Modelling the Hydrodenitrogenation of Aromatic N-Heterocycles in the Homogeneous Phase

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Recent legislation directed at reducing nitrogen levels in fossil fuels has led to numerous studies of the hydrodenitrogenation (HDN) process, whereby nitrogen is removed from organic compounds in petroleum feedstocks. In this review a comprehensive study of the coordination, activation, hydrogenation, hydrogenolysis and denitrogenation of N-heterocycles assisted by transition metal complexes in either fluid solution or single-site systems, is reported. Furthermore, similarities to the reactions occurring in the HDN process over commercial heterogeneous catalysts are also discussed.

Introduction

Under the business pull and environmental push, increasing research efforts are being made to design more efficient catalysts for the hydrodenitrogenation (HDN) of fossil fuels. To this purpose, studies applying molecular complexes have provided valuable mechanistic information on the adsorption modes of aromatic N-heterocycles as well as their hydrogenation and hydrogenolysis reactions. All relevant HDN modelling studies are reviewed in this paper that also provides a brief overview of the heterogeneous HDN mechanisms.

Petroleum and other fossil fuel feedstocks are contaminated by variable amounts of organic compounds containing sulfur, nitrogen and oxygen and, to a much lesser extent, by inorganic compounds, mainly in the form of metalloporphyrins. The presence of all these substances considerably damages the refining processes employed to upgrade feedstocks to product fuels, and ultimately lowers the quality of the latter. Indeed, besides poisoning the catalysts for the cracking and reforming reactions, hydrocarbons containing heteroatoms generate, upon combustion, dangerous polluting agents such as sulfur and nitrogen oxides (SO_x, NO_x).

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Claudio Bianchini (left) was born in Florence, Italy, in 1949 and received his ''Laurea'' in Chemistry from the University of Florence in 1973. Upon graduation, he joined the Chemistry Department as a bourse-holder (1974−1975). He then moved to the Research Center of the pharmaceutical industry A. Menarini in Florence (1976−1977) as research officer. In 1977, he was offered a position at ISSECC-CNR, Florence, by Prof. L. Sacconi. Currently Director of ISSECC, his research interests include homogeneous and heterogeneous catalysis (HDS, HDN, polymerisation and copolymerisation of olefins), asymmetric catalysis and organometallic reactions. He has authored about 300 papers and patents.

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MICROREVIEWS: This feature introduces the readers to the authors' research through a concise overview of the selected topic. Reference to important work from others in the field is included.

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The discovery of heavy oil reservoirs world-wide and the growing use of coal and oil shale for the production of fuels are pushing the petrochemical industry to invest an increasing amount of human and financial resources in the research and development of more efficient catalysts for removing heteroatoms from fossil fuels. This purification is currently carried out under hydrotreating conditions in the presence of heterogeneous catalysts and, depending on the element to be removed, involves four main chemical processes: hydrodesulfurisation (HDS), hydrodenitrogenation (HDN), hydrodeoxygenation (HDO) and hydrodemetalation (HDM) [Equations (1) to (4)].[1]

$$C_aH_bS + c\ H_2 \rightarrow H_2S + C_aH_d$$
Hydrodesulfurisation (HDS) (1)

$$C_aH_bN + c\ H_2 \rightarrow NH_3 + C_aH_d$$
Hydrodenitrogenation (HDN) (2)

$$C_aH_bO + c\ H_2 \rightarrow H_2O + C_aH_d$$
Hydrodeoxygenation (HDO) (3)

$$ML + a\ H_2 + b\ H_2S \rightarrow MS_b + LH_c$$
Hydrodemetalation (HDM) (4)

Of the four heterogeneous reactions outlined above, HDS has received, and is still receiving, the greatest attention for two principal reasons. Sulfur, contained in thiols, sulfides, disulfides and thiophenic molecules, is actually the most abundant heteroatom in fossil fuels and is also the element with the highest environmental impact. Furthermore, sulfur compounds are largely responsible for the poisoning of the hydrotreating catalysts. The importance of sulfur removal from crude oil feedstocks has therefore directed most of the R&D investments toward the HDS reaction, and in particular toward the design of more efficient heterogeneous catalysts. In parallel to studies under both actual and model reactor conditions, a considerable contribution to a better understanding of the HDS mechanism has been provided by homogeneous studies involving soluble metal complexes.[3−6] It is a common belief that many recent progresses in the field of heterogeneous HDS catalysis have been made with the contribution of the mechanistic information provided by the homogeneous studies.

Related to environmental push and business pull, increasing attention is now being paid to the HDN reaction. Indeed, the degradation of nitrogen compounds to ammonia and hydrocarbons consumes more hydrogen than any other hydrotreating reaction, and therefore any improvement in the efficiency of HDN catalysis would cause an immediate business advantage. From the environmental perspectives, nitrogen oxides and sulfur oxides contribute almost equally to the ravaging phenomenon known as "acid rain". Further, nitrogen oxides contribute to enhance the "greenhouse" effect and are certainly at the forefront in the undesired production of ground-level ozone that damages lung tissue, reduces lung function and sensitises the lungs to other irritants.[1,2]

Although nitrogen is largely produced in the combustion of air/hydrocarbon mixtures, the removal of nitrogen from feedstocks is of enormous importance and constitutes a major technological challenge for the 21st Century.

Nitrogen in petroleum and coal is contained in various organic compounds, which include five- and six-membered heterocycles, aliphatic and aromatic amines and nitriles. Some representative nitrogen compounds in fossil fuels are shown in Figure 1 (polyalkyl substitution is largely diffuse among cyclic compounds).

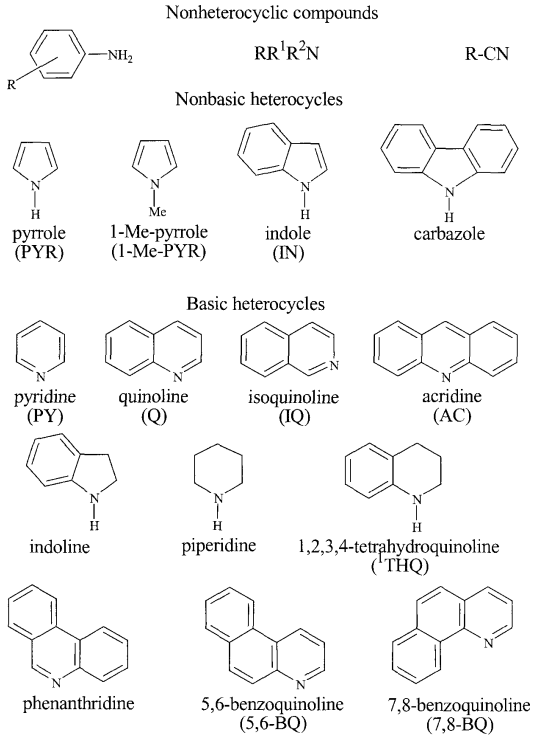


Figure 1. Some representative nitrogen compounds in fossil fuels

Amines and nitriles are less abundant and their degradation is efficiently performed under hydrotreating conditions applying commercial catalysts. The HDN of the aromatic heterocycles, generally pyrroles, indoles, quinolines and pyridines, is much more difficult to accomplish, even more than the HDS of fused-ring thiophenes. Moreover, HDN of the aromatic N-heterocycles requires a greater amount of H_2 than HDS of thiophenes, as the latter does not necessarily involve the saturation of the heterocyclic ring prior to hydrogenolysis.[1,7]

Although the intimate mechanism of metal-catalysed HDN is still far from being understood completely, a relatively rough mechanistic picture of this reaction is now available based on the combined efforts of heterogeneous and homogeneous studies. The former have provided data on product distribution, kinetics and selectivity, whereas the latter have contributed to the elucidation of the binding of the nitrogen substrates to metal centres and the mechanisms of fundamental steps such as the hydrogen-transfer from metal to coordinated substrate and the C-N bond scission.

Unlike HDS, no review article on homogeneous modelling studies of HDN has recently appeared, and therefore a complete overview of the interactions between single metal sites and N-heterocycles, alone or in combination with H_2, is missing in the relevant literature. Aimed at filling this gap, we have written this short review which takes into account

all recent results regarding the activation of N-heterocycles by soluble metal complexes, and also tries to provide some clues which will enable a comparison between heterogeneous and homogeneous HDN-related reactions.

The Heterogeneous HDN Reaction

General Information

In actual refinery reactors, HDN occurs simultaneously with all the other hydrotreating processes that include HDS, HDO, HDM, hydrodearomatisation (HDA), and hydrocracking. The reaction parameters are generally optimised for the HDS reaction, and therefore the experimental conditions and the catalysts employed are not the optimal ones for HDN, as the degradation of nitrogen compounds requires longer reaction times, as well as higher temperature and H_2 pressures than that of thiophenes.[1,7]

The HDN reaction is commonly performed at high temperatures (350−500 °C) and hydrogen pressures (200 bar), over heterogeneous catalysts composed of a γ-alumina support covered by metal sulfides. Mo or W are essential "components" but increased catalytic activity is achieved with the use of variable amounts of late transition metals such as Co, Ni, Ru, Rh, Ir, and Pt, which are called "promoters". Commercial catalysts are prepared by coimpregnation of γ-alumina with aqueous solutions of both a metal component salt (e.g. a Mo salt like $[NH_4][Mo_7O_{24}]$) and a promoter salt [e.g. a Co salt like $Co(NO_3)_3$], followed by reductive sulfidation with sulfur-containing compounds like H_2S, thiophene or CS_2. The Co and Mo exist primarily as Co_9S_8 and MoS_2.[8] The presence of H_2S during the reaction is believed to favour HDN, as it avoids the formation of metal oxides, which are much less active than metal sulfides. An active role of H_2S in the C−N bond scission step has also been demonstrated (vide infra).[9] The most efficacious HDN catalysts are based on Mo and Ni, probably because these catalysts exhibit the best performance in HDA.

In spite of significant progress in the field of surface characterisation (MES, EXAFS, FTIR, XAS, EPR spectroscopy, etc.), it has been concluded that the activity of the catalysts is related to sites located somewhere along the edges of small MoS_2 or Co(Ni)−Mo−S nanoclusters.[1a,10] In particular, the role of the promoters is still a matter of debate. According to a commonly accepted interpretation of HDS catalysed by "Co(Ni)−Mo(W)−S" phases,[1a,10,11] the active centres for the activation of the thiophenic molecules are the promoter atoms located at the edge plane of a MoS_2 single slab, whereas H_2 activation takes place on MoS_2 (or WS_2). The key role of the promoters in the activation of thiophenes has been confirmed by various homogeneous studies[3−6] that also agree with the conclusion that the desulfurisation requires the cooperation of more than one metal centre (component-promoter or promoter-promoter), and the multipoint coordination of the first C−S bond scission product (e.g. thiolate groups).[5a,12−14] A similar mechanistic picture may be proposed for HDN, e.g. the sulfur vacancies associated with Mo^{II} cations located at the edges of the MoS_2 crystallites are the sites where the hydrogenation of the N-heterocycles takes place, while the hydrogenolysis reactions would occur on acidic Mo−SH groups formed by interaction of M=S units with protons derived from the dissociation of H_2S over the catalyst surface.[1a]

It has been experimentally proven that aromatic nitrogen molecules undergo HDN via preliminary hydrogenation of the heterocyclic ring, followed by C−N bond scission (hydrogenolysis). The hydrogenation of the heterocyclic ring is necessary to reduce the high energy required to cleave the carbon−nitrogen bond that, in a typical N-heterocycle, is close to that of a C=N double bond.[7a]

Since the hydrogenation of the heterocycle to a saturated amine occurs prior to C−N bond cleavage, the position of the hydrogenation equilibrium actually controls the removal of the nitrogen atom, particularly when the hydrogenolysis rate is much slower than the hydrogenation rate. Unfavoured hydrogenation equilibria would result in a low concentration of saturated amine with the consequent decrease of the overall HDN rate. Accordingly, high pressures of H_2 are required for efficient HDN. The equilibrium constants for the hydrogenation of typical substrates such as quinoline (Q) and pyrrole (PYR) decrease with increasing temperatures as the ring reductions are exothermic. However, the hydrogenolysis and overall HDN equilibria are favourable, even at temperatures as high as 500 °C. Although the hydrogenation equilibria are unfavourable, the effect of higher hydrogen partial pressures, such as those used in industrial hydroprocessing, is to force the equilibria considerably toward the hydroprocessing products.[7a] Besides disfavouring the hydrogenation/hydrogenolysis equilibria, a low H_2 pressure may also lead to the undesired production of polycondensed N-heterocycles *via* catalytic dehydrogenation.[15] Indeed, kinetic modelling of the HDN process indicates that dehydrogenation of partially hydrogenated substrates such as tetrahydroquinoline (THQ) can be competitive with C−N bond cleavage, even in the presence of H_2.[7]

Adsorption Modes of N-Heterocycles over Heterogeneous Catalysts

In spite of many research efforts over the last twenty years and the progress made in developing surface spectroscopic techniques, very little is known about the detailed structure of the edges of the MoS_2 crystallites or Co(Ni)−Mo−S nanoclusters, as well as the nature of the active sites. This lack of information has strongly limited our knowledge of the interactions between N-heterocycles and the catalyst sites. As a result many hypotheses, often contradictory to each other, have been forwarded, but no precise conclusion has been reached.

A common belief is that basic heterocycles, such as Q, interact with the metal sites over the catalyst surface by two principal modes: *end-on* through the nitrogen atom and *side-on* through either ring (Figure 2). It is also agreed that in the absence of steric congestion provided by α-substituents, Q preferentially uses the nitrogen atom for interaction with the catalyst. In contrast, *side-on* coordination is fa-

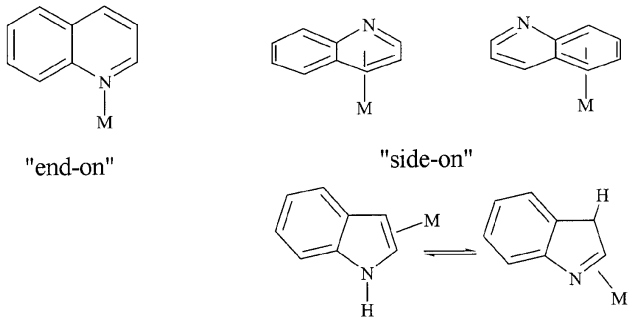


Figure 2. Postulated interactions of Q with the metal sites over the catalyst surface

voured for non-basic rings such as PYR and its higher homologues in which the nitrogen lone pair is not available for coordination.

In order to exemplify the level of uncertainty regarding the adsorption modes of N-heterocycles over the catalyst surface, Figure 3 shows the bonding modes of Q and THQ that have been proposed for HDN-active Ni^{2+} supported on SiO_2-Al_2O_3.[16]

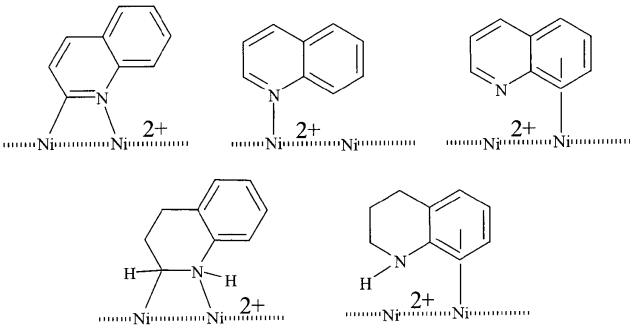


Figure 3. Proposed adsorption modes of Q and THQ over Ni^{2+} supported on SiO_2-Al_2O_3

HDN vs. Other Hydrotreating Processes

The nitrogen-containing compounds are more easily adsorbed over the catalyst surface than most of the heteroatom and aromatic compounds in fossil fuels. The adsorption of nitrogen compounds is so efficient that an almost continuous film may cover the catalyst surface. However, not all molecules undergo HDN due to the many possible unfavourable orientations. The strong tendency of nitrogen compounds for adsorption apparently disfavours adsorption of other substrates and ultimately inhibits other hydrotreating reactions, which, in some circumstances, may even favour HDN. Indeed, it has been found that the H_2S produced by HDS, although competing with the nitrogen compounds for adsorption (thus reducing the hydrogenation rate), promotes the hydrogenolysis step (vide infra).[9] Similarly, the H_2O formed in the HDO of many phenols and other O-heterocycles seems to enhance the overall HDN rate.[9a,17]

Principal Reaction Pathways and Mechanisms Proposed for Heterogeneous HDN

The principal reaction pathways proposed for the heterogeneous HDN of the model substrate Q[1,7,18] are shown in Scheme 1. A sequence of similar steps has also been suggested to occur for the HDN of PYR.

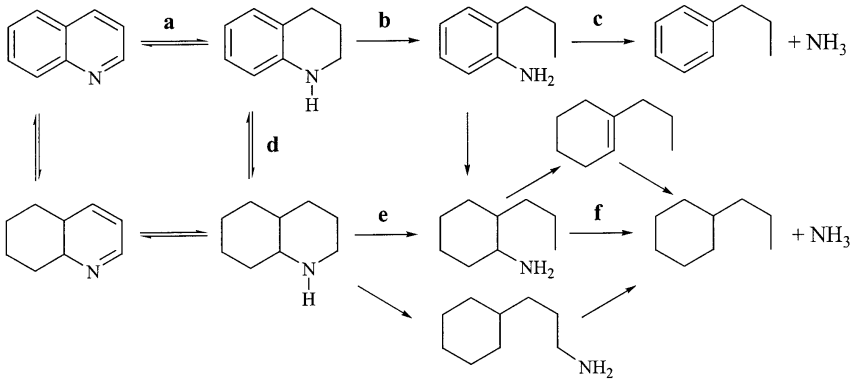
The most efficient and selective HDN of Q would proceed via the reaction sequence **a→b→c**, which does not involve the hydrogenation of the carbocyclic ring. The **a→b→c** sequence consumes less hydrogen than any other path, and also yields high quality product fuels as the residual aromaticity in the denitrogenated products increases the octane rating. However, most of Q undergoes HDN via the alternative sequence **a→d→e→f** that involves the hydrogenation of both rings and therefore consumes twice the amount of H_2, yielding propylcyclohexane. In neutral or basic media, the hydrogenation of the heterocyclic ring is faster than that of the carbocycle, i.e. the hydrogenation of Q to 1,2,3,4-tetrahydroquinoline (^{1}THQ) is faster than that of Q to 5,6,7,8-tetrahydroquinoline (^{5}THQ). In turn, the hydrogenation of ^{5}THQ to decahydroquinoline (DHQ) is faster than that of ^{1}THQ. This observation has been associated to the high π-electron density of the heterocyclic ring. It has been proposed that the hydrogenolysis of ^{1}THQ to *o*-propylaniline is slower than its hydrogenation to DHQ, because the adsorption of ^{1}THQ over the catalyst surface is hampered by its resonance form containing a double bond between the nitrogen atom and the proximal carbocyclic carbon atom.

Using the analogy of metal-catalysed hydrogenation of aromatics, it is proposed that the hydrogenation of N-heterocycles to saturated cyclic amines involves the formation of metal π-adducts, followed by a reductive π→s shift once the two consecutive hydrogen transfers have occurred from vicinal S−H groups. The mechanism is analogous to that reported by Kwart for the HDS of thiophene.[19] It has also been proposed that the metal centre activates the aromatic ring, behaving as an electrophile that delocalises the ring electron density.[7b]

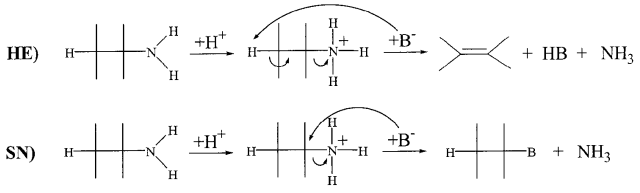
The hydrogenolysis of the C−N bonds in N-heterocycles is much more difficult to accomplish than the hydrogenation of the rings as well as the hydrogenolysis of C−S bonds. Indeed, homogeneous C−N scissions in N-heterocycles are very rare and exclusively stoichiometric in nature,[3c][3d] whereas several C−S bond insertions occurring in solution catalysts have been reported.[3−6] There is little doubt that the higher bond energy of C−N bonds as compared with C−S bonds (by 3−9 kcal mol^{-1}) contributes in making the catalysts less efficient for HDN than for HDS, under comparable experimental conditions.[7]

From a mechanistic viewpoint, the C−N bond cleavage has been suggested to occur through either a Hofmann-type elimination (HE) or a nucleophilic substitution (SN), both reactions being promoted by a base (Scheme 2).[20]

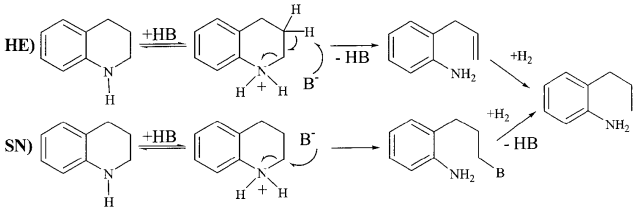
In this mechanistic picture, the first C−N bond cleavage in ^{1}THQ would require the cooperation of a protic acid whose conjugate base B^- may participate in either HE or SN mechanisms (Scheme 3). Many species present on the catalyst surface under hydrotreating conditions may act either as bases or nucleophiles: sulfydryl groups (SH^-) generated by the heterolytic splitting of H_2S, hydride ions (H^-), hydroxyl ions (OH^-) or even neutral molecules such as H_2S,



Scheme 1



Scheme 2



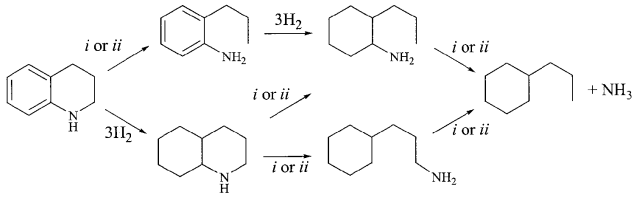
Scheme 3

H_2O, NH_3 or amines. In this mechanistic picture, the increase in the rate of hydrogenolysis by addition of H_2S, has been explained in terms of the enhanced production of H^+ and SH^- groups on the catalyst surface upon heterolytic splitting of H_2S.[7]

The second C−N bond cleavage to give NH_3 and *n*-propylcyclohexane completes the HDN process of Q consuming an overall amount of seven H_2 molecules per nitrogen atom. Furthermore, this step may occur through either HE or SN mechanisms.

It is worth noting that the saturation of the heterocyclic C_α atom is necessary to cleave the C−N bond *via* an SN mechanism, while both the C_α and C_β carbon atoms must have sp^3 hybridisation to allow for a C-N bond cleavage to occur *via* a HE mechanism. In the case of Q, this means that the hydrogenation of both rings is necessary to cleave the C−N bond *via* either mechanism, which is consistent with the formation of *n*-propylcyclohexane as the main HDN product (Scheme 4).

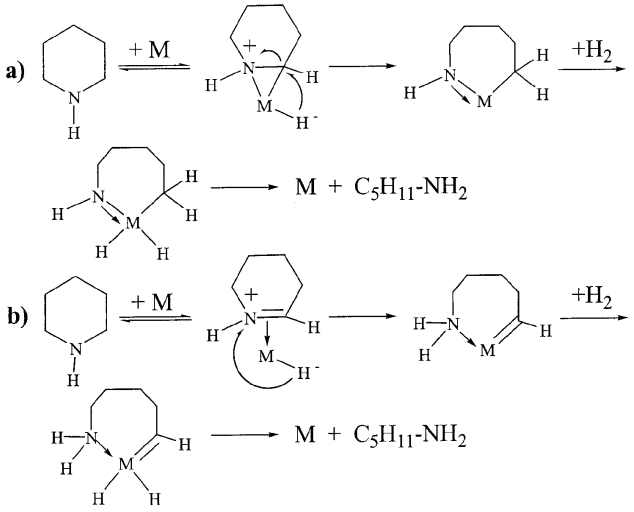
The interaction of the surface metal atoms with saturated N-heterocycles has been the object of model studies by Laine and co-workers.[7c,21] It has been suggested that the C−N scission in saturated heterocycles may not require acidic sites, but rather metal centres. Two possible pathways have been proposed for the HDN of piperidine which differ from each other with respect to the nature of the interme-



i = **HE** (+H^+, +B^-, -HB) + H_2
ii = **SN** (+H^+, +B^-) + (H_2, -HB)

Scheme 4

diate formed, either a metal alkyl species (**a**) or a metal alkylidene species (**b**) (Scheme 5). In either case, the first step has been suggested to involve the oxidative addition of the C−H bond adjacent to the nitrogen atom to give a metal(hydride) species. The subsequent migration of the hydride from the metal to either the C_α atom or the N atom of an η^2-piperidinyl ligand determines the nature of the intermediate that is ultimately hydrogenated to a primary amine.



Scheme 5

Model studies on the HDN of piperidine have also contributed to rationalise the beneficial effect of H_2S and H_2O on the rate of C−N hydrogenolysis. Nucleophilic attack by either molecule at the C_α atom would form sulfur-con-

taining intermediates that undergo hydrolytic C−N bond cleavage faster than in the absence of H_2S or H_2O.[7,9,17]

Similar mechanisms have also been proposed to account for the increased rate of C−N hydrogenolysis observed in the presence of other nucleophiles such as NH_3. However, under actual reactor conditions, the addition of NH_3 inhibits HDN, because NH_3 prevails over all the other nitrogen compounds for the interaction with the surface coordination vacancies.[7]

Homogeneous Modelling Studies

Homogeneous modelling studies involving soluble transition metal complexes represents one of the most fruitful approaches in providing mechanistic information on the elementary steps involved in the hydrotreating of fossil fuels. HDN model studies in solution are not as numerous and detailed as those involving HDS. Nonetheless, much of our current understanding of HDN is based on structural and reactivity information obtained in the homogeneous phase, in particular on four relevant issues: modes of bonding between N-heterocycles and metal centres, reactivity of coordinated N-heterocycles, elementary steps of metal-catalysed hydrogenation of N-heterocycles, insertion of metal centres into C−N bonds. A common strategy in HDN modelling is to react mononuclear or polynuclear metal complexes, containing either coordination vacancies or weakly bound ligands, with N-heterocycles.

Common model substrates are PYR, indole (IN), pyridine (PY), and Q together with their alkyl-substituted derivatives and/or their partially or completely hydrogenated products. These model substrates may be divided in two main categories according to the donor properties of the nitrogen atom. In compounds like PYR (pK_a = 0.4) and IN (pK_a = −3.6), the nitrogen lone pair is delocalised over the five-membered ring and is not available for interaction with electrophiles. In contrast, the nitrogen atom in PY (pK_a = 5.2) or Q (pK_a = 4.9) is a good nucleophile susceptible to attack by various electrophilic metal fragments. The different character of the nitrogen atom in the two types of substrates and the presence of aromatic carbocyclic rings is believed to remarkably influence their interaction with the heterogeneous catalyst surface and, consequently, the mechanisms for reduction. The homogeneous studies have indeed proved that both the basicity of the nitrogen atom and the presence of carbocyclic rings determine the binding mode of N-heterocycles to single metal sites, and ultimately control the further reactivity of the M−N heterocycle ensemble.

Binding Modes of N-Heterocycles in Transition Metal Complexes

A) Complexes with Pyrrole and Pyrrolyl Ligands

All known bonding modes of PYR and pyrrolyl ions, or their alkylated analogues, in mononuclear complexes are illustrated in Figure 4.

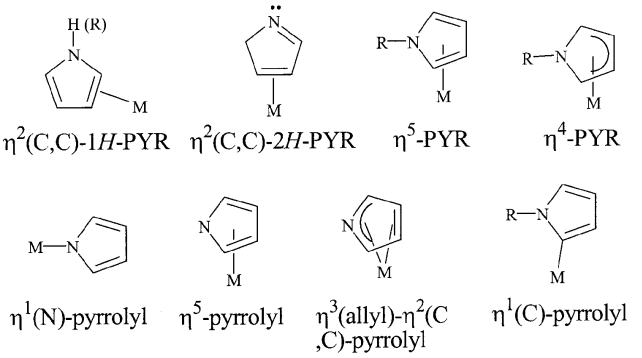


Figure 4. Known bonding modes of PYR and pyrrolyl ions in mononuclear complexes

No complex containing an η^1(N)-PYR ligand has ever been reported, even in the 3*H*-pyrrolidine structure which has been authenticated for IN (vide infra). The most numerous complexes are the η^5-PYR ones,[22] but some examples containing η^2(C,C)-PYR ligands have also been characterised.[23] The η^4 mode has been observed in one complex only.[24]

Metal complexes containing pyrrolyl ligands are ubiquitous in the periodic table, and common coordination modes are the η^1(N) and η^5 modes.[22a,25−27] However, depending on the nature of the supporting metal fragment, each bonding mode may be viewed as involving two distinct electronic forms.[27e]

The pyrrolyl group may be generated in situ by metal-assisted N−H activation of PYR,[26] or provided as a metal salt after N−H deprotonation with a base.[27] In the first case, a high-energy low-valent metal fragment is required to lower the energy barrier for N−H insertion, while $NC_4H_4^-M^+$ reagents (M = Na, K) are commonly reacted with electrophilic metal fragments. C−H bond activation to give η^1(C) pyrrolyl(hydride) metal complexes has also been described.[26c]

The interaction with polynuclear complexes to give an adduct containing intact PYR has never been reported. Either N−H and/or C−H bond activation is commonly observed, yielding bridging pyrrolyl ligands (Figure 5).[27a,27e,28,29]

Selective C−H bond cleavage of N-methylpyrrole is promoted by the dimer $[Cp^*IrH_3]_2$ ($Cp^* = C_5Me_5$), which, under comparable experimental conditions, is able to cleave both thiophene and 2-methylthiophene[28] (Scheme 6). This different reactivity is consistent with a higher energy barrier for C−N insertion than for C−S insertion, as is observed in heterogeneous HDN/HDS.

N−H activation, followed by two dehydrogenation steps has been found to transform pyrrolidine into an imidoyl ligand (Scheme 7).[30]

A particular type of pyrrolyl ligand is that found in the Mo dimer $[(Cp'Mo)_2(S_2CH_2)(\mu\text{-}S)(\mu\text{-}S\text{-pyrrolyl})]^+$, obtained by Rakowski DuBois upon nucleophilic attack by the electron-rich PYR molecule at the disulfide bond in $[(Cp'Mo)(\mu\text{-}S)_2(S_2CH_2)]_2^{2+}$ ($Cp' = C_5H_5$, C_5H_4Me) (Scheme 8).[31] A mechanism has been proposed which in-

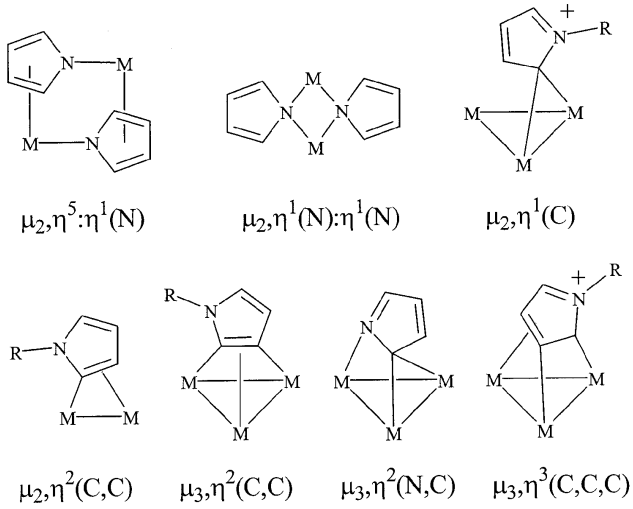
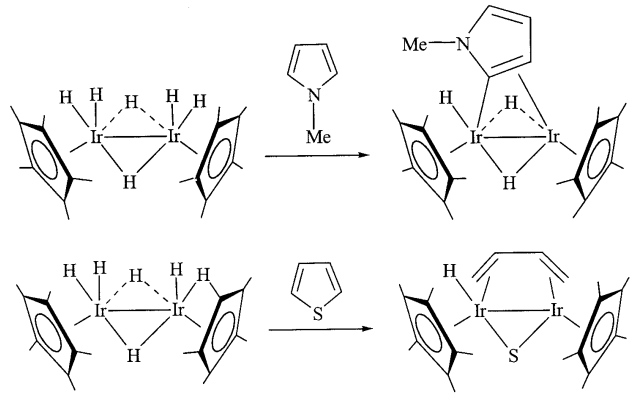


Figure 5. Bonding modes of pyrrolyl ligands in polynuclear complexes



Scheme 6

volves heterolytic scission of the S-S bond by the nucleophilic ring, followed by loss of a proton from the heterocycle to give a 1:1 mixture of μ-pyrrolylthiolate and μ-SH dimers. Alkyl-substituted pyrroles such as 1-Me-PYR or 1,2,5-Me_3-PYR behave similarly, but the regiochemistry of electrophilic addition may vary depending on the position of the substituent.

The ability of the pyrrole ring to attack S-S bonds is not diminished, neither when a metal is bound to the nitrogen atom as in Scheme 9 for $[ReCl_2(PMe_2Ph)_3(\eta^1(N)\text{-pyrrolyl})]$, nor when the nitrogen and a β-carbon atom are engaged in bonding to a metal and to a sulfur atom (Scheme 10). The selectivity for substitution at the β-position has been attributed to the steric bulk of pyrrole N-substituent.[31]

The formation of the unusual (η^1(C)-pyrrolyl)-SMo_2, Re-(μ,η^1(N):η^1(C)-pyrrolyl)-SMo_2 and Re-(μ,η^1(N):η^1(C):η^1(C)-pyrroldiyl)-$(SMo_2)_2$ groupings represents quite interesting models of the potential interaction of electron-rich N-heterocycles with a sulfided metal surface. Indeed, the presence of disulfide moieties over HDS/HDN catalysts has been demonstrated. Moreover, previous studies of thiophene adsorption over MoS_2 catalysts have hypothesised a S−S interaction between the surface sulfur and the substrate.[1,7]

B) Complexes with Indole, Indolyl, Indoline, and Indolinyl Ligands

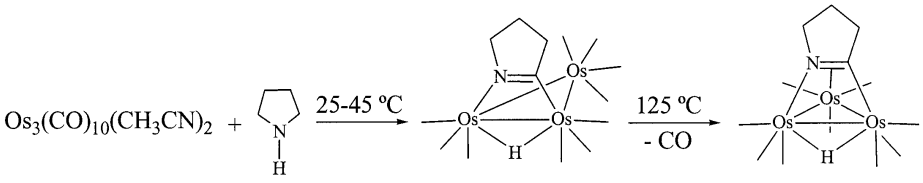
Indole (IN) differs from PYR by a condensed arene ring. This makes a great difference in the interaction with metal centres and produces a larger variety of possible coordination modes (Figure 6). Indeed, the presence of the carbocyclic ring allows IN to bind a metal centre using the arene ring, leading to the important η^6 mode.[32] Examples of η^1(N)-IN complexes have also been reported that may be better described as η^1(N)-3H-indolenine species.[33−35]

The indolyl anion coordinates mononuclear fragments using the nitrogen (η^1(N) mode),[26a][26e,35] the heterocyclic ring (η^5 mode),[32d,36] or the carbocyclic ring (η^6 mode).[32b]

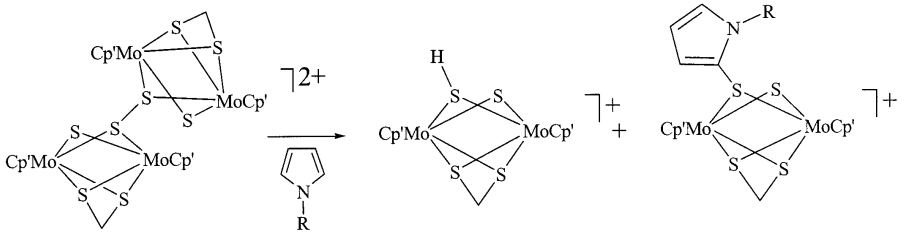
An interesting case of base-assisted η^6-IN → η^5-indolyl shift[32d] is illustrated in Scheme 11, while an acid-promoted η^1(N)-indolyl → η^1(N)-indolenine conversion[35] is shown in Scheme 12. Treating indolenine complexes with hydride produces η^1(N)-indolinyl derivatives.[32a][35b]

Electron-rich metal fragments can react with 2-substituted IN, yielding either kinetic C−H or thermodynamic N−H insertion products.[26d]

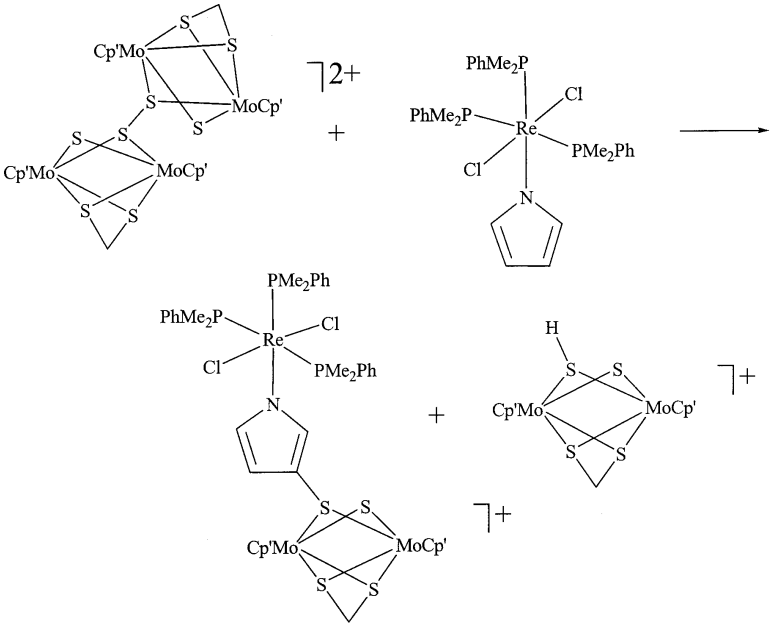
Like PYR,[31] 1-Me-IN has been found to react with the μ-S_2 tetramer $[(Cp'Mo\mu\text{-}S)_2(S_2CH_2)]_2^{2+}$ to give the elec-



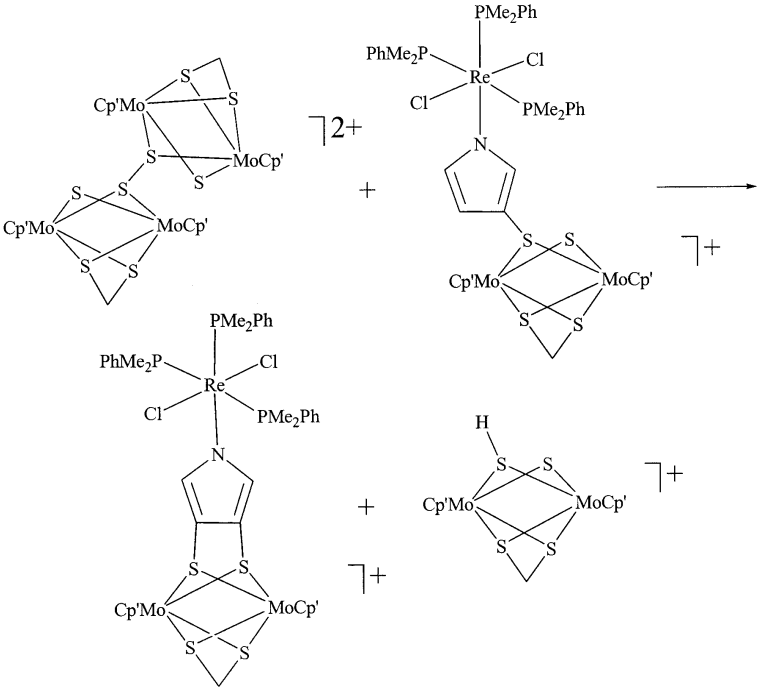
Scheme 7



Scheme 8



Scheme 9



Scheme 10

trophilic substitution product (Scheme 13). The reaction is mechanistically similar to that with PYR.

The coordination chemistry of indoline, obtained by selective hydrogenation of the heterocyclic ring of IN, has also been investigated.[32a] η^6 and η^1(N) Coordination modes, as well as their interconversion, have been reported.[31,35b,37] Of particular relevance are the studies carried out by Rakowski DuBois on the coordination, acid/base properties and activation of indoline by (*p*-cymene)Ru^{II} fragments.[32a,37] The complex [(*p*-cymene)Ru(η^1-indoline)$(CH_3CN)_2$)]$(OTf)_2$ converts to [(*p*-cymene)Ru(η^6-indoline)]$(OTf)_2$ upon gentle heating in CH_2Cl_2 and can be deprotonated to give the corresponding (η^1-indolinyl) complex[37] (Scheme 14). The reactivity of the latter compound is described in a following section.

The presence of the carbocyclic ring widens the range of possible bonding modes of IN to metal clusters.[34,38] As shown in Figure 7, IN, indolyl, indoline or indolinyl ligands may use both nitrogen and carbon atoms from either ring to bind metal centres.[34,38]

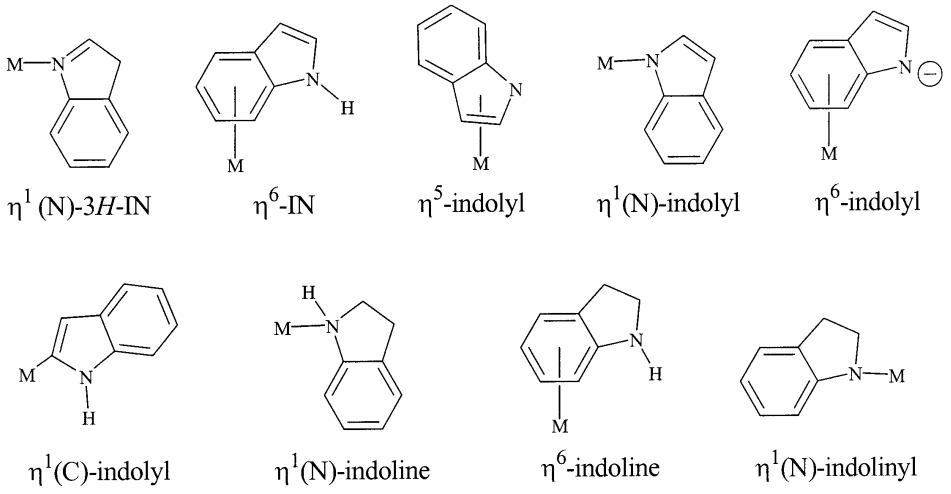
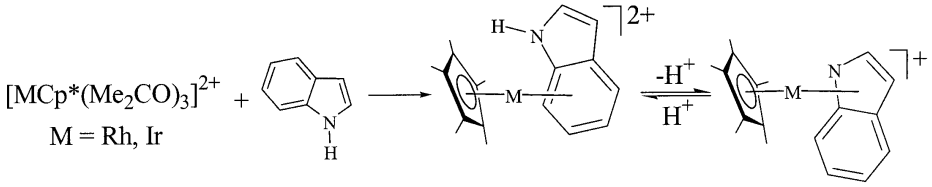
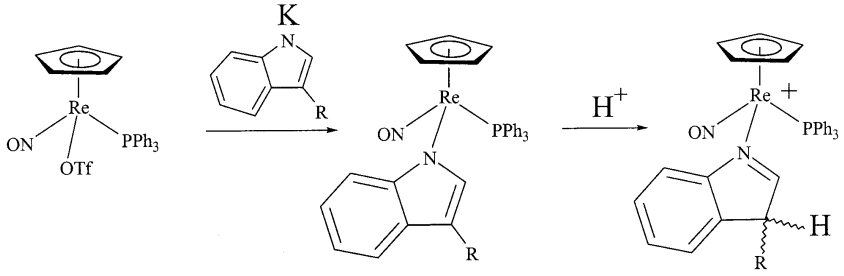


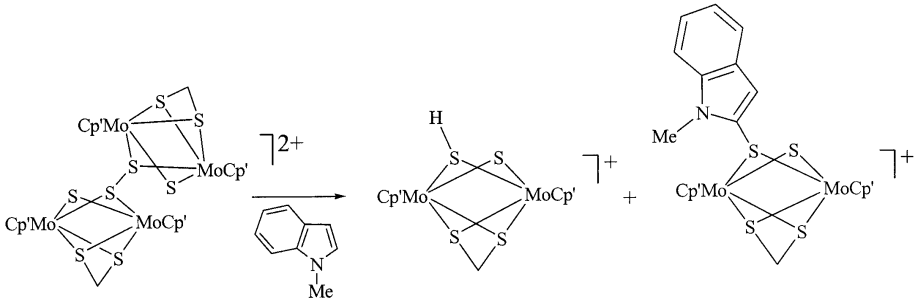
Figure 6. Known bonding modes of IN derivatives in mononuclear complexes



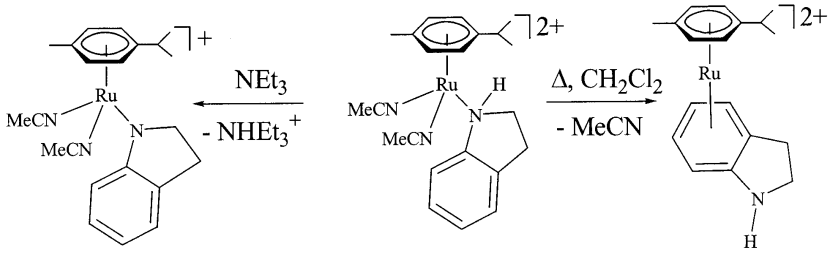
Scheme 11



Scheme 12



Scheme 13



Scheme 14

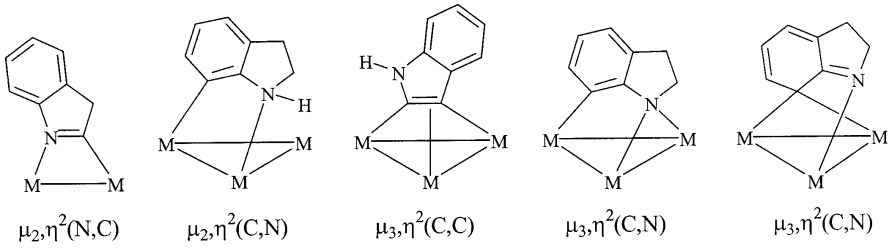


Figure 7. Bonding modes of IN to metal clusters

C) Complexes with Carbazole

The coordination chemistry of carbazole has scarcely been investigated. Only N−H bond activation to give η^1(N)-carbazoyl products has been reported.[26c,39] Interestingly, the reaction of [Cp*Rh(PMe_3)(H)(Ph)] with carbazole[26c] yields a C−H insertion kinetic product that thermally converts to a thermodynamic N-H insertion product (Figure 8).

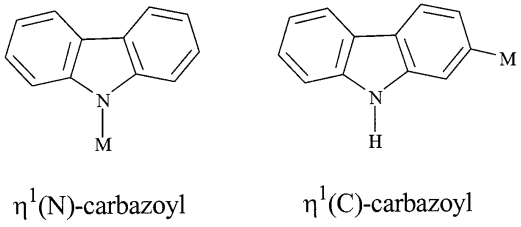


Figure 8. Known modes of carbazoyl coordination

D) Complexes with Pyridine, Quinoline, and Derivatives

The known bonding modes of PY and its alkyl-substituted derivatives to single metal sites are illustrated in Figure 9.

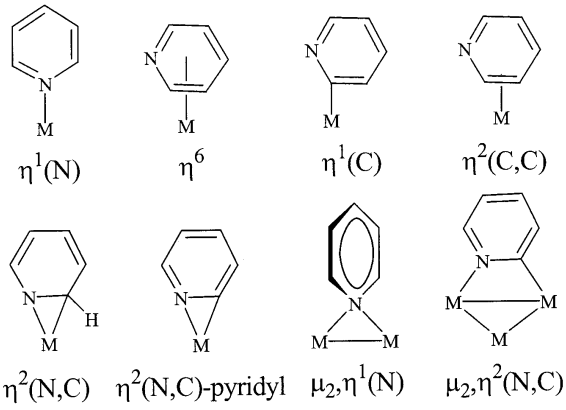


Figure 9. Known bonding modes of pyridine derviatives to single metal sites

The most common coordination for PY is through the nitrogen atom, which uses its lone pair for interaction with Lewis acceptors.[40,41] Unlike thiophene,[3−6] the nitrogen atom in η^1(N)-PY complexes is retained in the ring plane.[42] Formally, monohapto-PY complexes are also the η^1(C) ones obtained from C−H bond activation by electron-rich metal fragments.[43]

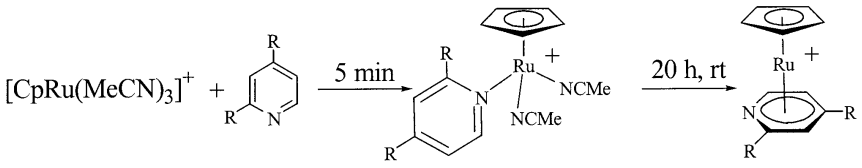
Another quite common coordination mode of PY is the η^6 mode, whose formation does not necessarily require the presence of alkyl substituents in the 2,6 positions of the ring to hinder the η^1(N) mode.[41,44]

Many homogeneous studies of PY coordination have centred on the η^1(N) and η^6 modes, and the factors controlling their interconversion and/or prevalence.[41] With the use of the isostructural and isolelectronic Ru^{II} and Rh^{III} complexes [Cp(or Cp*)M(CH_3CN)$_3$]$^{n+}$, Fish and co-workers have found that, in the absence of steric constraints, the η^1(N) mode prevails over the η^6 mode, particularly with the more electrophilic Rh^{III} centre.[41c] For example, [Cp*Rh(CH_3CN)$_3$]$^{2+}$ reacts with 2-methylpyridine and 2,6-dimethylpyridine yielding compounds of the formula [Cp*Rh(η^1(N)-PY)(CH_3CN)$_2$]$^{2+}$, while the sterically encumbered 2,4,6-trimethylpyridine[41c] forms the η^6 adduct [Cp*Rh(η^6-PY)]$^{2+}$. An interesting reactivity path is displayed by [CpRu(CH_3CN)$_3$]$^+$, in which the Ru^{II} centre is more electron-rich than Rh^{III} in the analogous complex. The greater propensity of Ru^{II} to stabilise the η^6 mode *via* π-backbonding from a filled metal orbital to a π* orbital of PY, has allowed Fish to follow the η^1(N)→η^6 interconversion of 2-methylpyridine and 2,4-dimethylpyridine illustrated in Scheme 15. The initially formed η^1(N) complex slowly loses MeCN and converts to the thermodynamic η^6-PY product. This rearrangement has been proposed to involve an η^4-PY intermediate.[41a,41d]

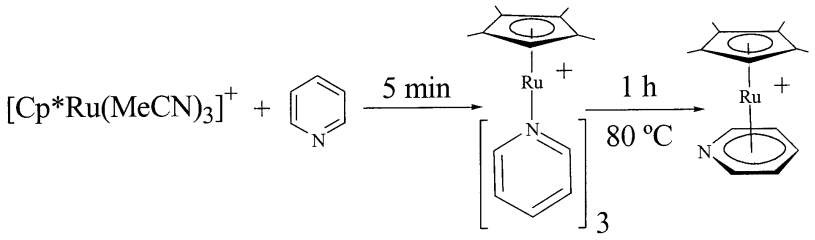
With unsubstituted PY, the stable adduct [CpRu(η^1(N)-PY)$_3$]$^+$ is obtained.[41d] However, when Cp* is employed to make the Ru centre more electron-rich, the complex [Cp*Ru(η^1(N)-PY)$_3$]$^+$ is a kinetic product that thermally converts to the corresponding η^6 derivative (Scheme 16).[41b]

The only example of PY acting as a bridge between two metal centres through the nitrogen atom has been found in Mo_2O_2[S_2P(O*i*Pr)$_2$]$_2$(μ-*O*)(μ-S)[μ,η^1(N)-PY] (Scheme 17).This compound is of particular relevance to HDN because of the presence of two Mo atoms in a sulfur-rich environment. In this Mo dimer, the PY ring is almost coplanar with the bridging O and S atoms, while the Mo-N distances are longer than regular Mo-N distances.[45]

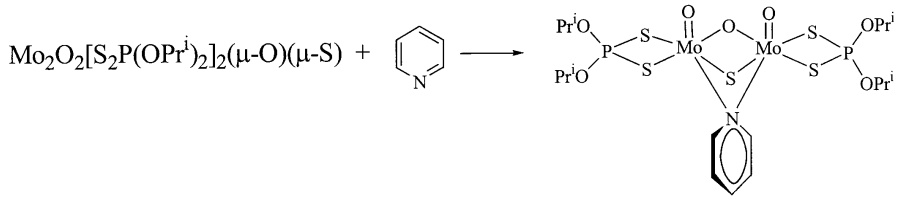
Another rare binding mode of a pyridine substrate is the η^2(C,C) mode which has been described by Taube and coworkers for 2,6-dimethylpyridine (lutidine) (Scheme 18).[46] This interesting coordination mode is exclusively stabilised by the electron-rich [Os(NH_3)$_5$]$^{2+}$ fragment, and rearranges to the η^1(N) mode a one-electron oxidation. The η^2(C,C)→η^1(N) rearrangement of lutidine raises much interest as it relates the bonding mode of the N-heterocycle with the metal oxidation state. Indeed, the active metal



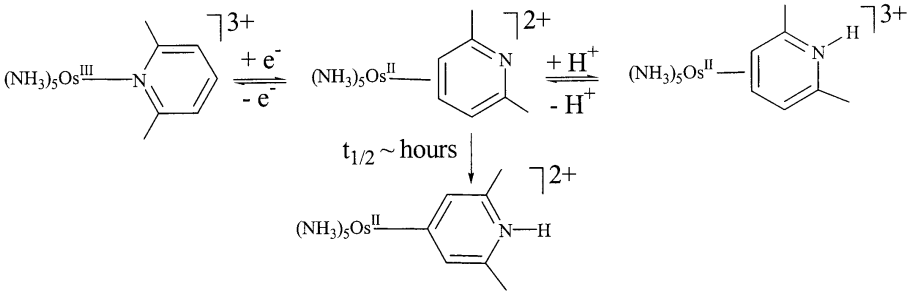
Scheme 15



Scheme 16



Scheme 17



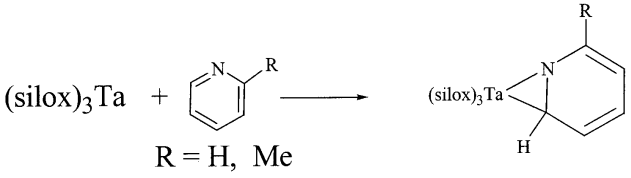
Scheme 18

centres of heterogeneous HDS/HDN catalysts may have different oxidation states due to electron-transfer processes involving both surface and bulk metal atoms.[1]

Interestingly, the η^2(C,C) mode of lutidine rearranges with time to give an Os^{II} lutidinium ylide. In contrast, the η^2(C,C) mode is maintained when $[Os(NH_3)_5(\eta^2$-lutidine$)]^{2+}$ is protonated to give a lutidinium derivative.

All the bonding modes that have been described so far represent valid models for the adsorption of PY over the catalyst surface. None of them, however, has been found to be a precursor to C−N bond scission. In contrast, the η^2(N,C) mode effectively activates the PY ring toward C−N scission. These C−N insertions will be commented on in a separate section, while the known η^2(N,C) metal complexes are reviewed below.

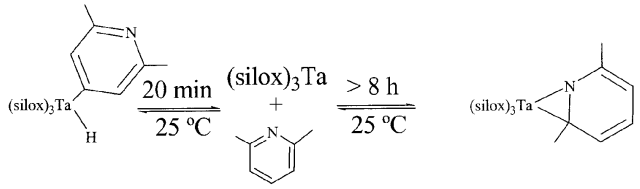
The first η^2(N,C)-PY complex, $[(silox)_3Ta(\eta^2$(N,C)-$NC_5H_5)]$, was prepared by Wolczanski in 1988 through the simple procedure illustrated in Scheme 19 (silox = tBu_3SiO^-).[47] The structure of $[(silox)_3Ta(\eta^2$(N,C)-$NC_5H_4R)]$ is consistent with a Ta^V metallaaziridine where the aromaticity of PY has been interrupted by strong Ta(dπ)→PY(π*) back-bonding.[47b]



Scheme 19

Reaction of $[(silox)_3Ta(\eta^2$(N,C)-$NC_5H_5)]$ with 2-picoline and lutidine give similar η^2(N,C) products whose formation have been proposed to occur by nucleophilic attack of the starting Ta^{III} compound at the LUMO of the N-heterocycle

(predominantly C=N π*). A detailed in situ NMR spectroscopic study with the sterically congested lutidine shows that C−H bond activation may compete kinetically with η^2(N,C) coordination (Scheme 20).



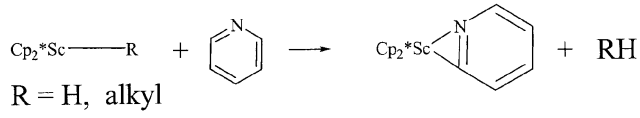
Scheme 20

Similar starting materials such as $(silox)_3M$ (M = Sc, Ti, V) react with PY in a conventional manner leading to η^1(N) derivatives.[47b] The absence of four electron repulsion problems in the Sc, Ti and V derivatives has been invoked to account for the selective formation of η^1(N) adducts.

Reduction of $[(silox)_3NbCl_2]$ with Na/Hg in PY affords a kinetic η^2(N,C)-PY product which thermally undergoes C−N insertion (vide infra).[47a]

Another Ta compound containing a η^2(N,C) pyridine ligand is $[(DIPP)_2ClTa(\eta^2(N,C)\text{-}2,4,6\text{-}NC_5H_2tBu_3)]$ (DIPP = $2,6\text{-}OC_6H_3iPr_2$) obtained by Wigley and co-workers by nitrile insertion into a tantallacyclopentadiene complex.[48]

Besides precursors to C−N bond scission, transients with η^2(N,C) pyridine ligands have been proposed to be critical to C_α−H activation leading to complexes containing a dihapto $NC_5H_4^-$ ligand.[49] The first of such compounds with unsubstituted PY, $Cp^*Lu(\eta^2(N,C)\text{-}NC_5H_4)$, was reported by Watson.[49b] A few years later, Bercaw reported the synthesis of $[Cp^*Sc(\eta^2(N,C)\text{-}NC_5H_4),]$[49a] while Ti derivatives with 2-substituted pyridines have been described by Teuben.[49c] A common synthetic procedure to these η^2(N,C)-pyridyl compounds involves the reaction of the substrate with alkyl or hydride complexes as shown in Scheme 21 for the Sc derivative. An in situ NMR spectroscopic study with the precursor Cp*ScMe has suggested the formation of the intermediate, the η^1(N)-PY adduct, prior to C−H insertion.[49a]



Scheme 21

PY uses the N atom and the C_α atom for coordination in the triosmium cluster $[Os_3(\mu\text{-}H)\ (\mu\text{-}NC_5H_4)(CO)_{10}]$, but two distinct metal centres are involved (Figure 9).[50]

The coordination chemistry of Q does not differ significantly from that of PY, except for the interactions with polynuclear metal complexes. In this case, the presence of the carbocyclic ring allows a larger variety of bonding modes.

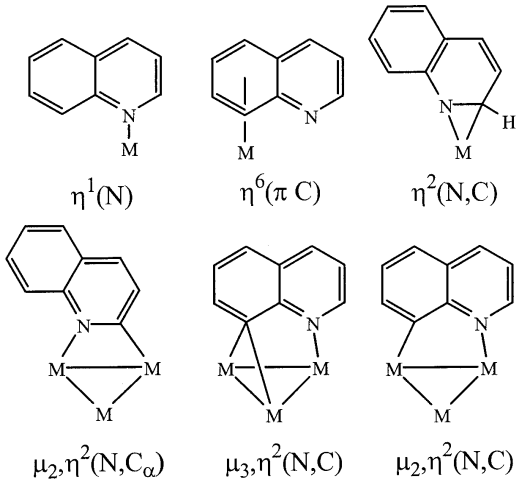


Figure 10. Known modes of Q coordination in transition metal complexes

Figure 10 summarises all the known coordination modes of Q in both mononuclear and polynuclear metal complexes.

Like PY, the most common coordination mode of Q in mononuclear complexes is the η^1(N),[40,41] which may be in equilibrium with the $\eta^6(\pi C)$.[41,44] No example of η^6coordination involving the heterocyclic ring (πN) has ever been reported.

An $\eta^1(N)\rightarrow\eta^6(\pi C)$ rearrangement analogous to that already described for PY is illustrated in Scheme 22.[41a][41d] The complex $[CpRu(CH_3CN)_3]^+$ reacts with Q yielding a kinetic η^1(N) product that converts to the thermodynamic $\eta^6(\pi C)$ derivative by decoordination of acetonitrile.

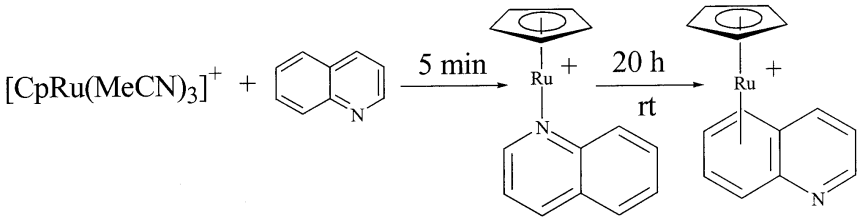
Substitution of Cp* for Cp increases the π back-bonding capability of the Ru centre, and the $\eta^6(\pi C)$ complex is formed in a straightforward manner with no evidence of the η^1(N) adduct.[41d]

The η^1(N)-Q mode may also be a precursor to the η^2(N,C) mode, as shown in Scheme 23, for the conversion of $[(DIPP)_3Ta\{\eta^1(N)\text{-}Q\}Cl_2]$ to $[(DIPP)_3Ta\{\eta^2(N,C)\text{-}Q\}]$ (DIPP = $2,6\text{-}OC_6H_3iPr_2$). This reaction requires an increase of the electron density at the metal centre to allow for an efficient $M(d\pi)\rightarrow Q(\pi^*)$ back-bonding interaction.[51]

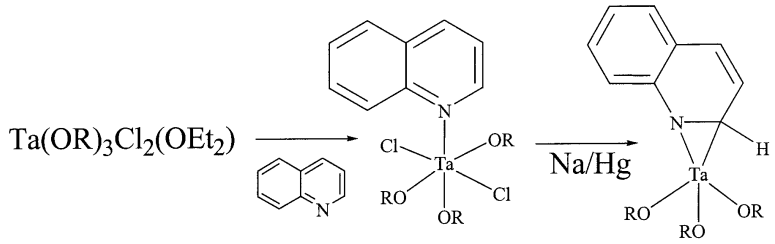
The multipoint activation of Q and alkyl-substituted quinolines has been studied with the clusters $Ru_3(CO)_{12}$ [52] and $Os_3(CO)_{10}(CH_3CN)_2$.[21a,53] The main bonding modes are summarised in Figure 10, while the reactivity of the resulting products will be reviewed in the next section. In all cases, N-coordination is accompanied by C-H insertion by an adjacent metal centre.

Tetrahydroquinoline (THQ) has been the subject of many studies aimed at investigating the dehydrogenation of partially reduced N-heterocycles over heterogeneous catalysts. $Ru_3(CO)_{12}$ reacts with THQ to give a bis-Q complex with a $\mu_2,\eta^2(N,C_\alpha)$ coordination mode (Scheme 24).[52] Dehydrogenation of THQ to Q has also been found to occur by reaction with either $[Os_3(CO)_{10}(CH_3CN)_2]$[53] or $Os_3(CO)_{12}$.[21a]

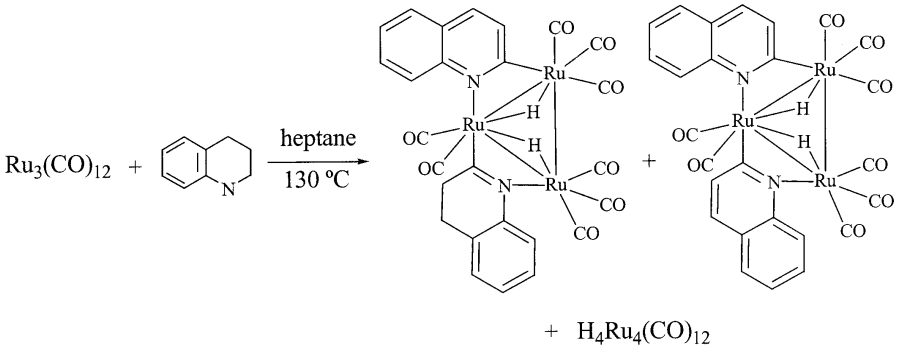
In conclusion, PY and Q exclusively use the nitrogen atom for coordination when the metal centre is electrophilic



Scheme 22



Scheme 23



Scheme 24

in nature and only one free site is available. When three coordination vacancies are available and the metal centre has filled dπ orbitals for πback bonding, the preferred bonding mode is the η^6, either πN or πC depending on the substrate. When two free sites are available, the electronic nature of the metal centre dictates whether the substrate binds the metal using two carbon atoms or the nitrogen and the C_α atom. Electron-rich systems based on late-transition metals prefer the olefinic η^2(C,C) mode, while electrophilic early-transition metal systems stabilise the η^2(N,C) mode. As will be shown in the next section, the binding mode of the N-heterocycle ultimately controls the reactivity of the activated substrate.

E) Complexes with Other Basic Polyaromatic N-Heterocycles

Isoquinoline, 5,6-benzoquinoline, 7,8-benzoquinoline, acridine, and phenanthridine have been found to bind single metal centres in either a η^1(N) or a η^6(πC) fashion.[41c,44a,53a]

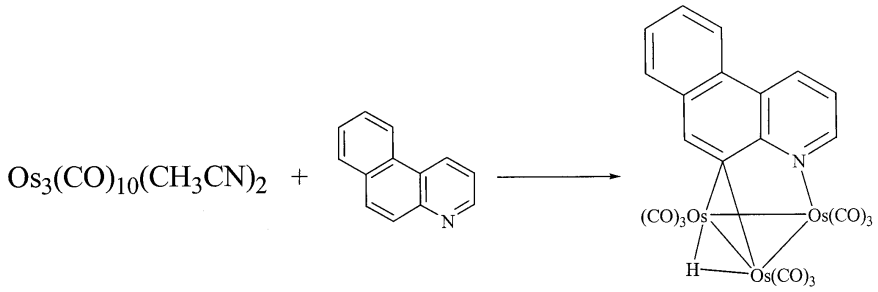
Like PY and Q, the triosmium cluster $[Os_3(CO)_{10}(CH_3CN)_2]$ reacts with polyaromatic N-heterocycles, such as 5,6-benzoquinoline and phenanthridine, yielding μ_3,η^2(N,C,C) complexes (Scheme 25).[53] Phenanthridine also forms a μ_2,η^2(N,C_α) complex similar to that with Q.

Reactivity of Coordinated N-Heterocycles

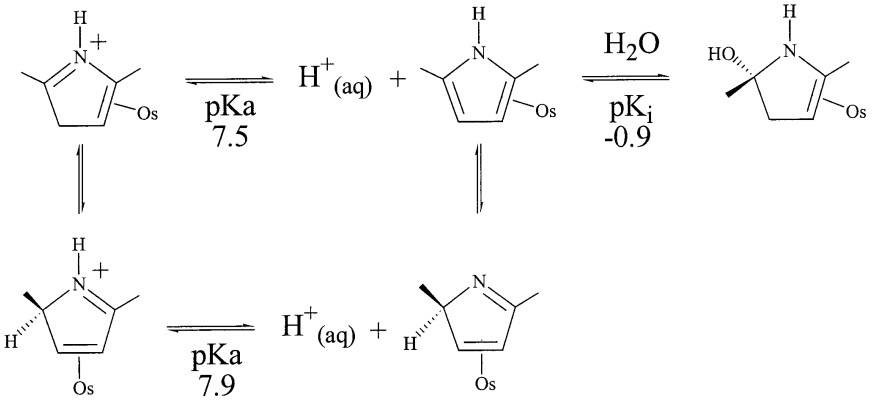
Upon coordination, the chemical reactivity of N-heterocycles is generally enhanced as compared with the free molecules. However, no general rule can be given. Indeed, besides the nature of the metal fragment, the reactivity of coordinated N-heterocycles depends on the substrate, the degree and regioselectivity of ring substitution, and the bonding mode. The reactivity studies reported in this section are just a selection of those that are representative of the possible chemical processes occurring during HDN. The catalytic hydrogenation reactions of N-heterocycles will be reviewed separately.

A) Pyrrole and Derivatives

In contrast to free PYR, which protonates at the α-position preferentially and under forcing conditions ($pK_a = -1$), η^2(C,C)-pyrrole in $[Os(NH_3)_5(2,3\text{-}\eta^2\text{-}2,5\text{-dimethylpyrrole})]^{2+}$, undergoes selective protonation by mild acids at the β-carbon away from the metal to produce a 3*H*-pyrrolium species (Scheme 26).[23a] In the presence of a weak base,



Scheme 25



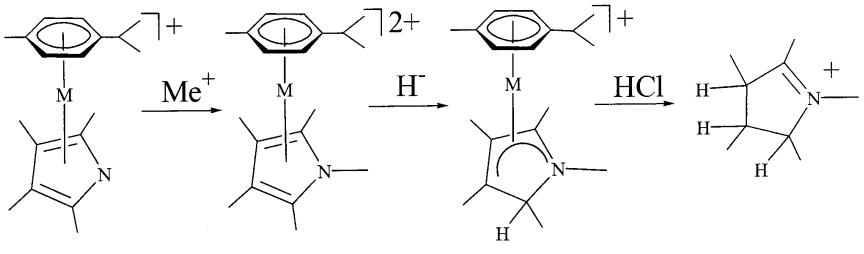
Scheme 26

the 3H-pyrrolium complex is converted into the 2H-pyrrolium tautomer that can be deprotonated at the nitrogen to give a neutral 2H-PYR ligand bonded to Os through the C_3-C_4 double bond. Nucleophilic addition of OH^-, from H_2O, to the enamine-like C=C bond in the starting η^2(C,C)-pyrrole complex has also been observed.

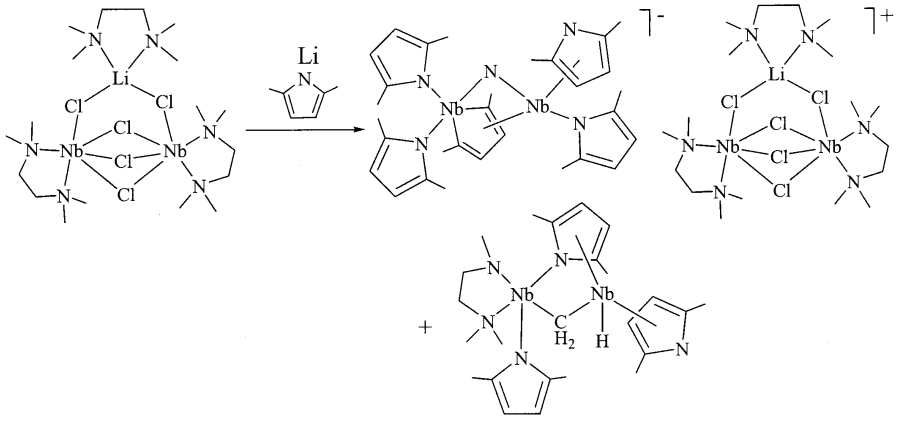
The η^5-pyrrolyl complexes [(*p*-cymene)M(NC_4Me_4)]OTf (M = Ru, Os) are readily converted into the corresponding η^5-PYR by selective alkylation at the nitrogen atom (Scheme 27).[22a] Interestingly, the η^5-PYR ligand in [(*p*-cymene)M($MeNC_4Me_4$)]($OTf)_2$ undergoes regio- and stereoselective hydride addition to an α-carbon atom to give a η^4-$MeNC_4Me_4H$ derivative. This compound reacts with protic acids, leading to further PYR reduction and dissociation from the metal as an iminium salt.

In a complex redox chemical process, the dimer [$(tmeda)_2$-Nb_2Cl_5Li(tmeda)] reacts with the 2,5-dimethylpyrrole lithium salt 2,5-$Me_2C_4H_2NLi$ to give a mixture of two products that have been confirmed by single-crystal X-ray analyses (Scheme 28) (tmeda = *N*,*N*,*N*′,*N*′-tetramethylethylendiamine).[27a]

The neutral product contains Nb^{III} and Nb^{IV} ions in different coordination geometries. The Nb^{IV} centre is coordinated by a terminal hydride ligand and by two η^5-pyrrolyl rings one of which is also η^1(N)-bonded to the Nb^{III} centre. The coordination of the latter metal is completed by another η^1(N)-pyrrolyl ligand, a bidentate tmeda molecule and a bridging CH_2 group that comes from the fragmentation of tmeda (N-Me cleavage, followed by C-H insertion). The anionic product [{(2,5-$Me_2C_4H_2N)_2Nb$}{(η^5-2,5-$Me_2C_4H_2N$)(2,5-$Me_2C_4H_2N$)Nb}(μ-N)(μ,η^1:η^1:η^4-1,4-$Me_2C_4H_2$)] is much more interesting as it contains a denitrogenated pyrrole ring. The anion, isolated as the $[(tmeda)_2Nb_2Cl_5Li(tmeda)]^+$ salt, contains two Nb^{IV}



Scheme 27



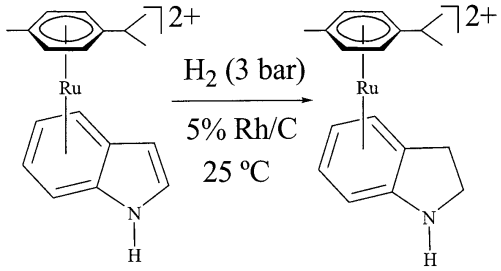
Scheme 28

centres connected by a nitride ligand and by a dienediyl group. Three η^1(N) and one η^5 pyrrolyl rings complete the coordination spheres.

The overall reaction (Scheme 28) thus corresponds to the simultaneous cleavages of C-N bonds in both the pyrrole ring and the saturated amine. The formation of the anionic product has been suggested to involve the cooperative attack of the two Nb^{II} centres on one pyrrolyl anion. The four electrons necessary to form the nitride and the dienediyl group are obtained from the five electrons provided by the oxidation of the four Nb^{II} centres during the formation of the anion and cation.

B) Indole and Derivatives

Besides undergoing deprotonation of the nitrogen atom to give η^5-indolyl complexes (Scheme 11), η^6-IN complexes are activated toward nucleophilic substitution at the carbocyclic ring,[32c,54] as well as reduction of the heterocyclic ring.[32a] Although the latter process has been found to involve a heterogeneous catalyst, 5% Rh/C, it is important to have demonstrated that η^6 coordination through the carbocyclic ring promotes the hydrogenation of the heterocyclic portion of the molecule to give an η^6-indoline complex (Scheme 29). Activation by carbanions towards nucleophilic addition has also been shown for η^6-indoline.[32a]



Scheme 29

A common reaction path of η^1(N)-indolyl complexes is their transformation into η^1(N)-indolenine derivatives upon selective protonation of the β-carbon atom (Scheme 12).[35]

The much lower propensity of N-heterocycles as compared with S- and O-heterocycles to undergo C-heteroatom insertion by metal fragments is shown by the reactions of $[Mn(CO)_3(\eta^6\text{-IN})]$, $[Mn(CO)_3(\eta^6\text{-BT})]$ (BT = benzothiophene) and $[Mn(CO)_3(\eta^6\text{-BF})]$ (BF = benzofuran) with $Pt(PPh_3)_3$ (Scheme 30).[55−57] Under comparable conditions, Pt inserts into the C_2-S[55] and C_2-O[56] bond of BT or BF, respectively, while the remote activation[55] of the IN heterocyclic[57] ring by $Mn(CO)_3$ exclusively results in N-H insertion with the formation of the heteronuclear trimer $[(CO)_3Mn(\mu^2,\eta^6,\eta^1(N)\text{-}C_8H_6N)]_2[Pt(PPh_3)_2]$.

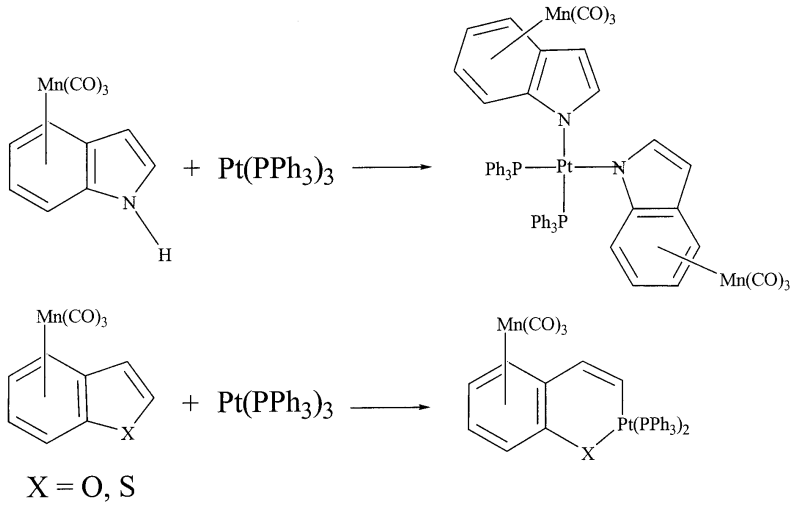
Unlike mononuclear species, polynuclear metal complexes containing bridging ligands derived from N−H or C−H activation of N-heterocycles (see Figure 5 and 7) generally behave as thermodynamic sinks and do not react further with H_2, nucleophiles or electrophiles even under harsh experimental conditions.

Dehydrogenation of indoline to indole by thermolysis of metal clusters containing C-H inserted indoline has been observed,[37] while indoline has been employed as a hydrogen source for the transfer hydrogenation of olefins in the presence of $[RhCl(PPh_3)_3]$.[57] A possible pathway for indoline dehydrogenation is shown in Scheme 31.

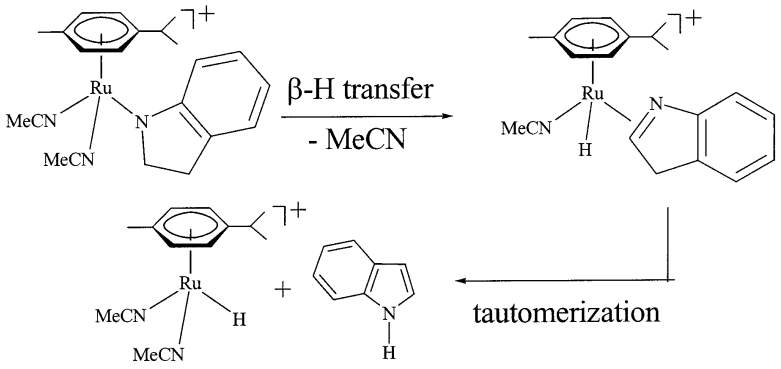
C) Pyridine, Quinoline and Derivatives

For PY the η^1(N) mode represents the simplest way of approaching a metal centre possessing a free coordination site. In the η^1-mode however, no activation of the heterocycle takes place. In order to increase the chemical reactivity of PY, a metal centre must have at least two free sites for coordination.

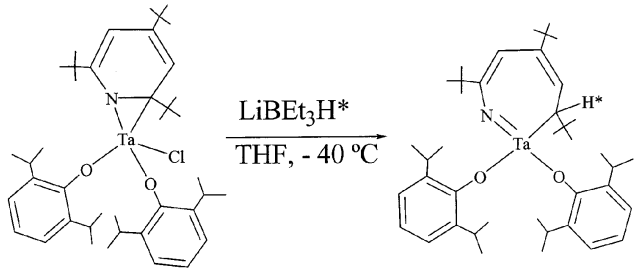
In the dihapto mode through two carbon atoms,[46] as in $[Os(NH_3)_5(\eta^2\text{-lutidine})]^{2+}$, the pyridine ring can be protonated intermolecularly at nitrogen, or even intramolecularly deprotonated at carbon as shown in Scheme 18. Although interesting, the transformations illustrated in Scheme 24 are by far less exciting than those observed when PY is activated by a metal centre through the η^2(N,C) mode: in this case, the HDN-crucial C−N bond cleavage may indeed occur. The first evidence for metal C−N insertion was reported by Wigley in 1992, who reacted the metallaaziridine complex $[(DIPP)_2ClTa(\eta^2(N,C)\text{-}2,4,6\text{-}NC_5H_2tBu_3)]$ with $LiHBEt_3$ in THF at low temperatures obtaining the C−N insertion product $[(DIPP)_2Ta\{=NCtBu=CHCtBu=CHCHtBu\}]$ (Scheme 32).[51d]



Scheme 30



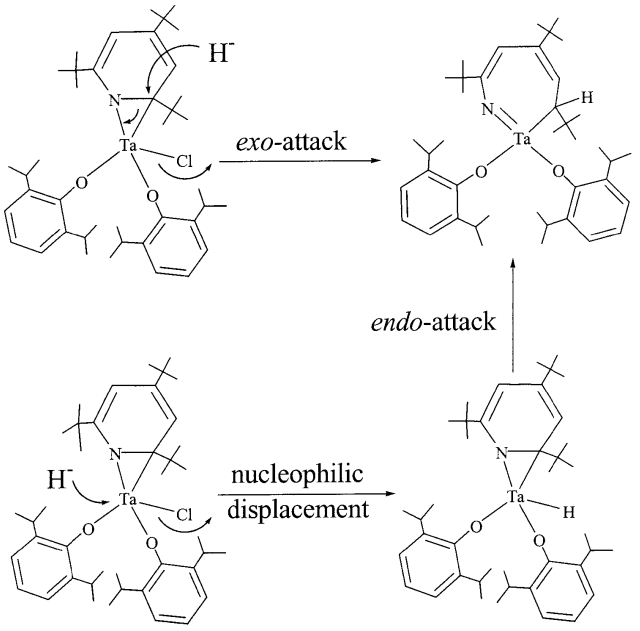
Scheme 31



Scheme 32

Experiments with carbon nucleophiles (RMgCl, MeLi) in place of $LiHBEt_3$, have provided valuable information to discriminate between the two possible pathways (*exo*-attack vs. *endo*-attack) to PY C−N scission (Scheme 33).[51b,51c] It has been established that the reaction occurs *via* an intramolecular *endo*-attack of the hydride that migrates to the PY Cα atom as a σ-nucleophile.

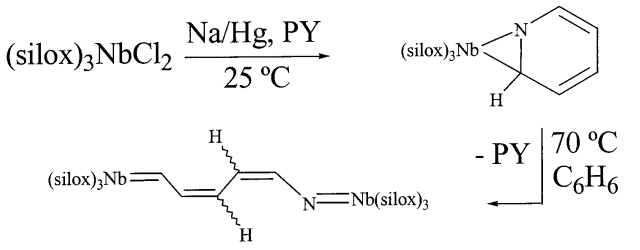
A major conclusion of Wigley's study is that bonding of PY in the η^2(N,C) fashion allows the Cα atom (a formal sp^2 carbon) to attain sp^3 hybridisation, and thereby renders this carbon atom susceptible to nucleophilic attack. However, the presence of the *t*Bu groups in $[(DIPP)_2ClTa\{\eta^2(N,C)\text{-}2,4,6\text{-}NC_5H_2tBu_3\}]$ is of mandatory importance for the occurrence of the nucleophile-promoted C-N bond cleavage. Indeed, neither the related Ta complex $[(silox)_3Ta\{\eta^2(N,C)\text{-}NC_5H_5\}]$[51a] nor the Q derivative $[(DIPP)_2Ta\{\eta^2(N,C)\text{-}Q\}]$[51a] undergoes C−N insertion upon nucleophilic addition. Nonetheless, Wigley's compound represents an excellent model to gain an insight into some relevant issues of HDN, e.g. it supports the hypothesis which states that the cobalt-promoter effect in the $MoS_2/\gamma\text{-}Al_2O_3$ catalyst is that where the electron density increases on the surface metal atoms *via* electron transfer.[1] Moreover, the fact that the C−N scission step occurs with the



Scheme 33

formation of an imido moiety (M=NR) is consistent with the ultimate elimination of ammonia by hydrogenolysis of the C−N inserted product.

An intriguing case of metal-assisted ring-opening of PY has been reported by Wolczanski using the low-valent $(silox)_3Nb$ fragment that binds PY in the η^2(N,C) mode (Scheme 34).[47a] Unlike $[(DIPP)_2ClTa\{\eta^2(N,C)$-2,4,6-$NC_5H_2tBu_3\}]$, $[(silox)_3Nb\{\eta^2(N,C)$-$NC_5H_5\}]$ undergoes C−N insertion by thermolysis in benzene at 70 °C only. The reaction gives 0.5 equiv. of PY and 0.5 equiv of $[(silox)_3Nb{=}CHCH{=}CHCH{=}CHN{=}Nb(silox)_3]$ as a thermodynamic mixture of *cis,cis*-, *trans,cis*-, *trans,trans*- and *cis,trans*-isomers.



Scheme 34

Hydrogenation and Hydrogenolysis of N-heterocycles Catalysed by Transition Metal Complexes

Under actual HDN conditions, the hydrogenation of N-heterocycles is much more facile than the subsequent C−N hydrogenolysis.[7] This trend is observed also when soluble metal complexes are used as models for heterogeneous HDN catalysts. Indeed, while several examples of hydrogenation of N-heterocycles to the corresponding cyclic amines (partially or fully saturated) have been reported, only one case of hydrogenolysis promoted by a homogeneous catalyst has been described so far. Moreover, the real nature of this hydrogenolysis process is still rather doubtful.

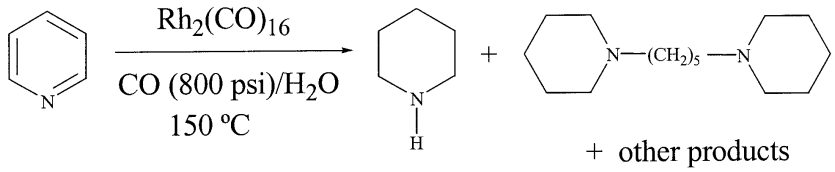
A) Hydrogenolysis of Pyridine

Under water-gas shift (wgs) conditions and in the presence of $Rh_6(CO)_{16}$, PY has been found to undergo both hydrogenation to piperidine and hydrogenolysis to various bis(piperidinyl)alkanes (Scheme 35).[58] The formation of the latter compounds has been proposed to involve extrusion of NH_3 from the intermediate 1,4-dihydropyridine to give glutaraldehyde, which in turn reacts with piperidine and hydrogen to form the bis(piperidinyl) products. The absence of both particulate metal in the reactor and reactivity when the rhodium metal was substituted for $Rh_6(CO)_{16}$ confirmed the homogeneous nature of the process. However, the lack of further studies supporting the homogeneity of this HDN reaction, the harsh experimental conditions (150 °C, 800 psi CO), and the proven capability of heterogeneous catalysts to promote the conversion of PY illustrated in Scheme 35,[59] have contributed in raising doubts on the homogeneous nature of the overall process.

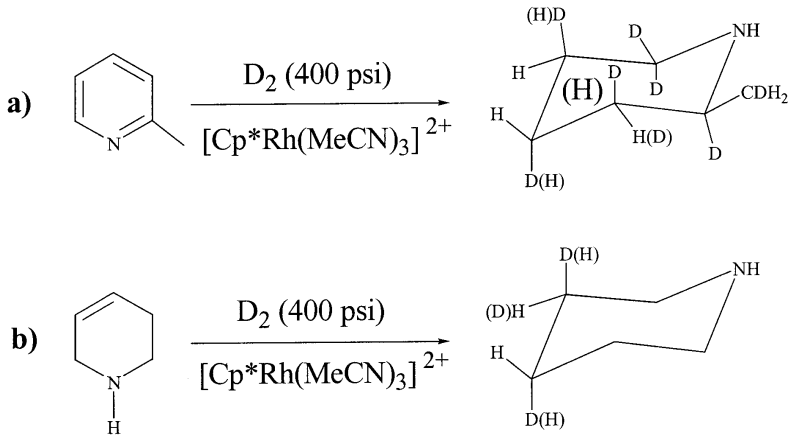
B) Hydrogenation of Pyridine, Quinoline, Indole and Derivatives

The first example of selective hydrogenation of PY to piperidine was reported in 1970 by Jardine and McQuillin.[60] The reaction was carried out in DMF at 1 bar H_2 in the presence of $Rh(PY)_3Cl_3/NaBH_4$. The same catalyst system was found to be effective for the reduction of Q to THQ (see below). In either case, no kinetic or mechanistic information was provided. In contrast, an in-depth study[61] is available for the hydrogenation of 2-methylpyridine to 2-methylpiperidine catalysed by $[Cp^*Rh(MeCN)_3]^{2+}$. Deuterium labelling experiments, competitive studies and reactions with isolated intermediates allowed Fish and co-workers to address many relevant issues regarding the hydrogenation of pyridines in the presence of this Rh^{III} precursor (Scheme 36a).[41,61]

On the basis of the deuteration pattern observed when D_2 was substituted for H_2, it was concluded that the reductions of the C=N and C=C bonds are reversible. The reversibility of H_2 addition to the C=N bond was suggested to be promoted by the allylic nature of the reduction product, i.e. $NH{-}CH_2{-}C{=}C$, which is highly activated toward rearomatisation of the N-ring by dehydrogenation. Another remarkable observation made by Fish was that six-membered mononuclear N-heterocycles such as PY and derivatives are much less prone to undergo hydrogenation than bi- and trinuclear N-ring compounds (e.g. quinolines, benzoquinolines, acridines) due to their higher resonance stabilisation energy. This finding led Fish to conclude that the initial C=N bond hydrogenation which actually disrupts the aromaticity of the molecule, is the most critical hydrogenation step in the overall reduction process. The reduction of 1,2,5,6-tetrahydropyridine (THPY) with D_2 in the presence of $[Cp^*Rh(MeCN)_3]^{2+}$ (exclusive deuterium incorporation in the C_3 and C_4 carbon atoms, Scheme 36b) and the independent synthesis of $[Cp^*Rh(\eta^1(N)$-THPY$(MeCN)_2]^{2+}$



Scheme 35



Scheme 36

provided two additional pieces of HDN-relevant information: i) η^1(N)-THPY complexes are not intermediate to piperidine production; ii) partially hydrogenated N-heterocycles are easily dehydrogenated to their aromatic precursors, thus confirming that C-N bond cleavage for cyclic amines is not thermodynamically favoured over rearomatisation.[61]

Laine's idea to use late transition metal carbonyls, capable of promoting the wgs reaction, for the hydrogenation of PY, prompted other researchers to follow this route. In all cases, however, polyaromatic heterocycles such as Q, 5,6-benzoquinoline (5,6-BQ), 7,8-benzoquinoline (7,8-BQ), acridine (AC) and derivatives, were employed as model substrates. In no case was the HDN of the N-heterocycle observed.

Under either wgs or synthesis-gas (sg) conditions, Fish employed a variety of metal carbonyls or phosphane-modified metal carbonyls for the reduction of polyaromatic heterocycles.[62] Selective hydrogenation of the heterocyclic ring was achieved with $Fe(CO)_5$, $Mn_2(CO)_8(PBu_3)_2$ and $Co_2(CO)_6(PBu_3)_2$. Under wgs conditions, $RuCl_2(CO)_2(PPh_3)_2$ and $H_4Ru_4(CO)_{12}$ proved to be inactive due to competitive coordination of CO, while efficient regioselective hydrogenation of the substrate was achieved using H_2 gas. In all cases, however, high temperatures (180−200 °C) were needed and very low turnovers [mol substrate (mol catalyst^{-1})] were obtained.[62] The reactivity of $Fe(CO)_5$ toward selective reduction of the heterocyclic ring under wgs conditions was also reported by Kaesz and co-workers for Q, isoquinoline (IQ) and AC.[63] Improved catalytic efficiency (up to 87 turnovers) was obtained adding both a base and a phase-transfer agent. Finally, various substituted quinolines and isoquinolines were selectively hydrogenated in the heterocyclic ring with $Rh_6(CO)_{16}$ under wgs conditions.[64] However, unlike PY,[58] no HDN product was formed. It was also reported that 4-methyl-Q was selectively converted into 4-methyl-THQ under wgs conditions, whereas 4-methyl-5,6,7,8-THQ was exclusively obtained using H_2 gas.[64]

It was possible to apply mild reaction conditions only with more complex ligand systems than CO, and hence study the mechanism and kinetics of hydrogenation of polyaromatic N-heterocycles.

The first detailed mechanistic studies of homogeneous hydrogenation of polyaromatic substrates have been reported by Fish and co-workers who employed the Rh^I and Ru^{II} precatalyts $[(PPh_3)_3RhCl]$[65] and $[(PPh_3)_3RuHCl]$[66] under mild experimental conditions (85 °C, 310 psi H_2, benzene). The Rh complex was actually shown to convert into $(PPh_3)_3Rh(H)_2Cl$ by treatment with H_2. As a general trend, the relative hydrogenation rates decreased in the order phenanthridine > AC > Q > 5,6-BQ > 7,8-BQ, which reflects the influence of both steric and electronic effects. All substrates were regioselectively hydrogenated at the heteroaromatic ring; only AC was converted into a mixture of 9,10-dihydroacridine and 1,2,3,4-tetrahydroacridine. The hydrogenation of Q was found to be inhibited by the presence of pyridines and THQ in the reaction mixture, due to competing coordination to the metal centre; all the other substrates had no appreciable effect on the rate of Q hydrogenation. In the case of the Rh catalyst, Q reduction was promoted in the presence of IN, PYR, carbazole and even of sulfur-heterocycles such as thiophene, benzothiophene and dibenzothiophene.

The substitution of D_2 for H_2 in the reduction of Q, catalysed by either $(PPh_3)_3RhCl$ or $(PPh_3)_3RuHCl$, provided the following pieces of information: i) the hydrogenation of the C=N bond is reversible; ii) the C_3-C_4 double bond is irre-

versibly hydrogenated in a stereoselective cis manner; iii) the C_8-H bond in the carbocyclic ring is activated (most likely by cyclometalation). Based on deuterium labelling experiments and of reactions with isolated compounds, Fish proposed a sound mechanism for the hydrogenation of Q with $[(PPh_3)_3Rh(H)_2Cl]$ or $[(PPh_3)_3RuHCl]$, which however, did not distinguish between intra- and intermolecular reduction of the C_3-C_4 double bond. This mechanism is not shown here for the simple reason that, some years later, the same author reported a similar and more complete mechanistic picture using $[Cp^*Rh(MeCN)_3]^{2+}$ as the catalyst precursor (vide infra).

The catalytic performances of $[(PPh_3)_3RuCl_2]$, $[(PPh_3)_3RhCl]$, $[(PPh_3)_3RuHCl(CO)]$, $[(PPh_3)_3OsHCl(CO)]$, $[Rh(cod)(PPh_3)_2]^+$ and $[Ir(cod)(PPh_3)_2]^+$ (cod = 1,5-cyclooctadiene) in the selective hydrogenation of Q to THQ have been investigated by Sánchez-Delgado and Gonzáles (150 °C, 30 bar H_2, toluene).[67] The Rh complex was by far the most active [initial rate ca. 200 mol Q (mol cat)$^{-1}$ h^{-1}], while the Os complex was the least efficient [initial rate ca. 5 mol Q (mol cat)$^{-1}$ h^{-1}]. The latter observation is consistent with the kinetic sluggishness of third-row metals. Some chemical factors affecting the activity of the Ru complex $[(PPh_3)_3RuHCl(CO)]$ were investigated in detail. Coordinating solvents such as MeCN or MeOH, or added ligands such as CO quenched the catalysis. The addition of acid or base gave adverse effects, the base acting as an inhibitor; water did not apparently affect the catalytic rate.

A study relating the rate of hydrogenation of Q to THQ with the nature of the metal centre has recently been reported by López-Linares and co-workers.[68] Several catalyst systems were prepared by adding either Tp or Tp* [Tp = tris(pyrazolyl)borate; Tp* = tris(3,5-dimethylpyrazolyl)borate] to toluene solutions of $[Rh(cod)Cl_2]_2$, $[Ir(cod)Cl_2]_2$, $[Ir(coe)Cl_2]_2$ (coe = cyclooctene) and $RuCl_2(MeCN)_4$. Preformed $TpIr(C_2H_4)_2$ was also tested. Rhodium formed the most active catalysts. As a general trend, the activity was found to increase with the ease of formation of Tp or Tp* complexes, while the presence of ligands capable of competing with Q for coordination decreased the hydrogenation rate, e.g. coe and ethylene which can undergo competitive metal insertion into sp^2 C−H bonds.

Deuterium gas experiments, monitored by both NMR spectroscopic and GC/MS analysis, and in situ high-pressure NMR spectroscopic reactions were very helpful to draw out the mechanism reported in Scheme 37 for the hydrogenation of Q to THQ catalysed by the Rh^{III} complex $[Cp^*Rh(MeCN)_3]^{2+}$ (40 °C, 500 psi H_2, CH_2Cl_2).[61] The regioselectivity and degree of deuterium incorporation are shown in the scheme just to help the reader in following the authors' conclusions.

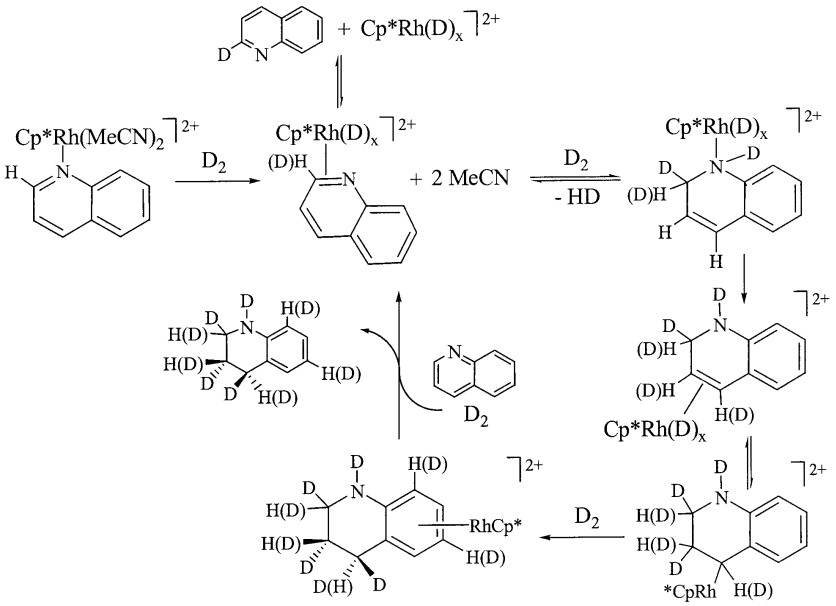
Salient features of the postulated mechanism are: i) η^1(N) bonding of Q to Rh with the loss of complexed MeCN, followed by the formation of a hydride; ii) reversible 1,2-N=C bond hydrogenation, most likely by a η^2(N,C) coordination as later shown by Wolczanski[47] and Wigley;[48] iii) migration of Cp*Rh from nitrogen to the C_3-C_4 double bond; iv) reversible C_3-C_4 double bond reduction; v) Cp*Rh complexation to the carbocyclic ring, followed by C_6-H and C_8-H bond activation; vi) $\eta^6(\pi C)$ coordination of THQ, followed by ligand exchange with Q to continue the catalytic cycle. In this mechanistic picture, the Rh centre goes through the catalytic process with the unusual III→V→III oxidation/reduction cycle. Some intermediate complexes[41e] in the catalytic cycle were isolated and characterised, i.e. $[Cp^*Rh(\eta^1(N)\text{-}Q)(MeCN)_2]^{2+}$ and $[Cp^*Rh(\eta^6(\pi C)\text{-}THQ)]^{2+}$. The critical role of η^1(N) coordination for selective nitrogen ring reduction was also demonstrated by the much higher catalytic activity of $[Cp^*Rh(MeCN)_3]^{2+}$ vs. the Ru analogue $[Cp^*Ru(MeCN)_3]^+$, which indeed forms a more stable $\eta^6(\pi N)$ complex.[41]

The mechanism illustrated in Scheme 37 also accounts for the $[Cp^*Rh(MeCN)_3]^{2+}$-assisted regioselective hydrogenation of pyridines, benzoquinolines, AC as well as indoles and benzothiophene.[61] The observation that the relative hydrogenation rates decreased in the order AC > Q > 5,6-BQ > 2-Me-Q > 2-Me-PY was attributed to both electronic and steric effects. In particular, the rate decreased with increasing basicity and steric hindrance at the nitrogen atom. A different case is represented by 7,8-BQ that showed the highest relative rate and, in competitive reactions, was found to remarkably enhance the rate of hydrogenation of Q and other substrates as well. It was proposed that the enhanced rate is due to a hydrogen transfer mechanism, which is consistent with the role of nitrogen compounds as hydrogen-donor solvents in coal liquefaction.[61]

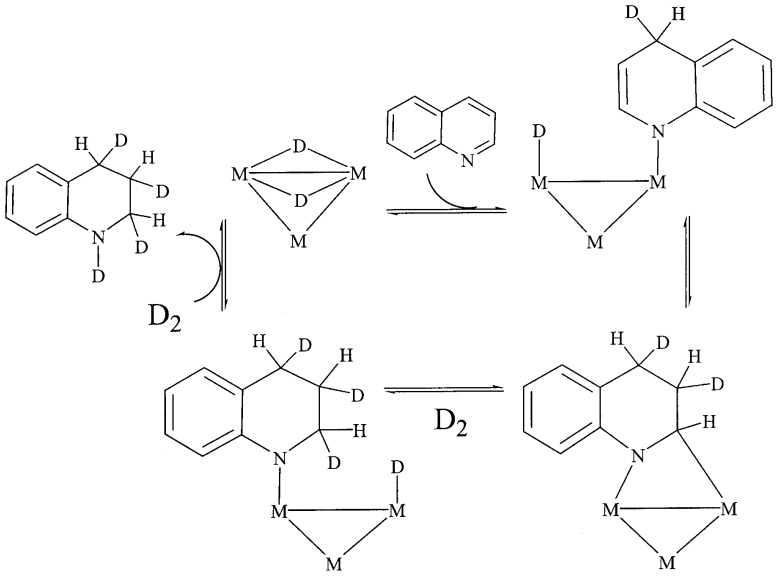
The deuteration pattern of THQ found by Fish is rather similar to that reported by Laine for the hydrogenation of Q with the clusters $H_2Os_3(CO)_{10}$ and $Os_3(CO)_{12}$, as well as real sulfided Co-Mo/γ-Al_2O_3 heterogeneous catalysts.[21a][69] Some differences in the deuteration pattern, in particular the presence of more deuterium in the 4-position and less in the 2-position, have been interpreted in terms of the occurrence of oxidative addition of the Os cluster to C-H bonds in Q and 1,4-hydrogenation as well (Scheme 38).

By combination of kinetic and chemical methods, and using $[Rh(cod)(PPh_3)_2]PF_6$ as the catalyst precursor, Sánchez-Delgado and co-workers have provided a further insight into the mechanism of the regioselective hydrogenation of Q to THQ.[70] The experimental rate law was $r_i = k_{cat}[Rh][H_2]^2$ with $k_{cat} = 50 \pm 6$ M^{-2} s^{-1} at 370 K and the following thermodynamic parameters were obtained: $\Delta H = 9 \pm 1$ kcal mol^{-1}, $\Delta S = -27.0 \pm 0.3$ eu. The isolation of $[Rh(cod)(Q)_2]PF_6$ at the end of the catalysis (370 K, ≤1 bar H_2, toluene), and the observation that the rate of hydrogenation of the partially reduced substrate dihydroquinoline (DHQ) was comparable with that of Q, allowed Sánchez-Delgado to propose the mechanism illustrated in Scheme 39.

The catalytic cycle starts with the displacement of PPh_3 by Q in the Rh^I precursor to give the bis-Q compound $[Rh(cod)(Q)_2]^+$, which then reacts with H_2 to give the Rh^{III} dihydride $[Rh(cod)(H)_2(Q)_2]^+$. After the C=N bond has been rapidly and reversibly reduced by two consecutive hydride transfers, a η^2(C,C)-DHQ complex is formed which



Scheme 37

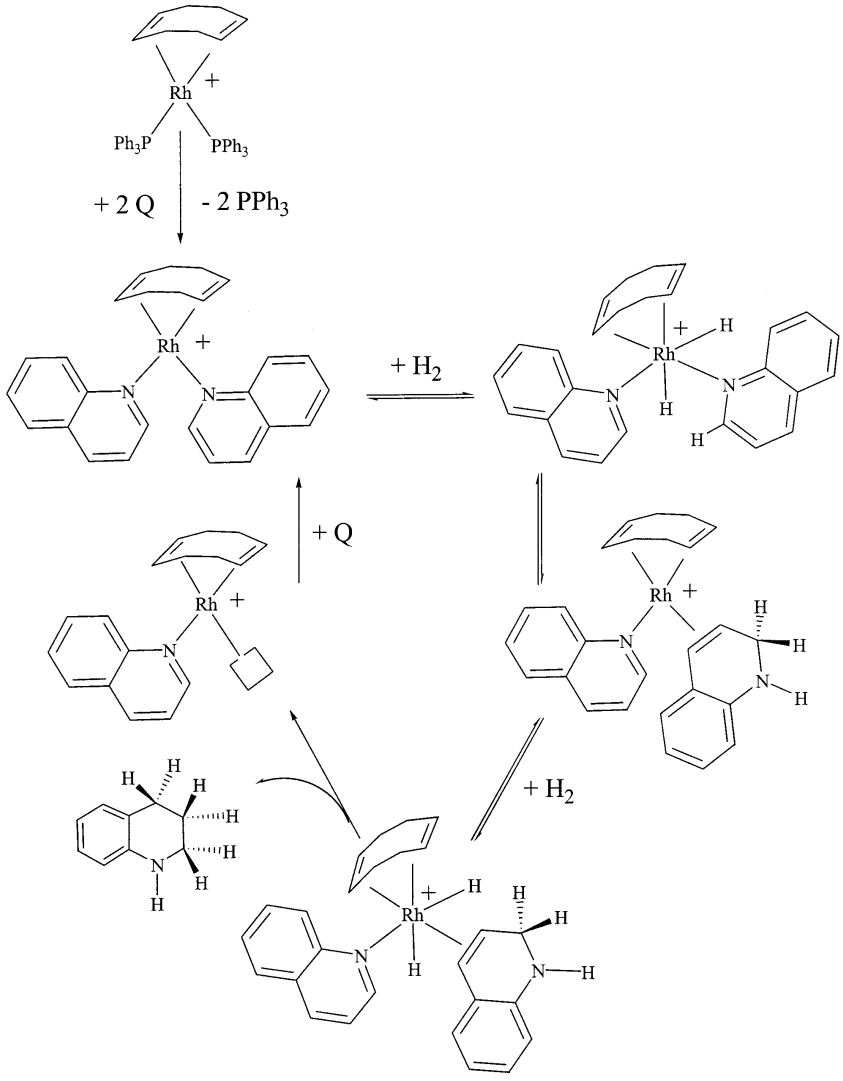


Scheme 38

slowly reacts with H_2 to give THQ. The irreversible displacement of THQ from rhodium by Q regenerates the bis-Q complex to continue the catalysis. According to the kinetic studies, the overall process that converts DHQ to THQ constitutes the rate-limiting step. Besides accounting for the kinetic results, the mechanism proposed by Sánchez-Delgado comprises steps that are commonly encountered in rhodium-catalysed olefin hydrogenation mechanisms where, unlike the Fish mechanism, the rhodium metal goes through the catalysis with the usual III→I→III reduction/oxidation cycle.

Kinetic studies for Q reduction to THQ have also been reported by Rosales and co-workers for the Ru^{II} complex $[RuH(CO)(MeCN)(PPh_3)_2]BF_4$.[71] At low hydrogen pressure, the experimental rate law $r_i = k_{cat}\,[Ru_0][H_2]^2$ (k_{cat} = 28.5 $M^{-2}\,s^{-1}$ at 398 K) was quite similar to that found by Sánchez-Delgado. In contrast, at high H_2 pressure, a first-order dependence of the reaction rate with respect to the hydrogen concentration was observed. The proposed mechanism involves a rapid and reversible partial hydrogenation of bonded Q, followed by a rate-determining second hydrogenation of DHQ.

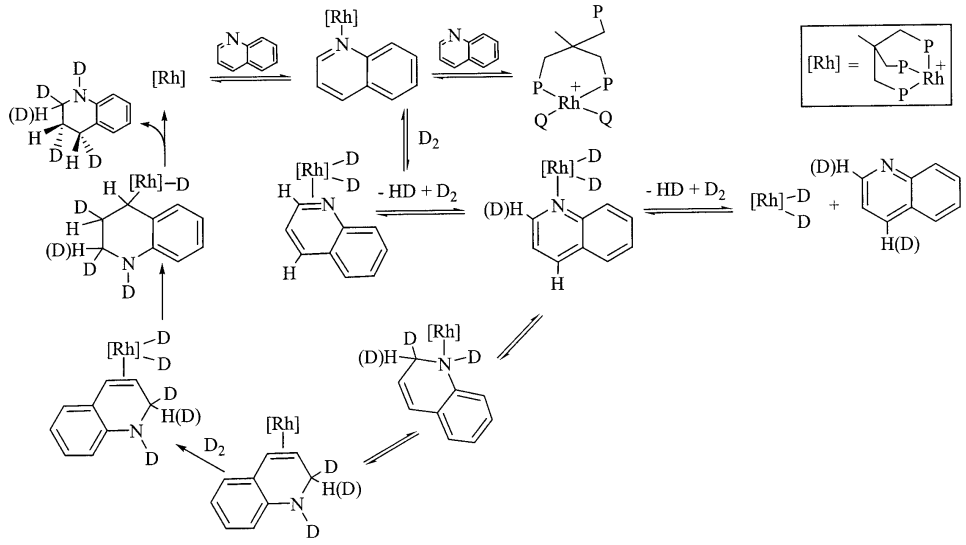
A zero-order dependence on the substrate concentration is not a general kinetic rule for the homogeneous hydrogenation of Q to THQ. A much more complex kinetic law was actually found for the reaction catalysed by the Rh^{I} complex [(triphos)Rh(DMAD)]PF_6 (triphos = $CH_3C(CH_2PPh_2)_3$; DMAD = dimethyl acetylenedicarboxylate).[72] Monitoring the formation of THQ with time by GC at a fixed temperature of 60 °C showed that the rate is



Scheme 39

first-order with respect to both H_2 (from 4 to 30 bar) and catalyst concentration (from 36 to 110 mM). In contrast, an inverse dependence of the hydrogenation rate with respect to Q concentration was found. The empirical rate law $r = k''\,[Rh][H_2][Q]^2$, where $k'' = k\,(a + b[Q] + c[Q]^2)^{-1}$, was proposed to account for the inhibiting effect of Q concentration and the experimental observation that the rate tends to be second-order for very low Q concentrations (< 30 mM) and zero-order for very high Q concentrations (> 70 mM). Depending on the concentration of Q, the experimental rate law thus simplifies to $r = k/c\,[Rh][H_2]$, to $r = k/a\,[Rh][H_2][Q]^2$ or to $r = k\,(b + c[Q])^{-1}[Rh][H_2][Q]$. On the basis of the kinetic study, deuterium labelling and high-pressure NMR spectroscopic experiments under catalytic conditions, as well as the identification of catalytically relevant intermediates, a mechanism was proposed which essentially differs from that reported by Sánchez-Delgado for the rate-limiting step, i.e. the reversible reduction of the C=N bond instead of that of the $C_3{=}C_4$ bond (irreversible) (Scheme 40). The overall hydrogenation of the C=N bond, which actually disrupts the aromaticity of Q, was proposed as rate-determining step also in light of the independent reduction of isolated 2,3-dihydroquinoline that, under comparable experimental conditions, was reduced faster than Q. Also, the lack of deuterium incorporation into the carbocyclic ring of both THQ and Q ruled out η^6-Q or η^6-THQ complexes.

The Rh catalyst generated from [(triphos)Rh(DMAD)]PF_6 underwent deactivation with time, due to the formation of catalytically inactive Rh^I monohydrido complexes by heterolytic splitting of H_2 promoted by the basic environment of the reaction.[73] The addition of an excess of strong protic acid such as triflic acid, CF_3SO_3H, to the catalytic mixture was sufficient to overcome this drawback and induce a remarkable rate enhancement: at 40 °C and 30 bar H_2, the tof [mol substrate (mol cat)$^{-1}$ h^{-1}] increased from 40 to 95 by addition of a 20-fold excess of acid.[72] The acid was shown to convert inactive Rh^I into active



Scheme 40

Rh^{III}. Based on this finding, the addition of strong protic acids was also found to be of mandatory importance for generating a catalytically active system from [(triphos)Ru(-MeCN)$_3$](O$_3$SCF$_3$)$_2$ which, under neutral conditions, is almost inactive for Q reduction. Indeed, treatment of the ruthenium compound with H_2 produces ammonia which preferentially coordinates, over Q, to the metal centre. Moreover, in the basic environment of the reaction, the presence of moisture[73a,74] was found to give the catalytically inactive dimer [(triphos)Ru(μ-OH)$_3$Ru(triphos)]$^+$. The protic acid inhibits the formation of both NH_3 adducts and the (μ-OH)$_3$ dimer, thus allowing the hydrogenation of Q to THQ to proceed smoothly with a tof of 65.[72]

The catalyst precursor [RuH(CO)(MeCN)$_2$(PPh$_3$)$_2$]BF$_4$ was also employed to catalyse the hydrogenation of various polyaromatic N-heterocycles under relatively mild conditions (125 °C, 4 bar H_2, xylene or toluene).[75] The reactivity order AC > Q >> 5,6-BQ > 7,8-BQ > IN > IQ was in line with previous trends and reflects steric and electronic effects. In particular, the greater propensity to reduction of AC as compared with Q was attributed to the higher resonance stabilisation energy of this latter, while the almost negligible reduction of IQ was accounted for by the higher basicity of the N atom in this substrate. A kinetic study was carried out for the reduction of AC to 9,10-dihydroacridine. Unlike Q, the experimental rate law was $r = k_{cat}$ [Ru][H_2] and the postulated mechanism involves, as the determining step, the hydrogenation of coordinated AC in [RuH(CO)(η^1(N)-AC)(MeCN)(PPh$_3$)$_2$]$^+$, yielding 9,10-dihydroacridine and the coordinatively unsaturated complex [RuH(CO)(MeCN)(PPh$_3$)$_2$]$^+$.

In homogeneous phase, IN is much more difficult to reduce than Q as shown by the limited number of known catalysts {e.g. (PPh$_3$)$_3$RuHCl[66] and [RuH(CO)(-MeCN)(PPh$_3$)$_2$]BF$_4$ [75]}, as well as their very scarce activity (tof's ≤1). Indeed, the η^1(N) coordination, which is critical for selective nitrogen ring reduction in Q, is virtually unknown for IN which prefers to bind to metal centres using the carbocyclic ring (vide infra). In the latter coordination mode, the C=N bond is not activated and too many sites at the metal centre are occupied so that the oxidative addition of H_2 is very difficult to accomplish. Consistently, the hydrogenation of IN is generally inhibited when the reaction mixture contains basic substrates such as Q, THQ, and PY. To the best of our knowledge, the only catalyst that is able to regioselectively hydrogenate IN to indoline with an acceptable tof is [(triphos)Rh(DMAD)]PF$_6$, on the condition that a protic acid is added to the catalytic mixture.[3a–3d,7] By using equivalent amounts of triflic acid and IN tof's as high as 100 were obtained already at 60 °C and 30 bar H_2. It was experimentally shown that indoline was actually formed by reduction of the protonated form of IN, the 3H-indolium cation which possesses a localised C=N bond.[72]

Aqueous-Biphase Hydrogenation of N-Heterocycles

The remarkable progress recently achieved in the field of water-soluble catalysts and the actual possibility of applying aqueous-biphase catalysis to large volume reactions[76] have encouraged the petrochemical industry to look at aqueous-catalysis as an alternative method for removing sulfur and nitrogen impurities from distillates. Recent publications[73c,77–79] and patents[80] show that the hydrogenation and hydrogenolysis of aromatic heterocycles in biphasic media is indeed technically feasible.

The selective hydrogenation of N-heterocycles has been achieved by researchers at PDVSA-INTEVEP with the use of water-soluble Ru^{II} catalysts stabilised by either triphenylphosphane trisulfonate (TPPTS) or triphenylphosphane monosulfonate (TPPMS) ligands.[77,80] As a general procedure, the catalysts were prepared in situ from RuCl$_3$·3H$_2$O and excess phosphane in water, and the resulting solution was added to a hydrocarbon solution containing various model N-heterocycles such as Q, AC, and IQ. The biphasic reactions were performed under relatively drastic experimental conditions (130–170 °C, 70–110 bar H_2) and gave

the selective reduction of the heterocyclic ring. It was generally observed that nitrogen compounds did not inhibit the hydrogenation of added thiophenic substrates. In fact, in some cases a promoting effect was observed. The beneficial effect of the N-compounds on the rate of hydrogenation of thiophenes has been attributed to the catalyst protection by amines, which are better nucleophiles than thioethers. As a matter of fact, the major ruthenium product isolated from the aqueous phase after hydrogenation of a BT/Q mixture with $RuCl_3 \cdot 3H_2O/TPPMS_{(excess)}$ in water/decalin was $RuHCl(TPPMS)_2(THQ)_2$ (**A** in Figure 11).

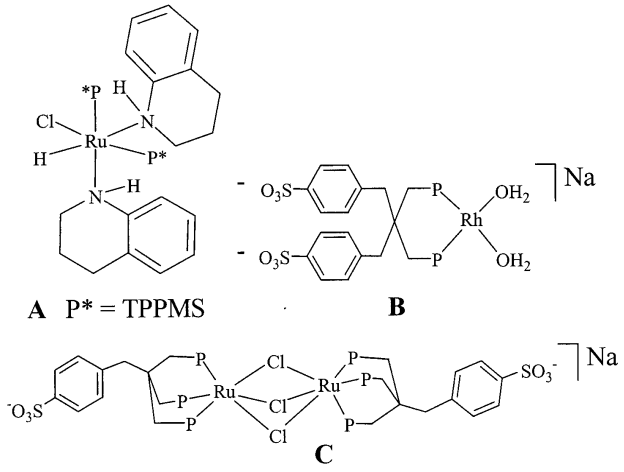


Figure 11. Water-soluble ruthenium complexes

The regioselective reduction of Q to THQ in water/hydrocarbon has been achieved also with bidentate and tridentate water-soluble ligands. In particular, the diphosphane $(NaO_3S(C_6H_4)CH_2)_2C(CH_2PPh_2)_2$ ($Na_2DPPPDS$) was found to form quite active systems in combination with rhodium and ruthenium.[5a,78] The Rh^I complex $[(DPPPDS)Rh(H_2O)_2]Na$ (**B** in Figure 11) was actually isolated and employed in water/*n*-octane to hydrogenate 1:1 mixtures of Q and BT at high temperatures (160 °C). Only the N-heterocycle was efficiently reduced (tof = 50), BT hydrogenation to 2,3-dihydrobenzothiophene (DHBT) being only marginal (tof = 2). A similar selectivity was found for the catalytic system $RuCl_3 \cdot H_2O/2Na_2DPPPDS$, prepared in situ. In contrast, the individual hydrogenation rates for Q and BT have been reported to be similar (tof = 30 at 140 °C, 30 bar H_2, water/*n*-heptane) and independent of the presence of either substrate when the dimeric complex $Na[\{(sulphos)Ru\}_2(\mu\text{-}Cl)_3]$ (**C** in Figure 11) was employed as precatalyst[79] [sulphos = tridentate ligand $^-O_3S(C_6H_4)CH_2C(CH_2PPh_2)_3$]. No attempt was made to determine whether the dimeric structure of the precursor was maintained during the catalysis. However, since the mononuclear complex $[(sulphos)Ru(MeCN)_3]^+$ has been found to catalyse the hydrogenation of BT to DHBT in water/decalin at a very similar rate,[79b] it is likely that disruption of the dimeric structure of C occurs under catalytic conditions. Under biphasic conditions, also the zwitterionic Rh^I complex (sulphos)Rh(cod) has been tested as a catalyst precursor for the hydrogenation of heterocycles. Although a modest catalyst for the hydrogenation of BT to DHBT, it is very efficient for the hydrogenation of Q to THQ (tof = 20 at 160 °C, 30 bar H_2, water/*n*-heptane).[79b]

Hydrogenation of N-Heterocycles by Supported Molecular Catalysts

In order to gain an insight into the reactivity of isolated metal surface sites under hydrotreating conditions, molecular catalysts of proven effectiveness for the hydrogenation of heteroaromatic rings have been heterogenised following different procedures.

The first of such approaches was reported by Fish in 1985. The molecular catalyst of choice was $Rh(PPh_3)_3Cl$, that the same author had shown to be active for the regioselective reduction of various polynuclear heteroaromatics.[81] The molecular precursor was tethered to 2% crosslinked phosphinated polystyrene-divinylbenzene and the resulting heterogeneous catalyst (**A** in Figure 12) was employed to hydrogenate Q, AC, 5,6-BQ and 7,8-BQ in benzene solution (85 °C, 310 psi H_2). The order of activity was identical to that in the homogeneous phase,[65] AC>Q>5,6-BQ>7,8-BQ, but the initial rates of the heterogeneous hydrogenations were from 10 to 20 times faster. This remarkable increased rate was essentially attributed to steric requirements surroundings the active metal centre in the tethered com-

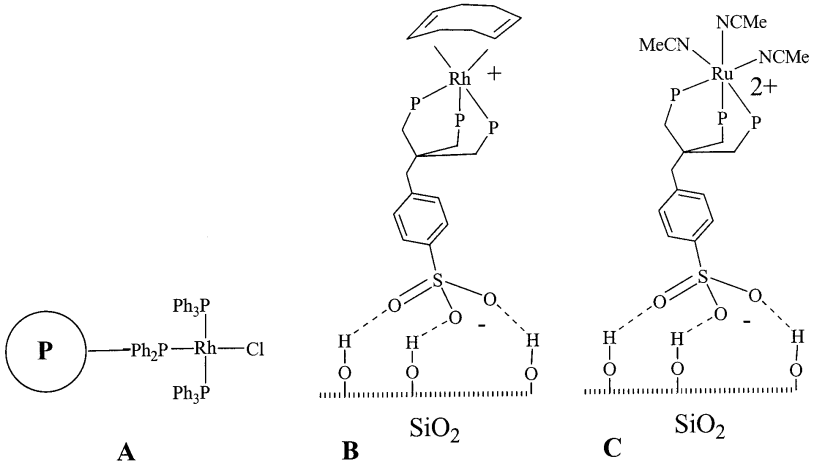


Figure 12. Supported molecular catalysts

plex, which apparently would favour the coordination of the N-heterocycles by disfavouring that of PPh_3. The regioselectivity of hydrogenation was even higher than that in the homogeneous phase as no formation of 1,2,3,4-tetrahydroacridine was observed. The deuteration pattern of the heteroaromatic ring after a catalytic reaction with D_2 was identical to that observed in the homogeneous phase, except for the lack of deuterium incorporation at position 8 of the carbocyclic ring. The supported catalyst was also employed to hydrogenate N-heterocycles in model coal liquid containing pyrene, tetralin, *p*-cresol, 2-methylpyridine and methylnaphthahalene. An increased rate was observed which was attributed to the ability of some constituents, especially *p*-cresol, to stabilise unsaturated rhodium species formed in the course of the catalysis.

The silica-supported hydrogen-bonded (SHB) rhodium complexes (sulphos)Rh(cod)/SiO_2 and [(sulphos)Ru(-MeCN)$_3$](SO$_3$CF$_3$)/SiO_2 (**B** and **C** in Figure 12), successfully employed to hydrogenate olefins in heterogeneous phase,[82][83] have been found to hydrogenate Q in *n*-octane (100 °C, 30 bar H_2) yielding selectively THQ with tof's as high as 100.[84] In line with the behaviour of the $Rh(PPh_3)_3Cl$/P-$Rh(PPh_2)_2Cl$ system,[81] both (sulphos)Rh(cod)/SiO_2 and [(sulphos)Ru(MeCN)$_3$](SO$_3$CF$_3$)/SiO_2 have been found to be more efficient catalysts than the homogeneous and aqueous-biphasic counterparts with triphos or sulphos ligands. The enhanced rate observed for the heterogeneous reactions has been attributed to the fact that, unlike in fluid solution systems, the heterogenised complexes do not undergo dimerisation to give catalytically inactive species.

Conclusions

The results described in this report define transition metal complexes as viable models for mimicking many steps occurring in heterogeneous HDN and allow the following conclusions to be drawn.

The η^1(N) and η^2(N,C) coordination modes of N-heterocycles are crucial for their hydrogenation and hydrogenolysis, respectively. In particular, it is evident that the regioselective hydrogenation of the heteroaromatic rings is effectively accomplished by late transition metals (promoters) in high oxidation states. Also, an acidic environment is generally found to promote efficient hydrogenation pathways. C−N bond cleavage is a difficult task that is best accomplished when the substrate uses the η^2(N,C) mode for binding an early transition metal in relatively low oxidation state. In all the cases reported, however, the C−N insertion step requires the transfer of a hydride ligand from the metal centre to the C−N carbon atom, which is consistent with a hydrolytic C−N insertion. The ultimate denitrogenation step apparently requires the cooperation of two metal centres as is commonly found for the homogeneous desulfurisation of thiophenes.[3−6,12] Accordingly, it does not seem likely that a single metal site can coordinate a N-heterocycle, insert into a C−N bond and finally remove the nitrogen atom.

Given the complexity of the HDN process and the many alternative or concomitant mechanisms that may be in operation even on the surface of the same catalyst, the homogeneous modelling studies must be considered with extreme caution. Most of the spectator ligands in solution reactions are actually not representative of the pool of ligands available to industrial hydrotreating catalysts. The model N-heterocycles generally employed (Q, PYR, IN) represent a fraction of nitrogen compounds in fossil fuels, and the environment of the reactions is extremely different. Nonetheless, we have shown here that many reactions involving transition metal complexes and N-heterocycles show sound analogies with related reactions occurring over the surface of heterogeneous catalysts. These analogies and the relative mechanistic information continue to give HDN modelling a great boost.

Acknowledgments

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