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Coordination Chemistry Reviews
196 (2000) 249–280

COORDINATION CHEMISTRY REVIEWS

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Kinetic studies as a tool for the elucidation of the mechanisms of metal complex-catalyzed homogeneous hydrogenation reactions

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Received 12 March 1999; accepted 25 May 1999

Contents

Abstract

The role of transition metal complexes as catalysts for homogeneous hydrogenation reactions has been extensively investigated during the last few decades. This paper reviews

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PII: S0010-8545(99)00168-X

recently disclosed work by a number of research laboratories including ours, which shows that the study of the kinetics of such processes is a particularly important tool which, if used in combination with spectroscopic techniques, isotope labeling, isolation of stable analogues and theoretical calculations, allows the elucidation of the mechanisms operating in a variety of homogeneous catalytic hydrogenation reactions.

Keywords: Kinetics; Mechanisms; Homogeneous hydrogenation

1. Introduction

Some of the most important applications of coordination and organometallic compounds over the past several decades have been associated with their use in homogeneous catalytic reactions, a number of which are actually practiced in large scale industrial processes [1]. The study of homogeneous hydrogenation reactions catalyzed by transition metal complexes has been far more extensive than that of any other catalytic process in solution, mainly because these reactions have proved to be amenable for detailed investigations and thus they have played a key role in the fundamental understanding of catalytic reactions in general. James has produced a classic book and an update on homogeneous hydrogenation which are obliged reading for anyone interested in the field [2a,b]; Oro et al. contributed with a more recent book on homogeneous hydrogenation [2c].

Some hydrogenation reactions are of great utility in practical applications in organic synthesis at the laboratory scale (e.g. $RhCl(PPh_3)_3$ is today a standard reducing agent [3]) and some enantioselective hydrogenation reactions are becoming a very important alternative in the industrial manufacture of fine chemicals and pharmaceuticals [4].

Although homogeneous catalytic hydrogenation has been known since 1938 [5], historically three key events have represented in our view, the most important breakthroughs concerning the introduction of new catalysts: (1) the discovery of $RhCl(PPh_3)_3$, commonly referred to as 'Wilkinson's Catalyst' [6], which marked the entry into modern homogeneous catalysis; (2) the report on cationic Rh and Ir phosphine complexes by Schrock and Osborn [7], which set the basis for the subsequent impressive development in asymmetric hydrogenation of prochiral substrates through the incorporation of chiral phosphine ligands [4]; and (3) the recent modification of Ru–phosphine systems by addition of N-donor ligands, which opened the way for a number of important discoveries by Noyori and others, most notably in the asymmetric hydrogenation of C=O bonds and other related reactions [8].

Although a great proportion of the published work has dealt with the hydrogenation of C=C bonds, a wide variety of other substrates have been investigated, such as acetylenes, carbonyl compounds, nitro groups and arenes [2]. Recently, the hydrogenation of nitrogen- and sulfur-containing aromatic substrates has received considerable attention by our groups and others because of their relation with the

industrially important hydrodenitrogenation (HDN) and hydrodesulfurization (HDS) processes (see Section 6).

The mechanistic aspects of homogeneous catalytic reactions have been addressed by a number of authors and some impressive developments have emerged over the years; nevertheless, this remains an area of constant evolution, as the understanding of many active systems is far from complete. Although one of the commonly cited advantages of homogeneous catalysts over their heterogeneous counterparts is that they are amenable to detailed mechanistic elucidation, a complete catalytic cycle is often difficult to establish since it involves several connected elementary steps and numerous labile species in equilibrium. Thus, the apparently simple reaction schemes which often appear to be 'plausible' on the basis of chemical intuition and knowledge, or even as a result of chemical or spectroscopic identification of a few species, may in fact correspond to systems of great complexity. It is only when such considerations are combined with the study of the reaction kinetics that a full understanding of the catalytic phenomenon may be attempted. On the other extreme, trying to understand the mechanisms of homogeneous hydrogenation reactions purely from a kinetic study of the overall process may also lead to incomplete or even erroneous conclusions. Possibly the best way to tackle this type of problem is through a combination of kinetic measurements of the overall catalytic reaction and of as many of the individual steps as possible, with other analytical tools (NMR spectroscopy being particularly useful), as well as the isolation and/or independent syntheses of stable intermediates or model compounds; also theoretical calculations may provide important additional information.

In view of this complex situation, it is not surprising that relatively few papers deal specifically with kinetic and mechanistic studies of homogeneous catalytic reactions. Perhaps the most remarkable examples of such work can be found in the pioneering studies carried out by Halpern (see below) which definitely must be considered as one of the major landmarks in homogeneous catalysis, as they set the basis for the continuing interest in this field.

In this article, we provide an account of recently published work concerning kinetic investigations of hydrogenation reactions catalyzed by soluble transition metal complexes. Because the extensive literature already cited [2] covers all the general aspects of homogeneous hydrogenation, rather than attempting a comprehensive coverage of the subject here we will concentrate on particularly important and/or recent examples, with some emphasis on results from our own laboratories in Caracas and Maracaibo, in order to illustrate the potential of kinetics as a tool for understanding catalytic reactions.

2. Hydrogenation of alkenes

2.1. Dihydride catalysts

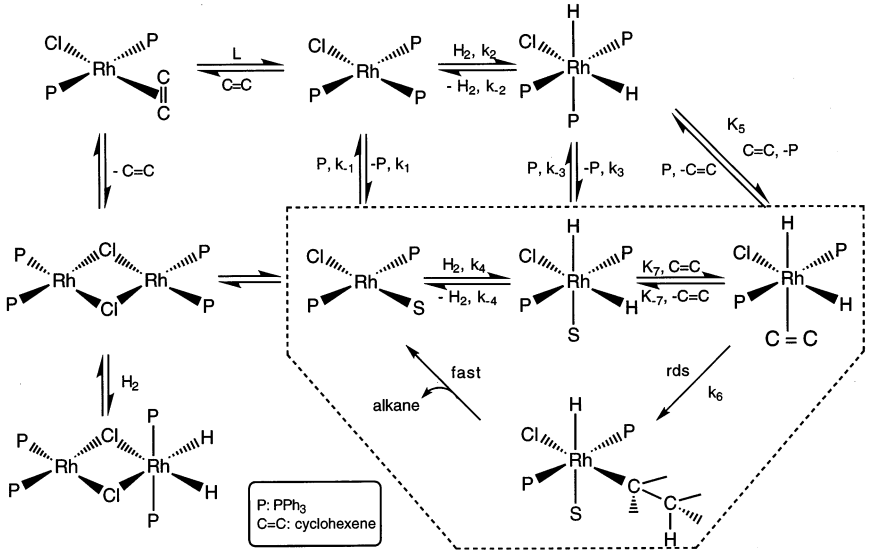
As mentioned above, the hydrogenation of C=C bonds is the most thoroughly

studied catalytic reaction in homogeneous phase. The mechanisms of olefin hydrogenation by use of Wilkinson's catalyst $RhCl(PPh_3)_3$, and of the cationic systems $[Rh(S)_2(P–P)]X$ (S = solvent, P–P = 1,2-bis(diphenylphosphino)ethane, diphos), and $X = PF_6^-$, BF_4^-) are classic examples of Halpern's successful analysis of kinetic and equilibrium parameters measured for individual reactions and for the overall catalytic process. These measurements, in combination with spectroscopic and other analytical tools, provided the right means for deducing the corresponding catalytic cycles depicted in Schemes 1 and 2, which have come to be widely known as the 'hydride route' and 'the olefin route', respectively.

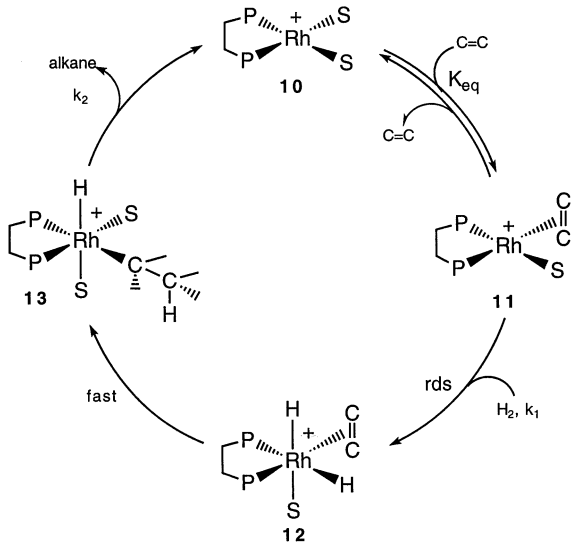
The rate law derived for the mechanism in Scheme 1 ('hydride route') is given by Eq. (1) (where C=C is cyclohexene and P is PPh_3):

$$[k_{cat}]^{-1} = \frac{[Rh_0]}{rate} = \frac{1}{k_6} + \frac{[P]}{K_5 k_6 [C{=}C]} + \frac{[P]}{K_1 k_4 [H_2]} \quad (1)$$

The beauty of this system rests in the fact that it allowed Halpern and his co-workers to measure directly each and every rate and equilibrium constant individually for the corresponding stoichiometric reaction. The remarkable coincidence of the values obtained from Eq. (1) with the measured catalytic rates, constituted a highly reliable test of the proposed mechanism. Moreover, several of the species in the peripheral cycle (Scheme 1, outside the dotted lines) could be properly characterized in the solid state and/or in solution, thus adding to the



Scheme 1. The mechanism for the hydrogenation of alkenes catalyzed by $RhCl(PPh_3)_3$.



Scheme 2. The mechanism for the hydrogenation of alkenes catalyzed by $[Rh(diphos)(solv)_2]^+$.

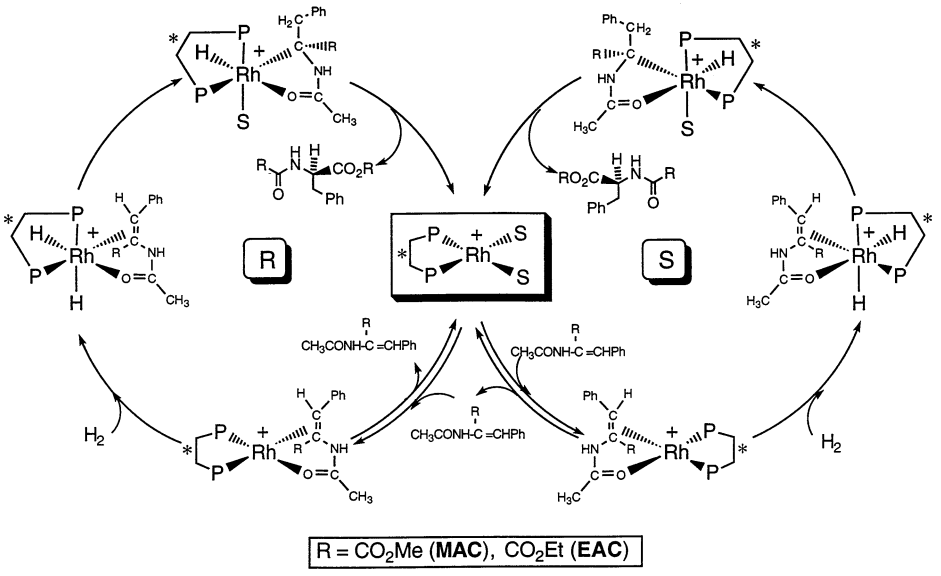
overall coherence of Halpern's proposal. An additional important information derived from these studies was that none of the stable complexes identified was actually involved in the catalytically operative (inner) cycle, which is good warning against proposing mechanisms solely on the basis of isolated or detected species. Finally, it should be mentioned that when the substrate was changed to styrene (a better coordinating olefin but otherwise closely related molecule) similar studies showed the mechanism to be slightly different, further illustrating the complexity of these reactions and the difficulty in trying to derive 'general mechanisms'.

Also of interest is the fact that on going to cationic complexes $[Rh(S)_2(diphos)]X$ containing a chelating diphosphine, the dominant mechanism of olefin hydrogenation, also elucidated by Halpern, involves an 'olefin path', as depicted in Scheme 2. An olefin complex [Rh(S)(olefin)(diphos)]X is formed in equilibrium with $[Rh(S)_2(diphos)]X$ before reaction with hydrogen takes place. Halpern was again able to measure the individual rate and equilibrium constants, and arrive at the rate law in Eq. (2):

$$r = k_{cat}[Rh]_0[olefin][H_2] \qquad k_{cat} = \frac{k_1 K_{eq}}{1 + K_{eq}[olefin]} \tag{2}$$

Also, most of the species involved were characterized by NMR and/or X-ray diffraction data.

Yet a further interesting extension of the mechanism described for $[Rh(S)_2(diphos)]X$ (Scheme 3) is the one proposed also by Halpern for proquiral olefins such as methyl(*Z*)- and ethyl(*Z*)-α-acetamidocinnamate (MAC and EAC, respectively) by use of rhodium complexes with chiral diphosphines, which is shown in Scheme 3. In this case two parallel pathways are possible which lead to the

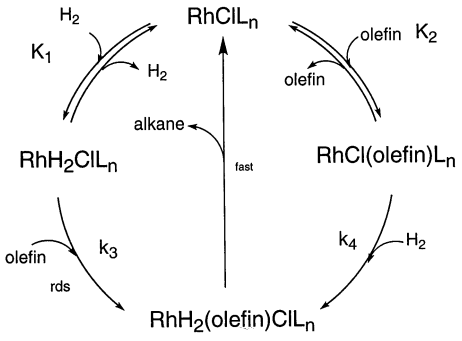


Scheme 3. The mechanism for the enantioselective hydrogenation of prochiral alkenes catalyzed by $[Rh(P–P^*)_2(solv)_2]^+$ (P–P* = chiral diphosphine).

formation of two diastereoisomers. Kinetic measurements together with NMR studies and the determination of absolute configurations of intermediates and products by X-ray diffraction, demonstrated that the minor intermediate diastereomer (which is not detected in solution!) reacts faster with hydrogen to yield predominantly the R isomer of the product, once again pointing to the danger of assuming that the major intermediates observed are always responsible for product formation. Although these studies can be found in any major textbook on organometallic chemistry and catalysis [9], the reader unfamiliar with Halpern's work is strongly advised to read the original papers [10–14].

Another important contribution to field is contained in a series of articles published by Taqui Khan and co-workers [15], who have extensively studied the kinetic and thermodynamic aspects of the homogeneous hydrogenation of olefins by, among others, rhodium and iridium complexes of the type $RhClL_n$, with monodentate, bidentate and tridentate phosphines as well as some arsines. For instance, using Rh with $L = PPh_2CH_2CH_2EPh_2$ (E = P, As) for the hydrogenation of cyclohexene (C=C), their results indicate that the catalytic cycle involves dihydride intermediates operating both through a hydride path and through an olefin path, as depicted in Scheme 4. The experimentally determined rate law for the catalytic hydrogenation, in accord with the proposed catalytic cycle, is of the form shown in Eq. (3):

$$r = \frac{k_3 K_1 [Rh]_0 [C{=}C][H_2]}{(1 + K_1[H_2])(1 + K_2[C{=}C])} \tag{3}$$



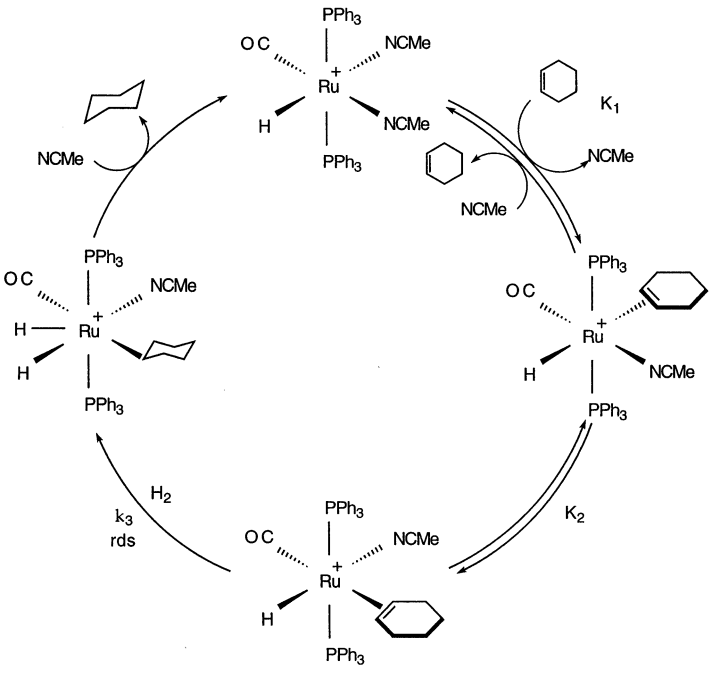
Scheme 4. The mechanism for the hydrogenation of alkenes catalyzed by $RhClL_n$ (L = monodentate or polydentate phosphine).

The kinetic measurements were complemented by use of ^{1}H- and ^{31}P-NMR spectroscopy in order to propose the mechanism of Scheme 4. Also interestingly, this group has provided a large amount of thermodynamic data, some of which is collected at the end of this article together with those from other authors. Although the interpretation of such data is at present difficult, some general considerations will be made in the appropriate Section.

2.2. Monohydride catalysts

Another important class of hydrogenation catalysts are in the form of monohydrido complexes, the prototypical one being $RuHCl(PPh_3)_3$, another early discovery by Wilkinson, who also provided some kinetic data for the overall reaction and the basic ideas of the mechanism operating in this case [16]. Recently, two kinetic and mechanistic studies of the hydrogenation of cyclohexene with ruthenium catalysts have come out of our laboratories. In both cases, the hydrogenation proceeds through mechanisms involving coordination of cyclohexene to monohydride intermediates, hydride migration to the olefin, oxidative addition of H_2 and reductive elimination of the product as the elementary steps of the cycles. Rosales and co-workers [17a] reported the use of $[RuH(CO)(NCMe)_2(PPh_3)_2]BF_4$ as the catalyst precursor. The experimental rate law was found to be $r = k_{cat}[Ru][C_6H_{10}][H_2]$ and $r = k_{cat}[Ru][H_2]$ at low and high concentrations of the substrate, respectively. These kinetic data were consistent with a mechanism involving a reversible displacement of the acetonitrile ligand *trans* to the hydride by cyclohexene, followed by an isomerization prior to the rate-determining addition of hydrogen (Scheme 5). As this mechanism consists of two equilibria preceding the rate-determining step (rds), the Equilibrium Approximation [18] could be applied, yielding the rate expression in Eq. (4):

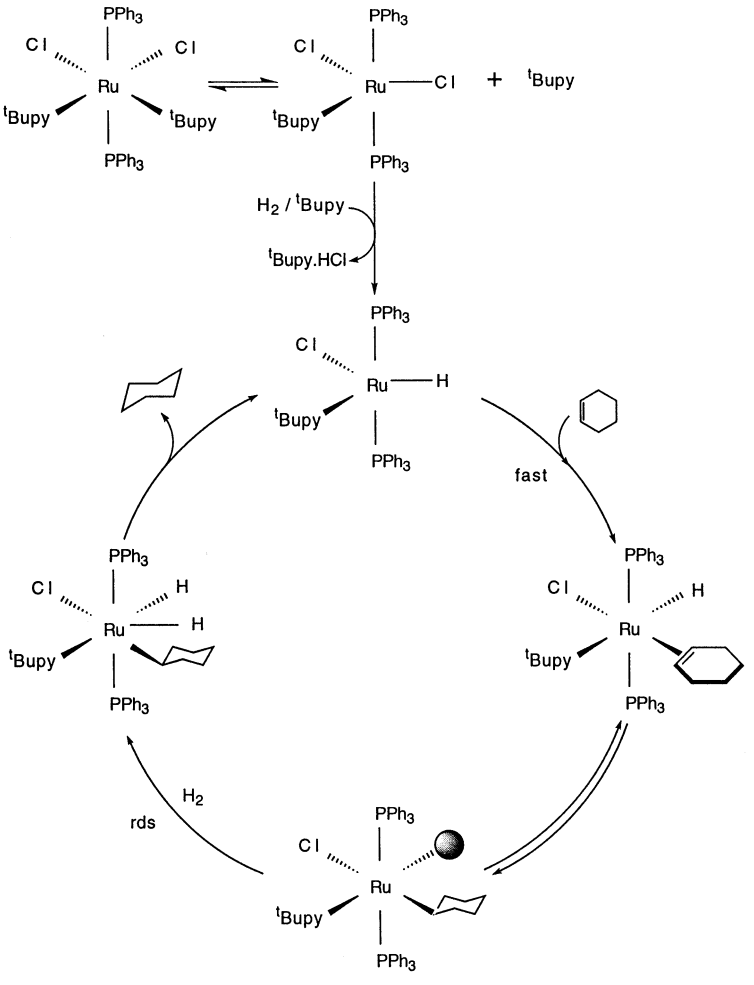
$$r = \frac{K_1 K_2 k_3 [Ru]_0 [C{=}C][H_2]}{[MeCN] + K_1(1 + K_2)[C{=}C]} \tag{4}$$



Scheme 5. The mechanism for the hydrogenation of cyclohexene catalyzed by $[RuH(CO)(MeCN)_2(PPh_3)_2]^+$.

which is in good agreement with the experimental rate law observed at both low and high substrate concentrations, as well as with other knowledge on the chemical behavior of this cationic ruthenium precursor previously reported by us [17b].

Bolaños and Sánchez-Delgado [19] described a kinetic study of the hydrogenation of the same substrate in presence of $RuCl_2(4\text{-}^t\text{Bu-py})_2(PPh_3)_2$. The rate of hydrogenation in this case was independent of the substrate concentration ($r = k_{cat}[Ru][H_2]$), which corresponds to a mechanism involving a fast coordination of cyclohexene to an electronically unsaturated monohydride species $RuHCl(4\text{-}^t\text{Bu-py})(PPh_3)_2$ (quickly formed from the initial dichloride under catalytic conditions), followed by a rate-limiting oxidative addition of H_2 and rapid reductive elimination of the cyclohexane product (Scheme 6). In this system, although the rds also seems to be the addition of dihydrogen, similar to the mechanism with the cationic ruthenium system, an important difference was related to the facile dissociation of the pyridine ligand from the catalyst precursor, which favors the formation of coordinatively unsaturated hydride species capable of effectively adding the olefin even at low substrate concentration.

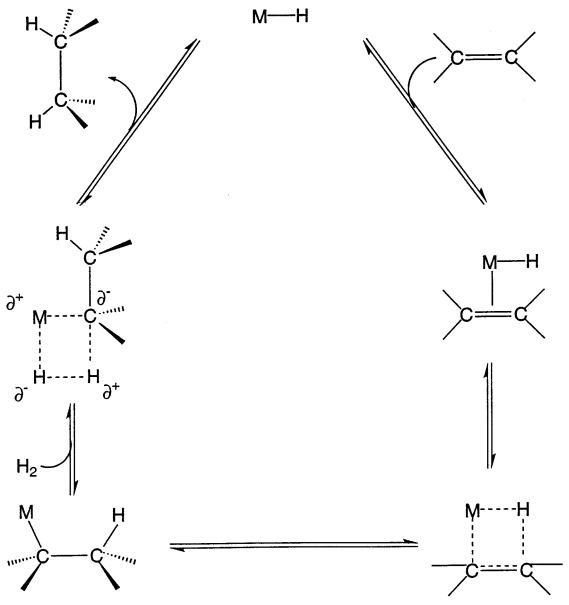


Scheme 6. The mechanism for the hydrogenation of cyclohexene catalyzed by $RuHCl(^tBu\text{-}py)_2(PPh_3)_2$.

2.3. Organolanthanide catalysts

Marks has provided a very interesting series of organolanthanide complexes of the general formulae $(Cp'_2MH)_2$, $Cp' = \eta^5\text{-}C_5Me_5$, M = La, Nd, Sm, Lu, and $(Me_2SiCp''_2MH)_2$, $Cp'' = \eta^5\text{-}C_5Me_4$, M = Nd, Sm, and Lu which are extremely active as olefin hydrogenation catalysts under very mild reaction conditions (25°C and 1 atm H_2) [20]. A very detailed kinetic analysis, together with substrate selectivities, labeling experiments and stoichiometric model reactions clearly showed that these complexes effect the hydrogenation through a mechanism involving a close coupling of olefin/hydride insertion followed by a four center hydrogenolysis, rather than via classical oxidative addition/reductive elimination sequences. In the

case of 1-hexene the rate law is $r = k[\text{cat}][H_2]$ suggesting a rapid exothermic Ln–H/olefin addition and a rate limiting M–C hydrogenolysis. In the case of cyclohexene $r = k[\text{olefin}][\text{cat}]^{1/2}[H_2]$ which implies a rate limiting Ln–H/olefin addition except for Cp'_2Lu for which $r = k[\text{olefin}][\text{cat}]$ which is indicative of a $(Lu–H)_2$/olefin addition as the rate limiting step. A general reaction network for these lanthanide catalysts is shown in Scheme 7.

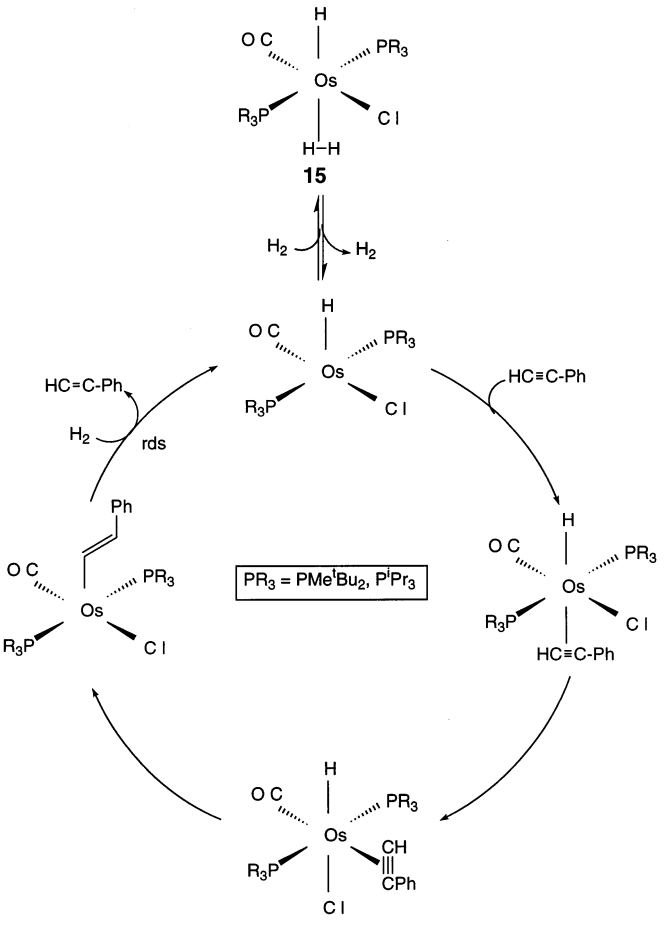


Scheme 7. The mechanism for the hydrogenation of alkenes by organolanthanide catalysts.

3. Hydrogenation of alkynes

Despite the fact that a number of complexes are known to reduce alkynes, some highly selectively to the corresponding alkene [2], detailed mechanistic knowledge like the one available for C=C bond hydrogenation has seldom being put forward. A particularly interesting example of such a mechanistic study was provided by Andriollo et al. [21] who found that the complexes $OsHCl(CO)(PR_3)_2$, $PR_3 = PMe^tBu_2$, P^iPr_3 (also termed the 'Zaragoza-Wurzburg catalysts' [22]) catalyze the sequential hydrogenation of phenylacetylene in 2-propanol solution at 60°C. Selectivities close to 100% were obtained for the hydrogenation of the alkyne to the alkene.

The kinetic investigation of the hydrogenation of phenylacetylene to styrene indicated a first-order dependence on catalyst, substrate and hydrogen concentrations ($r = k_{cat}[Os]_0[C{\equiv}C][H_2]$). Since the reactivity of the hydrido carbonyl complexes toward hydrogen and alkynes were also extensively studied, a well-founded

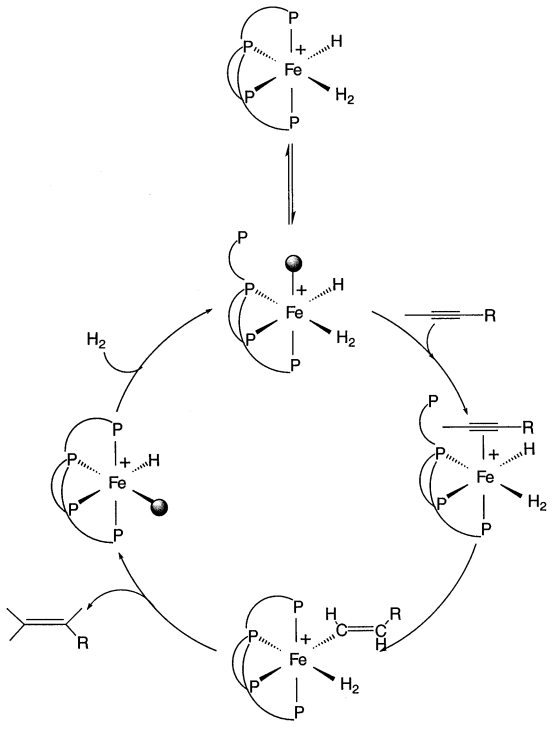


Scheme 8. The mechanism for the hydrogenation of phenylacetylene catalyzed by $OsHCl(CO)(PR_3)_2$ ($R = PMe^tBu_2$, P^iPr_3).

mechanism could be proposed in accord with the kinetics and the coordination chemistry, as shown in Scheme 8. The monohydrides react rapidly with hydrogen under ambient conditions to form the corresponding dihydrogen compounds $OsHCl(\eta^2\text{-}H_2)(CO)(PR_3)_2$. Furthermore, the hydrides react with phenylacetylene initially through coordination of the triple bond to Os (a stable analogue with $R'C{\equiv}CR'$, $R' = CO_2Me$ was isolated), followed by an isomerization into a stereochemistry in which the alkyne and the hydride are in mutually *cis* positions (followed by NMR) well suited for the insertion into the M–H bond to take place yielding the stable vinylosmium products $Os(CH{=}CHPh)Cl(CO)(PR_3)_2$. The slow step of this cycle is the reaction of these vinyl intermediates with hydrogen to yield styrene and regenerate the starting hydride.

In the absence of phenylacetylene, the same complexes catalyze the hydrogenation of styrene to ethylbenzene at rates of about ten times faster than those observed for C≡C bond reduction by a similar mechanism to that for the hydrogenation of the alkyne, although the reaction is zero-order with respect to hydrogen concentration ($r = k_{cat}[Os]_0[C{=}C]$) and so in this case hydrogen addition is not the rds. What is interesting is that these results clearly show that hydrogenation of styrene is the kinetically favored reaction, and thus the high selectivity for reducing the alkyne to the alkene must have a thermodynamic origin. This was found in the formation of the very stable vinyl–osmium intermediates which represent a thermodynamic sink that causes virtually all the osmium present to be tied up in this form, and consequently the kinetically unfavorable pathway becomes essentially the only one available in the presence of even small amounts of the alkyne. Another interesting study of sequential hydrogenation of alkynes by Rh complexes also incorporates kinetic data and a mechanistic proposal with many features in common with the one described in Scheme 8; for the sake of brevity this will not be further discussed here and the reader is referred to the original paper by Werner et al. [23a]. In a further publication by Oro and co-workers, the cationic complex $[Ir(COD)(\eta^2\text{-}Pr_2PCH_2CH_2OMe)]BF_4$ was also shown to be a good catalyst for the hydrogenation of phenylacetylene and the reaction mechanism was elucidated by a combination of kinetic, chemical and spectroscopic data [23b]. Although the main species observed under catalytic conditions was $[IrH(C_2Ph)(COD)(\eta^2\text{-}^iPr_2PCH_2CH_2OMe)]BF_4$ catalysis proceeds via a dihydrido–diolefin intermediate $[IrH_2(COD)(\eta^2\text{-}^iPr_2PCH_2CH_2OMe)]BF_4$ which reacts reversibly with phenylacetylene to yield $[IrH(CH{=}CHPh)(COD)(\eta^2\text{-}^iPr_2PCH_2CH_2OMe)]BF_4$, followed by a rate-determining reaction of the hydrido vinyl species with hydrogen to regenerate the dihydride and liberate the alkene product, in accord with the experimentally determined rate law $r = k[cat][P(H_2)]^2$. It is interesting to note that the diolefin is not hydrogenated during the alkyne hydrogenation cycle; also, in contrast with the findings for the neutral osmium catalysts described above, the high selectivity for triple bond hydrogenation in the case of the cationic Ir systems was ascribed to kinetic reasons, i.e. the alkyne competing favorably for the displacement of the OMe group of the ligand in comparison with the olefin.

Another interesting example of selective C≡C bond hydrogenation involves the *cis*-hydride dihydrogen complex $[(PP_3)Fe(H)(H_2)]BPh_4$, $PP_3 = P(CH_2CH_2PPh_2)_3$ which was found to be inactive for the hydrogenation of alkenes. A kinetic analysis led to the rate law $r = k[cat][alkyne]$; these data, combined with spectroscopic and chemical evidence led to the mechanism depicted in Scheme 9. A key feature of this mechanism is the fact that no decoordination of dihydrogen is required at any stage of the cycle and the vacant site is created by unfastening of one of the P-donor atoms. The binding of the alkyne to the metal center appears to be the rds [23c].

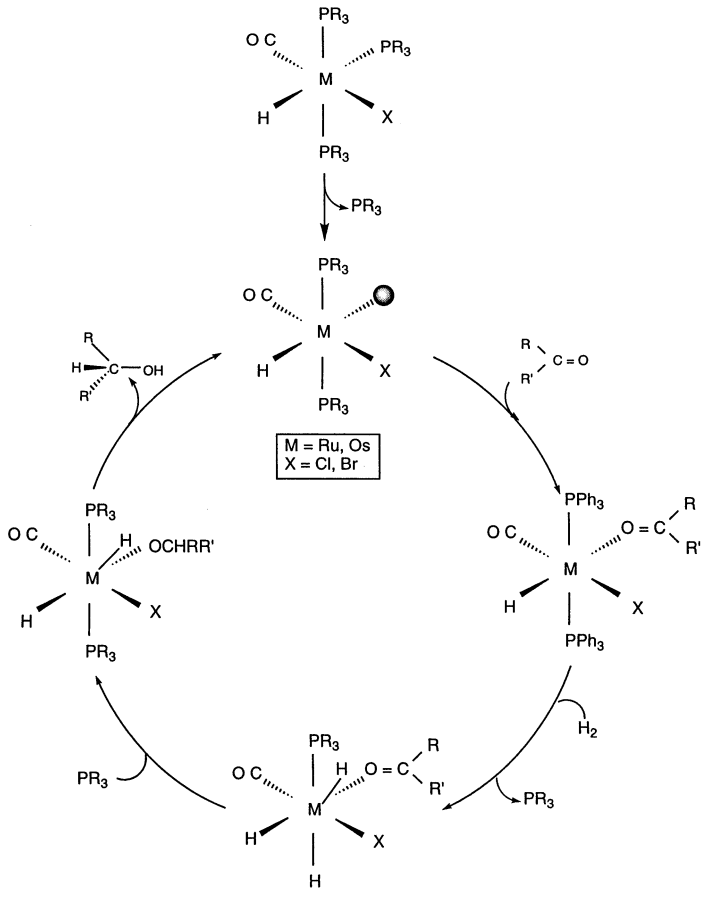


Scheme 9. The mechanism for the hydrogenation of phenylacetylene catalyzed by $[(PP_3)Fe(H)(H_2)]BPh_4$.

4. Hydrogenation of C=O and C=N bonds

The homogeneous catalytic reduction of aldehydes and ketones to their corresponding alcohols has received considerable attention. Hydrogenation by use of the complexes $MHX(CO)(PPh_3)_3$ (M = Ru and Os; X = Cl, Br) and its chloro- and hydride derivatives as the catalyst precursors has been extensively studied by Sánchez-Delgado and co-workers [24]. These early studies included some overall kinetic measurements as well as some mechanistic proposals, particularly for $MHCl(CO)(PPh_3)_3$ (Scheme 10). For carboxylate derivatives of the general formula $MH(OCOR)(CO)(PPh_3)_2$ the mechanism was similar to that in Scheme 10 except that the vacant coordination site required for the catalysis is formed by a bidentate–monodentate transformation of the carboxylate ligand, which in turn depends on the nature of the R group as demonstrated by a nice correlation between hydrogenation rates and the pK_a of the corresponding RCO_2H.

Halpern and Linn [25] carried out a kinetic and mechanistic study for the stoichiometric and catalytic reduction of cyclohexanone in the presence of anionic polyhydride ruthenium complexes *fac*-$[RuH_3(PPh_3)_3]^-$. They interpreted the data in terms of the stoichiometric reactions 5–7 which were studied individually (L = *c*-$C_6H_{10}O$, *c*-$C_6H_{11}OH$):



Scheme 10. The mechanism for the hydrogenation of aldehydes catalyzed by $MHX(CO)(PPh_3)_3]$ (M = Ru, Os; X = Cl, Br).

$$fac\text{-}[RuH_3(PPh_3)_3]^- + c\text{-}C_6H_{11}OH \overset{K_{eq}}{\rightleftharpoons} RuH_4(PPh_3)_3 + c\text{-}C_6H_{11}O^- \quad (5)$$

$$RuH_4(PPh_3)_3 + c\text{-}C_6H_{10}O \rightarrow RuH_2(PPh_3)_3L + c\text{-}C_6H_{11}OH \quad (6)$$

$$RuH_2(PPh_3)_3L + H_2 \rightarrow RuH_4(PPh_3)_3 + L \quad (7)$$

However, what was thought at the time to be $RuH_4(PPh_3)_3$ was later reformulated as a Ru(II) dihydrogen complex $Ru(H_2)(H)_2(PPh_3)_3$, which is actually just another member of the family $Ru(H)_2(L)(PPh_3)_3$ mentioned by Halpern, and the catalytic cycle originally proposed should be modified accordingly, in better accord with the involvement of the dihyrogen species now known to be present. The catalytic rate law for the overall Ru-catalyzed hydrogenation of cyclohexanone was found to be:

$$\frac{-\mathrm{d}[C_6H_{10}O]}{\mathrm{d}t} = k[\text{'}RuH_4(PPh_3)_3\text{'}][C_6H_{10}O] \quad (8)$$

which is essentially identical with that found for the stoichiometric reaction of '$RuH_4(PPh_3)_3$' with cyclohexanone (Eq. (6)). This proves that the only operative catalytic mechanism coincides with the combination of stoichiometric reactions investigated. From the temperature dependence of k (in the catalytic or stoichiometric reaction), the following activation parameters were deduced: $\Delta H^{\neq} = 15.0 \pm 1$ kcal mol^{-1}; $\Delta S^{\neq} = 34.2 \pm 3$ cal K^{-1} mol^{-1}.

Rosales and co-workers [26a] described a detailed kinetic and mechanistic study of the hydrogenation of benzaldehyde catalyzed by $[RuH(CO)(NCMe)_2(PPh_3)_2]BF_4$ in 2-methoxyethanol. The experimental rate law was found to be $r = k_{cat}[Ru][PhCHO][H_2]$, where $k_{cat} = 20$ M^{-2} s^{-1}. The activation parameters ($\Delta H^{\neq} = 4.6 \pm 0.5$ kcal mol^{-1}; $\Delta S^{\neq} = -40 \pm 2$ cal K^{-1} mol^{-1}; $\Delta G^{\neq} = 18 \pm 1$ kcal mol^{-1}) and the KIE value ($k_{cat(H)}/k_{cat(D)} = 1.2$) were also calculated.

The complex $[RuH(CO)(NCMe)_2(PPh_3)_2]BF_4$ reacts with both 2-metoxyethanol and benzaldehyde in chloroform to yield the corresponding mono- and disubstitution products.

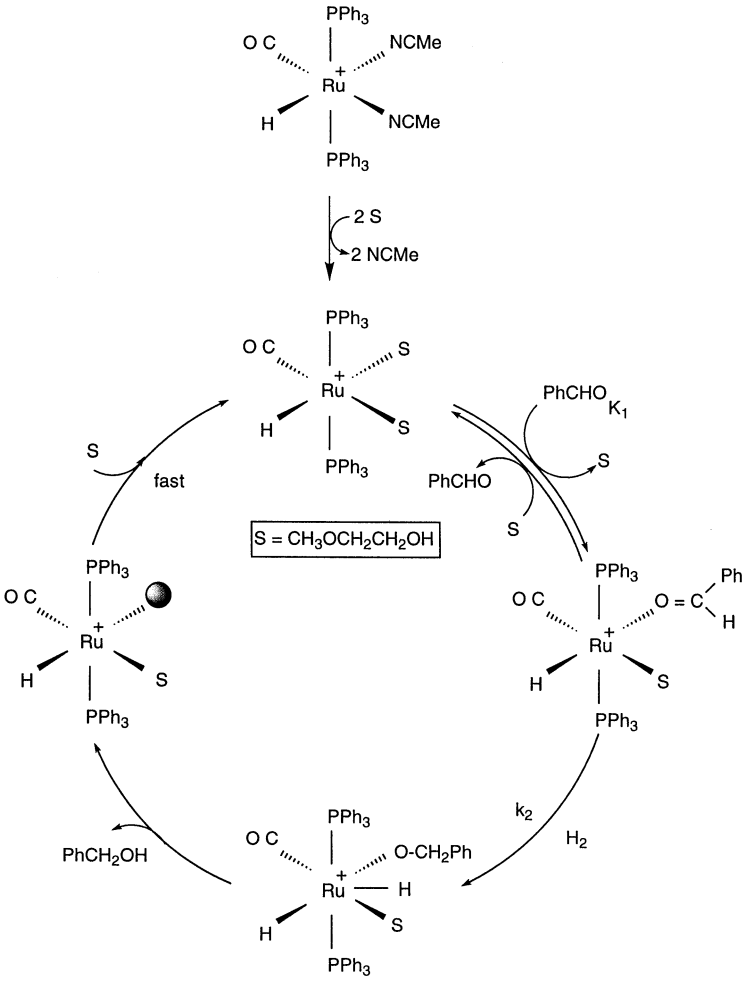
On the basis of the experimental findings, a general catalytic cycle for the $[RuH(CO)(NCMe)_2(PPh_3)_2]BF_4$-catalyzed hydrogenation of benzaldehyde was proposed, which is illustrated in Scheme 11. The solvated complex is proposed to be the initial species entering the cycle; then the incoming benzaldehyde will occupy the site *trans* to the hydride ligand to produce $[RuH(CO)(S)(PhCHO)(PPh_3)_2]BF_4$ through the equilibrium K_1. Oxidative addition of H_2 could lead to an 18-electron, 7-coordinated Ru(IV) trihydride, $[RuH_3(CO)(PhCHO)(PPh_3)_2]BF_4$, or $[Ru(H)(H_2)(CO)(PhCHO)(PPh_3)_2]BF_4$ which would rapidly evolve by transferring one hydride to the aldehyde to form $[RuH_2(CO)(OCH_2Ph)(S)(PPh_3)_2]BF_4$. Reductive elimination of benzyl alcohol generates the unsaturated species $[RuH(CO)(S)(PPh_3)_2]BF_4$, which will take up 2-methoxyethanol to restart the cycle.

Assuming that the rds is the oxidative addition of hydrogen (also supported by the KIE value) a rate law corresponding to this mechanism was derived as:

$$r = \frac{k_2K_1}{1 + K_1[PhCHO]}[Ru]_0[PhCHO][H_2] \quad (9)$$

It can be easily shown by inverting and reorganizing Eq. (9) that a plot of $[Ru]_0[H_2]/r$ versus the reciprocal of benzaldehyde concentration yields a straight line from which the values of k_2 (12.5 M^{-1} s^{-1}) and K_1 (1.9 M^{-1}) can be obtained. If the term $K_1[PhCHO] << 1$ in Eq. (9), the rate law expression can be approximated to $r = K_1k_2[Ru]_0[PhCHO][H_2]$, which is identical to the experimental rate law if $k_{cat} = K_1k_2$.

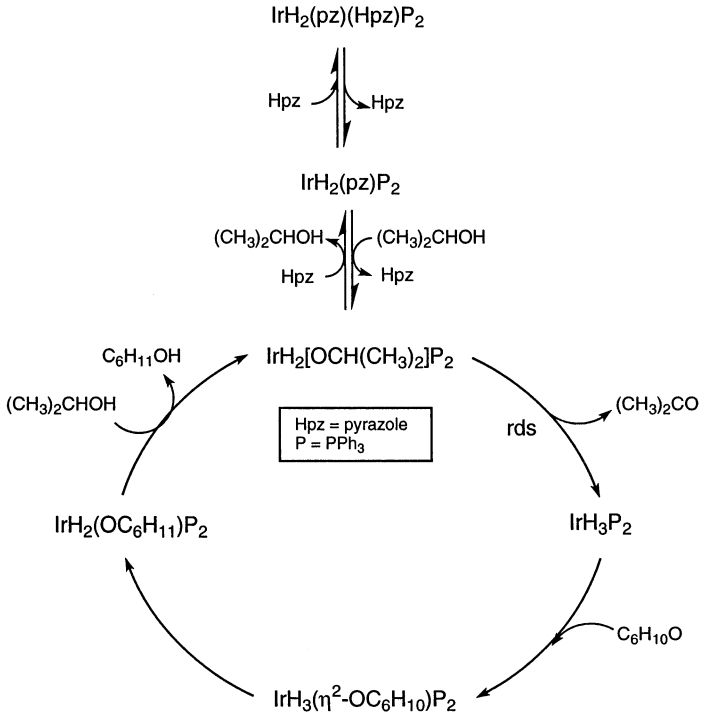
The hydrogenation of cyclohexanone with the same precatalyst followed somewhat different kinetics in the sense that zero-order on substrate concentration was found; this difference was explained in terms of a greater coordinative ability of the ketone as compared to benzaldehyde. A mechanism similar to that of benzaldehyde hydrogenation was proposed for the hydrogenation of cyclohexanone, with the difference that the catalytic species entering the cycle is $[RuH(CO)(S)(\eta^1\text{-}OC_6H_{10})(PPh_3)_2]BF_4$ instead of the bis(solvento) complex [26b].



Scheme 11. The mechanism for the hydrogenation of benzaldehyde catalyzed by $[RuH(CO)(MeCN)_2(PPh_3)_2]^+$.

In an interesting variation of the hydrogenation reaction, Oro and co-workers have studied the kinetic and mechanistic aspects of the hydrogen-transfer reaction from alcohols to ketones catalyzed by hydride complexes of osmium [27a] and iridium [27b] and by a dinuclear Ru–Ir system [27c]. In general, these reactions involve coordination of the ketone to a coordinatively unsaturated hydrido–metal intermediate, formation of alkoxy–metal species by insertion of the hydride ligand into the C=O bond, exchange of the alkoxy group by reaction with the hydrogen donor, which also acts as solvent and a β-elimination process as the elementary steps of the catalytic cycle. A particularly interesting case is the hydrogen-transfer of 2-propanol to cyclohexanone catalyzed by $IrH_2(pz)(Hpz)(PPh_3)_2$ (Hpz = pyra-

zole). The kinetic data of the reaction was accommodated by a rate expression of the form $r = a[\mathrm{Ir}]_0/(1 + b[\mathrm{Hpz}]^2)$, where a and b are constants. The mechanism deduced on the basis of this rate law and spectroscopic observations proceeds in accordance with Scheme 12, where the β-elimination process of the $OCH(CH_3)_2$ group linked to the metal center is the slow step of the reaction.



Scheme 12. The mechanism for the transfer hydrogenation of cyclohexanone catalyzed by $IrH_2(pz)(Hpz)(PPh_3)_2$ (pzH = pyrazole).

The catalytic hydrogenation of the C=N bond of imines has attracted considerable attention, as evidenced in a recent review by James covering the literature until 1996 [28]. However, this field is notably less developed than the reduction of C=O bonds; most of the work is concerned with testing a wide variety of complexes for activity and enantioselectivity, but few studies deal with the kinetics and mechanisms of such reactions.

Willoughby and Buchwald reported a kinetic and mechanistic study of the asymmetric hydrogenation of imines catalyzed by a chiral *ansa*-titanocene Cp'_2TiCl_2 (Cp'_2 = ethylene(bis-tetrahydroindenyl)), which revealed a rate law $r = k[\mathrm{Ti}][H_2]$. The mechanism consists of a rapid imine 1,2-insertion into a Ti–H bond, followed by a slow reaction of hydrogen with the resulting amide intermediate to produce the amine and regenerate the hydride. For a very interesting discussion of the nature of the active catalyst, the origin of the enantioselectivity and mechanistic details, the reader is referred to the original papers [29] and to James's review [28].

Very recently, a kinetic and mechanistic investigation of the hydrogenation of *N*,β-naphthylideneimine catalyzed by $[Ir(H)_2(PPh_3)_2(Solv)_2]^+$ was carried out in our laboratories [30]. The rate of hydrogenation was found to be first-order in substrate, catalyst, and hydrogen concentrations, which could be interpreted in terms of Eqs. (10)–(12) (C=N = *N*,β-naphthylideneimine, S = solvent THF, P = PPh_3):

$$[Ir(H)_2S_2P_2]^+ + C{=}N \overset{K_1}{\rightleftharpoons} [Ir(H)_2(RCH{=}NR')SP_2]^+ \quad (10)$$

$$[Ir(H)_2(RCH{=}NR')SP_2]^+ \overset{k_2}{\rightarrow} [IrS_2P_2]^+ + RCH_2NHR' \quad (11)$$

$$[IrS_2P_2]^+ + H_2 \overset{K_3}{\rightleftharpoons} [Ir(H)_2S_2P_2]^+ \quad (12)$$

This leads to a theoretical rate law of the form of Eq. (13):

$$r = \frac{k_2K_1K_3[Ir]_0[H_2][C{=}N]}{1 + K_3[H_2] + K_1K_3[H_2][C{=}N]} \quad (13)$$

from which the values of the various constants could be determined as $K_1 = 22.14$ M^{-1}, $k_2 = 5.2 \times 10^{-2}$ s^{-1} and $K_3 = 2432$ M^{-1}. Under standard catalytic conditions the denominator may be approximated to 1 and thus the theoretical law agrees well with the experimental one. The rds is probably the first hydride transfer to the substrate, as evidenced by in situ NMR measurements.

5. Hydrogenation of arenes

The hydrogenation of arenes is an important reaction for which only a few homogeneous catalysts have been found to be effective [31], and the kinetic and mechanistic details of such reductions remain largely unexplored and thus constitute an open interesting area for future research. Landis and Halpern studied the hydrogenation of 9-trifluoroacetylanthracene and 9-methylanthracene catalyzed by $[Rh(S)_2(diphos)]X$ (S = MeOH) and '$RuH_4(PPh_3)_3$', respectively [32,33].

The hydrogenation of 9-trifluoroacetylanthracene to 1,2,3,4-tetrahydro-9-trifluoroacetylanthracene catalyzed by the rhodium complex proceeds through the second-order rate law $r = k_{cat}[Rh][H_2]$, and can be interpreted in terms of a mechanism depicted by Eqs. (14)–(16), which is similar to that found for the hydrogenation of olefins with the same precatalyst.

$$[Rh(diphos)(anthracene)]^+ + H_2 \underset{rds}{\overset{k}{\rightarrow}} [Rh(diphos)(MeOH)_2]^+ + 1,2\text{-dihydroanthracene} \quad (14)$$

$$1,2\text{-dihydroanthracene} + H_2 \xrightarrow{[Rh(diphos)(MeOH)_2]^+} 1,2,3,4\text{-tetrahydroanthracene} \quad (15)$$

$$[Rh(diphos)(MeOH)]^+ + anthracene \overset{fast}{\rightleftharpoons} [Rh(diphos)(anthracene)]^+ \quad (16)$$

The activation parameters for this catalytic reaction were $\Delta H^{\neq} = 16.6 \pm 2$ kcal mol^{-1} and $\Delta S^{\neq} = -14 \pm 5$ cal K^{-1} mol^{-1}. The kinetic data for the hydrogenation of 9-methylanthracene to its corresponding 1,2,3,4-tetrahydro derivative using

the ruthenium complex indicate that this reaction proceeds through a catalytic cycle analogous to that established for the hydrogenation of cyclohexanone catalyzed by the same ruthenium precatalyst.

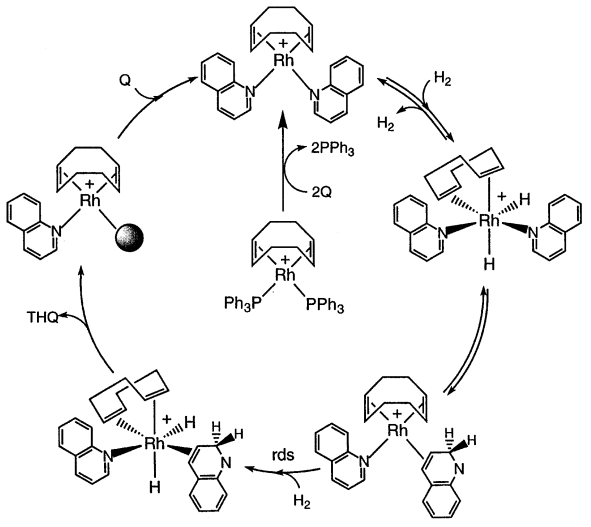
6. Hydrogenation of N- and S-heteroaromatic compounds

The hydrogenation of polynuclear heteroaromatic compound is an area of continued interest because of its relation to the industrially important hydrodenitrogenation (HDN) and hydrodesulfurization (HDS) processes. Kinetic and thermodynamic studies of heterogeneous HDN reactions indicate that the selective hydrogenation of the nitrogen-containing ring occurs prior to the C–N bond cleavage reaction [34], whereas in the case of S-heteroaromatics it is less clear whether hydrogenation occurs prior or subsequent to C–S bond cleavage [35]; in both cases, hydrogenation is regarded as a key step and hence the importance of understanding the details of such reactions.

Concerning nitrogen compounds, several homogeneous Ru, Os, Rh and Ir systems catalyze the regioselective hydrogenation of the N-containing ring in quinoline, isoquinoline, indole and benzoquinolines [36–40]. Although Fish has provided extensive spectroscopic studies and sound mechanistic proposals for the hydrogenation of quinoline and related molecules [36,37], few papers deal with the kinetic aspects of these reactions.

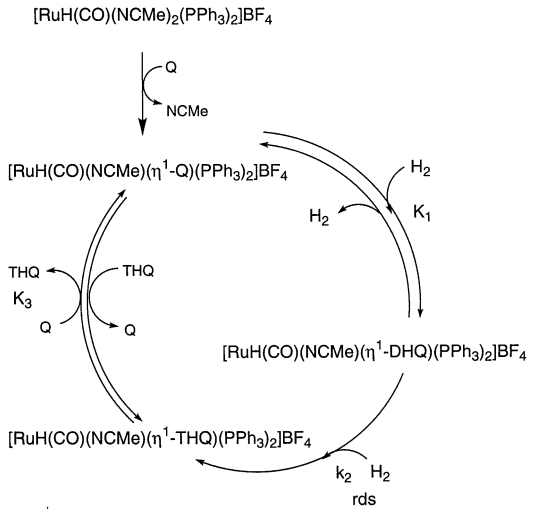
Sánchez-Delgado and co-workers described the regiospecific homogeneous reduction of quinoline (Q) to 1,2,3,4-tetrahydroquinoline (THQ) using $[Rh(COD)(PPh_3)_2][PF_6]$ as the catalyst precursor in toluene solution under mild reaction conditions [39]. The experimentally determined rate law was $r = k_{cat}[Rh][H_2]^2$, where $k_{cat} = 50 \pm 6\ M^{-2}\ s^{-1}$ at 370 K. The corresponding activation parameters were $\Delta H^{\neq} = 9 \pm 1$ kcal mol^{-1}, $\Delta S^{\neq} = -27.0 \pm 0.3$ cal K^{-1} mol^{-1} and $\Delta G^{\neq} = 19.1 \pm 0.3$ kcal mol^{-1}. It was shown that the complex $[Rh(COD)(\eta^1\text{-}N,Q)_2]PF_6$, rapidly formed under the reaction conditions, is actually the catalytically active species and the data are consistent with a mechanism involving a rapid and reversible hydrogenation of one coordinated quinoline to dihydroquinoline (DHQ) (similar to what happens on heterogeneous catalysts), followed by a rate-determining reduction of the DHQ intermediate to yield THQ. A detailed catalytic cycle accounting for these results was also postulated as shown in Scheme 13.

Rosales and co-workers [41] studied the kinetics and the mechanism of the hydrogenation of Q to THQ by using $[RuH(CO)(NCMe)_2(PPh_3)_2]BF_4$ as the precatalyst. It was found that the reaction was first-order in catalyst concentration, zero-order with respect to quinoline concentration, second-order on hydrogen concentration (which tends to first-order at higher pressure) and inverse-order on THQ concentration. The activation parameters obtained were $\Delta H^{\neq} = 10 \pm 1$ kcal mol^{-1}, $\Delta S^{\neq} = -27.5 \pm 0.5$ cal K^{-1} mol^{-1} and $\Delta G^{\neq} = 22 \pm 2$ kcal mol^{-1}. In independent experiments $[RuH(CO)(NCMe)_2(PPh_3)_2]BF_4$ was found to react with Q to yield $[RuH(CO)(NCMe)(\eta^1\text{-}N,Q)(PPh_3)_2]BF_4$, which was also isolated from

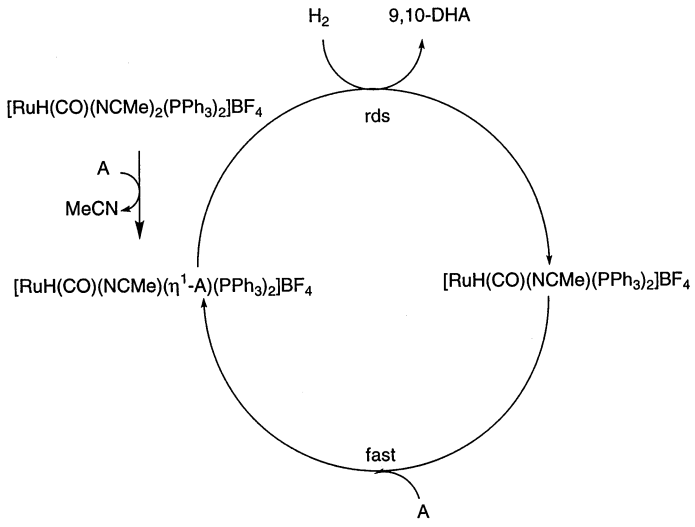


Scheme 13. The mechanism for the hydrogenation of quinoline (Q) catalyzed by $[Rh(COD)(Q)_2]^+$ (COD = 1,5-cyclooctadiene).

the hydrogenation runs. These experimental findings are consistent with a mechanism constituted by the catalytic cycle shown in Scheme 14. Complex $[RuH(CO)(NCMe)(\eta^1\text{-N,Q})(PPh_3)_2]BF_4$ is rapidly and reversibly hydrogenated to



Scheme 14. The mechanism for the hydrogenation of quinoline (Q) catalyzed by $[RuH(CO)(MeCN)_2(PPh_3)_2]^+$.



Scheme 15. The mechanism for the hydrogenation of acridine (A) catalyzed by $[RuH(CO)(MeCN)_2(PPh_3)_2]^+$.

form $[RuH(CO)(NCMe)(\eta^1\text{-DHQ})(PPh_3)_2]BF_4$. Further reaction with a second molecule of H_2 produces $[RuH(CO)(NCMe)(\eta^1\text{-THQ})(PPh_3)_2]BF_4$, in which the THQ is weakly coordinated through the nitrogen atom; the latter is considered to be the rds. Finally, the catalytic cycle is completed with the substitution of THQ by Q to regenerate the active monohydride. This mechanism led to the rate expression:

$$r = \frac{K_1 k_2}{1 + K_1[H_2]}\,[Ru]_0[H_2]^2 \tag{17}$$

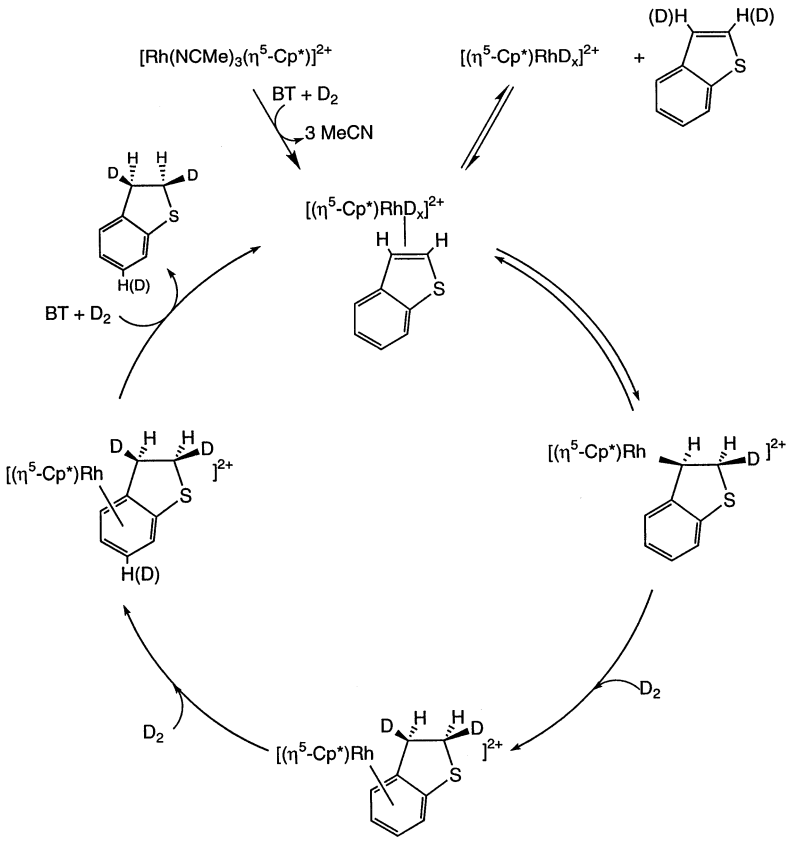
which explains why the dependence of the reaction rate with respect to H_2 concentration changes from 2 to 1 on going from low to high H_2 pressure. To further support this proposal, semiempirical SCF-CNDO/2 calculations were also employed to study this mechanism using simplified Ph_3 analogues. The main results indicate that: (i) the active species of the cycle is the *cis* isomer of complex $[RuH(CO)(NCMe)(\eta^1\text{-Q})(PPh_3)_2]BF_4$, (ii) the hydride in this intermediate migrates to C_2 of Q to form a complex with monohydroquinolinide ligand prior to the addition of H_2, (iii) the first hydrogenation occurs through heterolytic activation of dihydrogen, and (iv) a change in the coordination of DHQ from η^1 to $\eta^2\text{-}C_3,C_4$ is necessary to reduce this double bond [42].

For the regioselective homogeneous hydrogenation of acridine (A) to 9,10-dihydroacridine (DHA) catalyzed by the same complex, Rosales' results revealed a rate law $r = k[Ru][H_2]$, with activation parameters $\Delta H^{\neq} = 13 \pm 1$ kcal mol^{-1}, $\Delta S^{\neq} = -25 \pm 1$ cal K^{-1} mol^{-1} and $\Delta G^{\neq} = 22 \pm 1$ kcal mol^{-1}. The experimental findings are consistent with a mechanism (Scheme 15) involving $[RuH(CO)(\eta^1\text{-A})(NCMe)(PPh_3)_2]BF_4$ as the species entering in the catalytic cycle; the hydrogenation of this species to yield acridane and $[RuH(CO)(NCMe)(PPh_3)_2]BF_4$ is the rds,

followed by the rapid coordination of a new molecule of (A) to restart the catalytic cycle [42].

Concerning S-aromatic compounds, several mechanisms for the catalytic hydrogenation of benzothiophene (BT) to 2,3-dihydrobenzothiophene (DHBT) in homogeneous phase have been discussed in the literature. Fish and co-workers, based on deuteration experiments and detailed NMR studies, have elucidated a catalytic cycle for $[Rh(Cp^*)(MeCN)_3]^{2+}$ [37]. The main cycle (Scheme 16) starts with the η^2-coordination of BT to a rhodium polyhydrido species, followed by hydride transfer from the metal to the C_2 of the substrate. Reaction of the resulting 3-dihydrobenzothienyl intermediate with further hydrogen gives DHBT, which is finally displaced by a new molecule of the substrate; the intermediacy of a η^6-arene intermediate, preceding the last step, is suggested by the observed incorporation of deuterium in C_7 of the product DHBT.

Sánchez-Delgado and co-workers have provided further insight into the mechanism of this reaction catalyzed by the complexes $[M(COD)(PPh_3)_2]PF_6$, M = Rh, Ir,



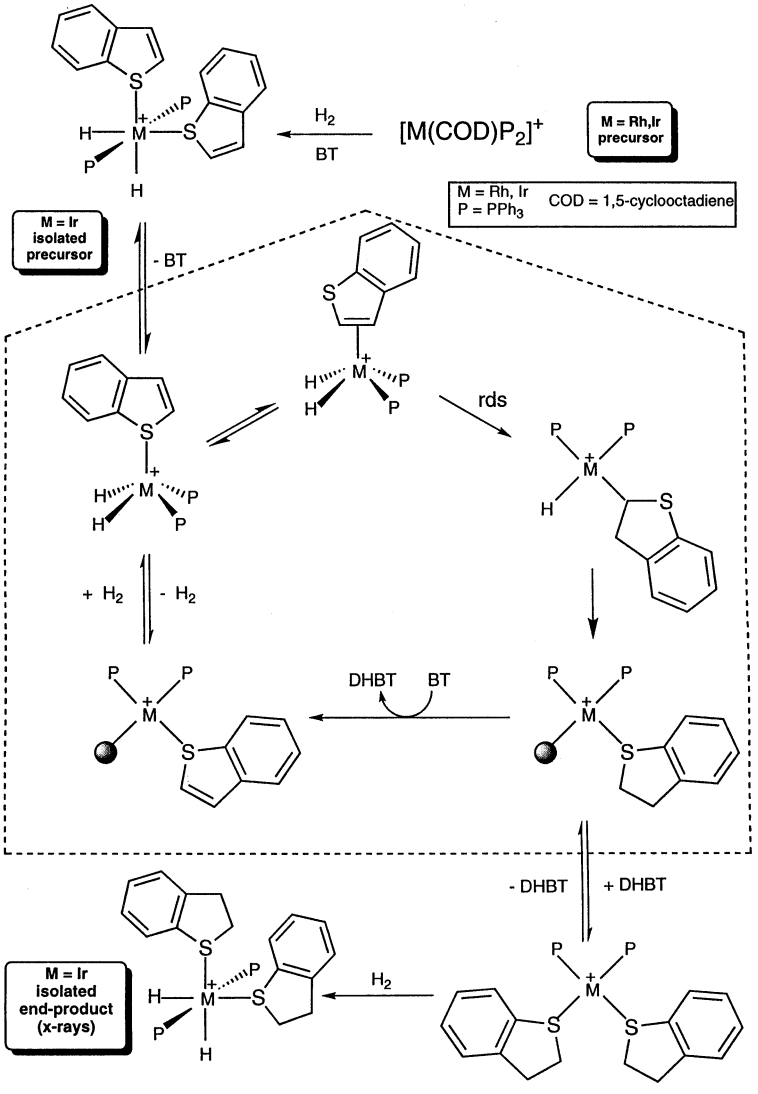
Scheme 16. The mechanism for the hydrogenation of benzothiophene (BT) catalyzed by $[Cp^*Rh(MeCN)_3]^{2+}$.

employing a combination of kinetic, chemical and theoretical methods [43]. Using the rhodium precatalyst in 2-methoxyethanol as the solvent provided rather slow rates and showed a first-order dependence on metal concentration, zero-order with respect to BT concentration and first-order on hydrogen concentration, which tends to zero-order at higher pressure ($r = kK_{eq}[Rh]_0[H_2]/1 + K_{eq}[H_2]$. The activation parameters were $\Delta H^{\neq} = 20.1 \pm 0.9$ kcal mol^{-1}, $\Delta S^{\neq} = -11.1 \pm 0.8$ cal K^{-1} mol^{-1} and $\Delta G^{\neq} = 23 \pm 3$ kcal mol^{-1}. More recently, Sánchez-Delgado and Bianchini [44] found that the same complexes are extremely active for the specific hydrogenation of BT to DHBT if 1,2-dichloroethane is used as the solvent, although the experimental rate law for the Rh-catalyzed reaction was found to be identical to that displayed in 2-methoxyethanol. Also, moving to iridium chemistry in chlorinated solvents opened the possibility not only of obtaining highly active catalysts, but also of isolating and characterizing some of the key species thought to be involved in the catalysis, such as $[Ir(H)_2(BT)_2(PPh_3)_2]PF_6$, a rather stable compound amenable to analytical and spectroscopic characterization, and $[Ir(H)_2(\eta^1\text{-S-DHBT})_2(PPh_3)_2]PF_6$, which was isolated from the catalytic runs and characterized by X-ray diffraction.

The experimental findings in these two papers led to a generic catalytic cycle for both systems, represented in Scheme 17. The species within the dotted lines are the ones believed to be directly participating in the hydrogenation catalysis. BT initially binds η^1-S to a M(III) dihydride (M = Ir, Rh); loss of a BT molecule yields $[Ir(H)_2(\eta^1\text{-S-DHBT})(PPh_3)_2]PF_6$ which is very likely in equilibrium with the isomeric dihydrido-η^2-BT complex. This olefin-like intermediate undergoes selective hydrogenation of the C_2=C_3 bond trough a hydrido-2-benzothienyl species, to yield intermediates containing the hydrogenated product $[M(\eta^1\text{-S-DHBT})(PPh_3)_2]^+$. Displacement of DHBT by a new molecule of BT produces $[M(\eta^1\text{-S-BT})(PPh_3)_2]^+$, which reacts with hydrogen to restart the cycle. The outer species do not participate directly in the catalysis and in fact, the accumulation of the bis DHBT product as the reaction progresses results in loss of activity.

Originally, it was thought that η^5-bonded BT complexes $[Rh(\eta^5\text{-BT})(PPh_3)_2]PF_6$ were involved in the hydrogenation cycle [43]; although some NMR evidence as well as theoretical calculations support the existence of such compounds, their participation in the catalysis is now believed to be minor, and thus the predominant catalytic cycle proceeds in the way described by Scheme 17 for both Rh and Ir, in 1,2-dichloroethane or in 2-methoxyethanol.

Yet a much more active catalyst precursor for the hydrogenation of BT was recently reported by Bianchini and Sánchez-Delgado [45] viz. the complex $[(triphos)Ru(NCMe)_3][BF_4]_2$ in THF solution. The rate of the hydrogenation reaction was found to be first-order in catalyst, substrate and hydrogen concentration. In addition, the intermediates $[(triphos)RuH(NCMe)_2]^{2+}$ and $[(triphos)RuH(DHBT)(NCMe)]^{2+}$ could be adequately characterized by their independent synthesis and/or NMR observations at low and high pressures of hydrogen, all of which led to the mechanism represented in Scheme 18, in agreement with the chemical data and the experimental rate law (at low H_2 pressures):



Scheme 17. The mechanism for the hydrogenation of benzothiophene (BT) catalyzed by $[Rh(H)_2(BT)_2(PPh_3)_2]^+$

$$r_i = \frac{K_1 k_2}{1 + K_1[BT]} [Ru]_0[BT][H_2] \quad (18)$$

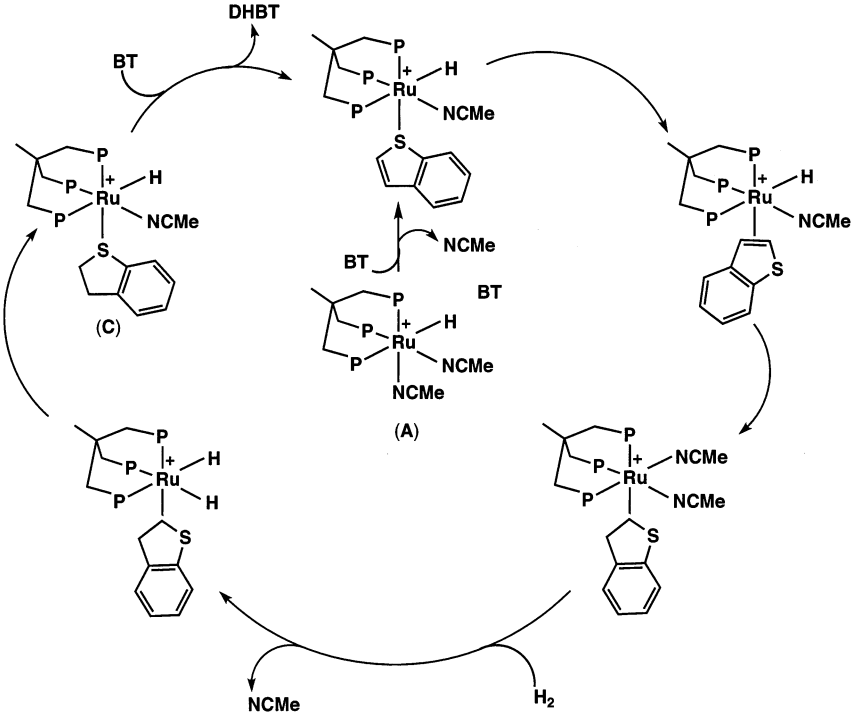
where $k_2 = 250\ M^{-1}\ s^{-1}$ and $K_1 = 5\ M^{-1}$.

The formation of species **A** (Scheme 18) has been demonstrated by independent preparative and in situ NMR experiments; transfer of two hydrides to coordinated BT generates the complex $[(triphos)RuH(DHBT)]^+$ (**C**), which was observed by in situ NMR measurements. The fact that only **A** and **C** were observed by NMR,

together with the fact that no deuterium incorporation was observed in either unreacted BT or the arene ring of DHBT indicates that the transfer of hydrides to coordinated BT is rapid and irreversible, while coordination of BT to **A** and dissociation of DHBT to regenerate **A** and restart the cycle must be reversible reactions.

This mechanism differs from the one previously deduced for the hydrogenation of BT by Rh- and Ir-PPh_3 complexes, in that the latter displayed a zero-order dependence on substrate concentration, and a rate-limiting hydride transfer to coordinated BT. Otherwise, the elementary steps which compose the proposed cycle are similar to the ones described in other BT hydrogenation mechanisms, and closely related to well known C=C bond hydrogenation cycles.

Interestingly, at high pressures the nitrile ligands were also reduced to the corresponding $EtNH_2$, which then suffered a redistribution reaction to yield NEt_3, NEt_2H and NH_3. The presence of these amines did not affect the catalytic rates.



Scheme 18. The mechanism for the hydrogenation of benzothiophene (BT) catalyzed by [Ru-(triphos)$(MeCN)_3]^{2+}$.

7. Hydrogenation by water soluble complexes

Liquid biphasic catalysis is rapidly emerging as a very useful technology, as for instance in the SHOP process and the Ruhr Chemie-Rhone Poulenc hydroformylation process [1]. A number of water soluble ligands have been reported to be adequate for this type of reaction, but sulfonated phosphines have attracted by far the greatest attention. Several groups have studied hydrogenation reactions in water [46] and reasonable intermediates and mechanisms have been advanced, partly on the basis of direct chemical and/or spectroscopic data, and partly derived from analogies with well known non-sulfonated phosphine systems; relatively little information is still available concerning the kinetics of such processes. Joó and co-workers have provided [47] kinetic data for the reaction of $RuCl_2(TPPMS)_2$ (TPPMS = *meta*-sulfonatophenyl-diphenylphosphine) with hydrogen to yield the corresponding hydride $RuHCl(TPPMS)_{2,3}$ according to a rate law which is first-order in [Ru], first-order in [H_2] and independent of [TPPMS]. This system was then used to catalytically hydrogenate crotonic and pyruvic acids, and a full kinetic analysis was carried out. The mechanism for crotonic acid was explained in terms of a reversible reaction of $RuHCl(TPPMS)_2$ with the substrate to yield an alkyl intermediate, followed by a rate-determining reaction with hydrogen to produce butyric acid and regenerate the hydride. In the case of pyruvic acid, a similar mechanism was proposed except that in this case the active catalyst seems to be the tris(phosphine) complex $RuHCl(TPPMS)_3$. The same complex was found to be also active for aldehyde hydrogenation, and a detailed kinetic study was provided for benzaldehyde [48]. Clearly, further work is needed in the kinetics of liquid biphasic catalytic reactions.

8. Hydrogenation by metal clusters

The use of carbonyl clusters as catalysts for hydrogenation reactions has been the subject of a number of papers, an important question actually being whether the cluster itself is the species responsible for the hydrogenation. The fact that the cluster is recovered from the catalytic reaction, or is the only species spectroscopically observed under catalytic conditions has been taken as evidence for cluster catalysis but such data must always be interpreted with caution. It is sufficient to transform a very small (undetectable) amount of the cluster into a very reactive mononuclear fragment to obtain a highly active catalytic solution [49].

Doi and co-workers [50] carried out kinetic and mechanistic studies for the hydrogenation of ethylene by use of $H_4Ru_4(CO)_{12}$ as the precatalyst. The hydrogenation rate was found to be first-order with respect to cluster concentration, while it increased to constant values with increasing ethylene and hydrogen pressure. An inverse dependence of the reaction rate on CO pressure was also observed. On the basis of the kinetics, complemented by some spectroscopic measurements, a reasonable catalytic cycle was proposed, as outlined in Eqs. (19)–(23):

$$H_4Ru_4(CO)_{12} \overset{K_1}{\rightleftharpoons} H_4Ru_4(CO)_{11} + CO \tag{19}$$

$$H_4Ru_4(CO)_{11} + H_2 \overset{K_2}{\rightleftharpoons} H_6Ru_4(CO)_{11} \tag{20}$$

$$H_4Ru_4(CO)_{11} + C_2H_4 \overset{K_3}{\rightleftharpoons} H_3Ru_4(CO)_{11}(C_2H_5) \tag{21}$$

$$H_3Ru_4(CO)_{11}(C_2H_5) + H_2 \overset{k_4}{\rightleftharpoons} H_4Ru_4(CO)_{11} + C_2H_6 \tag{22}$$

On the basis of this mechanism, the rate of ethane formation is given by:

$$r = \frac{k_4K_3[Ru]_0[C_2H_4][H_2]}{1 + K_2[H_2] + K_3[C_2H_4] + [CO]/K_1} \tag{23}$$

in accord with a cluster catalyzed reaction.

Basset and co-workers [51] found the silica-supported cluster $Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}OSi\equiv)$ to be an efficient catalyst for the gas–solid hydrogenation of ethylene. The reaction was found to be zero-order in ethylene and first-order in hydrogen. The kinetic results together with volumetric and IR measurements on this system and on the soluble analogue $Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}OPh)$ led to a mechanism involving the intact triosmium framework in all the steps conforming the catalytic cycle; a facile $3e \leftrightarrow 1e$ interconversion of the surface oxygen ligand was said to provide the appropriate energy balance for cluster catalysis without fragmentation.

Sánchez-Delgado and co-workers [52] reported that a number of tri- and tetranuclear osmium clusters can serve as catalyst precursors for hydrogenation of cyclohexene under moderate reaction conditions; the fact that some structure–activity relationships could be established led to the idea that the intact clusters could be the actual catalytic species. More detailed work by this group on the kinetics of styrene hydrogenation with neutral and anionic tetrahedral and butterfly shaped tetraosmium clusters showed that the hydrogenation rate is first-order with respect to the concentration of styrene and hydrogen; the turnover frequency, however, increased with decreasing cluster concentration. These results, together with other relevant data, were interpreted in terms of cluster fragmentation yielding low concentrations of highly active species of lower nuclearity. This type of fragmentation was proposed as a general phenomenon for reactions catalyzed by simple metal carbonyl clusters [53]. On the other hand, Cabeza et al. demonstrated by use of kinetic arguments combined with other appropriate techniques that the hydrogenation of alkynes is catalyzed by intact metal clusters, mainly on the basis of a first-order rate dependence on cluster concentration [54].

In conclusion, it is now recognized that cluster catalysis is possible and also that fragmentation into lower nuclearity fragments is a facile process, and therefore caution should be observed in proposing mechanisms for cluster catalyzed reactions. It seems that detailed kinetic studies may be the best way to distinguish between these two possibilities.

9. Activation parameters

A number of the papers referred to in previous sections report activation parameters which are certainly of interest. Since such data is still relatively scarce and definitely scattered, their interpretation is at this point far from straightforward. It has seemed useful, however, to collect such data in this article for future reference (Table 1), and also to include at least the following few comments which are in order:

- It must be kept in mind that the majority of the data correspond to apparent activation parameters.
- The values of $\Delta H^{\neq}$ range from 3 to 20 kcal mol^{-1}, generally distributed at < 10 kcal mol^{-1} for C=C bond hydrogenation and > 10 kcal mol^{-1} for polar bond hydrogenation (C=O, C=N, C=S). The corresponding $\Delta S^{\neq}$ values are all negative (-11 to -64 eu)—except interestingly, for Wilkinson's catalyst ($\Delta S^{\neq} = +1$ eu)—as could be expected for highly-ordered transition states in which reactants come together at the metal center of the catalyst. Despite the rather wide range of $\Delta H^{\neq}$ and $\Delta S^{\neq}$ values, the overall $\Delta G^{\neq}$s vary much less, between 15 and 25 kcal mol^{-1}, most of them being around 20 kcal mol^{-1}.
- For C=C bond hydrogenation by dihydride catalysts, $\Delta H^{\neq}$, via the hydride route $> \Delta H^{\neq}$ for the olefin route, while $\Delta S^{\neq}$ values follow the opposite trend.
- Very marked solvent effects may be observed on activation parameters, like for instance in the hydrogenation of benzothiophene by Rh phosphine complexes for which $\Delta H^{\neq}$ drops from about 20 to 3 kcal mol^{-1} on changing from 2-methoxyethanol to the less strongly coordinating 1,2-dichloroethane. This could have important implications, since it indicates that solvation effects which are often not taken into account on deriving rate laws may in fact be determining for some key steps of the catalytic cycle.

Again, the data available is definitely insufficient to be of any predictive value at this moment, but at least some general trends appear to be emerging. It is hoped that these considerations will stimulate further kinetic and thermodynamic measurements, particularly of well-defined individual elementary steps, along with overall catalysis, in order to reach a much broader data base which might allow clearer conclusions in the near future.

10. Final remarks

We hope to have demonstrated throughout this review that kinetic studies provide a powerful tool for the determination of the mechanisms of homogeneous catalytic reactions, if they are used in combination with other chemical, spectroscopic and theoretical methods. In particular, the use of IR, UV–vis, and multinuclear NMR spectroscopies have allowed the identification or detection of many intermediates in homogeneous catalytic hydrogenation. Isotope labeling experiments (particularly deuteration in the case of hydrogenation reactions) has proved to be very useful in obtaining further mechanistic information (e.g. identifying the

Table 1
Activation parameters for the homogeneous hydrogenation of unsaturated compounds

Substrate	Catalyst	$\Delta H^{\neq}$ (kcal mol^{-1})	$\Delta S^{\neq}$ (cal K^{-1} mol^{-1})	$\Delta G^{\neq}$ (kcal mol^{-1})	Ref.
Cyclohexene	$RhCl(SbPh_3)_3$	7.5	−46.2	21.3	[15c]
	$RhCl(AsPh_3)_3$	5.5	−51.0	20.7	[15c]
	$RhCl[Ph_2P(CH_2)_2AsPh_2]_2$	3.1	−57.5	20.2	[15c]
	$RhCl(PPh_3)_3$	18.2	1.0	17.9	[15c]
	$RhCl[Ph_2P(CH_2)_2PPh_2]_2$	4.0	−49.0	18.6	[15c]
	$IrCl(S)(PPh_3)_2$	5.1	−50.0	20.0	[15d]
	$IrCl(S)[Ph_2P(CH_2)_2PPh_2]$	4.0	−53.0	19.8	[15d]
	$IrCl(PPh_3)(Ph_2P(CH_2)_2PPh_2)$	3.5	−55.0	19.9	[15d]
	IrCl(triphos)	6.7	−46.0	20.6	[15d]
	$IrCl(NP_3)$	7.5	−43.0	20.3	[15d]
	$K[Ru(EDTA\text{-}H)Cl]\cdot 2H_2O$ [a]	16.0	−21.0	22.3	[15a]
	$Ru(EDTA\text{-}H)(PPh_3)$ [a]	13.1	−31.0	22.3	[15a]
	$K[Ru(EDTA\text{-}H)(CO)]\cdot 2H_2O$ [a]	10.9	−36.0	21.6	[15a]
	$K[Ru(EDTA\text{-}H)SnCl_3]\cdot 2H_2O$ [a]	7.7	−40.0	19.6	[15a]
	$Na[Ru(EDTA\text{-}H)N_3]\cdot 2H_2O$ [a]	3.7	−63.7	22.7	[15b]
	$Na[Ru(EDTA\text{-}H)N_3]\cdot 2H_2O$	16.4	−22.0	23.0	[15b]
	$[Ru(EDTA\text{-}H)(NO)]BF_4$ [a]	7.6	−40.8	19.7	[15b]
	$[Ru(EDTA\text{-}H)(NO)]BF_4$	12.0	−34.0	22.1	[15b]
	$[RuH(CO)(NCMe)_2(PPh_3)_2]BF_4$	9.1	−33.2	20.1	[17]
	$RuHCl(^tBu\text{-}py)_2(PPh_3)_2$	4.0	−46.8	17.8	[20]
Styrene	$OsHCl(CO)(P^iPr_3)_2$	14.3	−13.2	18.2	[21]
Phenylacetylene	$OsHCl(CO)(P^iPr_3)_2$	10.1	−24.5	17.4	[21]
	$OsHCl(CO)(PMe^tBu_2)_2$	11.0	−26.7	19.0	[21]
Benzaldehyde	$[RuH(CO)(NCMe)_2(PPh_3)_2]BF_4$	4.6	−40.0	18.0	[26]
Cyclohexanone	$[RuH(CO)(NCMe)_2(PPh_3)_2]BF_4$	6.0	−46.9	20.3	[27]
	$[OsH(CO)(NCMe)_2(PPh_3)_2]BF_4$	11.2	−32.3	21.5	[55]
	$Ru(H)_2(H_2)(PPh_3)_3$	15.0	−34.2	25.2	[25]
N,β-Naphthylideneimine	$[Ir(H)_2(THF)_2(PPh_3)_2]PF_6$	4.0	−33	14	[30]
9-Trifluoroacetylanthracene	$Rh(S)_2[Ph_2P(CH_2)_2PPh_2]^+$	16.6	−14.0	20.8	[32]
Quinoline	$Rh(COD)(PPh_3)_2^+$	9.0	−27.0	19.1	[39]
	$[RuH(CO)(NCMe)_2(PPh_3)_2]BF_4$	10.0	−27.5	22.0	[41]
Acridine	$[RuH(CO)(NCMe)_2(PPh_3)_2]BF_4$	12.9	−24.1	21.5	[42]
Benzothiophene	$Rh(COD)(PPh_3)_2^+$ (in 2-MeO–EtOH)	20.1	−11.1	23.0	[43]
	$Rh(COD)(PPh_3)_2^+$ (in 1,2-dichloroethane)	2.9	−41.3	16.0	[44]
	$Ir(H)_2(BT)_2(PPh_3)_2^+$ (in 1,2-dichloroethane)	5.1	−31.7	15.0	[44]

[a] Olefin route.

rds of the cycle, or establishing the stereoselectivity of the addition of hydrogen to the substrate or verifying the reversibility of an elementary step). However, the more meaningful evaluations of the mechanisms of catalytic reactions have been achieved by measuring and examining the kinetic and equilibrium parameters for individual steps of the catalytic cycle, as well as for the overall process. Only when all these studies can be combined to coherently fit the experimentally determined rate-law of the catalytic reaction, the overall mechanism can be considered to be understood.

Clearly, the kinetic and mechanistic aspects of homogeneous hydrogenation and other catalytic reactions remain a very open area of research in which many important contributions are still to be expected; we hope to have stimulated some interest so that other workers join those already involved in this fascinating aspect of catalytic science.

Acknowledgements

We would like to thank the continuous financial support provided by IVIC, CONDES (LUZ) and CONICIT over the years for our own work described in this article. Also, the enthusiasm and the excellent work of former students and technicians whose names appear in the pertinent bibliographic references is gratefully acknowledged. R.A.S.-D. thanks the John Simon Guggenheim Foundation (New York) for a Fellowship and the Chemistry Department of the University of California, Berkeley, for a Visiting Scholar position during which this article was written.

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