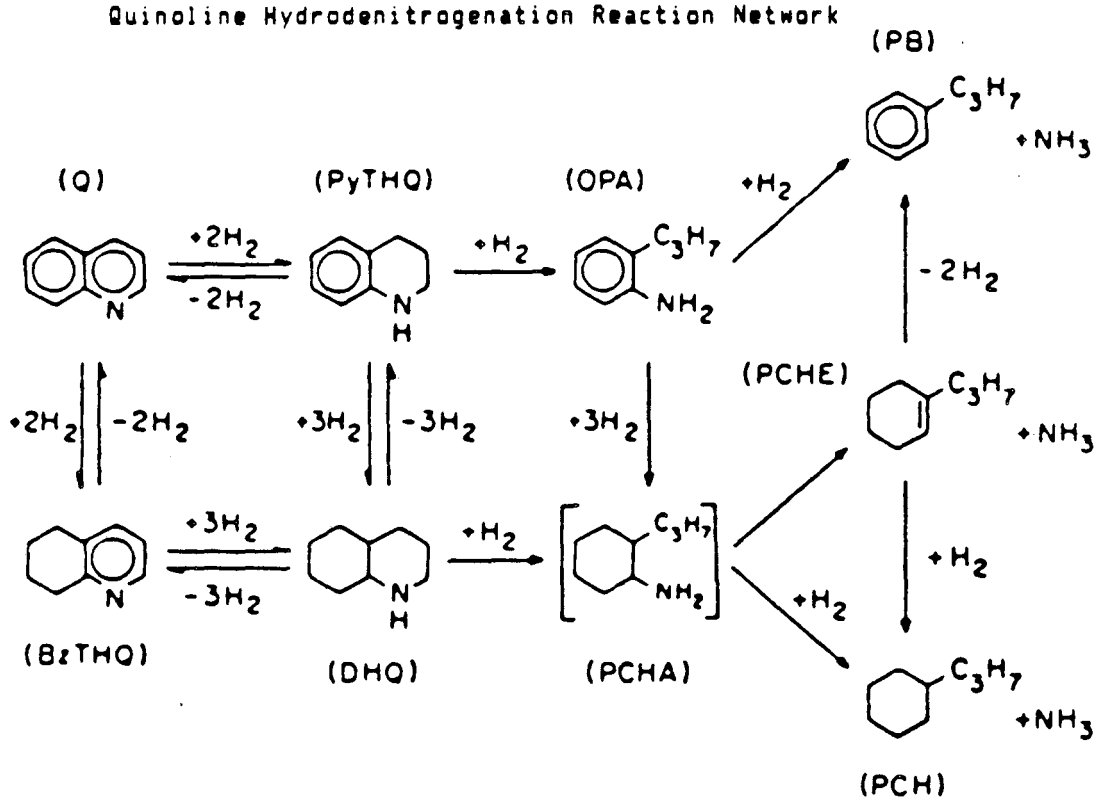
An example of the overall reactions involved in the HDN process are illustrated in Figure III.1[88]. Here the nitrogen containing compound, quinoline, has been used as a model for the complex mixture of nitrogen compounds present in an actual refinery feed. The reaction network is quite involved, but the principal pathway leads from quinoline to the fully saturated decahydroquinoline and ultimately to propylcyclohexane and ammonia. It is necessary to fully reduce the nitrogen containing ring prior to the removal of nitrogen.

The reduction of the nitrogen containing ring is necessary prior to the removal of nitrogen because the stability of the original carbon-nitrogen aromatic bonds. The average bond strength of a carbon-nitrogen multiple bond is approximately the same as a carbon-carbon multiple bond, but a carbon-nitrogen single bond is approximately 25 kcal/mol weaker than a carbon-carbon single bond. Thus, saturation of the nitrogen containing ring facilitates the selective cleavage of the carbon-nitrogen bonds. Unfortunately, saturation of the nitrogen containing ring is accompanied by the hydrogenation of the other aromatic ring in quinoline (under the processing conditions of HDN described above), leading to hydrogen consumption in excess of that required simply to remove the nitrogen.

Nearly four times as much hydrogen is consumed in

FIGURE III.1

Quinoline Hydrodenitrogenation Reaction Network



Q	quinoline
PyTHQ	Py (or 1,2,3,4) - tetrahydroquinoline
BzTHQ	Bz (or 5,6,7,8) - tetrahydroquinoline
DHQ	decahydroquinoline (cis and trans isomers)
OPA	o - propylaniline
PCHA	propylcyclohexylamine
PB	propylbenzene
PCHE	propylcyclohexene
PCH	propylcyclohexane

producing propylcyclohexane as was needed to reduce and remove the nitrogen from quinoline. Hydrogen is an expensive commodity, and this is particularily so if processing a hydrogen poor material, such as a coal liquid, since the hydrogen must all come from an external source. The desired product of quinoline hydrodenitrogenation is propylbenzene, the result of the minimum hydrogen consumption pathway.

III.B HETROGENEOUSLY CATALYZED C-N BOND CLEAVAGE

III.B.1 INTRODUCTION

The nature of the hydrodenitrogenation reaction and the approach to it taken in this study have been discussed in the general introduction. In the study that follows a preliminary survey has been made of the ability of several materials to heterogeneously catalyze the cleavage of the carbon-nitrogen bonds in 1,2,3,4-tetrahydroquinoline to form alkyl anilines and alkyl benzenes. This work is intended as a basis for the further study of catalysts identified as able to cleave the carbon-nitrogen bonds without reducing the aromatic ring in tetrahydroquinoline.

A quick examination was made of the use of a variety of compounds as catalysts. Various bulk metals and metal oxides, as well as a fluid catalytic cracking catalyst, were found to be entirely inactive or to promote only the dehydrogenation of tetrahydroquinoline to form quinoline. Several supported nickel catalysts, and one supported rhodium catalyst, all showed the activity desired to varying degrees. Two of these, a 30% Ni/SiO_2 catalyst prepared in our laboratory and a 50% Ni/SiO_2 catalyst supplied as a gift by United Catalyst (C46-7-03), were chosen for further studies, in which proposed intermediates in the HDN reaction of 1,2,3,4-tetrahydro-quinoline were used as substrates. These results indicate that free radical processes may be involved in the C-N

cleavage, and that the action of the various nitrogen bases present during reaction is critical in moderating the catalyst activity. TEM characterization of the 30% Ni catalyst indicates a bimodal distribution of nickel crystallites, with 2000 angstrom and 200 angstrom range crystallites present.

These reactions were all carried out in the tube reactor described in the experimental section. This system is patterned on a similar reactor designed and used by Dr. W. Maier in studies of high Pt loaded silica catalysts for the HDN reaction of quinoline[82]. The temperature regulation was not perfect, a 5°C change either way was typical during a run due to variation of the mains supply voltage. The hydrogen pressure was one atmosphere, chosen deliberately in an attempt to prevent aromatic reduction to give undesired cyclohexane derivatives, the flow through the reactor was 30 cc/min.

A syringe pump was used to admit reactants at 0.14 cc/hr. The reactants entered the reactor dropwise, and vaporized along the wall of the reactor. Thus the flow rate was not controlled except in an average sense, however this was adequate for the survey nature of this study. Powdered or granular catalysts were used as received, the two catalysts from United Catalyst were in the form of extrudates and were ground and sieved to 40-325 mesh before packing into the reactor. The reproducibility of runs was only fair, for the reasons discussed above. In

order to do more accurate kinetics runs a new system is being designed currently, one which allows for much tighter controls of the temperature and flow rates.

The product mixtures were in general quite complex, with 50 or more major and trace components. The major components (those present at concentrations exceeding approximately one percent) were identified by GCMS and then verified by comparison to known standards, except for 2-methylaniline and 2-ethylaniline, which were not available as standards at the time. The gas analyses were performed on a Varian 3700 GC with a 6' Poropac PS column, FID detection, and a temperature program of 40°C to 200°C at 15°C/min, with an initial 2 min. hold at 40°C. This instrument could detect hydrocarbon gasses to approximately 1 ppm.

III.B.2 RESULTS AND DISCUSSION

Survey of Catalysts:

Table III.2 summarizes all of the results of this survey. In the table and discussions that follow, percentages of products are expressed in mole percents, while percentages of metals in supported catalysts refer to weight percents. Two main types of reactivity were identified, dehydrogenation of 1,2,3,4-tetrahydroquinoline to form quinoline, and C-N bond cleavage to form several alkyl derivatives of aniline and benzene. In some cases 5,6,7,8-tetrahydroquinoline was also formed.

Bulk nickel and manganese, chromia- zirconia and a fluid catalytic cracking zeolite were all found to be catalytically inactive towards 1,2,3,4-tetrahydroquinoline. In these cases small amounts of quinoline were formed (less than 5%), similar small amounts of quinoline were also formed when the reactor was packed with glass beads. This is due to the thermal, uncatalyzed, dehydrogenation of 1,2,3,4-tetrahydroquinoline, which we had also observed occuring in the GC injector port under some conditions, as discussed in the experimental section (IV).

With the zeolite, experiments were also carried out in which 1,2,3,4-tetrahydroquinoline was diluted in tetralin to 0.4% by volume, and the mixture fed into the reactor. As expected, the cracking activity of the catalyst was almost entirely inhibited, due to the interaction between

TABLE III.2

Summary of Heterogeneous Catalyst Results
Using 1,2,3,4-Tetrahydroquinoline as Substrate

Catalyst	Results
Bulk Nickel (powder)	Inactive
Bulk Manganese (powder)	Inactive
Cr_2O_3 (powder)	Inactive
ZrO_2 (powder)	Inactive
Zeolite (fluid cat. cracking)	Inactive
Bulk Copper (granules)	Dehydrogenation[1]
8% Cu,8% Ni/SiO_2[3]	Dehydrogenation
5% Ni/SiO_2[3]	Dehydrogenation, C-N Cleavage[2]
5% Rh/SiO_2[4]	Dehydrogenation, C-N Cleavage
30% Ni/SiO_2[3]	Dehydrogenation, C-N Cleavage
50% Ni/SiO_2[5]	Dehydrogenation, C-N Cleavage
60% Ni/Al_2O_3[5]	Dehydrogenation, C-N Cleavage

CONDITIONS: Approx. 1cc each catalyst, T = 250°C - 350°C, 0.14 cc/hr 1,2,3,4-tetrahydroquinoline, 30 cc/min-H_2 at 1 atm. Analysis by capillary gas chromatography.

NOTES:
1) Formation of quinoline.
2) Formation of alkyl anilines and alkyl benzenes.
3) Prepared as described in experimental section.
4) Donated by Dr. A. Bell's research group (UC Berkeley).
5) Donated by United Catalyst.

the basic nitrogen compound and the acidic cracking sites within the zeolite. There was no trace of any nitrogen containing material in the products from these reactions, leading to the conclusion that the small amount of tetrahydroquinoline in the feed must be irreversibly absorbed and decomposed to coke within the catalyst.

Bulk copper granules and an 8% Cu,8% Ni on silica catalyst prepared in our laboratory were both found to be efficient dehydrogenation catalysts. The copper metal gave quinoline in yields as high as 70% (400°C), while at 340°C the Cu/Ni catalyst gave more than 90% quinoline. 5,6,7,8-tetrahydroquinoline was also formed by the bimetallic catalyst in small amounts, varying from 5.3% at 260°C to 1.6% at 340°C. This product is presumably formed by the hydrogenation of quinoline, and is the thermodynamically favored reduction product of quinoline under these conditions[80]. It was formed as well in some of the reactions described below.

All of the supported nickel catalysts and a supported rhodium catalyst exhibited the C-N bond cleavage activity that was being sought. In none of these cases were any appreciable amounts of cyclohexane derivatives observed, with the exception of 5,6,7,8-tetrahydroquinoline, which may be regarded as a cyclohexane derivative.

These catalysts also all caused dehydrogenation of 1,2,3,4-tetrahydroquinoline to quinoline, in addition to forming 5,6,7,8-tetrahydroquinoline in some cases. Since

these are not desired products, the usefulness of these catalysts must be judged by the ratio of bond cleavage products to quinoline and 5,6,7,8-tetrahydroquinoline, as well as by the overall conversion of 1,2,3,4-tetrahydroquinoline.

The most active catalyst was a 50% Ni/SiO_2 material provided as a gift by United Catalysts. At 250°C, 0.26 g of this material gave approximately 50% aniline or benzene derivatives, quinoline and 5,6,7,8-tetrahydroquinoline comprised about 30% of the products. Next in activity, but lower by a considerable amount, was a 30% Ni/SiO_2 catalyst prepared as described in the experimental section. At its maximum activity (as discussed below the activity of this catalyst was hard to reproduce), and at approximately 340°C, 0.86 g of this material provided 45% anilines and benzenes, and about 35% quinoline, with very little 5,6,7,8-tetrahydroquinoline being formed. With both catalysts the total conversions of 1,2,3,4-tetrahydroquinoline were 95% or better. These catalysts were examined further as detailed below.

The other three catalysts were not as satisfactory. The 5% Rh/SiO_2 catalyst was found to give more than 50% quinoline and 5,6,7,8-tetrahydroquinoline (up to 20% of the latter product at 260°C), versus about 30% C-N bond cleavage products. The total conversions found were from 90% at 260°C to 99% at 300°C.

The 5% Ni/SiO_2 catalyst (prepared by us) gave

conversions under 80% at 320°C, 1 g catalyst. Quinoline made up 55% to 65% of the products, the anilines and benzenes only about 5% total. The 60% Ni/Al_2O_3 catalyst gave low conversions at well, at 260°C, 0.25 g of this catalyst gave less than 70% conversion, 50% of the products were quinoline and 5,6,7,8-tetrahydroquinoline and 9% were aniline or benzene derivatives.

This last result is interesting, when compared to the high activity shown by 50% Ni/SiO_2. It is not clear if the low activity of the 60% Ni/Al_2O_3 is due to the different support material or to a difference in the dispersal of the metal. We are currently conducting morphological studies of these two catalysts in order to help understand this difference.

Further Study of Highly Loaded Nickel on Silica Catalysts:

Because of their relatively high C-N cleavage activity the 30% and 50% nickel on silica catalysts were examined in more detail than the other catalysts. Table III.3 gives some of the results obtained with the 30% Ni/SiO_2 catalyst prepared in our laboratory (see experimental section IV).

The first two columns are the results for the reaction of 1,2,3,4-tetrahydroquinoline at two different temperatures. The principal products are identified, in

TABLE III.3

Results using 30%Ni/SiO_2 Catalyst[1]

Substrate :	1,2,3,4-THQ	1,2,3,4-THQ	2-Pr-aniline	Pr-benzene
Temperature:	320°C	360°C	320°C	320°C
Products (mol%)[2]:				
Benzene	8.4%	12.2%	19.3%	trace
Toluene	1.4%	1.8%	2.9%	trace
Et-Benzene	trace	trace	trace	0.0%
Pr-Benzene	trace	trace	5.3%	0.0%
Aniline	27.5%	18.9%	9.3%	0.0%
2-Me-aniline	7.2%	2.7%	5.7%	0.0%
2-Et-aniline	trace	trace	trace	0.0%
2-Pr-aniline	trace	trace	37.0%	0.0%
Quinoline	34.0%	44.5%	0.0%	0.0%
5,6,7,8-THQ	trace	trace	0.0%	0.0%
1,2,3,4-THQ	5.3%	3.5%	5.8%	0.0%
Indole	6.5%	9.1%	trace	0.0%
2-Me-indole	2.1%	0.9%	2.3%	0.0%
Unidentified	7.6%	6.4%	12.4%	0.0%

CONDITIONS: 0.86 g catalyst, 0.14 cc/hr substrate, 30 cc/min H_2 at 1 atm. Products identified by GCMS and verified by comparison with standards (except 2-methylaniline and 2-ethylaniline).

NOTES:

1) This catalyst prepared as described in the experimental section. The activity of this catalyst was not constant, but decayed with storage. Also, the preparation was difficult to reproduce exactly. The results given in the table are for the most active batch of catalyst, later results with this batch and with others gave quinoline productions as high as 60%, with 1,2,3,4-tetrahydroquinoline as the substrate. The C-N cleavage products were all present in lower amounts, but with relative proportions similar to those in the above table.

2) Not included in the product normalization is the amount of gaseous products obtained. For a 340°C 1,2,3,4-tetrahydroquinoline run the hydrocarbon gasses produced were analyzed by gas chromatography to give 99.5% methane, 0.1% ethane, 0.4% propane and ca. 0.02% butane. Ammonia was also produced.

both cases several unidentified products were also obtained in trace amounts, the total amount of these is in the last row of the table. These results were obtained with the most active batch of catalyst at the highest point in its activity, which occured after about 10 runs. The preparation and stability of this catalyst were not well reproduced, other batches gave up to 60% quinoline and proportionally less aniline and benzene products, although these latter products occured in the same relative proportions.

The anticipated reactions, based on the known HDN mechanisms as discussed in section III.A, would be the ring opening of 1,2,3,4-tetrahydroquinoline to form 2-propylaniline, and the further cleavage of the C-N bond in this compound to form propyl benzene. Interestingly, neither propyl nor ethyl substituted anilines and benzenes were found in more than trace amounts, The principal C-N cleavage products were aniline, 2-methylaniline, benzene and toluene. This would indicate that the cleavage of alkyl C-C bonds is facile on this catalyst, quickly converting the propyl side chains to methyl groups. The cleavage of this methyl group from the aromatic ring is then less facile, this would be expected from bond strength considerations.

The average bond strength of an alkane C-C single bond is 85 kcal/mole, a benzylic bond (one distant from an aromatic ring, such as the terminal methyl group in ethyl

benzene) is even weaker, 72 kcal/mole. The bond strength of the methyl group in toluene however is approximately 100 kcal/mole. Thus conversion of propyl derivatives to methyl derivatives would be expected to be much more facile than the conversion of methyl derivatives to unsubstituted aromatics. This would explain the small amounts of ethyl derivatives of benzene and aniline found relative to propyl and methyl derivatives, as well as the larger amounts of the methyl derivatives relative to aniline and benzene.

Dehydrogenation to quinoline was a significant reaction, and increased with increasing temperature. Very little 5,6,7,8-tetrahydroquinoline was produced by this catalyst though, indicating perhaps that it is a poor hydrogenation catalyst for quinoline (which is presumed to be an intermediate in the formation of 5,6,7,8-THQ). The reaction of quinoline with this catalyst remains to be investigated, and will be helpful in understanding the hydrogenation activity of the catalyst.

Both indole and 2-methylindole were produced in significant amounts. It is assumed that these products are formed by the ring closure of 2-propylaniline, as other experiments would seem to indicate. The formation of these products will be discussed in more detail later in this section.

The effect of raising the temperature on the overall HDN efficiency is mixed. At the higher temperature more denitrogenated products (benzene and toluene) are

produced, but more quinoline is generated as well. The total amount of C-N cleavage products decreases by 10% as the temperature is raised, the total amount of quinoline produced increases by about the same amount. This indicates that the dehydrogenation reaction has a higher activation energy that the overall "activation energy" of the HDN process, and so running at lower temperatures is advantageous as long as the total conversions are good. If the quinoline could be recycled, re-reduced to 1,2,3,4-tetrahydroquinoline and fed back into the reactor, then the efficiency of the whole process would be much improved and there would be an advantage to higher temperatures, where production of benzene and toluene are highest.

Both 2-propylaniline and propylbenzene were also investigated as feeds, since these compounds are proposed as intermediates in the cleavage reactions, the results are in the last two columns of the table.

2-propylaniline gave an interesting distribution of products. As expected methyl and unsubstituted anilines and benzenes were major products. Interestingly, propyl benzene was also found in significant amounts, but very little ethylbenzene was seen. This is in qualitative agreement with the bond strength values presented above, in which transformation of propylbenzene to ethylbenzene is energetically less favored than transformation of ethylbenzene to toluene.

Both 1,2,3,4-tetrahydroquinoline and 2-methylindole

were formed in significant amounts, indicating that these product may be formed from propylaniline in the tetrahydroquinoline reaction as well. In both cases these products can result from a hydrogen abstraction from the propyl chain on propylaniline, followed by attack of the resulting primary or secondary carbon radical on the amino group, resulting in tetrahydroquinoline directly, or in 2-methylindoline, which could then dehydrogenate to form 2-methylindole. Indole, formed in traces, could be the result of the cleavage of the methyl group from 2-methyl-indole. The exact nature of these reactions is however not apparent to us at this time, further experiments are necessary. Products such as these have been observed by Satterfield in the conventional HDN of quinoline[91].

Propylbenzene was almost entirely degraded to gaseous products under the same conditions as used for propylaniline. Only a trace of benzene and toluene wee found. This indicates that the poisoning action of the various nitrogen bases present in the other reactions is critical in moderating the activity of the catalyst. In the absence of any poisoning the catalyst is much more active and aromatics undergo nearly complete hydrogen-olysis. This is an important finding, since in any actual HDN reaction the concentration of nitrogen bases is far lower than in our reactions. It would be necessary to somehow moderate the catalyst activity for it to be practical when used with lower nitrogen content feeds.

The gasses formed from these reactions were collected and analyzed. The gas was collected in a water trough, so that ammonia was absorbed into the water and only the hydrocarbons collected. Ammonia was presumed to be present in the initial gas mixture, as indicated by odor, pH of aqueous solutions, and its low boiling point. The presence of methylamines cannot be ruled out by this evidence but this seems very unlikely based on other workers results.

The hydrocarbon gasses were found to be almost entirely methane (99.5%), with traces of ethane (0.1%), propane (0.4%) and butane (0.02 %). The methane is presumably formed from the cleavage of aromatic side chains, some could also be formed by the complete hydrogenolysis of aromatics, but larger amounts of other hydrocarbon gasses would be anticipated as well. Due to the simple nature of our system mass balance closure could not be established, and so the amount of aromatic compounds undergoing complete hydrogenolysis (if any) is unknown. The nature of the formation of the higher hydrocarbon gasses is not clear, propane and ethane may be formed by direct cleavage of propyl and ethyl side chains, or by reactions between methyl and ethyl radicals. Butane cannot be formed by the cleavage of side chains, none of which are 4 carbons long, and so must only be formed by radical reactions.

Table III.4 gives the results of a set of experiments using a 50% Ni/SiO_2 catalyst supplied by United Catalyst

TABLE III.4

Results using 50%Ni/SiO_2 Catalyst
(United Catalyst C46-7-03)

Substrate :	1,2,3,4-THQ	1,2,3,4-THQ	2-Pr-aniline	Pr-benzene
Temperature:	250°C	260°C	250°C	250°C
Products (mol%)[1]:				
Benzene[2]	9.2%	15.8%	29.9%	trace
Toluene[2]	1.8%	2.8%	4.3%	trace
Et-Benzene	trace	trace	trace	0.0%
Pr-Benzene	trace	trace	20.8%	0.0%
Aniline	9.4%	16.7%	6.0%	0.0%
2-Me-aniline	14.3%	20.0%	5.4%	0.0%
2-Et-aniline	8.6%	8.6%	1.4%	0.0%
2-Pr-aniline	2.0%	1.6%	21.5%	0.0%
Quinoline	14.3%	9.8%	0.0%	0.0%
5,6,7,8-THQ	14.1%	5.9%	0.0%	0.0%
1,2,3,4-THQ	4.7%	1.6%	trace	0.0%
Indole	2.7%	3.1%	trace	0.0%
2-Me-indole	5.0%	4.5%	trace	0.0%
Unidentified	13.9%	9.6%	10.7%	0.0%

CONDITIONS: 0.26 g catalyst, 0.14 cc/hr substrate, 30 cc/min H_2 at 1 atm. Products identified by GCMS and verified by comparison with standards (except 2-methylaniline and 2-ethylaniline).

NOTES:

1) Not included in the product normalization is the amount of gaseous products obtained. For the 1,2,3,4-tetrahydroquinoline runs the hydrocarbon gasses produced were analyzed by gas chromatography to give at least 99.8% CH_4, other hydrocarbons (if present) were below the detection threshold of the instrument. Ammonia was also produced.

2) For the 1,2,3,4-tetrahydroquinoline runs the amount of these two products varied considerably. The above are the highest values, amounts as low as 2.2% benzene, 0.8% toluene were obtained at 250°C. The amounts of the other products were more reproducible.

(C46-7-03). The results were similar to those discussed above, and so in the discussion that follows primary attention will be given to the differences between the two catalysts.

The most obvious, and important, difference between the two catalysts is the much higher activity of the 50% Ni material. At temperatures 100°C lower than those used above, and with one-third as much catalyst, similar total conversions of 1,2,3,4-tetrahydroquinoline were obtained. While part of this increase in activity is probably due simply to the higher metal content of the 50% Ni catalyst, most must be due to improved dispersion of the nickel in this catalyst, or to other physical features of the catalyst. This catalyst is produced by a proprietary process specifically to achieve high hydrogenation activity towards aromatics under higher pressures of hydrogen than that used in our work. The relation between this intended activity and the reactions we have observed is not clear.

Relative to the 30% Ni material, more ethyl and propyl aniline were produced by this catalyst, and more 5,6,7,8-tetrahydroquinoline. The higher production of this latter material is presumably due to the improved hydrogenation characteristics of this catalyst, but the reason for the higher production of the longer chain alkyl anilines is unknown. Less quinoline was produced by this catalyst, and more importantly the amount of quinoline production fell as the temperature was raised. The amount of 5,6,7,8-tetra-

hydroquinoline lowered as well, additional evidence for the production of this material from quinoline. This is unlike the behavior of the other catalyst, although quantitative comparisons are risky when two such disparate sets of conditions are compared. The overall efficiency of nitrogen removal and C-N cleavage increase with temperature, as does total conversion. This is a much better situation than with the 30% catalyst, in which the HDN reactions and the dehydrogenation reaction both increased with temperature.

More 2-methylindole than indole was produced by this catalyst, the opposite of the results with the 30% catalyst. Indole is presumable produced by the cleavage of the methyl group from 2-methylindole, although some could as well be produced by the cyclyzation of ethylaniline. The reduced production of indole by the 50% Ni catalyst is consistent with the relatively higher production of propyl and ethylaniline, in both cases a reduced activity towards C-C bond cleavage as compared with the other catalyst is indicated.

The reaction of 2-propylaniline with the 50% Ni catalyst gave quantitatively different results than with the 30% Ni catalyst. A much larger amount of propylbenzene was produced relative to aniline. This indicates that cleavage of the C-N bond in propylaniline is much more facile than cleavage of the C-C bonds in the propyl chain with this catalyst. Very little formation of indoles or

1,2,3,4-tetrahydroquinoline occured with this catalyst.

The reaction of propylbenzene over this catalyst gave the same results as with the 30% Ni material, virtually complete hydrogenolysis. Again, this points out the importance of the nitrogen bases as catalyst poisons in this system.

Finally, a gas analysis of the hydrocarbon gasses produced by this reaction revealed at least 99.8% methane, with other gasses, if present, below the detection limit of the instrument. The absence of these gasses is probably not significant, since they were present in such small concentrations in the 30% Ni sample. Again, the predominante reaction seems to be one carbon degradation of aromatic side chains to generate methane.

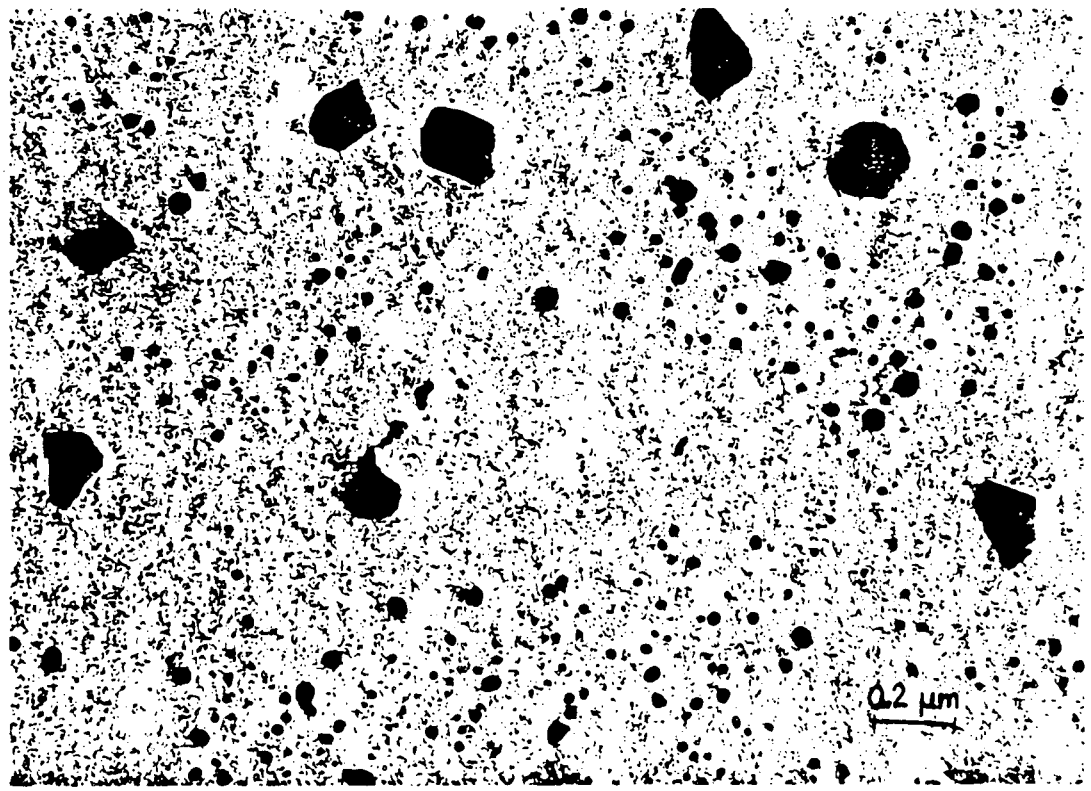
Characterization of 30% Ni/SiO_2 Catalyst:

Work was also begun during this study to characterize the various catalysts that proved to be active. Figure III.5 shows a transmission electron micrograph of the 30% Ni catalysts, this micrograph was obtained on a electron microscope at Chevron (Richmond) by Dr. I. Chan.

This micrograph revealed a bimodal distribution of nickel crystallites, with many small crystallites in the 200 angstrom size range and a few larger crystals in the 2000 angstrom range. Although not visible in this picture, coke deposits were also found on the surface. A chemical

FIGURE III.5

Transmission Electron Micrograph of 30% Ni/SiO_2 Catalyst



analysis of this same catalyst showed a 0.13% carbon content.

At this time we are not sure of the significance of these findings. It is planned to obtain similar micrographs of other batches (use and unused) of this catalyst. The reproducibility of the 30% catalyst preparation was poor, and the activity of the catalyst changed with time. We hope to be able to use these micrographs as a guide in understanding the reasons for the different activities of various batches of the catalyst.

A preliminary XPS study of this same catalyst has revealed both metallic and oxidized nickel on the surface. The oxidized nickel is present in small amounts, the lack of an accurate calibration standard prevents quantification. The oxidized nickel may not be present under the actual reaction conditions, but instead could be formed upon exposure of the catalyst to air. Samples of freshly used catalyst which have not been exposed to air are currently being prepared to help resolve this point.

III.C CONCLUSIONS AND PROPOSED FUTURE WORK

The preliminary nature of this work prevents any extensive conclusions about the nature of reactions producing the various products observed. Nevertheless, the results with the 30% and 50% nickel on silica catalysts clearly demonstrate that hydrodenitrogention can be carried out without excessive reduction of aromatic structures.

Figure III.6 illustrates in a compact fashion the general results obtained with the highly loaded nickel catalysts. 1,2,3,4-tetrahydroquinoline is assumed to be in equilibrium with quinoline, and through quinoline with 5,6,7,8-tetrahydroquinoline. Recent results that we have obtained with quinoline and the 50% nickel catalyst reinforces the idea of this proposed equilibrium, as both 1,2,3,4 and 5,6,7,8-tetrahydroquinoline were formed from quinoline.

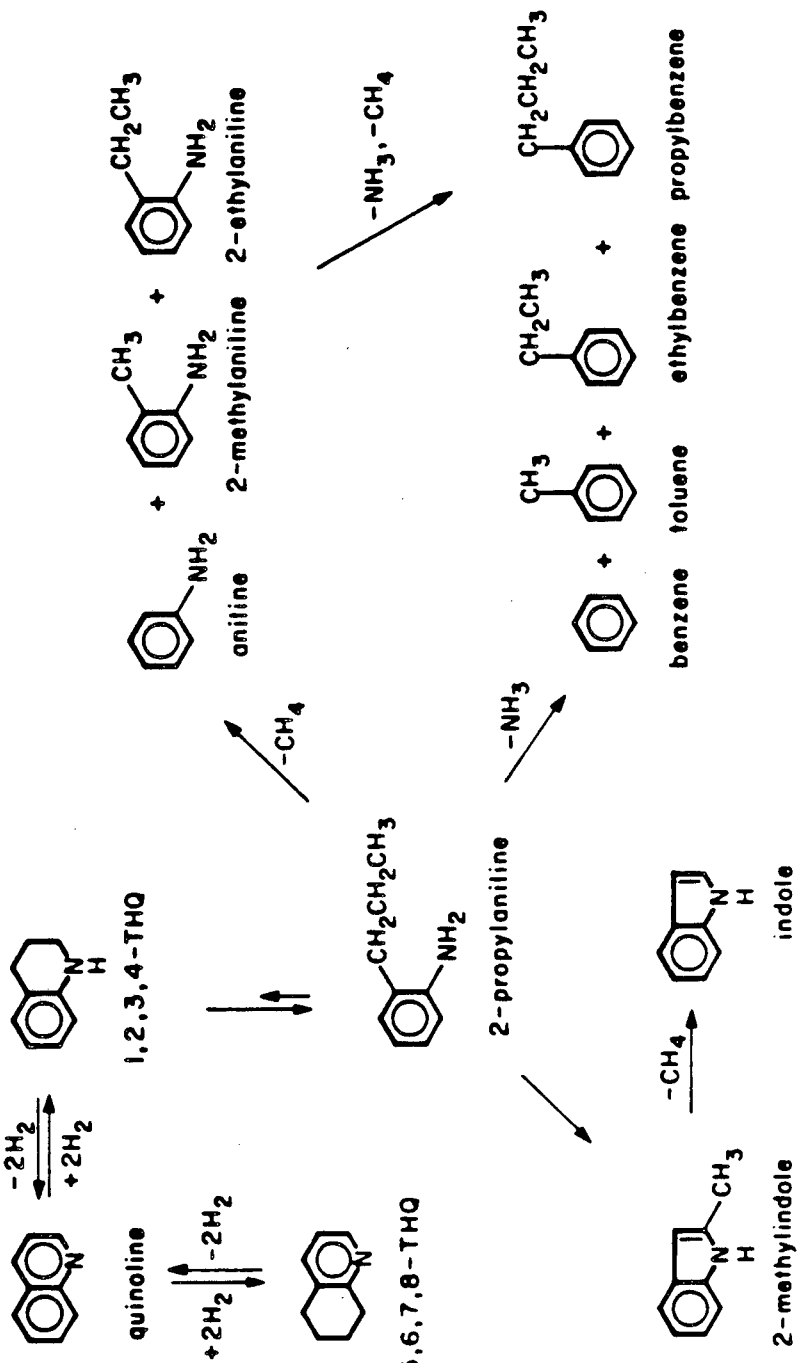
1,2,3,4-Tetrahydroquinoline may also be converted to 2-propylaniline. As indicated, our results with 2-propylaniline as a reactant indicate that this step may be slightly reversible as well.

2-Propylaniline is assumed to be the parent compound for the other major products. Cyclization of this compound can lead to 2-methylindole and indole. Successive losses of carbons from the propyl side chain leads to the aniline derivatives. Cleavage of the carbon-nitrogen bond followed by propyl side chain gives the various derivatives of benzene. The benzene derivatives can also be directly

FIGURE III.6

Proposed 1,2,3,4-Tetrahydroquinoline Reaction Network

With 30% and 50% Ni/SiO_2 Catalysts



formed from the aniline derivatives by C-N cleavage, as indicated.

A new reactor system is currently being designed. It will permit more accurate flow rates, and on line gas chromatography, simplifying analysis of product, as well as reactant, mixtures. This system should provide more consistent results than the simple tube reactor used in the present study.

A variety of substituted anilines could be used as substrates to help understand the factors leading to the cyclyzation products formed from 2-propylaniline. 5,6,7,8-tetrahydroquinoline and quinoline both should also be investigated as substrates. The activity towards quinoline is particularily important, as this will allow determination of the equilibrium (if it exists) between quinoline and 1,2,3,4-tetrahydroquinoline under reaction conditions.

The 30% and 50% nickel catalysts need to be better characterized. The surface area of both materials needs to be determined, and as well the oxidation state of the nickel at the surface under reaction conditions. Studies of the nickel distribution on the surface of the catalysts are also important. As described above, the 30% catalyst had a bimodal distribution of nickel crystallites. The relationship between this distribution and the activity of the catalyst remains to be discovered.

SECTION IV

EXPERIMENTAL METHODS

Materials:

All substrates and pure metals and metal oxides used in the HDN studies were purchased from Aldrich Chemical Co. and were used as received, except for quinoline and 1,2,3,4-tetrahydroquinoline, which were distilled and stored over 4A molecular sieves, and 7,8-benzoquinoline, which was vacuum sublimed to remove a dark colored impurity. All substrates were analyzed by GC prior to use and were found to be greater than 99% pure.

Chlorotris(triphenylphosphine)rhodium(I) was either purchased from Alfa Inorganics or Strem Chemical or was provided as a gift from Engelhard Industries. The polymer supported $RhCl(PPh_3)_3$ was purchased from Strem Chemical. Dichlorotris(triphenylphosphine)ruthenium(II) was provided as a gift from Engelhard Industries. Dicarbonyldichlorobis(triphenylphosphine)ruthenium(II) was purchased from Strem Chemical.

Solvents were obtained from various sources, and were purified before use. Tetrahydrofurane was distilled either from lithium aluminum hydride or from benzophenone ketyl, and stored under nitrogen. All other solvents were distilled from benzophenone ketyl or dried over molecular seive and also stored under nitrogen.

Instrumentation:

The capillary gas chromatography analyses were performed on an HP5880A instrument, with flame ionization detection. The carrier gas was grade A helium. For the rate experiments, when rapid separation was required, a 15m X 0.35 mm DB-5 (J and W) capillary column was used with the following conditions: 50°C-200°C with a 1.5 min initial hold at 50°C and a 10°C/min temperature rise to 200°C with a 10 min hold at 200°C. For the heterogeneous catalyst experiments, where the product mixtures were complex, enhanced separation was obtained using the above mentioned column under the following conditions: 35°C to 250°C at 3°C/min. A 30 m X 0.25 mm methyl silicone column was also used for these more complex mixtures, with the following temperature program: 50°C to 250°C at 5°C/min. Compounds were identified either by comparison with standards or by GC-MS as described below.

9,10-Dihydroquinoline, 9,10-dihydroacridine and 1,2,3,4-tetrahydroquinoline were all occasionally observed to dehydrogenate to various degrees in the gas chromatograph. This was a significant problem with the two dihydro compounds, where up to 50% of the injected material could dehydrogenate. In these cases co-injection of pyridine with the sample frequently was able to inhibit dehydrogenation. The pyridine presumably poisons to slight catalytic activity of acidic sites in the injector port.

The GC-MS analyses were performed on a Finnigan 4023 quadropole mass spectrometer with a 30 m X 0.31 mm DB-5 (J and W) capillary column, temperature programmed from 45°C to 300°C at 4°C/min. Headspace gas analyses were performed on a CDC magnetic sector mass spectrometer.

The NMR spectrometers used were either the 250MHz or 200MHz instruments with Nicolet computers located in the Department of Chemistry, UC Berkeley, or a 400MHz Bruker NMR spectrometer located at the NBS-NML laboratory, Gaithersburg, MD. A capillary tube containing a CCl_4 solution of trimethylphosphite was used as a standard for the phosphorus spectra (shift = 141 ppm).

Procedure for NMR Experiments:

Samples for NMR analysis were generally prepared in a Vacuum Atmosphere dry box, in an argon atmosphere. The various rhodium hydride samples for NMR spectra (see section II.B.3) were prepared as follows. A weighed amount of chlorotris(triphenylphosphine) rhodium (I) in a 5mm NMR tube was passed into the drybox along with a small cylinder of hydrogen connected to a 20 cm hypodermic needle (approx 200 cc of H_2 at 20 psi). One ml of solvent (generally CCl_2D_2, Chemical Dynamics) was measured into the tube and the solvent level marked with a grease pencil. Hydrogen gas was then bubbled slowly into the tube through the needle until the color changed from yellow brown to a golden yellow color, indicative of the formation

of the dihydride. Extra solvent was then added to the tube to bring the level back to the mark, replacing that which had evaporated. Finally, any added substrates were measured into the tube, which was sealed with a rubber septum or a plastic cap and Parafilm.

For the experiments with cresol and the rhodium hydride, the cresol was generally added through the septum cap immediately before the NMR spectrum was taken, allowing for easy comparison with spectra of the same sample taken before addition of the cresol. The cresol was taken from a small septum capped vial that was filled in the drybox.

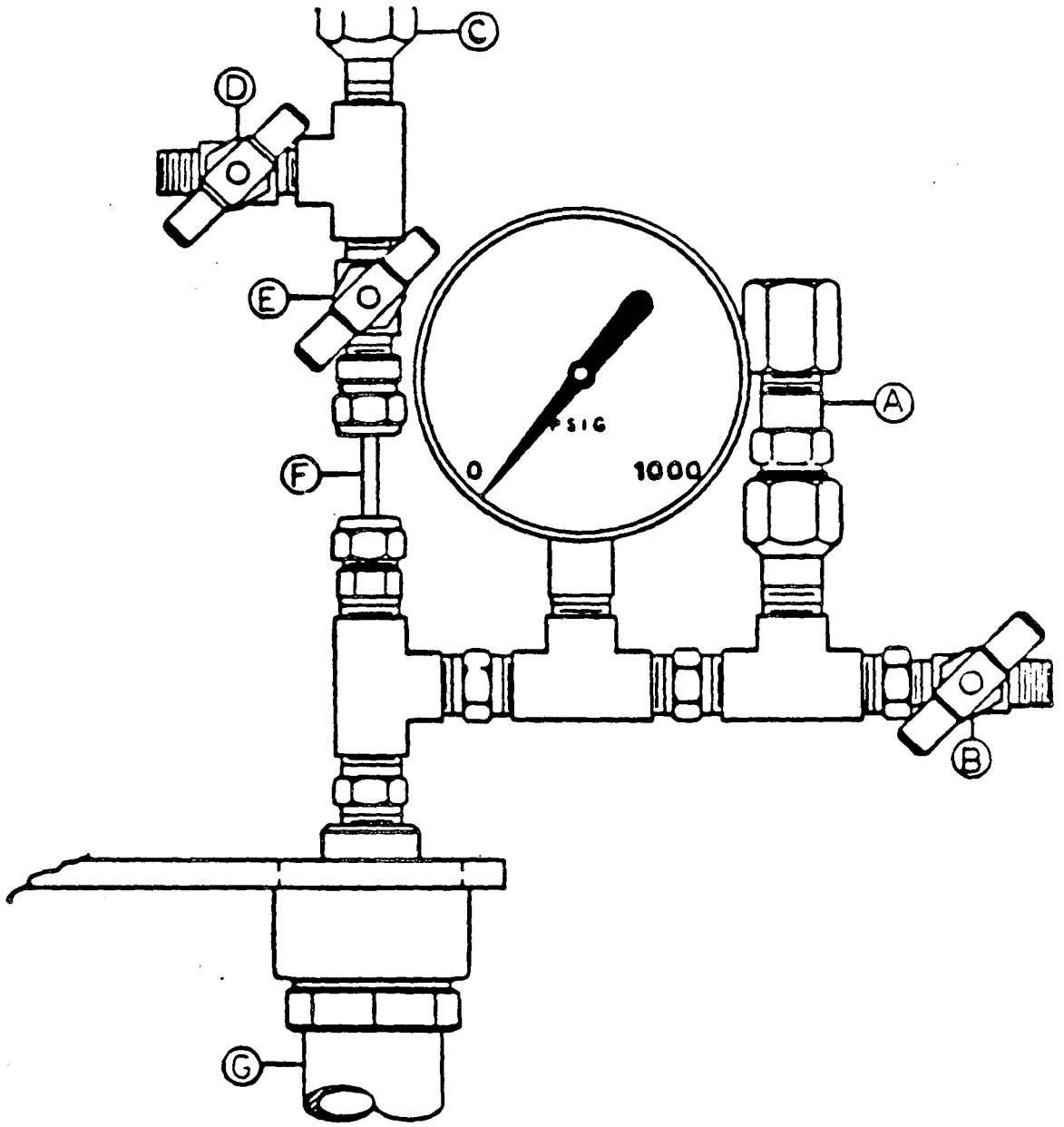
High Pressure Hydrogenation Apparatus:

Most of the high pressure hydrogenations were carried out in a Paar 1991 ACK, kinetic apparatus, designed by us in conjunction with Paar Instrument Co. A diagram of this apparatus appears in Figure IV.1. Some reactions were carried out in a batch reactor system which was identical to the apparatus in the figure except that the dip-tube assembly was absent. The procedure described below is that for the dip-tube apparatus, the batch reactor was used in a similar manner, but allowed only for the analysis of the final reaction mixture after a given reaction period.

The use of the 1991 ACK apparatus is illustrated by the following typical experiment. To the 45 ml reactor cup was added 0.1 mmole of catalyst and 1.0 mmole of substrate dissolved in 20 ml of dry, deaired solvent, along with a

FIGURE IV.1

Paar 1991 ACK Kinetic Apparatus



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small magnetic stirring bar. The reactor cup, G, was attached to the sampling head. The hydrogen gas line was attached to valve D, with valves E and B open. The system was then purged carefully with hydrogen gas for approximately 1 min., valve B was then closed and the reactor allowed to pressurize to the desired value, after which valves D and E were closed.

The reactor was then placed in a thermostatted oil bath, regulation was maintained to within 1°C with an on/ off type temperature controller. Good regulation was acheived with this simple type of controller by supplying most of the heat through an unregulated hot plate, the controlled heat was supplied by an immersion heater, th wattage of which was adjusted to be just sufficient to maintain the reactor temperature. The temperature of the bath was monitored until equilibrium was achieved, typically within 5 minutes, and the time of half approach to equilibrium was taken to be the starting time of the reaction.

At regular intervals samples were withdrawn for analysis by gas chromatography. A syringe needle that reached to the top of valve E was inserted through the septum, a cut off syringe body on the needle served as a sample cup. Valve E was (carefully) opened and approximately 100 ul of sample allowed to flow into the sampling cup. A small sample was then drawn from the cup and injected into the gas chromatograph. After the

sampling cup was removed valve D was opened and valve E opened (again with care) to force the reaction mixture back into the reactor. The pressure gauge was watched for a small pressure jump that accompanied the complete forcing back of the sample. Valves D and E were then closed and valve B used to bleed out a small amount of gas (if necessary) to readjust the hydrogen pressure to its inital value. This entire sampling operation was carried out in less than 1.5 min, and samples were typically withdrawn at 30 to 60 min intervals.

In this manner four to six data points were obtained, at low enough conversions that the conversion vs time data was linear (pseudo-zero order conditions). The data was analyzed by linear least squares regression on an Apple II computer to provide an initial rate of reduction.

For the polymer supported catalysts the above procedure was slightly modified. The catalyst was weighed out and placed in a small wire screen basket which was attached to the end of the dip tube, allowing just enough clearance at the bottom of the reactor for the stir bar.

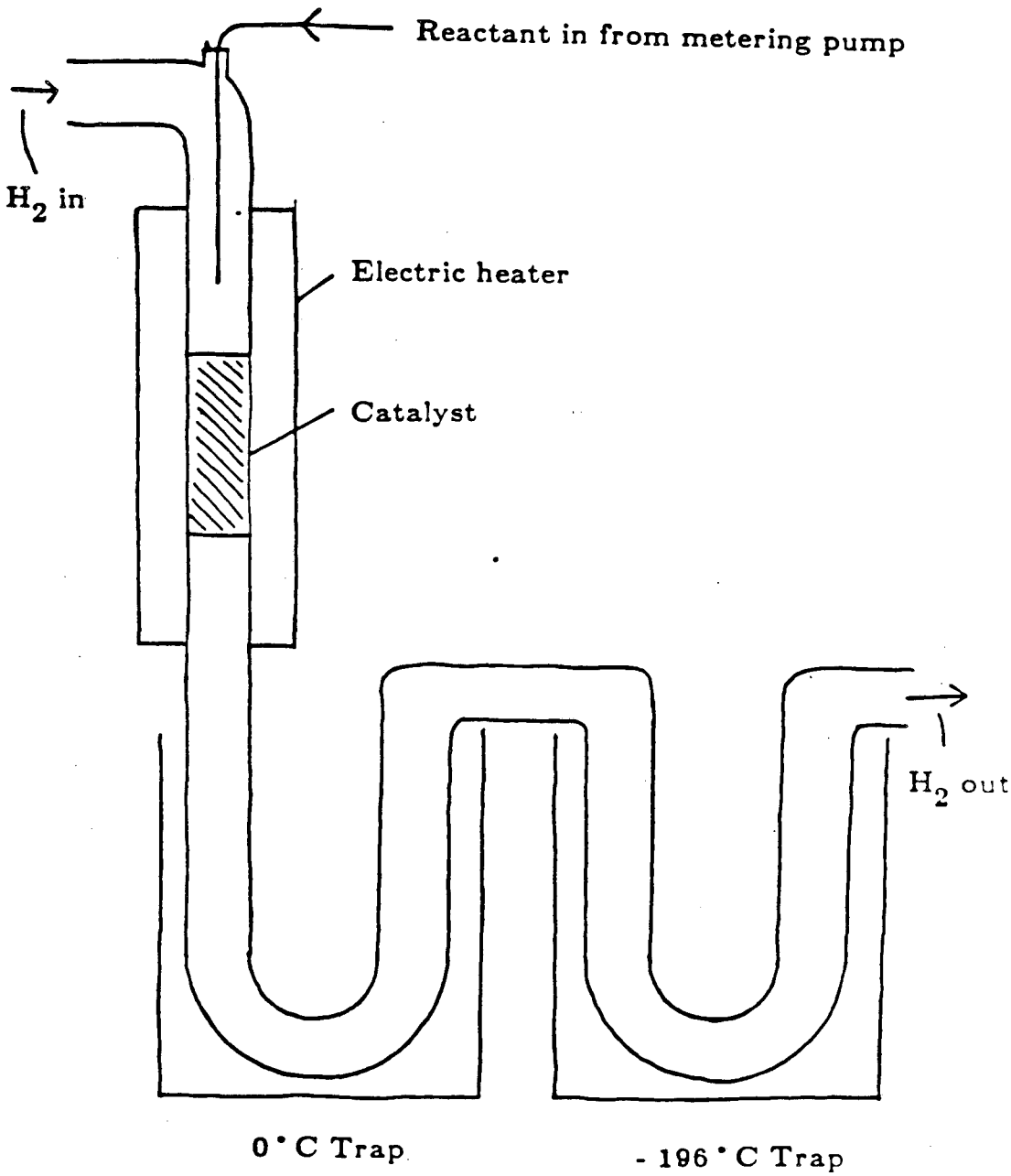
Heterogeneous Catalyst Reactor:

A diagram of the reactor used for the heterogeneously catalyzed reactions is in Figure IV.2. This reactor is patterned after a similar system used by Dr. W. Maier, UC Berkeley, Dept. of Chemistry[82].

The design of this reactor was made simple to

FIGURE IV.2

Schematic of Hydrodenitrogenation Reactor



facilitate the rapid examination of several catalysts. The catalyst was weighed out and placed in the tube between two pieces of glass wool. The catalysts supplied by United Catalyst were in the form of extrudates, and were ground and seived to 40-325 mesh before being placed in the reactor.

The reactor tube was inserted into a quartz tube electric heater. This heater was controlled by a variac, and the temperature monitored with a thermocouple meter. Temperature control could be maintained to within 5°C.

Hydrogen was admitted through a fitting on the top of the tube, the flow of hydrogen was monitored by a rotometer and controlled by a needle valve on the hydrogen tank. A bubbler was inserted into the hydrogen line immediatly before the reactor to prevent the admittance of air into the hydrogen line. The substrate was introduced through the top fitting as well. A 10 cm syringe needle was inserted through a septum, and adjusted so that the tip of the needle was clear of the heated zone. This prevented oxidation and plugging of the needle. The substrate was slowly metered into the reactor using a syringe pump, and vaporized as it flowed down the wall of the reactor tube. The temperature was always maintained above the boiling point of the substrate to facilitate vaporization.

After flowing through the catalyst the reaction mixture was lead through two traps, the first was maintained at 0°C by an ice bath, the second at -196°C

by liquid nitrogen. In general products with a boiling point above approximately 100°C condensed in the first trap, with all other products collecting as solids in the second trap.

After a reaction was complete the reactor was cooled to room temperature and the traps removed from the cold baths. If desired, as the traps warmed the gasses evolved were trapped in a schlenk tube or similar flask, which was inverted in a water trough. After warming to room temperature the traps were rinsed either with acetone or hexane. Acetone was the preferred solvent due to the total solubility of all products in it, but had the disadvantage of slowly reacting with the anilines in the product mixture. Samples in acetone were only stable for a few days. Hexane solutions were more stable, but the hexane had to be warmed slightly to solubilize all the components in the product mixture. To assure that all products of reaction were collected approximately 5 ml of solvent was first admitted through the top of the tube reactor, to wash any condensed material off of the walls of the tube. The traps were then removed from the tube and together rinsed with 10 ml of solvent. The resulting solution was analyzed by gas chromatography or GC-MS.

SECTION V

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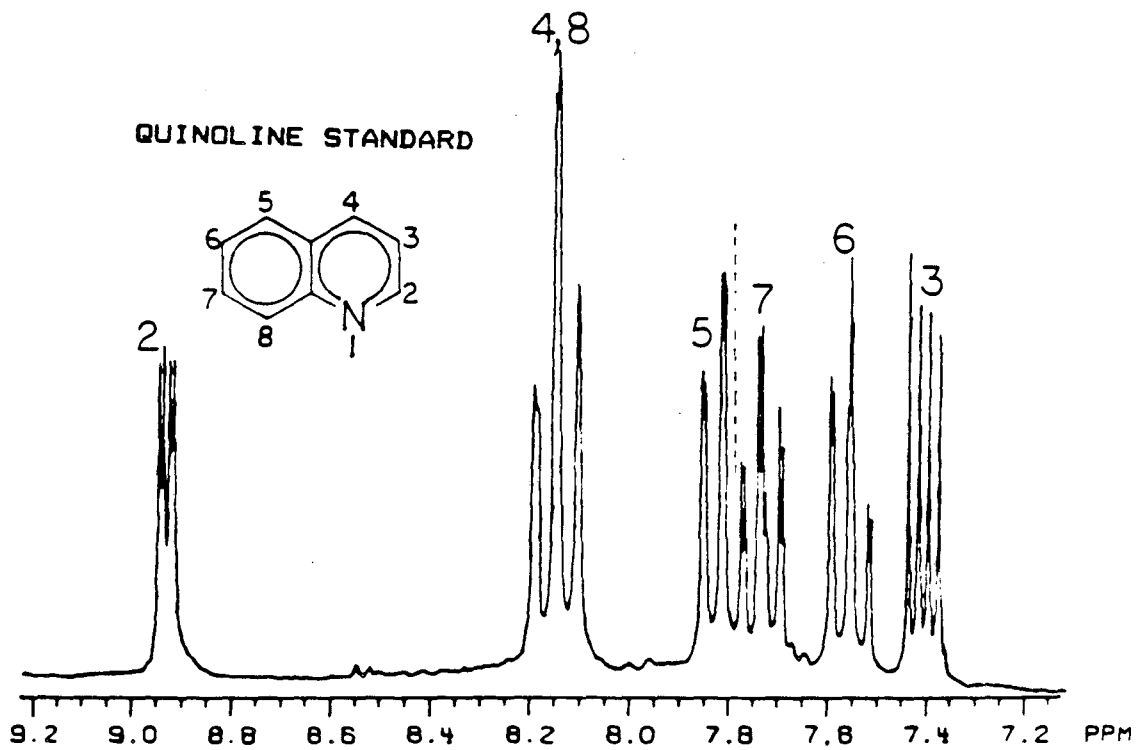
SECTION VI

APPENDIX

p188 - Quinoline Standard and Unreduced Quinoline Remaining in D_2 Reduction of Quinoline Using $RhCl(PPh_3)_3$

p189 - 9,10-Dihydrophenanthridine Standard and 9,10-Dihydrophenanthridine by D_2 Reduction of Phenanthridine Using $RhCl(PPh_3)_3$


QUINOLINE STANDARD
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4
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3
7
2
8
N
1
2
4,8
5
7
6
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9.2
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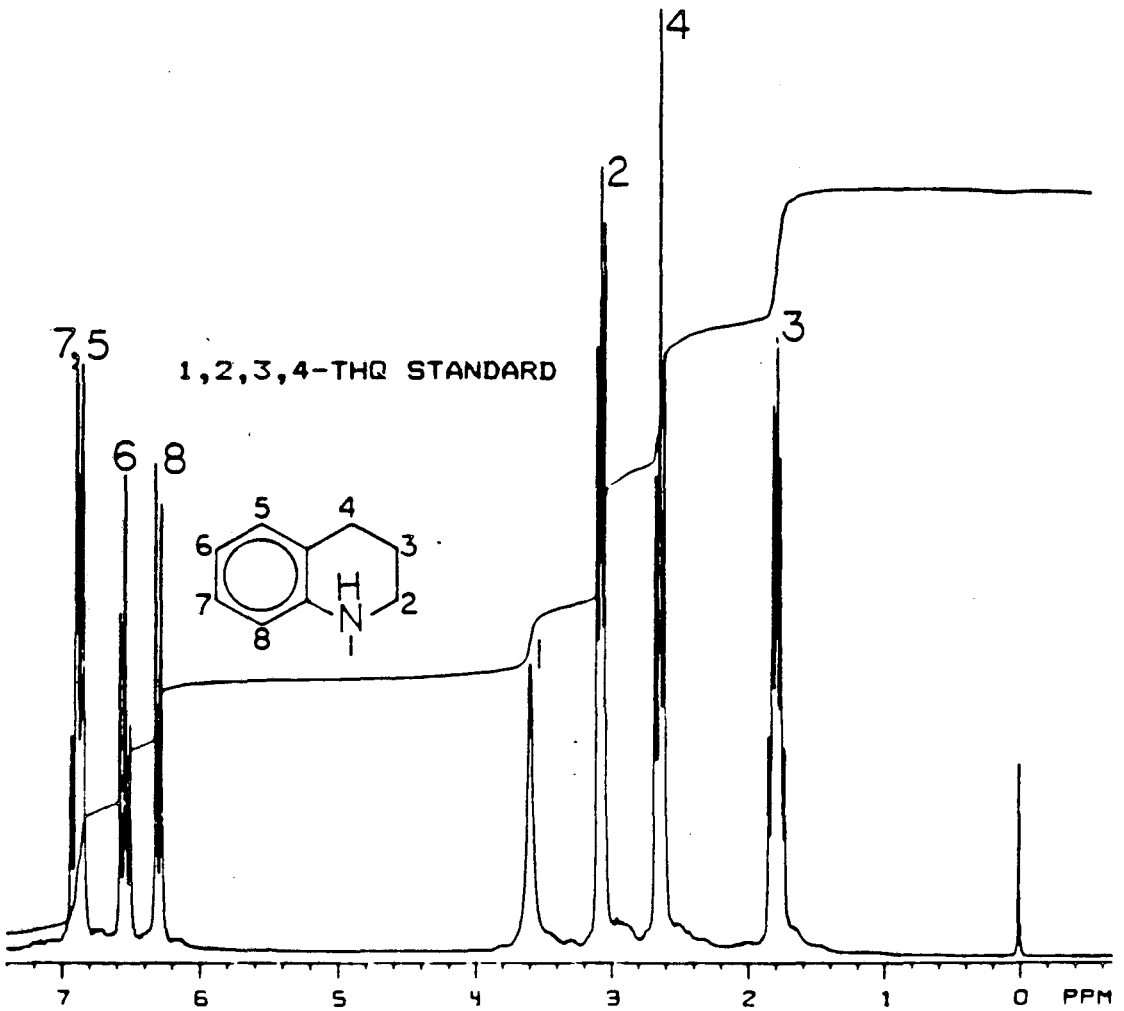
7.2
PPM


7,5
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1,2,3,4-THQ STANDARD
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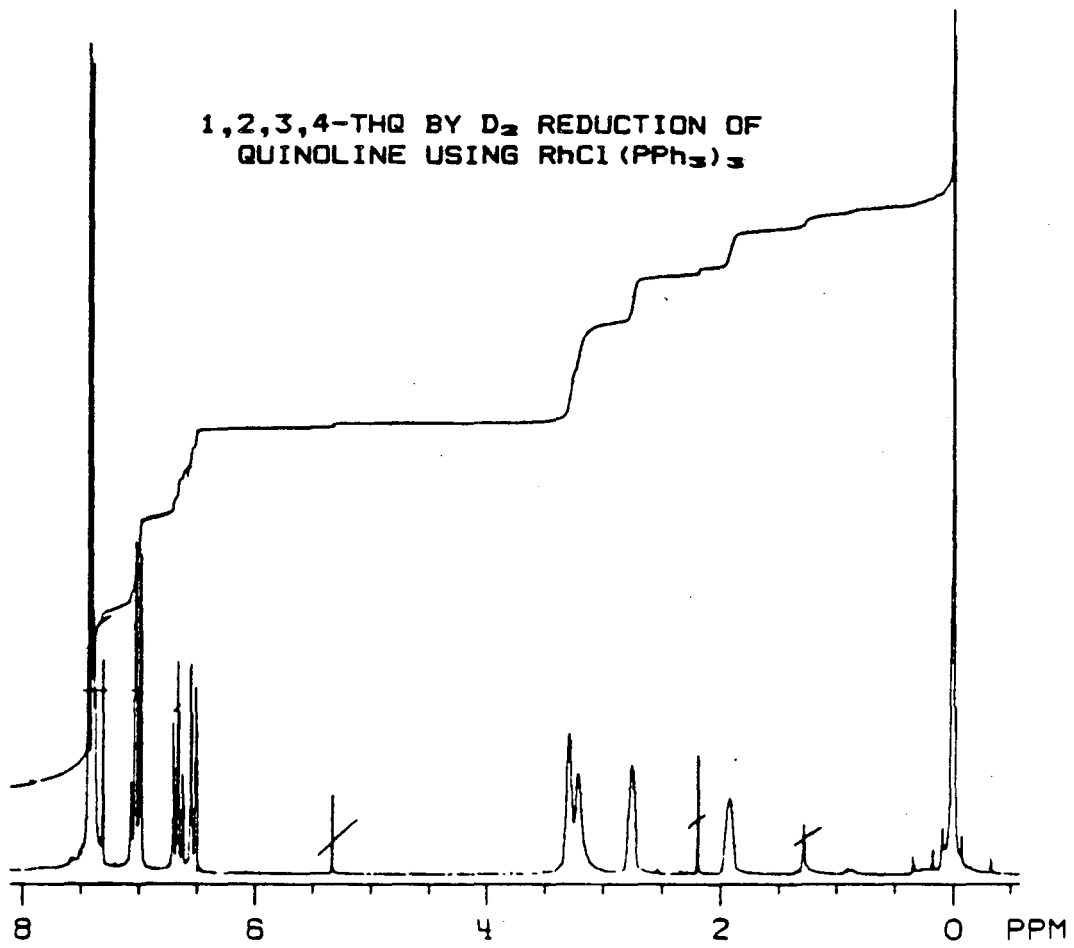
PPM


1,2,3,4-THQ BY D_2 REDUCTION OF
QUINOLINE USING $RhCl(PPh_3)_3$
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4
2
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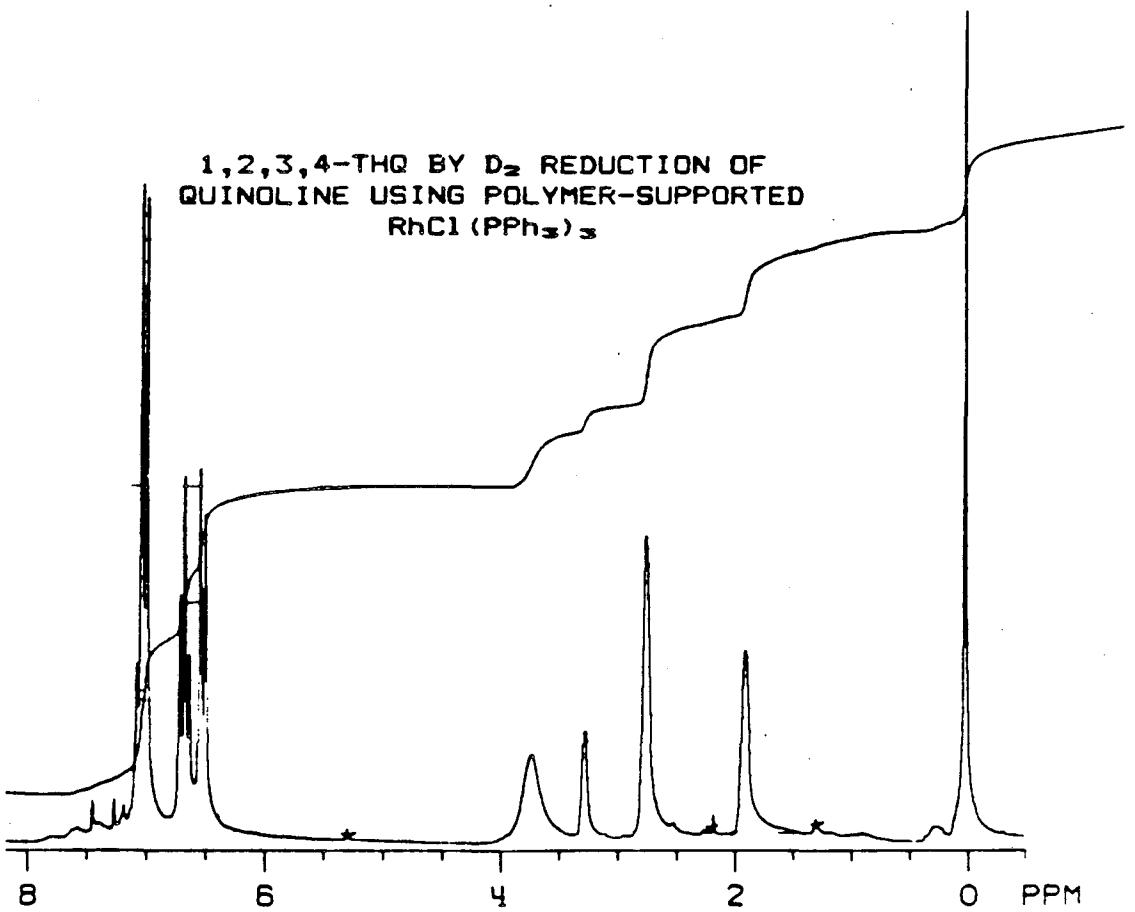
PPM


1,2,3,4-THQ BY D_2 REDUCTION OF
QUINOLINE USING POLYMER-SUPPORTED
$RhCl(PPh_3)_3$
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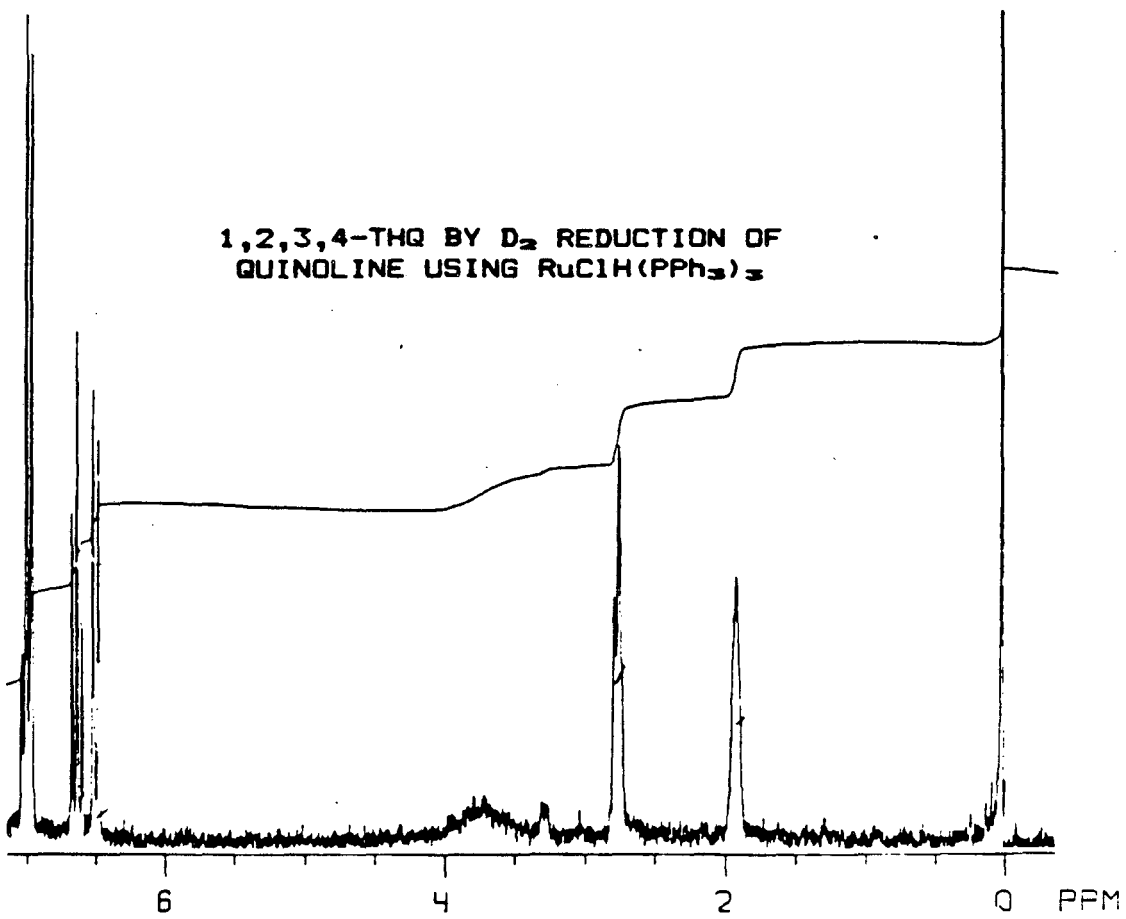
0
PPM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QUINOLINE USING $RuClH(PPh_3)_3$
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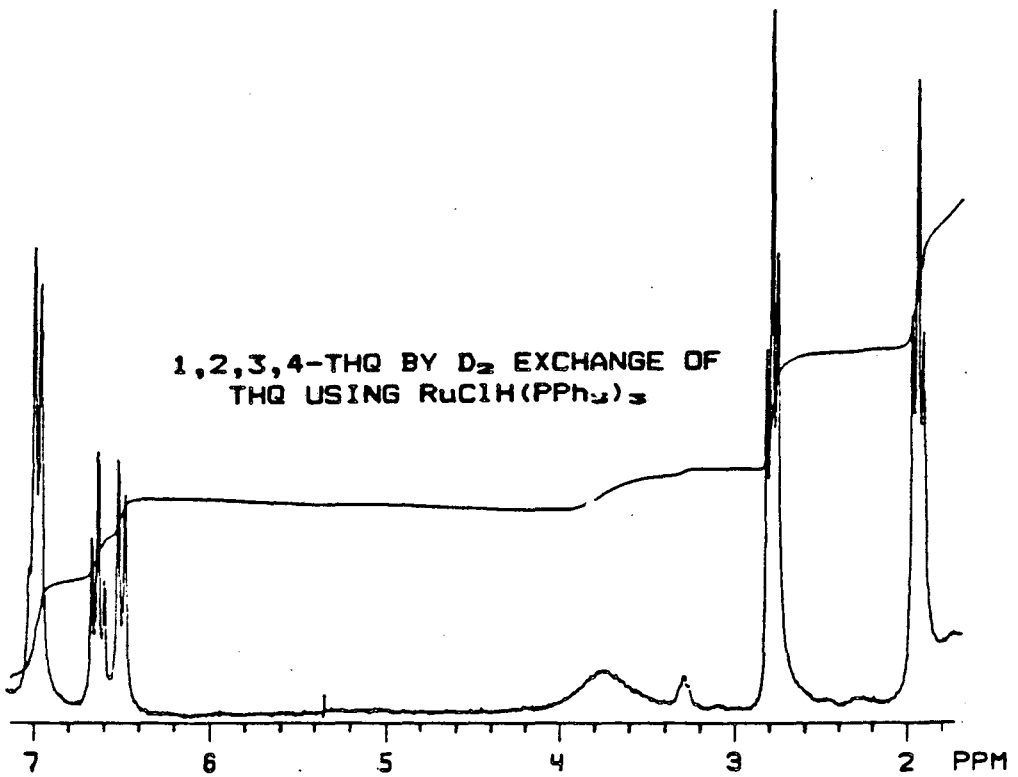
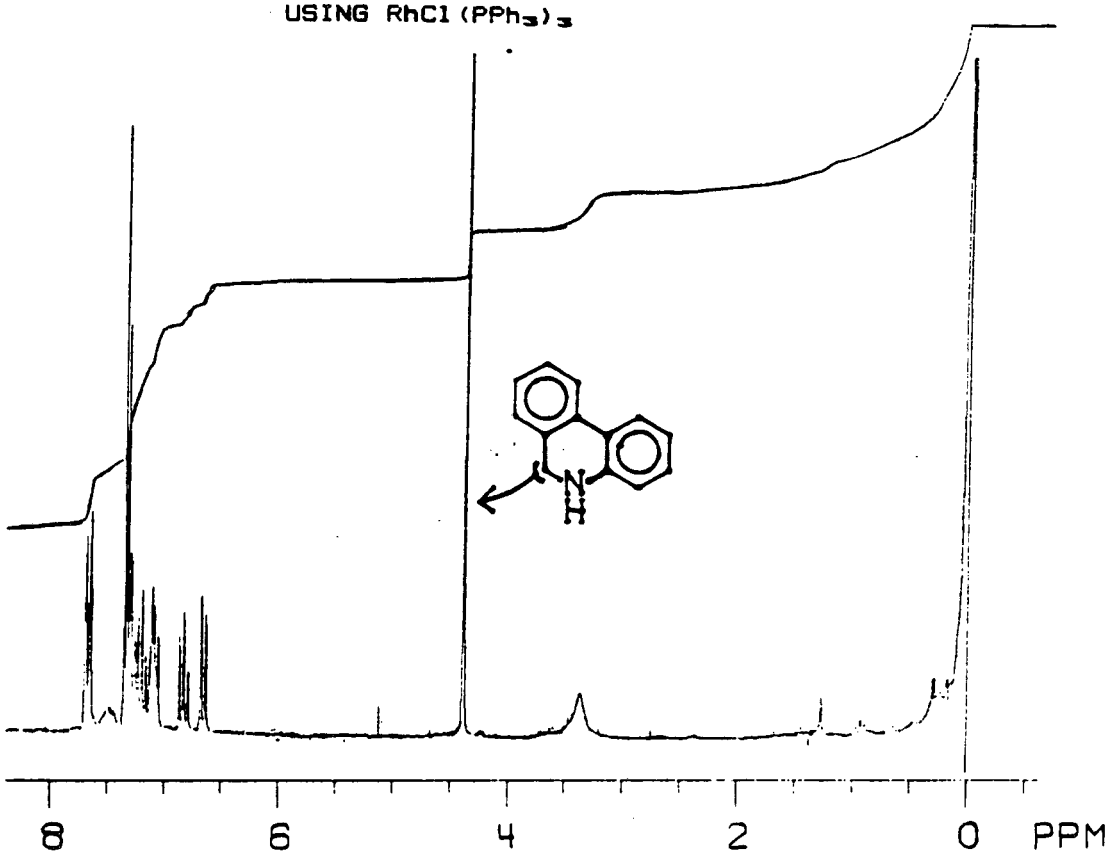
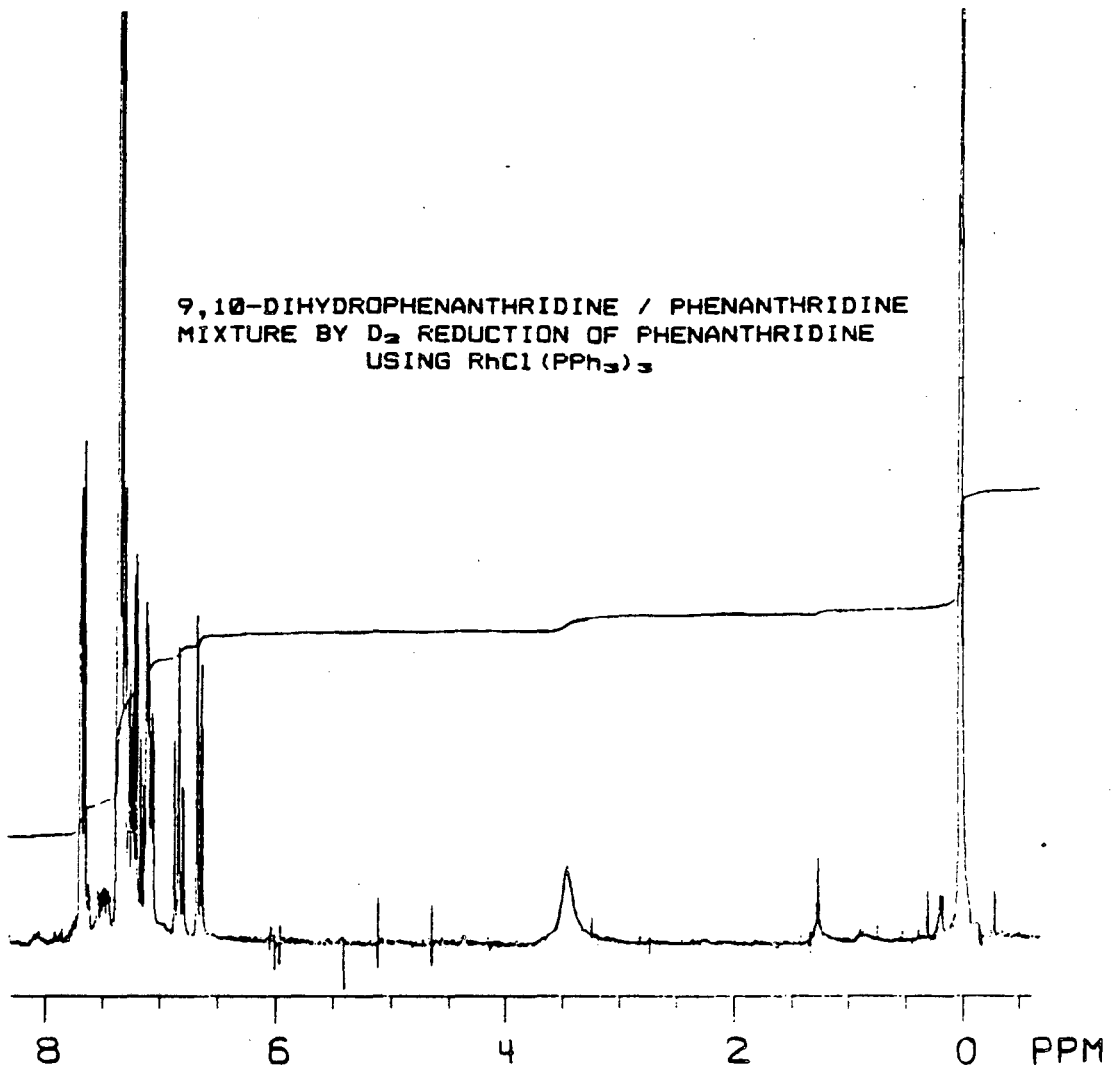
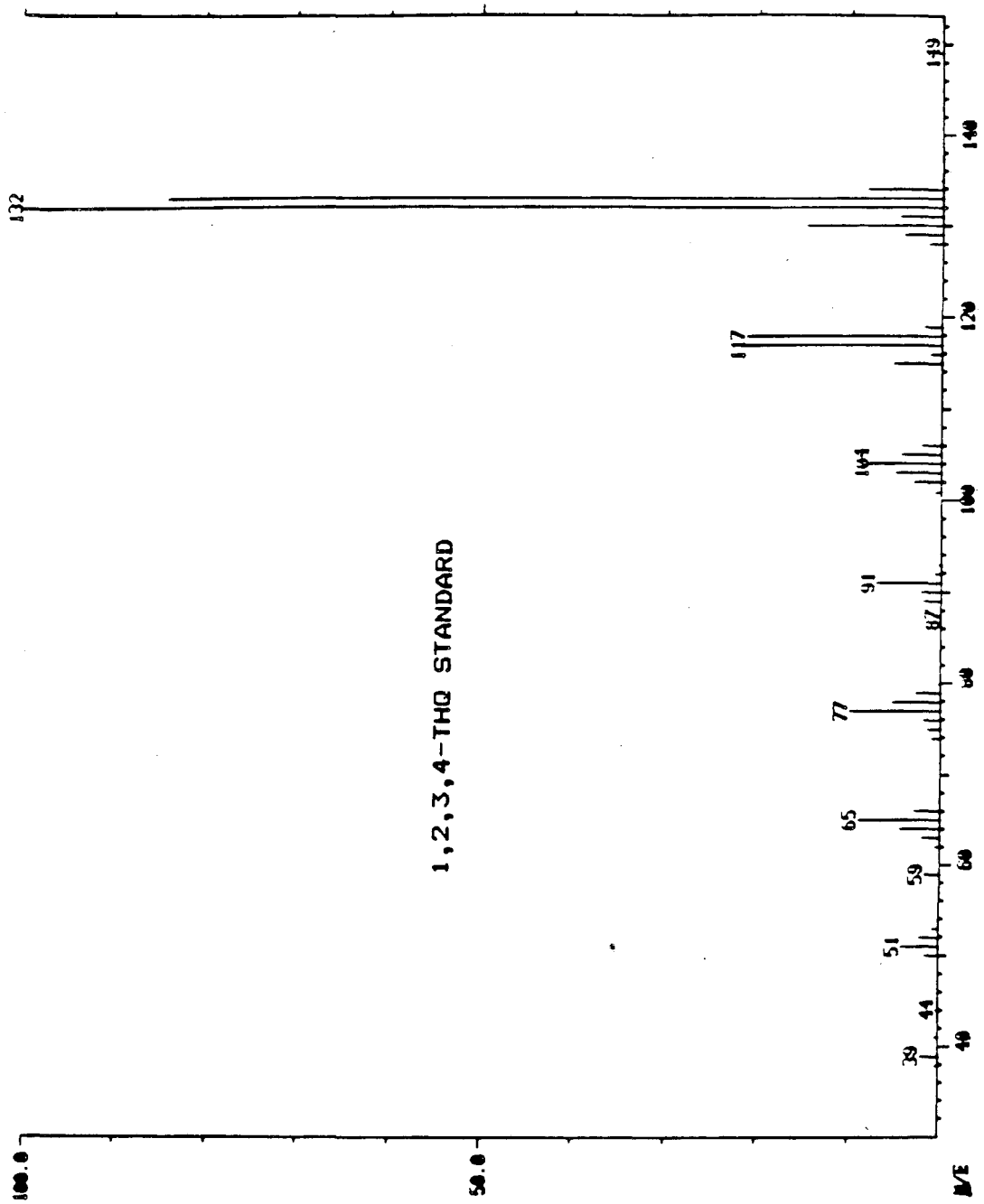
4
2
0
PPM

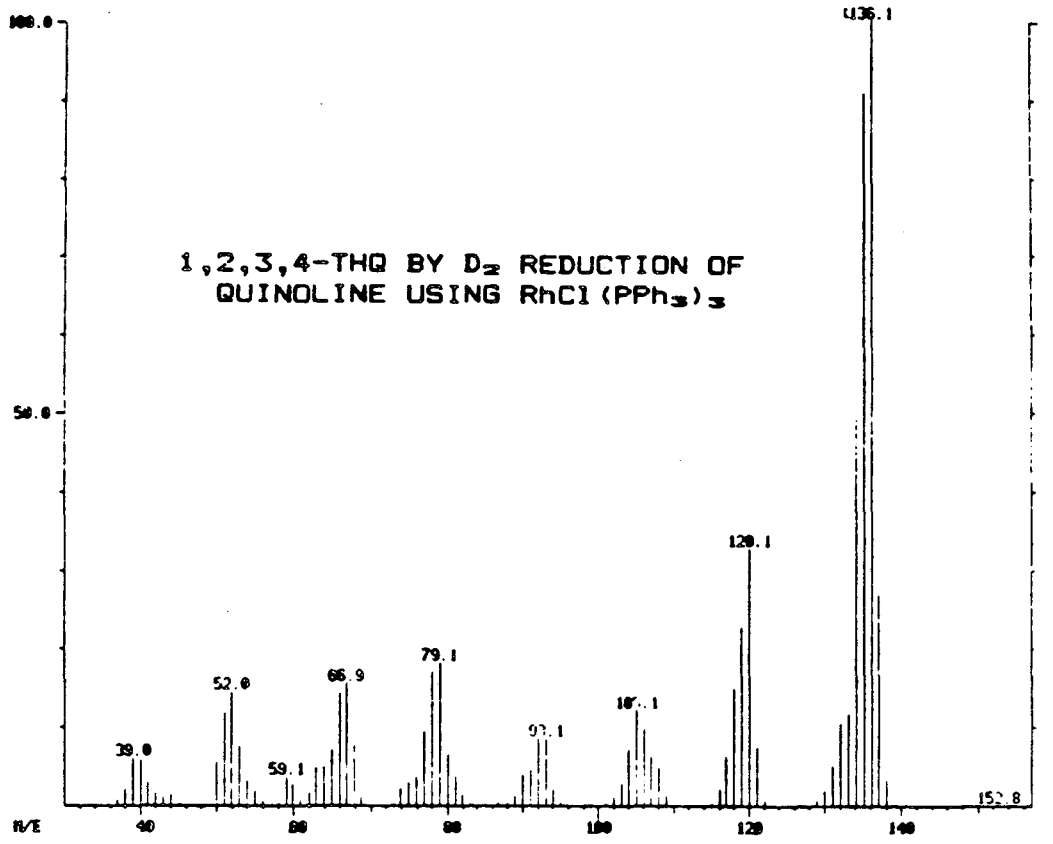

1,2,3,4-THQ BY D₂ EXCHANGE OF
THQ USING RuClH(PPh₃)₃
7
6
5
4
3
2
PPM

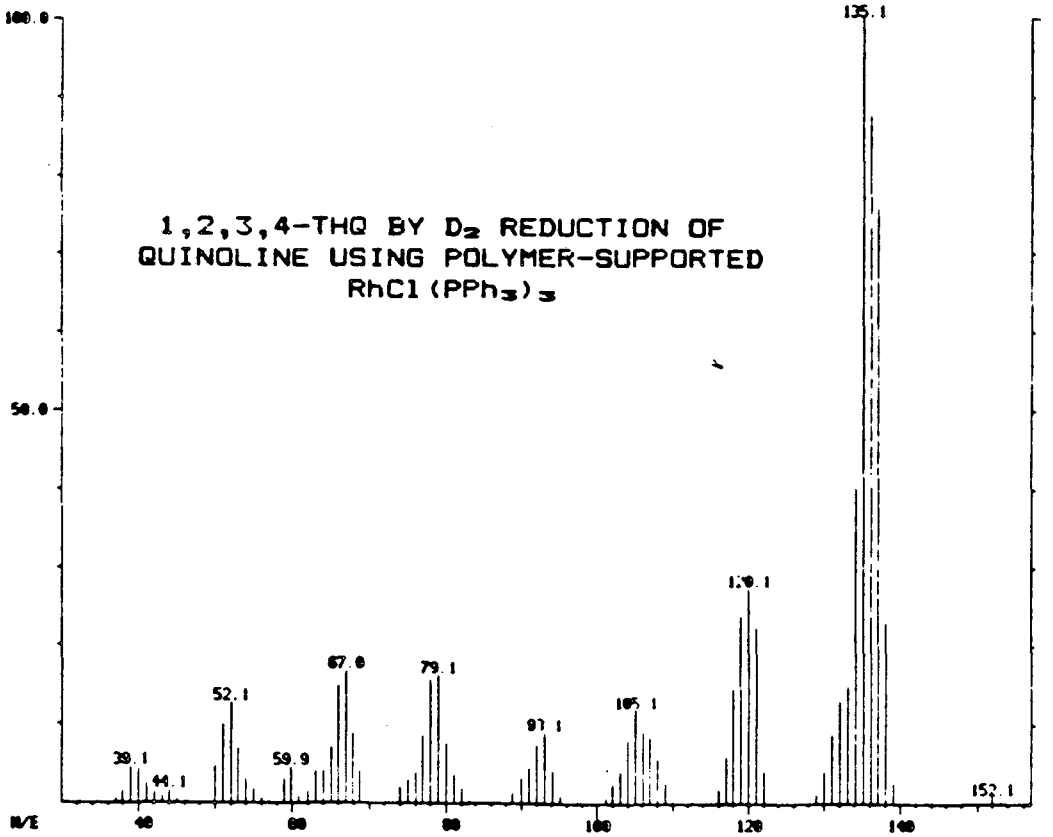
9,10-DIHYDROPHENANTHRIDINE / PHENANTHRIDINE
MIXTURE BY H_2 REDUCTION OF PHENANTHRIDINE
USING $RhCl(PPh_3)_3$

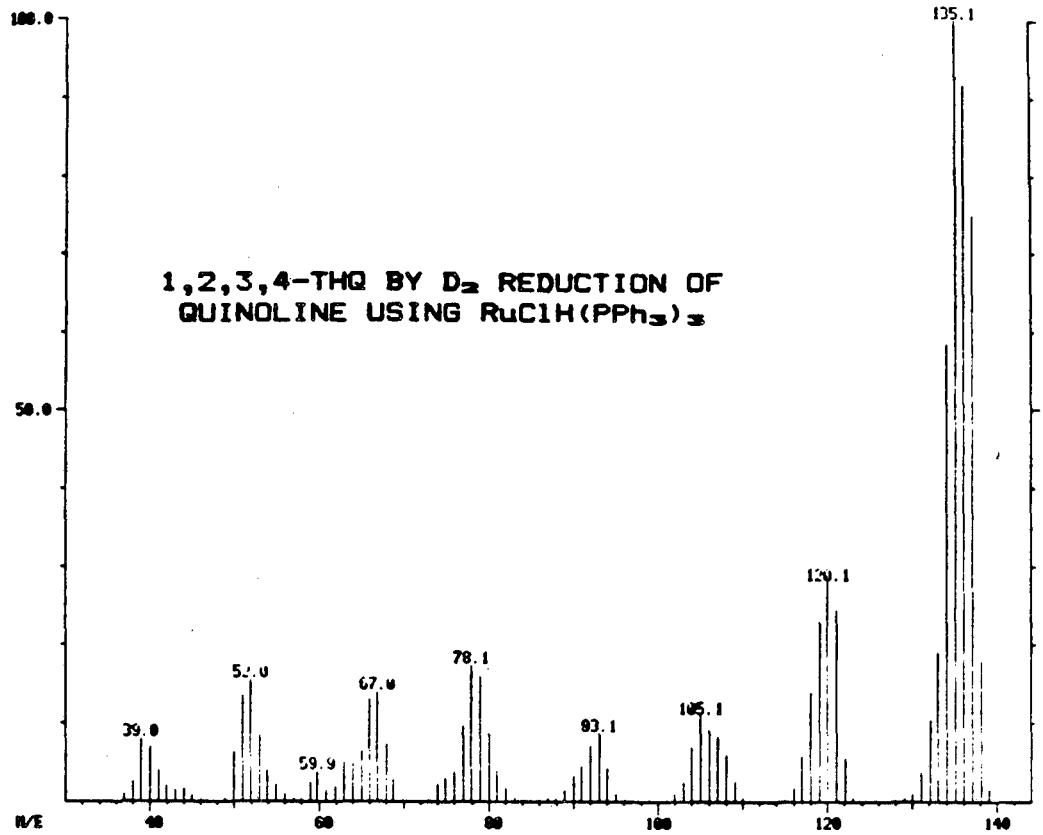


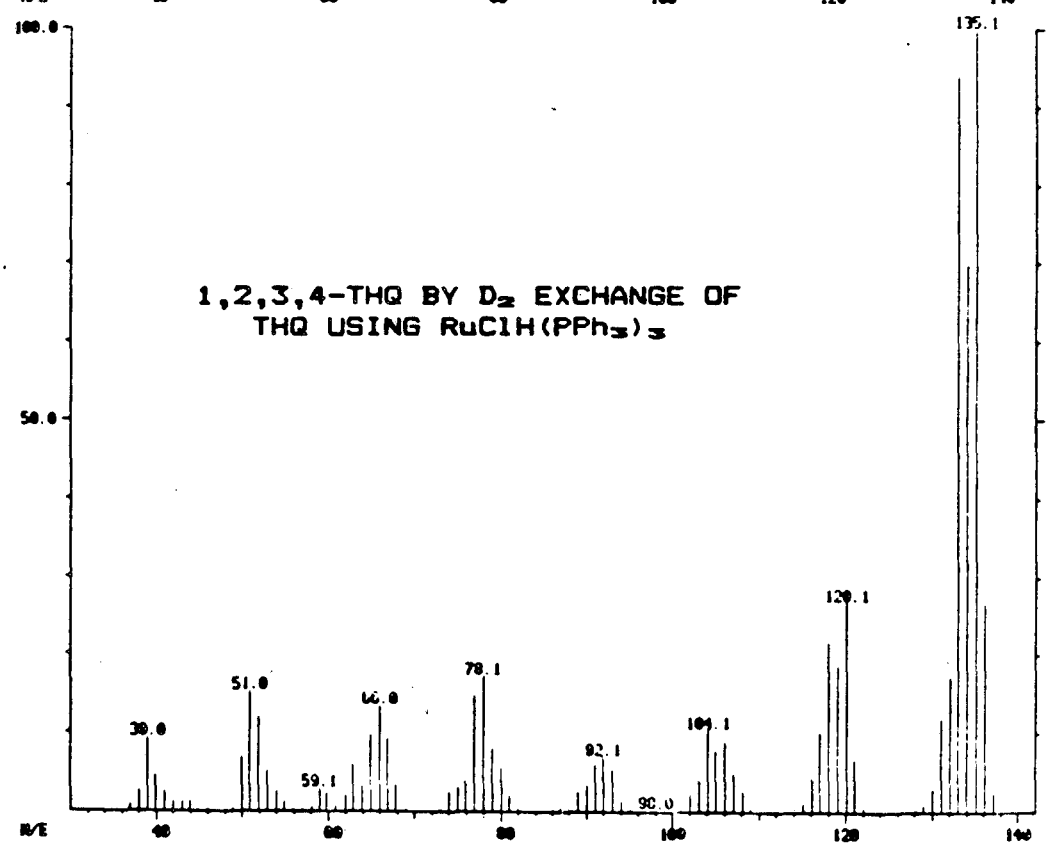

9,10-DIHYDROPHENANTHRIDINE / PHENANTHRIDINE
MIXTURE BY D_2 REDUCTION OF PHENANTHRIDINE
USING $RhCl(PPh_3)_3$
8
6
4
2
0
PPM

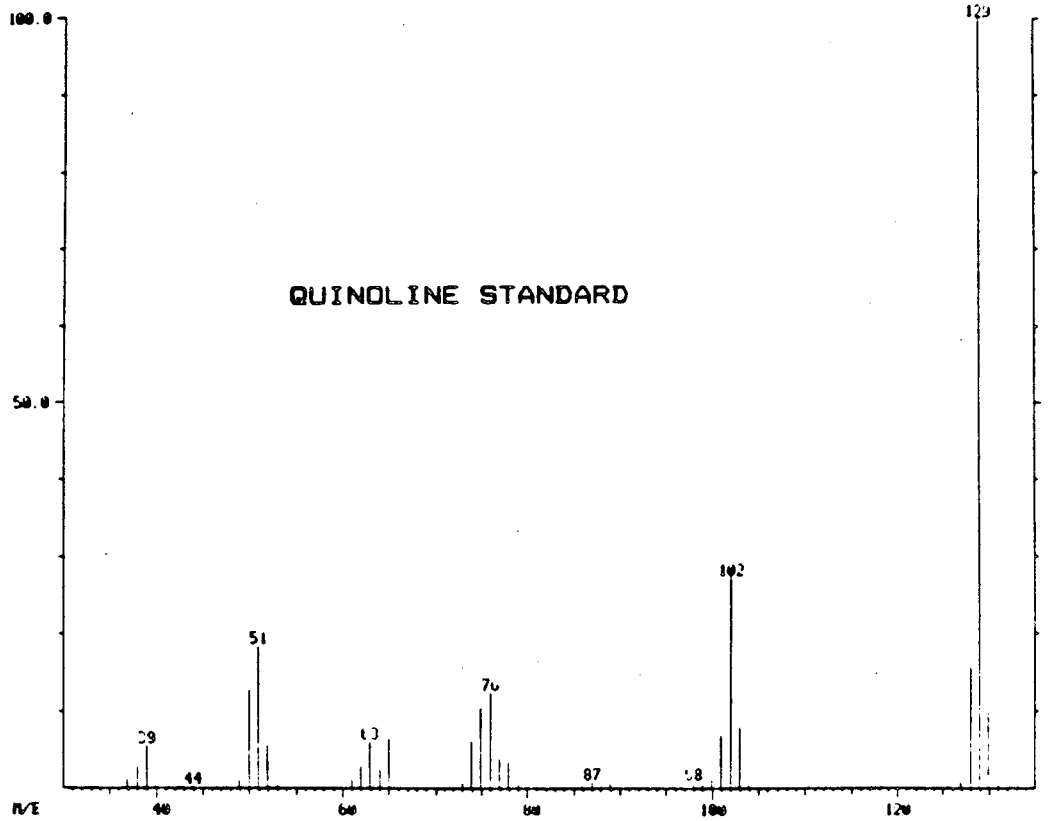

1,2,3,4-THQ STANDARD
132
117
91
77
65
59
51
44
39
100.0
50.0
M/E

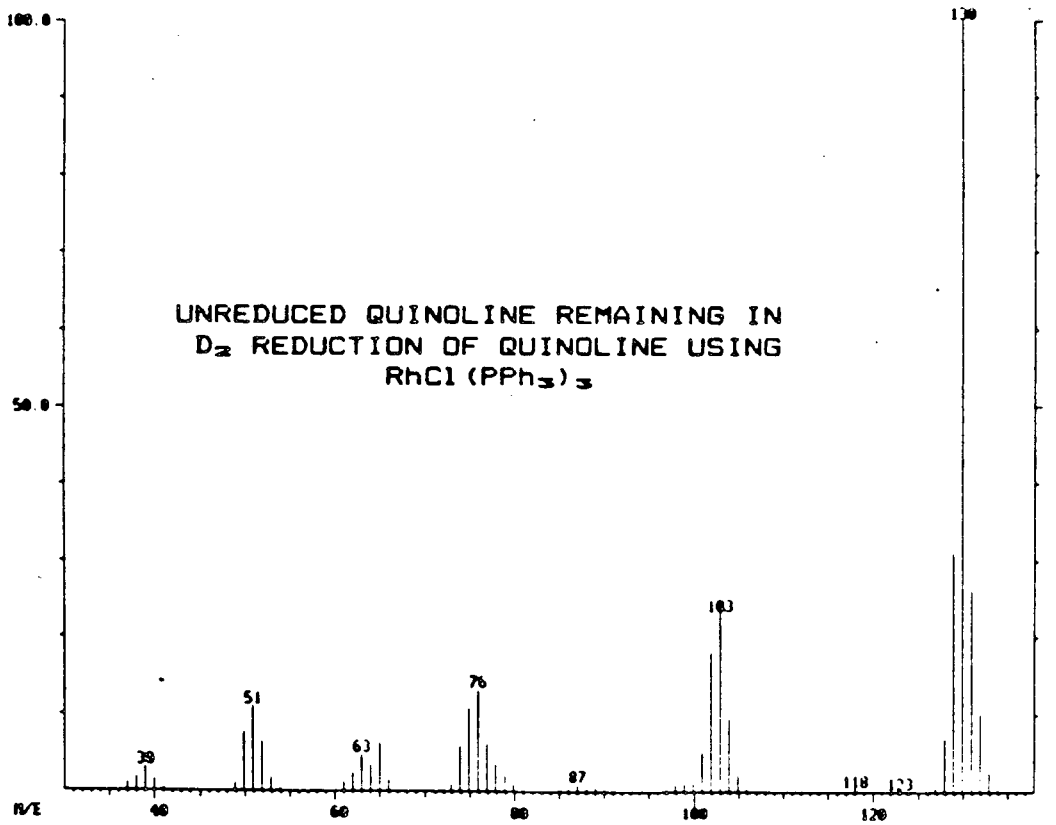

1,2,3,4-THQ BY D_2 REDUCTION OF QUINOLINE USING $RhCl(PPh_3)_3$
100.0
50.0
136.1
120.1
79.1
66.9
52.0
39.0
59.1
93.1
107.1
152.8
M/E
40
60
80
100
120
140

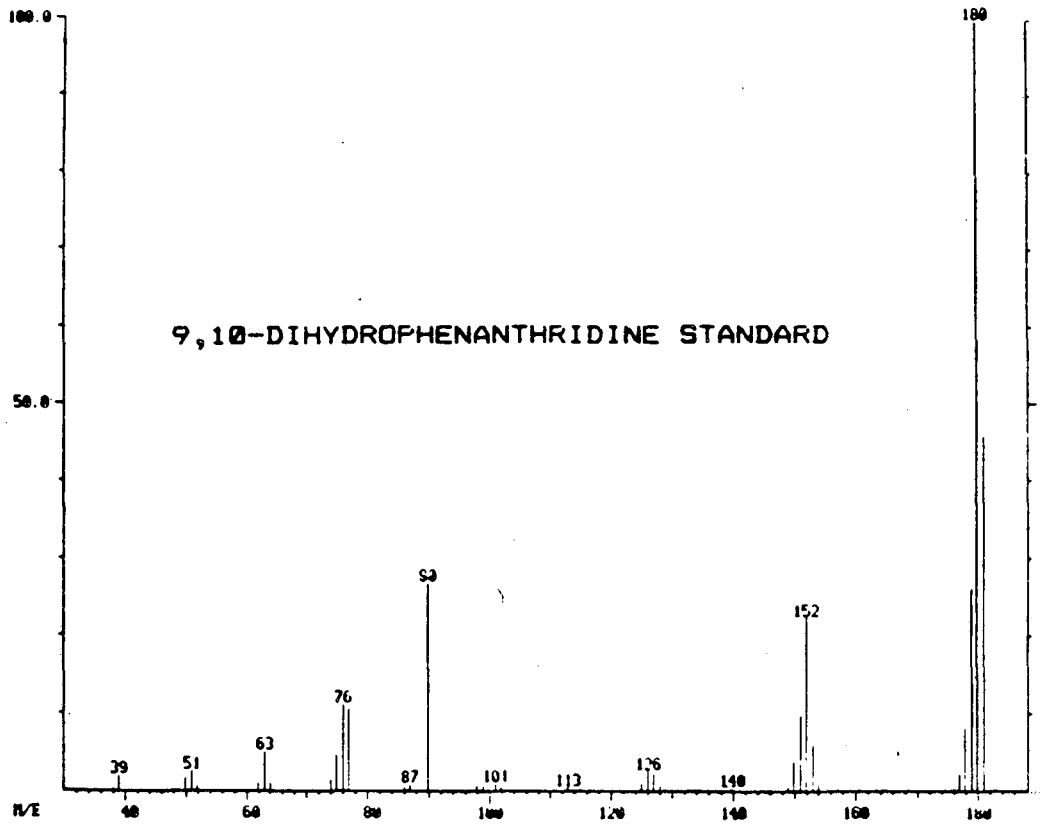

1,2,3,4-THQ BY D_2 REDUCTION OF QUINOLINE USING POLYMER-SUPPORTED $RhCl(PPh_3)_3$
100.0
50.0
135.1
120.1
79.1
67.0
52.1
39.1
44.1
59.9
91.1
105.1
152.1
M/E
40
60
80
100
120
140

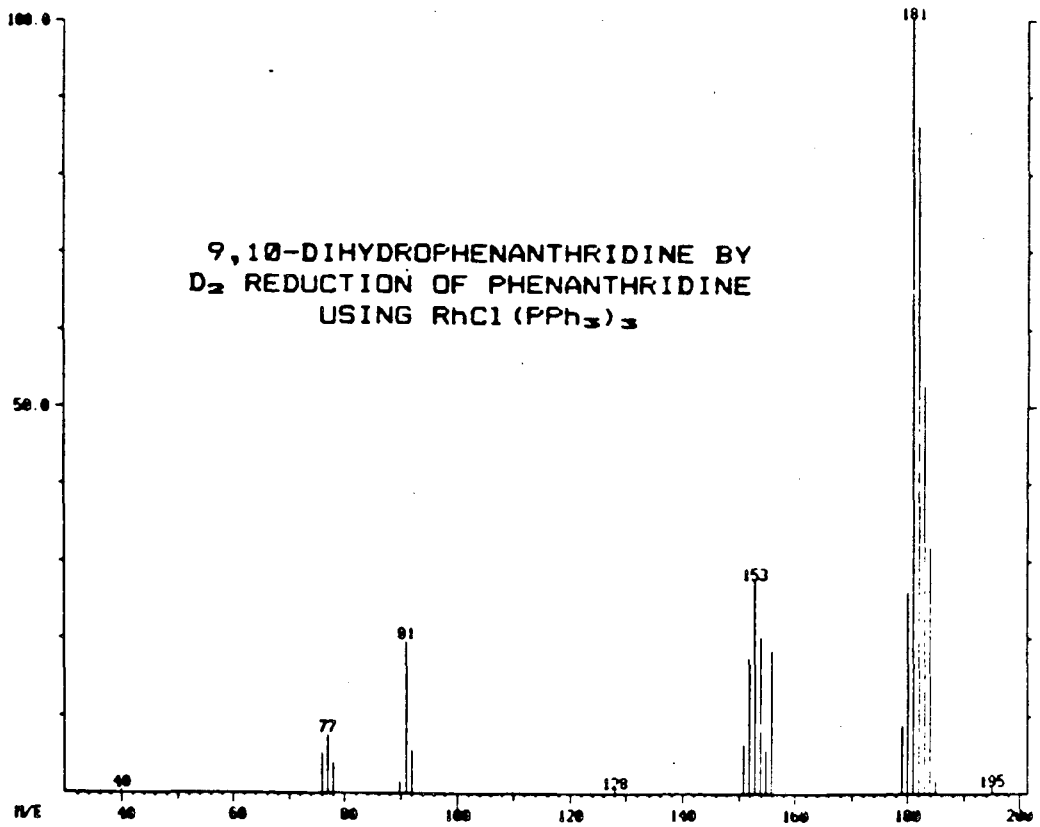

1,2,3,4-THQ BY D_2 REDUCTION OF
QUINOLINE USING $RuClH(PPh_3)_3$
100.0
50.0
M/E
135.1
120.1
78.1
67.0
52.0
39.0
59.9
93.1
105.1
40
60
80
100
120
140


1,2,3,4-THQ BY D_2 EXCHANGE OF
THQ USING $RuClH(PPh_3)_3$
100.0
50.0
M/E
135.1
120.1
78.1
51.0
38.0
59.1
92.1
90.0
104.1
40
60
80
100
120
140


QUINOLINE STANDARD
100.0
50.0
M/E
129
102
51
76
39
44
63
87
40
60
80
100
120


UNREDUCED QUINOLINE REMAINING IN
D2 REDUCTION OF QUINOLINE USING
RhCl(PPh3)3
100.0
50.0
M/E
130
103
51
76
39
63
87
118
123
40
60
80
100
120


9,10-DIHYDROPHENANTHRIDINE STANDARD
100.0
50.0
180
93
152
76
63
39
51
87
101
113
126
140
M/E
40
60
80
100
120
140
160
180


9,10-DIHYDROPHENANTHRIDINE BY
D2 REDUCTION OF PHENANTHRIDINE
USING RhCl(PPh3)3
100.0
50.0
181
153
91
77
40
178
195
M/E
40
60
80
100
120
140
160
180
200

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