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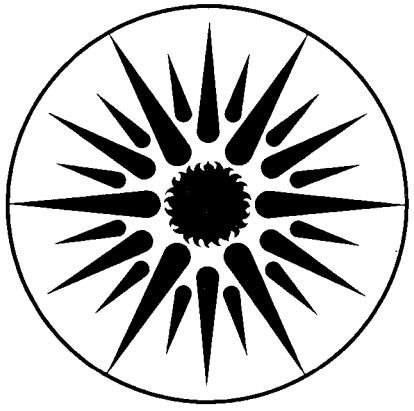

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Homogeneous Catalytic Hydrogenation of Aromatic Hydrocarbons and Heteroaromatic Nitrogen Compounds: Synthetic and Mechanistic Aspects

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Abstract:

The synthetic and mechanistic aspects of the homogeneous catalytic hydrogenation of mono and polynuclear aromatic hydrocarbons and the corresponding heteroaromatic nitrogen compounds will be reviewed. A comparison of the regioselectivities under various hydrogenation conditions for both classes of compounds will be discussed for a wide variety of transition-metal complexes with regard to substrate binding at the metal center and the role of free radical intermediates in metal carbonyl hydride reactions, where substrate does not bind to the metal center prior to hydrogen transfer. The polynuclear heteroaromatic nitrogen compounds appear to hydrogenate more readily, under similar reaction conditions, than the polynuclear aromatic hydrocarbons. The relative rates of hydrogenation of a variety of heteroaromatic nitrogen compounds as well as compounds that inhibit and enhance selective hydrogenation of the nitrogen-containing ring will be addressed. A relatively new spectroscopic technique, high pressure nuclear magnetic resonance spectroscopy, will be shown to be a powerful tool to elucidate the mechanisms of the regioselective hydrogenation of polynuclear heteroaromatic nitrogen compounds.

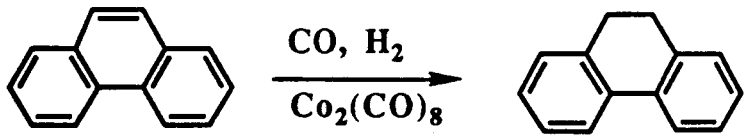
Introduction

The use of homogeneous catalysts to effect the selective hydrogenation of polynuclear aromatic and heteroaromatic nitrogen compounds found its impetus in studies on the use of these compounds as models for similar structures found in coal. The practical importance being that hydrogen up-grading and removal of nitrogen as well as sulfur from fossil fuels are dependent somewhat on the regioselectivity of the hydrogenation reactions. Since transition-metal, homogeneous hydrogenation catalysts are known to operate at lower temperatures and lower pressures of hydrogen gas in comparison to their heterogeneous counterparts and, more importantly, are more selective, this then makes them interesting complexes to study from a synthetic and mechanistic point of view.[1]

In this chapter, the synthetic scope and known mechanistic aspects of the homogeneous catalytic hydrogenation chemistry of aromatic hydrocarbons and the corresponding heteroaromatic nitrogen compounds will be reviewed. This will include the studies using Fe, Co, Mn, Rh, and Ru complexes under water gas shift (CO, H_2O); synthesis gas (CO, H_2); and hydrogen (H_2, alone) reaction conditions. The bonding mode of the polynuclear aromatic and heteroaromatic nitrogen ligands will be also be addressed to ascertain its important role in the regiochemistry of these selective reductions. The mechanisms of homogeneous catalyzed reductions are often characterized by kinetic evidence and the use of deuterium labelling as well as other spectroscopic information that may not always clearly define the exact pathway of the catalytic reaction. The recent advent of high pressure NMR spectroscopy will provide needed information about homogeneous hydrogenation mechanisms in real-time, and an example of the usefulness of this powerful technique will be presented for the regioselective reduction of quinoline to 1,2,3,4-tetrahydroquinoline with a cationic organorhodium complex.

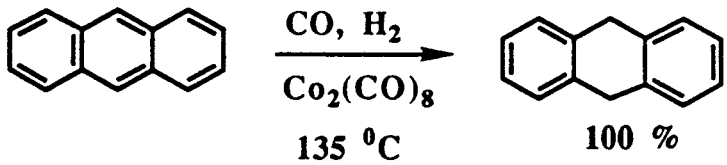
Hydrogenation of Mono and Polynuclear Aromatic Hydrocarbons

The earlier reports by Friedman and Wender and their co-workers in this relatively unstudied area of homogeneous catalysis were concerned with polynuclear aromatic compounds such as phenathrene with CO and H_2 in the presence of $Co_2(CO)_8$ (eq1).[2]



(1)

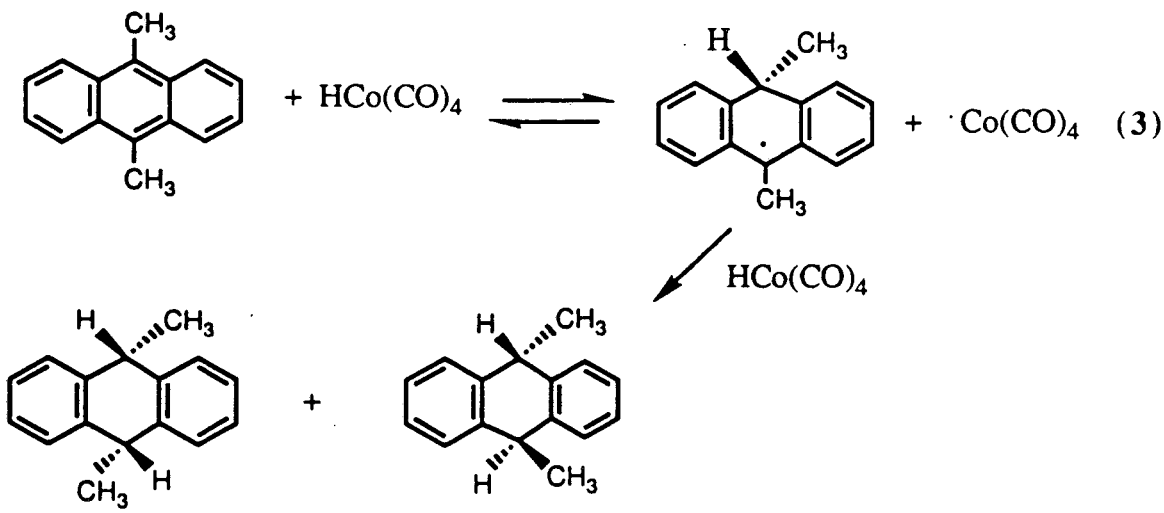
However, the linear polynuclear aromatic compounds such as anthracene were found to be more active under the hydrogenation conditions and at lower temperatures (eq 2).[2]



(2)

The results can be rationalized by the mechanism of hydrogenation, which was elucidated by several groups[3a-c] and entails the formation of $(CO)_4CoH$ followed by hydrogen radical addition to the aromatic nucleus to give a carbon radical.[3a] The carbon radical then abstracts a hydrogen from another cobalt hydride to form product. The free radical mechanism is also supported by reduction of 9,10-dimethylanthracene to provide a ~1:1 mixture of *cis* and *trans*- 9,10-dihydro-9,10-dimethylanthracene (eq3).[3c]

$$H_2 + Co_2(CO)_4 \rightleftharpoons 2HCo(CO)_4$$



(3)

A similar mechanism was found for the manganese analogue, $HMn(CO)_5$, for the reduction of 9,10-dimethylanthracene to a 1:1 mixture of the *cis* and *trans* dihydro derivatives.[4] One reason that the linear hydrocarbons are more reactive than their bent analogues is that in these latter cases the formation of the benzyl radical is accompanied by the stabilization of two phenyl groups not one (eq 3). This lowers the activation energy for H· radical addition and has a profound effect on the rate of reaction.

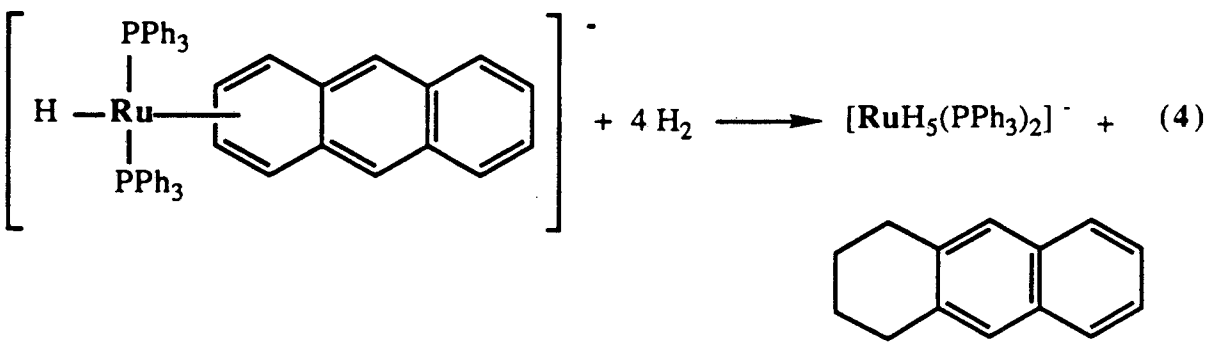
Several years ago, Fish and co-workers were intrigued by the possibility of using carbon monoxide and water in the presence of a base, i.e., water-gas shift conditions (wgs), as a reducing agent (in situ generation of transition-metal carbonyl hydrides) for polynuclear aromatic model coal compounds.[5-7] Thus, they reacted anthracene, phenanthrene, and pyrene with a number of transition-metal carbonyl complexes [$M_X(CO)_Y$ M = Fe, Co, Mn, Rh, Ru, W, Mo, Cr,] and found that only anthracene was reduced to 9,10-dihydroanthracene with Mn, Co, and Fe carbonyls, while the other polynuclear aromatic compounds and transition-metal carbonyls studied were inactive. They concluded that this metal carbonyl reactivity was based on the least reactive water-gas shift catalysts having the best hydrogenation activity, i.e., hydrogenation of polynuclear aromatic substrate being competitive with loss of hydrogen gas, and also provided clear evidence that the hydrogen came from H_2O by substituting D_2O for H_2O and finding 9,10-dideuteroanthracene.[5]

Fish and co-workers also found that under synthesis gas (sg) conditions (CO, H_2), with $Mn_2(CO_8(Bu_3P)_2$ as the catalyst, better yields of 9,10-dihydroanthracene were obtained when compared to yields under wgs conditions.[5-7] Again, they found, as did others,[2] that the linear polynuclear aromatic compounds were more reactive under either wgs or sg conditions.

The question of why Ru carbonyls were not very good catalysts under wgs conditions was answered when CO was removed from the reaction mixture using $Ru(Cl)_2(CO)_2(Ph_3P)_2$ as a catalyst with anthracene as the substrate.[5] It was found that the regioselectivity changed dramatically in going from Mn and Co carbonyls under wgs or sg conditions to Ru under base and H_2 conditions. Thus, with the former catalysts, 9,10-dihydroanthracene was the exclusive product, while the latter Ru carbonyl catalyst provided, regioselectively, 1,2,3,4-tetrahydroanthracene. The differences in mechanism

were evident in that with the Ru carbonyls substrate binding to the metal center was a prerequisite for reduction to occur, while with the Mn and Co carbonyls this was not necessary, since changes in the carbon monoxide pressures were independent of product formation.

Consequently, carbon monoxide must act as a competitive inhibitor with polynuclear aromatic substrates for the Ru metal center. Halpern and co-workers have studied the mechanism of selective anthracene hydrogenation with Ru polyhydrides. They were able to clearly show that anthracene binds η^4 to the Ru metal center, via the reaction of fac-$[RuH_3(PPh_3)_3]^-$ with anthracene, followed by the isolation and identification of $[RuH(Ph_3P)_2$anthracene$]K$, and demonstrate that it forms 1,2,3,4-tetrahydroanthracene upon reaction with H_2 (eq 4).[8a] Halpern and Landis have also determined that the $[Rh(diphos)(\eta^6$-anthracene$)]^+$ complex reacts with H_2 to give 1,2,3,4-tetrahydroanthracene, again via a presumed η^4 hydride intermediate.[8b]



The more difficult to hydrogenate mononuclear aromatic compounds, such as benzene, have been the object of several studies and a brief review of this area would be of interest. While benzene and its derivatives were readily hydrogenated to cyclohexane with heterogeneous catalysts, similar reactivity with homogeneous catalysts has proven to be more difficult. One reason is that providing definitive evidence for a homogeneous reaction that is free of any "heterogeneous component" is not always easy, and another is the high

activation energy barrier for arene ring hydrogenation that is needed in order to overcome the resonance stabilization energies of arenes.

Among the more important studies in the area of benzene hydrogenation, were those of Muetterties and co-workers.[9,10] They discovered that simple organocobalt compounds of general formula, η^3-$C_3H_5Co[P(OR)_3]_3$ (R= CH_3, C_2H_5, C_3H_7), readily hydrogenated aromatic hydrocarbons in a steroselective manner at ambient temperature and low pressures of H_2; the most unique property of this homogeneous catalyst is that it provides all *cis* cyclohexane. However, one drawback is that it deactivates readily by hydride transfer to the allyl group to produce propene.

While the mechanism of hydrogenation of the arenes with the Co catalysts appears complex, a discussion of what is known is important. The first step apparently is the loss of the allyl ligand as propane and formation of a 14 e^- complex, $HCo[P(OR)_3]_2$, which can then form a η^4-benzene complex, $HCo[P(OR)_3]_2(\eta^4$-$C_6H_6)$. Thus, by a series of H additions to one face of the coordinated arene followed by oxidative addition of H_2 to cobalt a postulated sequence of η^4-η^3-η^3-η^4-η^3-η^3-η^2-η^1 hydrogenated arene complexes can be envisioned.[10] The last complex, $C_6H_{11}CoH_2[P(OR)_3]_2$, reacts to provide *cis* cyclohexane and $HCo[P(OR)_3]_2$, which then starts the catalytic cycle again.

The catalytic system also does not appear to undergo H-D exchange with aromatic hydrogens; with C_6H_6 and D_2 or C_6D_6 and H_2 the same product, $C_6H_6D_6$, is formed. However, it does appear that it can exchange hydrogen on a CH_3 group on the toluene reduction product, methylcyclohexane. The synthetic scope shows a pronounced steric requirement with the following order of arene reactivity: benzene > toluene > xylene > mestilyene > 1,2,4,5-tetramethylbenzene > 1,2,3-trimethylbenzene >>> hexamethylbenzene. The electronic effect is also pronounced with electron-withdrawing groups, F, CN, and NO_2, on an arene ring causing the systems to be unreactive.

Among the many factors that are important for arene hydrogenation to proceed is η^4 coordination, which lowers the aromatic resonance stabilization energy (bent arene) and provides a driving force for arene ring hydrogenation. The formation of η^4 as well as η^2 arene complexes may well be critical for any successful arene hydrogenation catalyst. For example, bis(hexamethylbenzene)ruthenium(0), with one arene ring in a η^4 coordination and the other η^6 is a long-lived catalyst for arene ring hydrogenation; it is thought that η^4 coordination (16e^-) is important in that it can oxidatively add H_2.[11,12] In related studies,

Bennett and co-workers discovered that a (hexamethylbenene)ruthenium (μ-chloro)(μ-dihydrido) dimer was an efficient arene hydrogenation catalyst.[13,14] Again η^4 coordination appears to be important in the postulated mechanism of arene ring hydrogenation with this system. Maitlis and co-workers found that the catalyst precursor with the formula $[Cp^*RhCl_2]_2$ (Cp^* = pentamethylcyclopentadienyl) was also efficient for arene hydrogenation in the presence of a base co-factor such as triethylamine.[15,16] The base is thought to be required to neutralize the HCl that is formed in the heterolytic cleavage of H_2 to form the active catalyst. High *cis* stereoselectivity was observed with disubstituted benzene derivatives and predominant formation of 1,2,3,4-tetrahydroanthracene from anthracene was also observed, again indicative of the importance of η^4 coordination.

Recently, Taube and co-workers discovered some interesting η^2 arene complexes, $(NH_3)_5Os(\eta^2\text{-}C_6H_6)$ that provided cyclohexene upon reaction with H_2 using a heterogeneous surface, Pd / C.[17,18] Other arene hydrogenation studies with purported homogeneous Rh complexes that included $[(PhO)_3P]_2(AcAc)Rh(I)$[19] and Rh amino acid complexes (anthranilic, N-phenylanthranilic)[20] were also published; the former paper did not provide enough information on catalyst stability and the latter complexes were not characterized structurally, therefore, making it difficult to fully understand this system. Larsen and co-workers have recently described a homogeneous ionic hydrogenation system that consisted of $H_2O{\cdot}BF_3$, H_2, and $(CH_3CN)_2PtCl_2$. This catalytic system reduced benzene, naphthalene, substituted naphthalenes, and other polynuclear arene derivatives. While mechanistic studies are still to be performed, it is possible that protonation provides a carbonium ion intermediate and this is trapped by a PtH complex. Thiols and thiophenols quench hydrogenation activity by presumably forming PtSR complexes that are inactive.[21]

The mechanisms of all these arene hydrogenation complexes depends on disruption of the aromaticity of the arene ring and it is obviously an area that needs further study. More examples of η^4 and η^2 arene complexes are necessary as is the study of these reactions using high pressure NMR techniques, which will be discussed in a subsequent section.

Hydrogenation of Mono and Polynuclear Heteroaromatic Nitrogen Compounds

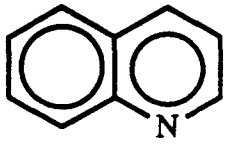
Prior to 1981, relatively little was known about the regioselective reductions of heteroaromatic nitrogen compounds, even though this class of model coal compounds is highly important to study from a fundamental point of view as well as from the fact that these compounds are prevalent in petroleum products and are an economic and environmental concern.[5] The earlier studies were able to demonstrate that quinoline, a representative polynuclear heteroaromatic nitrogen model coal compound, could be reduced regioselectively to 1,2,3,4-tetrahydroquinoline (THQ) (eq 5) under strictly hydrogenation [H_2, $RhCl_2Py_2(DMF)BH_4$][22] and under sg conditions [CO, H_2, $Mn_2(CO)_8(BuP)_2$].[23]

(5)

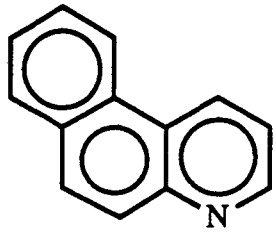
As well, Laine and co-workers were able to demonstrate that $Rh_6(CO)_{16}$ under wgs conditions (CO, H_2O) catalyzed the reduction of pyridine to piperidine and other piperidine derivatives.[24]

This basically was the state of the art with regard to heteroaromatic nitrogen compound homogeneous hydrogenation chemistry and in 1981 Fish and co-workers initiated a program to elucidate the synthetic scope and the mechanism of the selective hydrogenation of polynuclear heteroaromatic nitrogen compounds.[5-7] The important discovery that under a wide variety of conditions regioselectivity of the nitrogen ring was maintained, i.e., wgs, sg, and H_2 alone, provided a common characteristic for all these homogeneous hydrogenation reactions; however, profound differences in mechanism prevailed with respect to the transition-metal catalyst. In addition, the polynuclear heteroaromatic nitrogen compounds were far more reactive under all the homogeneous hydrogenation conditions studied than their carbon analogues, eg, acridine > anthracene.[5,6]

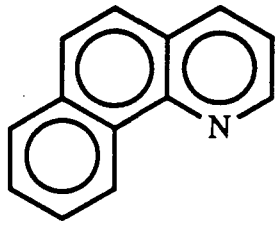
The Mn, Fe, and Co carbonyl complexes studied under wgs or sg catalytic conditions with quinoline, 5,6- and 7.8-benzoquinolines, acridine, and phenathridine were found to proceed independently of CO pressure, i.e., binding to the metal center was not rate limiting.



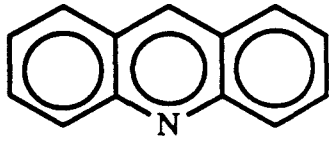
Quinoline



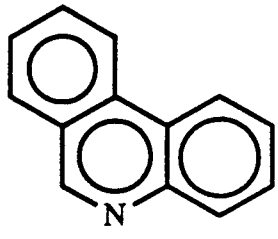
5,6-Benzoquinoline



7,8-Benzoquinoline



Acridine



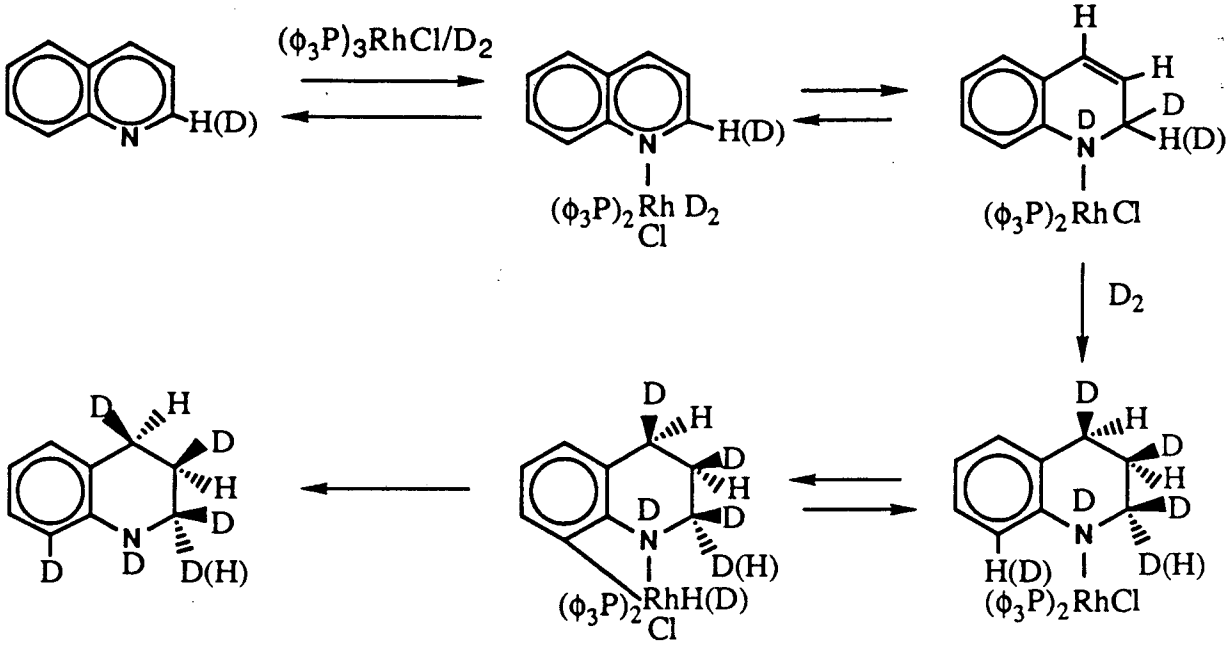
Phenanthridine

Kaesz and co-workers did an extensive study of the $Fe(CO)_5$ catalyzed reductions of polynuclear heteroaromatic nitrogen compounds under wgs reaction conditions.[25] They found a similar regioselectivity for the nitrogen ring and speculated that $[HFe(CO)_4]^-$ is the active catalyst and that an electron transfer mechanism prevails. Alternatively, it was found that the Ru carbonyls, $Ru(Cl_2)(CO_2)(Ph_3P)_2$ and $H_4Ru(CO)_{12}$,were inactive in the presence of carbon monoxide; again, as with the polynuclear aromatic compounds, binding of the nitrogen compound to the metal center appears to be a pre-rate determining step.[5] Thus, CO was acting as a competitive inhibitor under wgs or sg conditions. Murahashi and co-workers studied the selective hydrogenation of a variety of substituted quinoline derivatives under wgs conditions with $Rh_6(CO)_{16}$ as the catalyst.[26] Apparently, this Rh carbonyl cluster catalyst is able to reduce the quinoline compounds in the presence of CO, unlike the Ru carbonyl cluster complexes, which are inhibited in the presence of CO. As well, they notice a change in regioselectivity when the hydrogenation reaction is carried out with H_2 alone at 150 °C; from 4-methyl-1,2,3,4-tetrahydroquinoline (wgs) to 4-methyl-5,6,7,8-tetrahydroquinoline. This may be due to Rh carbonyl cluster catalyst decomposition at 150 °C to Rh metal; the fate of this Rh complex at the reaction temperature required is not mentioned by these workers and is suspect.

In their quest for a more active homogeneous catalyst for selective hydrogenation of

polynuclear heteroaromatic nitrogen compounds, Fish and co-workers discovered that $(Ph_3P)_3RhCl$ and $(Ph_3P)_3RuCl_2$ were excellent catalyst precursors for this purpose.[27-29] They defined structure-activity relationships with the above-designated model coal nitrogen compounds and found the order to be as follows: phenanthridine >> acridine >> quinoline > 5,6-benzoquinoline >> 7,8-benzoquinoline. They also found that pyridine and methyl derivatives totally quenched the hydrogenation of quinoline to 1,2,3,4-tetrahydroquinoline. This is indicative of competitive pyridine binding at the metal center, while the product THQ had a similar effect. Interestingly, they also found compounds such as pyrrole, carbazole, thiophene and, in particular, p-cresol enhanced the initial rate (% / min) of quinoline hydrogenation with the Rh catalyst by a factor of 1.5-2.5.

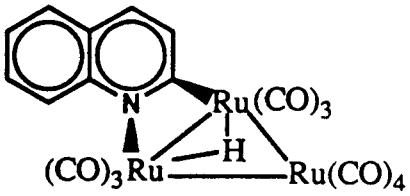
Substitution of deuterium gas for hydrogen gas allowed some insights into the mechanism of hydrogenation for these catalysts and is shown in the following scheme for the Rh catalyst.



Several important observations concerning this mechanistic scheme are as follows: Quinoline and D_2 (H_2) binding to the Rh metal center provides the driving force for reduction of the C=N bond; a reversible process, which provides D for H exchange at the 2-position of quinoline. Reduction of the 3,4 double bond occurs with *cis* stereochemistry, while exchange of the aromatic hydrogen at the 8-position is a consequence of a cyclometallation reaction. This latter exchange at the 8-position from the reduced nitrogen ring intermediate was proven by using 1,2,3,4-tetrahydroquinoline as the starting substrate in the above scheme and finding that the 8-hydrogen was exchanged for deuterium; no other H exchange was found by NMR analysis.[27]

The differences between the Rh and Ru catalysts were pronounced: the initial rates of hydrogenation of the nitrogen substrates for Ru / Rh was a factor of 3; the Ru catalyst was inhibited by several nitrogen compounds as with the Rh catalyst, but no rate enhancement was observed as was shown for the Rh catalyst with the above-mentioned compounds; D for H exchange of positions 2 and 8 was found for 1,2,3,4-tetrahydroquinoline with the Ru catalyst.[28,29]

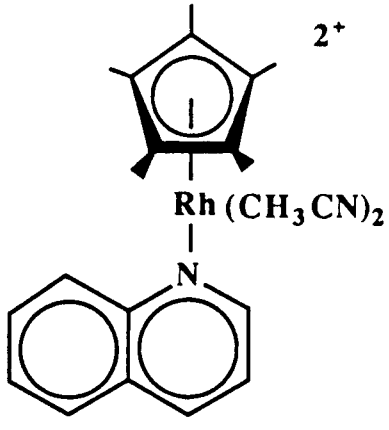
Studies on the bonding of quinoline, 1,2,3,4-tetrahydroquinoline, phenanthridine, and 9,10-dihydrophenanthridine with $Ru_3(CO)_{12}$ by Fish and co-workers[30] and similar studies with $Os_3(CO)_{12}$ and pyridine, quinoline, and 1,2,3,4-tetrahydroquinoline by Laine and co-workers[31] provided dimetallazacyclobutenes; potential models for cluster catalyst interactions with nitrogen heterocyclic compounds under hydrogenation conditions. Unfortunately, in the hydrogenation reaction of $Ru_3(\mu\text{-}H)(\mu,\eta^2\text{-quinoline})(CO)_{10}$, the cluster appears to be a sink for hydrogen with the formation of the very stable $H_4Ru_4(CO)_{12}$ and release of quinoline (eq 6).[30]



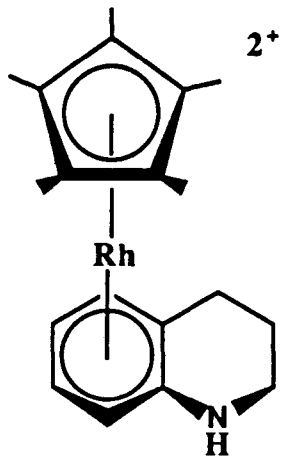
$$\xrightarrow[85\ ^{\circ}C,\ \text{toluene}]{500\ \text{psi}\ H_2} H_4Ru_4(CO)_{12} + \text{Quinoline} \quad (6)$$

The importance of understanding the bonding mode of polynuclear heteroaromatic nitrogen compounds to Rh metal centers can be directly related to the mechanism of selective hydrogenation of these compounds. In order to provide critical information on role of N(η^1) or π (η^6)-bonding in the selective hydrogenation of quinoline and related derivatives, Fish and co-workers initiated bonding and catalysis studies with η^5-pentamethylcyclopentadienylrhodium dication derivatives ($Cp^*RhL_nX_2$, L = p-xylene, $[CH_3CN]_3$, $[CH_3COCH_3]_3$; X= PF_6, BF_4) with a variety of mono and polynuclear heteroaromatic nitrogen compounds.[32]

The reaction of quinoline with $Cp^*Rh(CH_3CN)_3^{2+}$ provided an air and moisture sensitive complex, $Cp^*Rh(\eta^1, \text{N-quinoline})(CH_3CN)_2^{2+}$:



The reaction of this complex with traces of H_2O provided a crystalline derivative, $[Cp^*Rh(\eta^1, N\text{-quinoline})(OH)]_2^{2+}$, whose single crystal X-ray structure unequivocally verified N-bonding to Rh. Alternatively, reaction of $Cp^*Rh(CH_3CN)_3^{2+}$ with THQ gave the $Cp^*Rh(\eta^6\text{-THQ})^{2+}$ complex:



The significance of determining the N-bonding in the $Cp^*Rh(\eta^1, N\text{-quinoline})(CH_3CN)_2^{2+}$ complex and the $\pi(\eta^6)$-bonding in $Cp^*Rh(THQ)^{2+}$ was the fact that the synthetic precursor to these two complexes, $Cp^*Rh(CH_3CN)_3^{2+}$, was an efficient catalyst or catalyst precursor for the selective hydrogenation reaction of quinoline to THQ; this represents the first example of an organorhodium cationic complex acting as a catalyst for this conversion.[32] Thus, it appears from this result that N-bonding of the quinoline to the Rh metal center is necessary for selective hydrogenation of the nitrogen ring. The relative rates of hydrogenation (based on quinoline as the standard with an initial rate of 1% / min) were determined for quinoline, isoquinoline, and 2-methylquinoline and were found to be 1, .03, and 0.43, respectively in methanol at 80 °C.

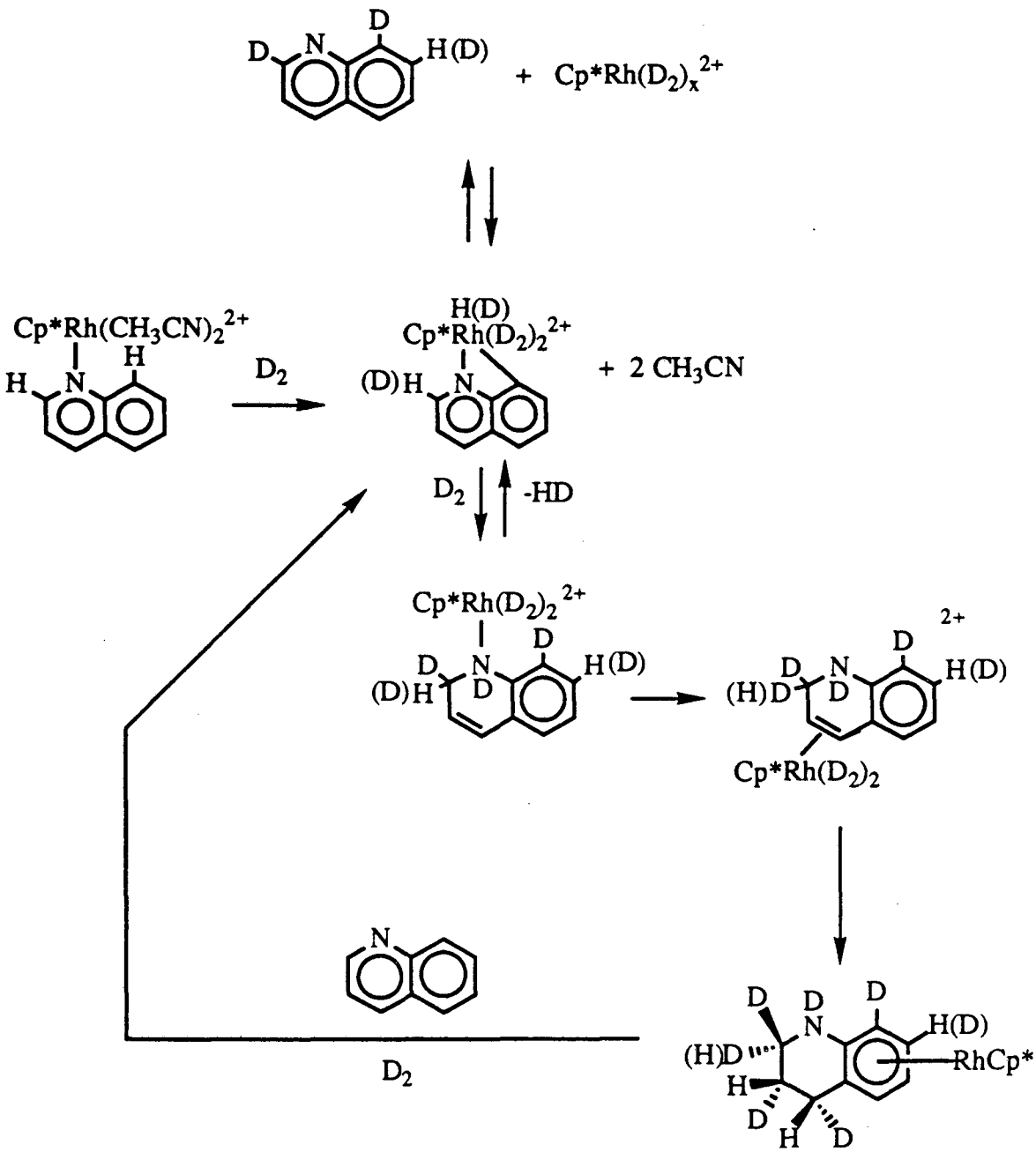
Recent results by Fish and Baralt have shown that solvent has a dramatic effect on the initial rate of quinoline hydrogenation; dichloroethane increasing the initial rate of quinoline hydrogenation over methanol by a factor of ~3.[33] The methanol apparently can reduce the quinoline hydrogenation rate by competing with quinoline for the Rh metal center. A similar solvent effect during quinoline hydrogenation was discovered by Sanchez-Delgado and co-workers with $HClRu(CO)(Ph_3P)_3$ as the catalyst and toluene, acetonitrile, and

methanol as solvents. They compared the % conversion of quinoline to THQ for the three solvents and found that acetonitrile quenched the hydrogenation activity, while in toluene, the % conversion was 9 times that in methanol.[34]

High Pressure Nuclear Magnetic Resonance Studies: The Mechanism of Quinoline Hydrogenation with Cp^*Rh^{2+}

The advent of high pressure nuclear magnetic resonance spectroscopy (HPNMR) provides the catalysis chemist with an opportunity to observe, in real -time, the catalytic reaction of interest.[35] Thus, Fish and Horvath and co-workers have studied the selective hydrogenation of quinoline with $Cp^*Rh(CH_3CN)_3^{2+}$ as the catalyst using the HPNMR technique.[36] The $Cp^*Rh(\eta^1$, N-quinoline$)(CH_3CN)_2^{2+}$ complex, which is shown above, was prepared *in situ* in the sapphire HPNMR tube in methylene chloride-d_2 at probe temperature (30 °C). The NMR spectrum was run and the Cp*Rh signal at 1.78 ppm as well as quinoline hydrogens from ~ 7.4-8.9 ppm were present. The HPNMR tube was then pressurized to 500 psi with D_2 gas and spectra were recorded at probe temperature for 23h.

The scheme shows the results of these HPNMR experiments and they are as follows: (1) the hydrogen on the 8-position of quinoline at 8.2 ppm is rapidly exchanged for deuterium prior to any nitrogen ring hydrogenation, while the signal for the starting complex at 1.78 ppm disappears with a concomitant formation of free acetonitrile; (2) the hydrogen on the 2-position of quinoline at 8.9 ppm is exchanged in a reversible process as nitrogen ring reduction (1,2-N=C) proceeds, while hydrogen exchange at 7.75 ppm assigned to the 7-position also occurs to a small extent , but as yet, via an unknown mechanism; (3) the reversible reduction of the N=C bond places ~1.5 deuteriums at the 2-position of the product THQ; (4) we speculate that Cp^*Rh^{2+} migrates to the 3,4-double (η^2) from nitrogen, after C=N bond reduction, and stereoselectively reduces the olefin via a *cis* addition of D_2; (5) the Cp*Rh then coordinates to the benzene ring (η^6), and this $Cp^*Rh(\eta^6$-THQ$)^{2+}$ complex then undergoes a ligand exchange with the 14 fold excess of quinoline over $Cp^*Rh(CH_3CN)_3^{2+}$ to start the catalytic cycle again.


D
N
H(D)
D
+ Cp*Rh(D2)x2+
Cp*Rh(CH3CN)2 2+
H
N
H
D2
H(D)
Cp*Rh(D2)2 2+
(D)H
N
+ 2 CH3CN
D2
-HD
Cp*Rh(D2)2 2+
D
D
N
H(D)
(D)H
D
2+
D
D
N
H(D)
(H)D
D
Cp*Rh(D2)2
N
D2
D
D
D
N
H(D)
(H)D
RhCp*
H
D
H
D

The similarities to the above-mentioned proposed mechanism with $(Ph_3P)_3RhCl$ and its Ru analogue are apparent; however, the sequence of events were different. Clearly, this powerful HPNMR technique will allow more reliable information on homogeneous catalysis mechanisms than was previously known and further studies on other mono and polynuclear heteroaromatic nitrogen substrates are being carried out.

Conclusions

In this perusal of what is known about mono and polynuclear aromatic ring hydrogenation, it appears that new catalysts need to be discovered for these transformations and that more mechanistic information, particularly on the role of η^4 arene coordination during hydrogenation, is necessary. Studies on the regioselective hydrogenation of polynuclear heteroaromatic nitrogen compounds, under strictly H_2 conditions, has revealed that N-bonding to the organoRh and Ru centers is mandatory for selective hydrogenation to take place. The HPNMR technique will be able to answer questions about homogeneous catalysis mechanisms in real time that will provide new insights into these interesting reactions. It is the hope of this author that this review will stimulate other workers in these areas to follow new directions.

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