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Catalytic processes involving dihydrogen complexes and other sigma-bond complexes

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The discovery of dihydrogen complexes, $L_nM(H_2)$, pointed to direct transfer of hydrogen from coordinated H_2 ligands to substrates as an operable pathway in catalysis both in homogeneous and heterogeneous systems. Sigma complexes, $L_nM(\eta^2\text{-H–X})$ ($X = H$, Si, C, etc), are indeed relevant in hydrogenation as well as silane alcoholysis and methane conversion.

KEY WORDS: hydrogenation; homogeneous catalysis; heterogeneous catalysis; dihydrogen complexes; hydride; sigma complexes; silane; silane alcoholysis; methane; heterolytic cleavage; oxidative addition; electrophilic complexes; isotopic exchange; hydrogenase.

1. Introduction

Catalytic hydrogenations are the largest man-made chemical reactions in the world: all crude oil is treated with hydrogen in hydrotreating processes and billions of tons of ammonia are produced worldwide by the Haber process. Metal hydride complexes formed by oxidative addition (OA) of the H–H bond in H_2 had early on been known to be a part of homogeneous catalytic cycles and were well-characterized species. However the discovery by Kubas and coworkers in 1983 of coordination of a nearly intact dihydrogen molecule (H_2) to a metal complex has led to a new paradigm in chemistry [1,2].

η^2-H_2 complex dihydride complex

Molecules containing only strong "inert" σ-bonds such as H–H in H_2 and C–H in alkanes had previously been believed to be incapable of stable binding to a metal. However, dihydrogen complexes (referred to as η^2-H_2 or H_2 complexes) that were only assumed to be unobservable intermediates in dihydride formation can be isolatable species, as exemplified by the first H_2 complex, $W(CO)_3(P^iPr_3)_2(H_2)$ (figure 1) [1,2].

The H–H distance is elongated to 0.89 Å from 0.75 Å in free H_2, indicating the bond is only partially broken. Hundreds of H_2 complexes have now been established and in many cases the nearly intact H_2 ligand is reversibly bound as in physisorbed H_2. These species are part of a class of compounds called *σ-complexes*, which refers to the side-on 3-center interaction of the bonding electron pair in H–H or other X–Y bonds with M.

One of most important initial questions was whether *direct transfer* of hydrogens from an η^2-H_2 ligand rather than a dihydride can take place in catalytic hydrogenation. This would avoid the need for completely breaking the strong H–H bond (104 kcal/mol), giving lower energy pathways for catalysis. Although this is difficult to prove conclusively, evidence now exists that certain reactions, e.g. styrene hydrogenation, involve transfer of metal-bound H_2 to substrate. As will be shown, Noyori's elegant asymmetric catalytic hydrogenation systems that led to the Nobel Prize have recently been found to contain H_2 complexes as part of the catalytic cycle. Perhaps the best example of the direct involvement of σ-complexes is catalytic silane alcoholysis, the mechanism of which employs two different σ-complexes: $M(\eta^2\text{-Si–H})$ and $M(\eta^2\text{-}H_2)$. New mechanisms for hydrosilylation other than the standard Chalk–Harrod mechanism [3] are being uncovered and appear to involve silane σ-complexes. The main focus of this article is then on systems that involve σ-complexes in catalytic cycles either directly or secondarily, i.e. as reservoirs for catalytic species. Importantly, the principles derived primarily from homogeneous systems can also apply to heterolytic catalysis, and a strong interface exists here with wide open potential. For example, only a few studies have been carried out on σ-complexes in the solid state or supported on solids.

1.1. General features of sigma complexes

A variety of σ-bonds have been found to interact intermolecularly (σ-complex) or intramolecularly (agostic) with metal centers as shown in scheme 1 [1].

In principle *any X–Y bond can coordinate to a metal center M* providing steric and electronic factors are

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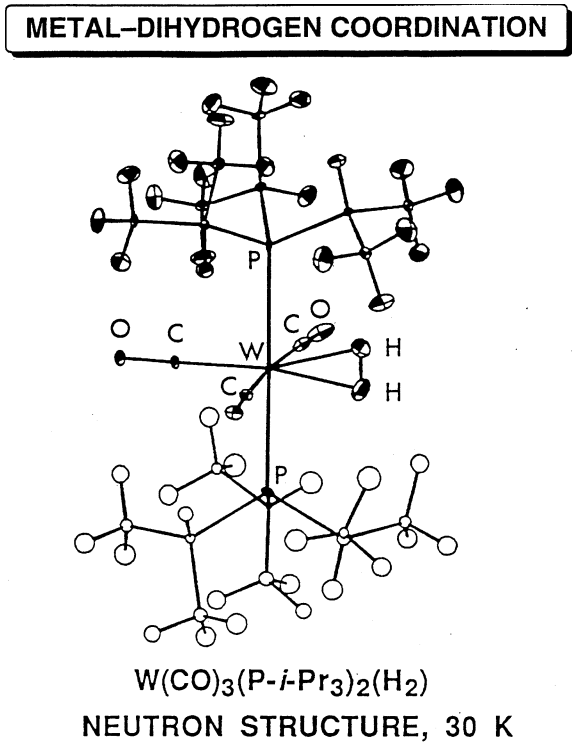
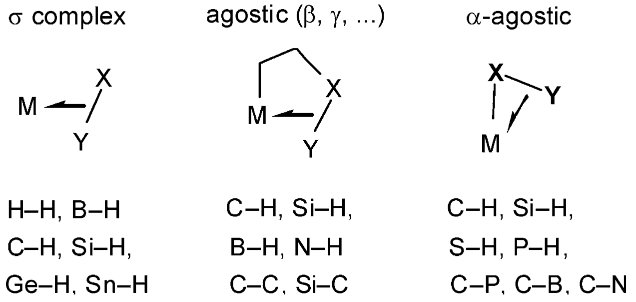


Figure 1. Molecular structure of $W(CO)_3(P^iPr_3)_2(H_2)$ showing intact H–H bond elongated to 0.82(1) Å. Lower phosphine is disordered. The actual H–H distance is longer (0.89 Å from solid state NMR) because rapid rotation of the H_2 results in foreshortening of the neutron distance.



σ complex	agostic (β, γ, ...)	α-agostic
H–H, B–H	C–H, Si–H,	C–H, Si–H,
C–H, Si–H,	B–H, N–H	S–H, P–H,
Ge–H, Sn–H	C–C, Si–C	C–P, C–B, C–N

favorable, e.g. substituents at X and Y do not block the metal's access. Sigma complexes have several features favorable over classical hydrides and related species in both homogeneous and heterogeneous catalyst systems. Foremost is that the *oxidation state of the metal does not change* on binding of e.g. molecular H_2, whereas formation of a dihydride involves oxidative addition (OA), i.e. increasing the metal oxidation state by two. Also H_2 ligation involves *no change in coordination number*, and H_2 ligands thus have greater kinetic acidity than classical hydrides of similar structure. H_2 ligands also have greater thermodynamic acidity than hydrides, which is important factor in the ability of H_2 ligands to protonate substrates such as olefins and N_2. Analogous increased acidity of C–H bonds in transient unstable metal–alkane σ-complexes is expected to be important in alkane activation such as catalytic conversion of methane to methanol.

The 3c–2e bonding in M–H_2 and other σ-bond complexes is stabilized by *backdonation (BD)*, i.e. the retrodative donation of electrons from a filled metal *d* orbital to the σ* orbital of the H–H bond. This is analogous to the Dewar–Chatt–Duncanson model for olefin coordination in figure 2 [4,5].

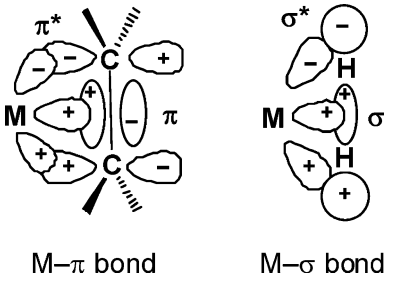
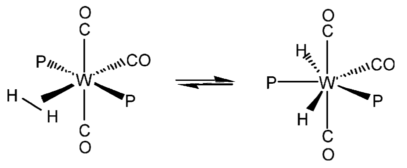


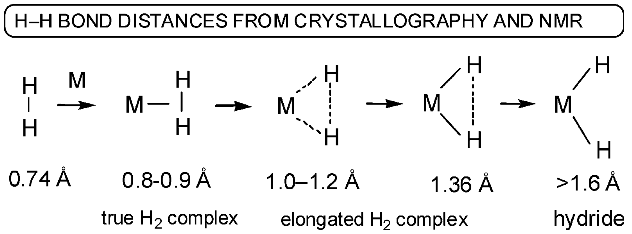
Figure 2. Dewar–Chatt–Duncanson model for olefin coordination (left) and bonding model for H_2 coordination (right).

BD is crucial in activating the H–H bond towards homolytic cleavage to dihydride ligands. If the backbonding becomes too strong, e.g. if more electron-donating co-ligands are put on M, the σ-bond cleaves to form a dihydride because of overpopulation of $H_2\sigma^*$. There is a fine line between H_2 and dihydride coordination, and in some cases *equilibria* between the two forms have been observed in solution (equation 1).

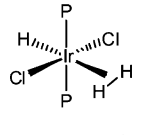


(1)

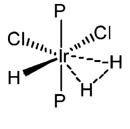
The entire reaction coordinate for the activation (elongation of the H–H bond) and OA of H_2 to a metal can be mapped out and related to the degree of BD. This is dramatically demonstrated by the remarkable "stretching" of the H–H distance, d_{HH}, as displayed within the large regime of known complexes with H_2 bound to different metal–ligand fragments (scheme 2) [1,5].



The d_{HH} is relatively short (0.85–0.90 Å) and reversibly bound in "true" H_2 complexes, as exemplified by **1**, much like in physisorbed H_2· The activation of H_2 is very sensitive to the nature of the metal, the ancillary ligands, and the overall charge. Third-row metals, strongly donating ligands, and neutral charge favors elongation or splitting of H–H, while first-row metals, electron-withdrawing ligands, and positive charge shortens the H–H distance. The nature of the ligand *trans* to H_2 has a particularly powerful influence. For example, strong π-acceptors such as CO (and also strong σ-donors such as H) greatly reduce BD, and d_{HH} is normally < 0.9 Å in complexes with CO trans to H_2, regardless of ligand set or overall charge. Conversely, complexes with mild σ-donor ligands such as H_2O trans to H_2 or π-*donors* such as Cl, have elongated H–H bonds (0.96–1.34 Å). This is dramatically demonstrated by the isomers shown below containing H_2 trans to H or Cl.



H–H = < 0.9 Å

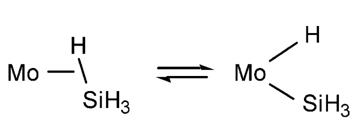


H–H = 1.11 Å

Most of the structure and bonding principles such as this have been extensively and accurately modeled computationally, and the interplay between experiment and theory in M–(η^2-H_2) and M–hydride systems has been remarkably effective [6]. Importantly, any of the structures shown in scheme 2 could be involved in catalytic processes, as will be discussed below.

There are strong interrelationships between activation of H_2 and other σ-bonded molecules such as alkanes and silanes. Among the greatest challenges in chemistry is the quest for a stable alkane complex and conversion of CH_4 in natural gas to liquid fuels, e.g. methanol [7]. Although H_2 (as well as silanes and germanes) can bind to metal centers in stable fashion at ambient temperature, alkanes cannot, although an unstable $CpRe(CO)_2$(cyclopentane) complex has been observed by solution NMR at low *T* [8]. The structure and bonding principles in σ-coordination and activation of H_2 also have application in certain biological systems, and understanding the binding site in hydrogenase enzymes [9] may lead to efficient biomimetic methods for converting seawater to hydrogen fuel. H_2 complexes have been implicated in solar energy conversion schemes based on the photoreduction of water [10]. Water gas shift and related H_2-producing reactions undoubtedly proceed *via* transient H_2 complexes.

Silanes containing at least one Si–H bond (hydrosilanes) have been demonstrated to bind in η^2-Si–H fashion [11,12], and closely analogous germane complexes, e.g. $Mo(CO)(PP)_2(GeH_2Ph_2)$ (PP = bidentate phosphine), have recently been found (figure 3) [12]. In this and related σ-complexes, the E–H bond (E = Si, Ge) is asymmetrically coordinated, i.e. the E atom is further from the metal than H, giving the appearance of a hydride bridging the M and E atoms. There is a very fine balance here between σ coordination and oxidative addition of the germane Ge—H bond. Merely replacing one phenyl on the germane with H, i.e. reacting GeH_3Ph instead of GeH_2Ph_2 with the formally unsaturated precursor $Mo(CO)(Et_2PC_2H_4PEt_2)_2$, leads to the germyl hydride, $MoH(GeH_2Ph)(CO)(Et_2PC_2H_4PEt_2)_2$. The η^2-SiH_4 structure can even exist in equilibrium with its OA tautomer on the $Mo(CO)(PP)_2$ fragment [12].



This is entirely analogous to η^2-H_2 systems (equation 1). Coordinated Si–H distances in silane complexes vary widely similarly to that in H_2 complexes.

The above SiH_4 binding and Si–H cleavage are exciting because they are possible models for the binding of $CH_4$to metal centers and subsequent C–H bond breaking to form methyl hydrides. The structure of the Mo–silane complex in figure 3 and its germane, dihydrogen, and agostic analogues is significant because it

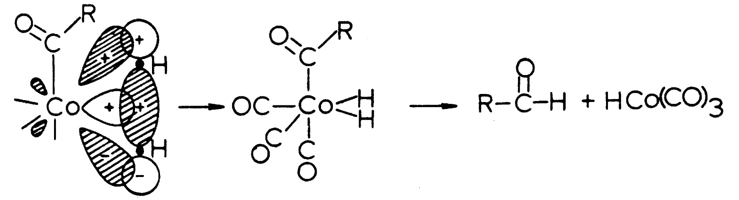


Figure 3. Molecular structure of $Mo(CO)(GeH_2Ph_2)(Et_2PC_2H_4PEt_2)_2$. Distances: $Ge–H_{Mo} = 2.08(6)$ Å; $Ge–H_E = 1.49(7)$ Å; $Mo–Ge = 2.6368(7)$ Å; $Mo–H_{Mo} = 1.72(6)$ Å.

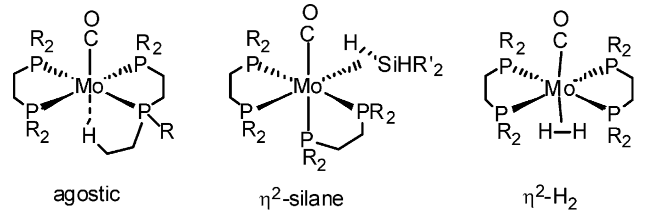
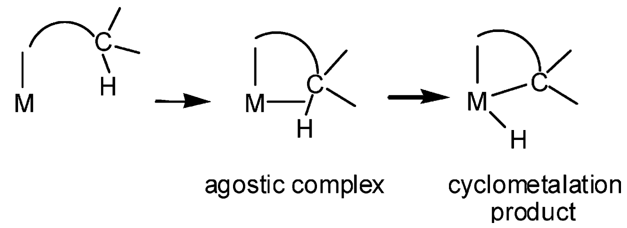


Figure 4. Structures of agostic complexes (R = Ph, ^{t}Bu), silane and analogous germane complexes (R = Et, Ph) and H_2 complexes (R = Ph).

allows comparison of the ease of activation of H–H, C–H, Si–H, and Ge–H bonds, as shown in figure 4 [12].

Although the $Mo(CO)(PP)_2$ fragment does not bind alkanes in stable fashion, it does form a weak agostic C–H interaction with a C–H bond of the phosphine. This isolatable complex is a precursor for the silane and germane complexes (the agostic interaction falls away on ligand addition). The ease of OA of σ-bonds on the Mo complexes gives the following comparison: Ge–H > Si–H∼H–H > > C–H. This also correlates with the degree of backdonation from the metal to the σ* orbital of the σ-bond, which directly influences the ease of bond cleavage. Thermodynamic factors, particularly relative bond strengths, also play a critical role in the ease of bond breaking [12]. OA of the Ge-H bond is easier than that for Si–H because of the relative weakness of the Ge–H bond, despite the fact that the Mo–Ge bond is also weaker. In general, the ease of OA of molecular hydrogen is between that of germanes and silanes because the M–H bonding energy in the dihydride product of OA is much higher than Mo–Si and Mo–Ge bonding energies, offsetting the higher H–H bond energy compared to Si–H and Ge–H bonds. For alkane C–H bond activation, calculations show that OA is much more difficult because the loss of the high C–H bond energy (comparable to or greater than that for H–H) is not as well compensated for by the energy of formation of the Mo–C bond due to the relative weakness of Mo–C bonds. Thus the agostic C–H bond is always weakly σ coordinated in this system and does not undergo OA (cyclometallation, see below), in line with the difficulty of OA of C–H bonds shown calculationally.

The above agostic interactions with phosphines are important in stabilizing electronically unsaturated complexes (16e or even 14e) that may be relevant in catalysis since many homogeneous catalysts employ phosphine ligands. Agostic interactions thus can "reserve" binding sites for coordination and activation of reactants and substrates such as H_2 [1a]. The first H_2 complexes (e.g. $W(CO)_3(P^iPr_3)_2(H_2)$ in figure 1) were indeed prepared by H_2 addition to 16e $M(CO)_3(PR_3)_2$ (M = Mo, W) stabilized by an agostic interaction [13]. A large variety of agostic M...H–X interactions are known, as shown in scheme 1 [14]. For example, α-agostic C–H interactions are quite common in unsaturated alkyl and alkylidene complexes. OA of the agostic C–H bond is very common and referred to as cyclometallation (or orthometallation) (scheme 3) [15].

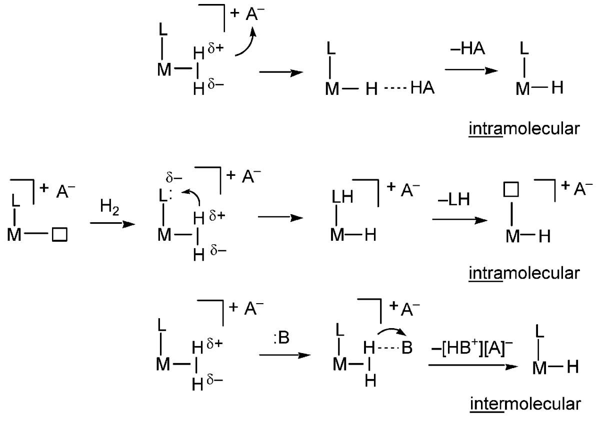


Cyclometalated species are important in organic synthesis, catalysis, asymmetric synthesis, and photochemistry.

1.2. Heterolytic cleavage of σ-bonds

There are two different pathways for cleavage of H–H (and X–H bonds): homolytic cleavage to a dihydride and heterolytic cleavage, i.e. breaking the H–H bond into H^+ and H^- fragments. Both paths have been identified in catalytic hydrogenation and are available for other σ-bond activations. Heterolytic cleavage is one of the oldest and most widespread reactions of H_2 on metal centers [16,17]. H_2 can bind in stable fashion to very electron-deficient cationic metal complexes that favor heterolysis nearly as well as to more electron-rich

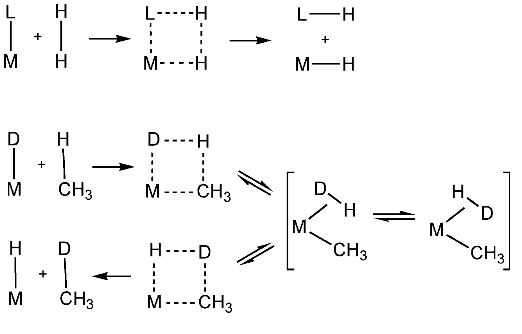
M. A proton can then split off from the H_2 ligand and migrate to either an external Lewis base (intermolecular) or a ligand/anion (intramolecular) as shown in scheme 4.



□ = COORDINATIVELY UNSATURATED SITE (e.g. 16e) OR WEAK SOLVENT LIGAND

Especially on electron-poor cationic complexes, the H_2 ligand becomes highly acidic, i.e. polarized towards $H^{\delta-}$-$H^{\delta+}$ where the highly mobile H^+ readily transfers. Free H_2 is an extremely weak acid with a pK_a near 35 in THF, but when H_2 is bound to a highly electrophilic cationic metal center, *the acidity of* H_2 *gas can be increased spectacularly, up to 40 orders of magnitude*. The pK_a of H_2 can become as low as −6 and thus *the acidity of* $\eta^2 - H_2$ *becomes as strong as that in sulfuric or triflic acid* [18]. *Intramolecular* heterolysis involves proton transfer to a *cis*-ligand L (e, g, H or Cl) or to the counteranion of a cationic complex. This can occur *via* a so-called *cis-interaction*, which essentially is a hydrogen-bonding like interaction of H_2 with a *cis*-ligand [1,6]. *Intermolecular* heterolysis involves protonation of an external base B to give a metal hydride (H^- fragment) and the conjugate acid of the base, HB^+. This is essentially the reverse of the protonation reaction commonly used to synthesize H_2 complexes (all the reactions in scheme 1 can be reversible), and the $[HB]^+$ formed can relay the proton to internal or external sites. Although heterolysis of H_2 can occur *via* several mechanisms that may or may not involve H_2 complexes as intermediates, emphasis will be placed on the latter here. Considerable research has also been carried out on heterolytic activation of hydrogen involving classical hydride systems or unidentified transient species. Important data on the thermodynamics of H_2 splitting and the hydride donor abilities of $[MH(PP)_2]^+$ (M = Ni, Pd, Pt; PP = diphosphine) have recently been reported by DuBois and Curtis [19]. The dicationic complexes $[M(PP)_2]^{2+}$ heterolytically cleave H_2 in equilibrium fashion in the presence of bases such as amines to give protonated amine and $[MH(PP)_2]^+$. The involvement of a dihydrogen (and/or dihydride) complex could not be identified, illustrating the frequent problem encountered in activation of σ-bonds, namely does the mechanism involve a σ-complex, i.e. $M(\eta^2\text{–}H_2)$ (or generically $M(\eta^2\text{–X–H})$), or oxidative addition to M(X)(H)?

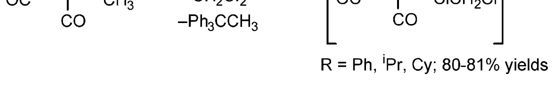
Intramolecular heterolysis is closely related to well-known *σ-bond metathesis* processes that generally occur on less electrophilic centers, especially d^0 systems (equation 2) [1,6].



(2)

Although the heterolytic process here is formally a concerted "ionic" splitting of the H–H or H–X bond as often illustrated by a 4-center intermediate with partial charges, the mechanism does not have to involve such charge localization. In other words the two electrons originally present in the H–H bond do not necessarily both go into the newly formed M-H bond while a bare proton transfers onto L or, at the opposite extreme, an external base. The term σ-bond metathesis is thus actually a better description and may comprise more transition states than the simple 4-center intermediate, as shown in the lower half of equation 2. Here transient coordination of H_2 to the metal cis to $L = CH_3$ can even be the initial step, and rotation of the σ-bound H–H (or H–D) can occur to give isotopic scrambling.

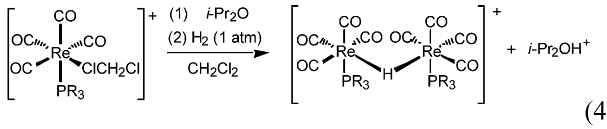
A crucial initial step in heterolysis of σ-bonds is generation of a complex with either a coordinatively unsaturated site or more commonly a site occupied by a weak, easily displaceable ligand such as a solvent molecule. For example, dichloromethane is very convenient here because it is an excellent solvent for cationic complexes and forms isolable complexes despite the high lability of the CH_2Cl_2 ligand. A good synthetic route to CH_2Cl_2 complexes is abstraction of a methyl ligand using a trityl salt with a low coordinating anion such as BAr_F ($B[3,5\text{-}C_6H_3(CF_3)_2]_4^-$). For example treatment of [*cis*-$Re(Me)(CO)_4(PR_3)$] with $[Ph_3C][BAr_F]$ in CH_2Cl_2 solution produced [*cis*-$Re(CO)_4(PR_3)(CH_2Cl_2)$][BAr_F] (equation 3) [20].



(3)

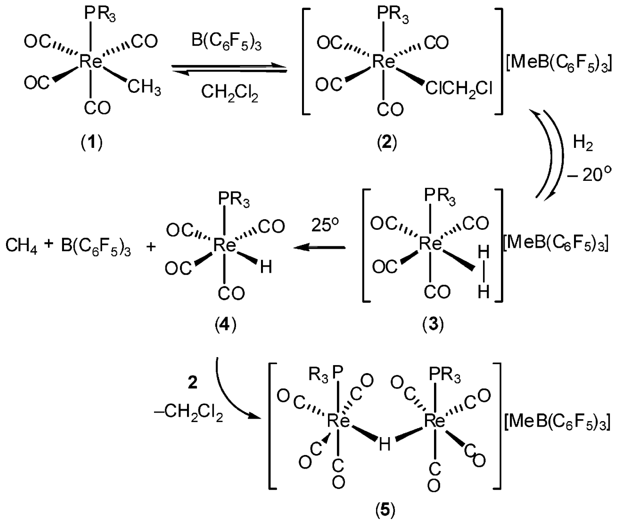
In these highly electrophilic complexes, the CH_2Cl_2 is labile and can be displaced by H_2 to form

$[Re(CO)_4(PR_3)(H_2)]^+$. The H_2 ligand is now quite acidic (pK_a estimated to be 1 to −2) and can protonate diisopropyl ether *via* intermolecular heterolytic cleavage (equation 4).



(4)

An interesting case of heterolysis of H_2 that could potentially occur in catalytic cycles involves protonation of borane anions. We have found that the d^6 rhenium(I) complex, **1**, is in nearly 1:1 equilibrium with **2**, formed by methyl abstraction by $B(C_6F_5)_3$ to give the $MeB(C_6F_5)_3^-$ counterion (scheme 5) [20c].

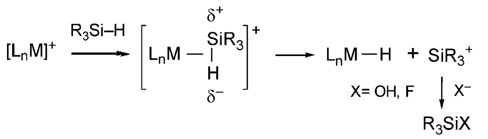


This indicates that the electrophilicity of the $[Re(CO)_4(PR_3)]^+$ fragment is similar to that of $B(C_6F_5)_3$. **2** reacts under H_2 atmosphere below room temperature to form equilibrium amounts (~5%) of the H_2 complex, **3**. On warming the solution, methane, $B(C_6F_5)_3$, and *cis*-$Re(CO)_4(PR_3)H$, **4**, form apparently by protonation of the anion $MeB(C_6F_5)_3$ by the acidic H_2 in **3**. **4** is not observed by NMR, but presumably quickly reacts with unreacted **2** (or **3**) to form the hydride-bridged dimer **5**, which is a "thermodynamic sink" in these systems (it is also the product in equation 4). Such protonation of a borane anion has precedence as reported by Bianchini where the H_2 complex is also unstable and is generated from H_2 gas (equation 5) [21].

$$[IrH_2(H_2)(triphos)]^+[BPh_4]^- \rightarrow IrH_3(triphos) + BPh_3 + benzene \quad (5)$$

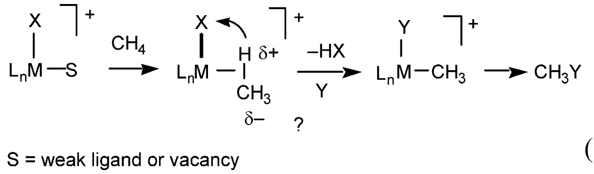
A mononuclear hydride results here as the final organometallic product (unlike unobserved **4** in scheme 5). Another possible scenario in scheme 5 is *intermolecular* heterolysis of H_2, e.g. protonation of the Me group in equilibrium quantities of **1** by the acidic H_2 in **3** to give CH_4, **2**, and **4**.

Other σ-bonds can be cleaved heterolytically, particularly on electrophilic cationic M. For coordinated Si–H bonds, the coordinated bond becomes polarized in the opposite sense $Si(\delta^+)$–$H(\delta^-)$, i.e. the Si becomes positively charged (equation 6).



(6)

Very reactive silylium ions are eliminated that scavenge nucleophiles such as adventitious water, solvent, or abstract fluoride from normally unreactive anions such as $B(C_6F_5)_4^-$. An important question thus is whether C–H bonds in alkanes, particularly CH_4, can likewise bind to "superelectrophilic" metal centers to form a σ-alkane complex that can be split heterolytically where proton transfer to a *cis*-ligand (or anion) takes place followed by functionalization of the resultant methyl complex (equation 7).



(7)

Intramolecular heterolytic cleavage of C–H in a fleeting σ-alkane complex may occur in alkane conversions such as Shilov-like [10] conversions of CH_4 that will be discussed below.

2. Reactions of dihydrogen complexes relevant to homogeneous catalysis

2.1. Introduction

Several decades prior to the discovery of H_2 complexes, reactions of H_2 with transition metal complexes had been intensely studied because of the widespread importance of catalytic hydrogenation and oxidative addition processes in chemistry [22]. A retrospective account of homogenous catalytic hydrogenation was published in 1980 by a pioneer in the field, Jack Halpern [23]. When Halpern began his studies in 1953, heterogeneous hydrogenation predominated and documented examples of homogeneous catalytic activation of H_2 by metal complexes were extremely rare. Indeed, metal hydrides were not even well characterized and generally accepted until after this time. One notable early example of homogeneous hydrogenation involved hydroformylation of olefins (the oxo process) catalyzed by cobalt carbonyl complexes (equation 8).

$$RCH = CH + H_2 + CO \xrightarrow{[Co_2(CO)_8]} RCH_2CH_2C(=O)H \quad (8)$$

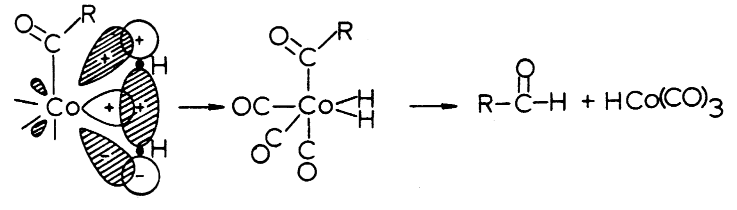
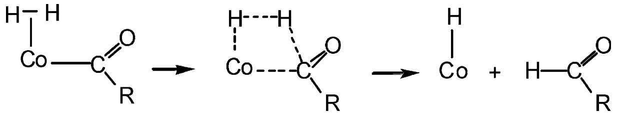
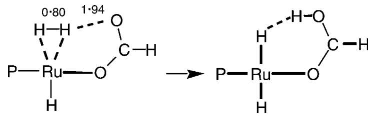


Figure 5. The hydrogenolysis of acylcobalt carbonyls by molecular hydrogen.

This reaction was discovered in 1938 by Roelen [24] and has received extensive study. After our discovery of H_2 complexes in 1983, it was surprising to come across a review article by Orchin [25] published in 1972 on the mechanism of the oxo reaction which contained the precise bonding picture (figure 5) for η^2-H_2 coordination that we now know to be true. Orchin even stated that the bonding involves backdonation to σ^* entirely analogous to that in metal–olefin π-bonding. The possibility of actually isolating an η^2-H_2 species was not mentioned, but he did state "the incipient dihydro species is capable of hydrogenolyzing the Co–COR bond" as shown above. Theoretical calculations many years later indeed support Co(η^2-H_2) intermediates in the oxo reaction [26,27]. One possibility is that hydrogen is transferred to an acyl ligand *via* a 4-center intermediate



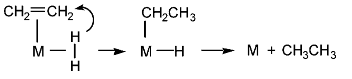
η^2–H_2 with $d_{HH} = 0.83$ Å binds initially and forms the 4-center intermediate with $d_{HH} = 1.14$ Å and $d_{CH} = 1.37$ Å (**Eq. 25**). The σ^* orbital of H_2 can interact with the bonding Co–C orbital on $CH_3(O)C$–$Co(CO)_3$ much like in the known interaction of coordinated H_2 with cis-ligands as exemplified in scheme 4 and observed experimentally and calculationally in a variety of H_2 complexes [1,6]. Related to this are calculations on hydrogenation of CO_2 to formic acid catalyzed by *cis*-$RuH_2(PH_3)_4$ model complexes that indicate a reaction mechanism involving a *six-membered* σ-bond metathesis (equation 9) [28].



(9)

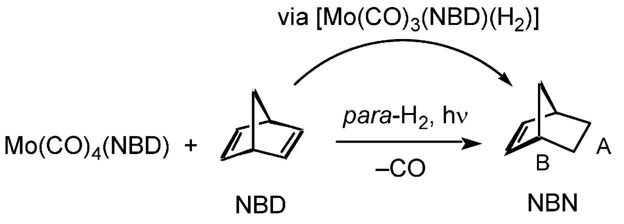
2.2. Direct transfer of hydrogen from H_2 ligands

A key question in figure 5 is whether η^2-H_2 *directly* transfers H-atoms to the acyl ligand above or other substrates such as olefins (equation 10), i.e. *without* the need for cleavage to the dihydride.

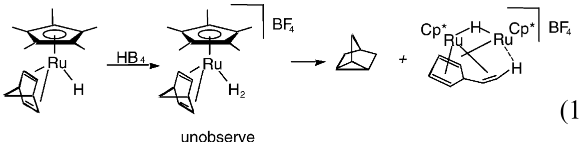


(10)

Proven examples of equation 11, which can be considered to involve initial intramolecular heterolytic cleavage of an H_2 ligand, or even M(olefin)(H_2) complexes are relatively rare. Unstable group 6 complexes $M(CO)_4$(norbornadiene)(H_2) detected by IR are proposed as intermediates for photocatalytic hydrogenation of norbornadiene to norbornene and nortricyclene involving direct reaction of H_2 ligands [29]. Jia has also reviewed such reactions of (norbornadiene)(H_2) and related complexes on various metal centers [30]. Evidence for direct transfer of the hydrogens in H_2 ligand to co-bound substrates is limited however, partly because it is difficult to prove absolutely that cleavage of the H–H bond does not first occur. Parahydrogen induced polarization (PHIP) [31] is useful in the detection of short-lived reaction intermediates in hydrogenation processes and provides crucial evidence here. The Mo–norbornadiene (NBD) complex in scheme 6 forms an unstable H_2 complex on photolysis that is proposed to directly transfer H_2 to NBD to form norbornene (NBN) [29b].



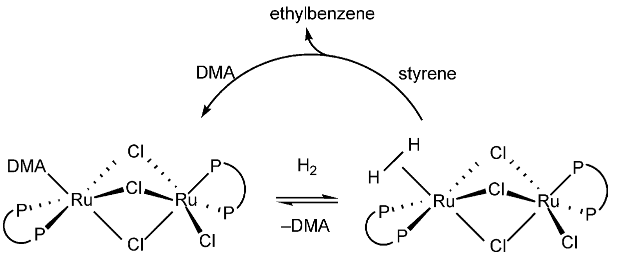
In situ NMR studies of the photocatayzed reaction in scheme 6 show that the nuclear spin polarization from *para*-H_2 is transferred to protons at the A and B positions of the NBN product. This can only occur if the H–H bond in the presumed [$Mo(CO)_3$(NBD)(H_2)] intermediate is not first cleaved to dihydride ligands before the hydrogens are transferred to the coordinated NBD. Intramolecular hydrogen transfer was also supported by the fact that decay of IR signals does not depend on H_2 pressure [29a]. Protonation of an olefin–hydride complex to generate [M(olefin)(H_2)]$^+$ and observation of transfer of protons from η^2-H_2 to the olefin could prove direct reaction of H_2 ligands, as in equation 10 where NBD is seen to be hydrogenated to nortricyclene and a dinuclear hydride (equation 11) [18b,30,32].



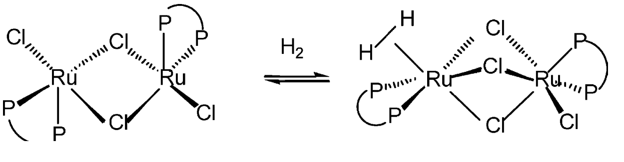
(11)

Although the Ru–H_2 complex is not detected, a similar cyclooctadiene dihydrogen complex is seen by NMR. Also displacement of the aquo ligand in $[Cp^*Ru(NBD)(H_2O)]^+$ by H_2 (50 atm) leads to nortricyclene. Equation 11 could be a form of ionic hydrogenation (Section 2.3), and detailed mechanistic studies will be required to unravel whether direct transfer from η^2-H_2 to olefin occurs here. Calculations indicate that a stepwise transfer of hydrogens occurs to the olefinic carbons.

James [33] provides excellent kinetic, NMR, and tensiometric evidence for a dinuclear Ru–H_2 complex transferring both hydrogens to styrene in DMA solution (scheme 7), DMA = *N*,*N*-dimethylacetamide; PP = $Ph_2(CH_2)_4Ph_2$).

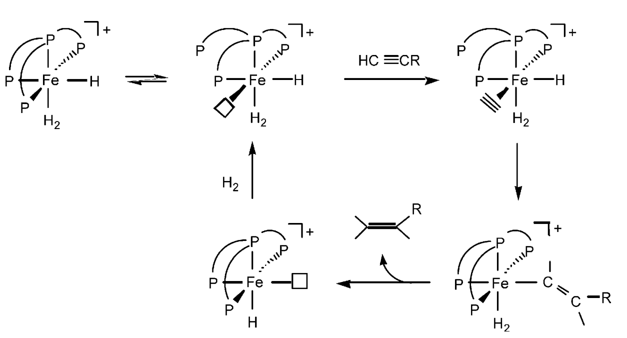


Although NMR data for the H_2 complex in the catalytic system is tenuous, it is a known complex [34] formed by a novel rearrangement reaction that undoubtedly exists in equilibrium with the DMA solvent in scheme 7.



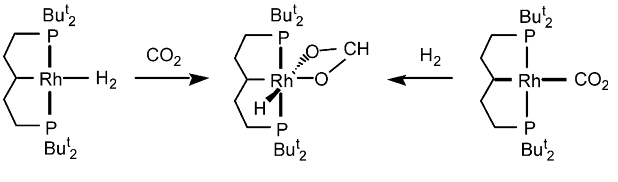
The first-order dependence on total Ru concentration, the first- to zero-order dependence on styrene concentration, and the fractional dependence on H_2 concentration are best interpreted in terms of the mechanism in scheme 7. Importantly, no hydride ligands are present in addition to or in equilibrium with the η^2-H_2 complex.

Prior to this, catalytic hydrogenation of alkynes to alkenes using $[FeH(H_2)(pp_3)]^+$, which contains a hydride, was proposed by Bianchini to involve intramolecular transfer from η^2-H_2 to a σ-vinyl ligand (scheme 8) [35].



The H_2 is not labile here and an open site is created by dissociation of a phosphine arm. The alkene elimination step is intramolecular heterolysis of η^2-H_2. This system is notable in that Fe-based homogeneous catalysts are very rare in industry although common in enzymatic systems.

A T-shaped 14e rhodium(I) complex containing a rigid P–C–P pincer ligand reversibly binds H_2 (**6**) and CO_2 (**8**) giving net insertion of CO_2 into the H_2 complex (scheme 9) [36].

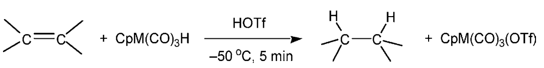


(6) **(7)** **(8)**

The hydrido-formate **7** quantitatively forms either upon treating **6** with CO_2 or **8** with H_2 at room temperature. In the latter case predissociation of CO_2 from **8** presumably takes place, followed by insertion of the displaced CO_2 into **6**, although concerted H_2 addition to **8** cannot be excluded. Significantly, this is the first demonstration of reaction of an H_2 complex with CO_2 and one of the clearest examples of direct reaction of η^2-H_2 since a dihydride tautomer is not observed here. Although the crystal structure of **6** is not known, NMR and other evidence points to a true H_2 complex.

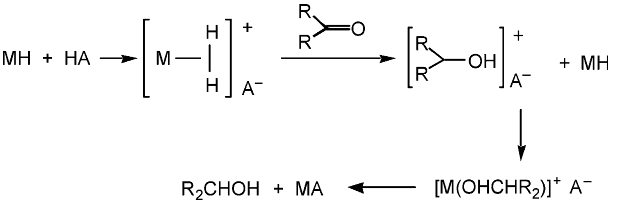
2.3. Catalytic hydrogenation on electrophilic complexes

Heterolytic activation of H_2 on electrophilic complexes is particularly important in catalytic hydrogenation. An early example dates back to 1938 when Calvin reported that copper(I) salts such as Cu(I) acetate catalyzed hydrogenation of substrates such as quinone [37]. The acetate anion here is protonated to form acetic acid, a good example of intramolecular heterolysis of H_2 *via* proton transfer to an anion (scheme 4). More recently, electrophilic activation of H_2 has been found to be valuable in *ionic hydrogenation* reactions. In 1989 Bullock reported that a mixture of an organometallic hydride such as $CpMoH(CO)_3$ and a strong acid such as HO_3SCF_3 reduces sterically hindered olefins to alkanes *via* protonation to carbocations, followed by hydride transfer from the metal hydride (equation 12) [38].



(12)

Several other examples have since been reported, including hydrogenation of alkynes, ketones, enamines, and C = N bonds in iminium cations [39]. It is likely that an acidic H_2 (or dihydride) complex is involved in the proton transfer step of some of these reactions (scheme 10).



A cationic dihydrogen complex, $[CpRu(dppm)(H_2)]BF_4$ (10 mol%), was indeed shown to catalyze ionic hydrogenation of an enamine in 71% yield [39d].

Another good example of a catalytic hydrogenation process proposed to involve heterolysis of H_2 on an acidic cationic H_2 complex is shown in figure 6 [40]. Treatment of the silyl enol ether **1a** with H_2 in the presence of a catalytic amount of **2** in benzene at 50 °C for 3 h gives the cyclohexanone **3a** and Me_3SiH in nearly quantitative yield. Based on studies using D_2, the initial step is thought to involve proton transfer from η^2-H_2 in **4** in figure 6 to the oxygen atom of **1a** to give **3a**, the neutral hydride **5**, and Me_3SiOTf from the triflate anion. The latter can accept a hydride to form known **2**, which then converts back to **4** under H_2.

The discovery by the recent Nobel-laureate, Ryoji Noyori, of asymmetric hydrogenation of ketones to alcohols catalyzed by *trans*-$RuCl_2$[(S)-binap][(S,S)-dpen] (binap = [1,1′-binaphthalene-2,2′-diylbis(diphenylphosphane)]; dpen = diphenylethylenediamine) is one of the best examples of catalysis employing heterolysis of H_2 complexes [41]. The reaction is quantitative within hours, gives enantiomeric excesses (ee) up to 99%, and shows high chemoselectivity for carbonyl over olefin reduction. The nonclassical bifunctional catalytic cycle is novel and involves heterolysis of H_2 to form the active ruthenium hydride as a key step (figure 7) which differentiates this new class of Ru(II) catalysts from structurally similar classical hydrogenation catalysts. The presence of NH_2 functionality in the diamine ligand is crucial for catalysis. First, the mixed-ligand $RuCl_2$ complex **2** is converted to the RuHX complex **3** (X = H or OR) with the aid of alkaline base and a hydride source, H_2, and isopropanol solvent. The catalytic cycle involves two ground-state components, **3** and its didehydro complex **4**, that are linked by transition states **TS1**and **TS2**. The NH_2 proton in **3** is key in delivering hydrogen to the ketone, while the amide nitrogen in **4** cleaves H_2. In both steps, the Ru centers and the ligands directly cooperate in the bond-breaking and bond-forming processes. The 18e Ru hydride **3** reacts with the ketone *via* a six-membered, pericyclic transition state **TS1**, giving the 16e complex **4** and alcohol product. The hydrogenating ability of coordinatively saturated **3** originates from the charge alternating $H^{\delta-}$–$Ru^{\delta+}$–$N^{\delta-}$-$H^{\delta+}$ arrangement which meshes well with the $C^{\delta+} = O^{\delta-}$ dipole. Thus, the hydride on Ru possesses sufficient nucleophilicity, while the NH moiety exhibits a

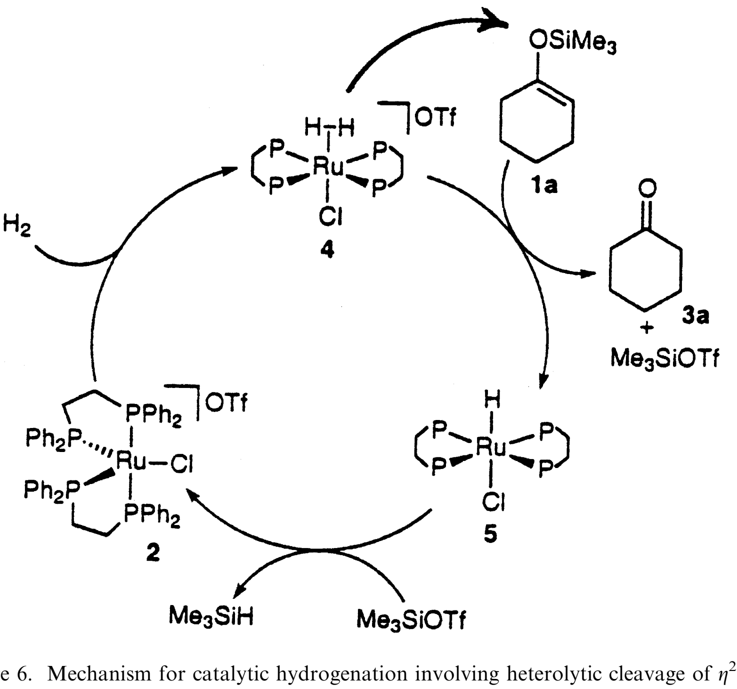


Figure 6. Mechanism for catalytic hydrogenation involving heterolytic cleavage of η^2-H_2.

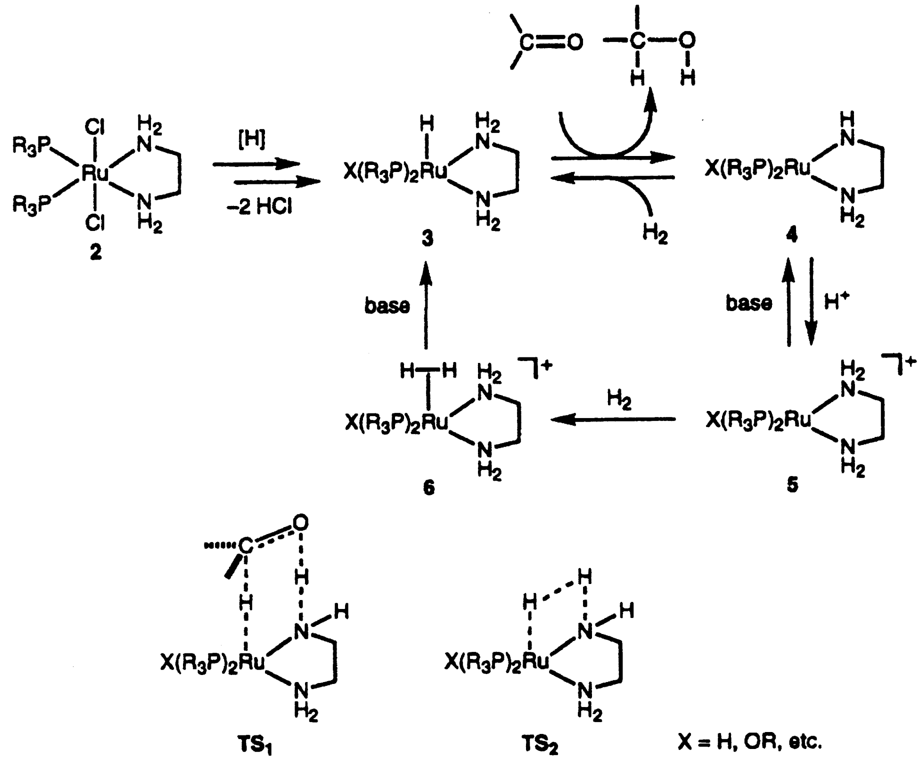
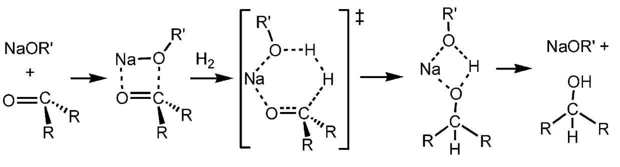


Figure 7. Mechanism for catalytic hydrogenation in Noyori's system.

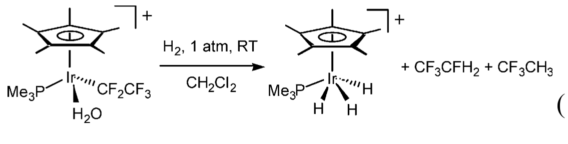
hydrogen-bonding ability to activate the carbonyl function. Because of the unique $Ru^{\delta+}$–$N^{\delta-}$ dipolar bond, **4** splits H_2 heterolytically *via* **TS2** to restore the hydride **3**. Alternatively, **3** may be regenerated from **4** and H_2 by way of **5** and the H_2 complex **6** by action of protic medium and base. The mechanism is novel in that it does not require the interaction of a carbonyl moiety with the metal. Neither a Ru-ketone complex nor a Ru alkoxide is involved in the mechanism, and the alcohol forms directly from the ketone. This nonclassical mechanism also explains the high functional selectivity for the C=O group. When the chiral "molecular surface" of the Ru hydride recognizes the difference of ketone enantiofaces, asymmetric hydrogenation is achieved. This is different from the earlier BINAP–Ru chemistry where the enantioface differentiation is made within the chiral "metal template" with the assistance of heteroatom/metal coordination.

Studies of reaction processes related to the Noyori systems show that heterolysis of H_2 ligands is the critical step in the catalytic mechanism [42]. Several isomers are possible catalysts and Morris's study of ketone hydrogenation catalyzed by isomers of $RuH_2(PPh_3)_2$(diamine) indicates that the isomers with *cis*-phosphines are more active [42e]. Thus the *cis*-phosphine donor arrangement inherent in the Noyori-type catalysts containing enantiopure diphosphine ligands is an important structural feature. Remarkably, base-catalyzed hydrogenation of ketones *without transition metals* is known and has some mechanistic similarities to the Noyori system (scheme 11) [42f, g].



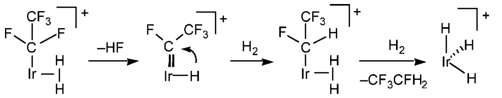
The hydrogenation is first order in ketone, H_2, and alkoxide base in agreement with a 6-membered cyclic transition state. The assembly of the latter is a major rate-limiting factor as indicated by *ab initio* calculations showing large entropic contributions to the barriers [42g]. Casey recently studied the mechanistic reverse of hydrogen elimination from a hydroxycyclopentadienyl ruthenium hydride, and it appears to involve heterolysis of bound H_2 mediated by alcohols [42d]. All of these systems underscore the growing importance of alcohols or alkoxides in promoting heterolysis of H_2 in metal (or even nonmetal) bifunctional catalysis.

Another recent development is hydrogenolyses of *C–F bonds* triggered by heterolytic activation of H_2 on cationic Ir complexes with piano stool geometry (equation 13) [43].



(13)

Hughes proposed that H_2 displaces H_2O and transfers a proton to form HF and a carbene ligand that is then hydrogenated to give a fluorohydrocarbon product (equation 14).

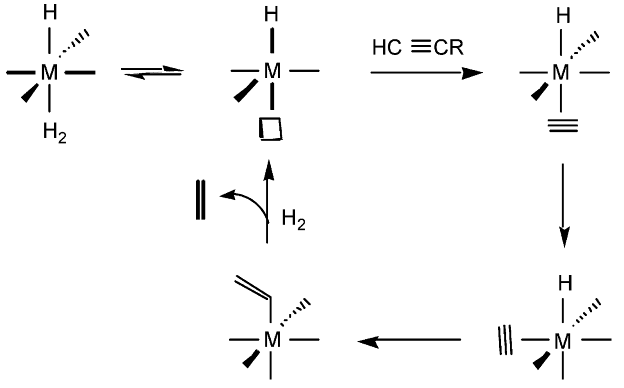


(14)

The water displaced by H_2 was proposed to be involved in the proton transfer, e.g. H_3O^+ may be formed from H_2 heterolysis and protonate the αa-C–F bond.

2.4. Hydrogenation catalyzed by H_2 complexes in a precursor role

Many catalytic and stoichiometric reactions access H_2 complexes as *precursors*, as summarized in reviews by Jessop and Morris [44] and Esteruelas and Oro [45]. As Morris points out, it is remarkable that H_2 complexes serve as catalysts because efficient hydrogenation catalysts have at least two very labile accessible sites for simultaneous hydrogen and substrate binding and are usually electron-rich, which reduces the activation energy for hydride transfer. Stable H_2 complexes normally have converse properties, e.g. only one open coordination site (the H_2 binding site). In the above examples of direct H_2 ligand reactivity, open coordination sites for catalytic reactivity were often created by unusual rearrangements or dissociations. However, the presence of a hydride ligand in addition to labile η^2-H_2 allows a straightforward catalytic pathway, and several catalytic systems possess $MH(H_2)$ formulations (scheme 12)



The loss of H_2 (usually trans to H) opens a site for binding of the unsaturated substrate, which in most cases are alkynes (as in scheme 12), alkenes, or ketones. The hydride migrates to substrate, followed by hydrogenolysis to final product, which could involve an η^2-H_2 intermediate and/or 4-center transition state. The H_2 complex thus functions as a reservoir of unsaturation and stabilizes the catalyst system against decomposition. Because excess H_2 is usually present in hydrogenations, the η^2-H_2 behaves similar to a weakly coordinated solvent molecule and can compete with solvent binding as in scheme 7. Catalysts include both neutral and cationic systems with labile H_2 such as $OsHCl(H_2)(CO)P_2$ [45–47], $RuH_2(H_2)P_3$ [48–53], $RuH_2(H_2)P_2$ [51,54,55], $[MH(H_2)P_4]^+$ (M = Fe, Ru, Os) [35,56–64], $[IrH_2(H_2)P_3]^+$ [65–67], and $Tp^*RuH_2(H_2)$ [68]. Some patented processes include hydrogenation of nitriles and nitro compounds, e.g. hydrogenation of adiponitrile to hexamethylenediamine in butylamine solvent containing $RuHCl(H_2)(PCy_3)_2$ catalyst under H_2 at 60 °C [51].

The $[MH(H_2)(pp_3)]^+$ system extensively studied by Bianchini and coworkers [35,57–59] highlights the importance of differences in M–H_2 bond strengths (Os > Fe > Ru) on the selective hydrogenation of alkynes to alkenes. The Fe congener is one of the most stable H_2 complexes and reactions with alkynes under one atm of H_2 produce only alkenes (with one exception) *via* the mechanism in scheme 8 where the H_2 remains attached while the alkyne coordinates.

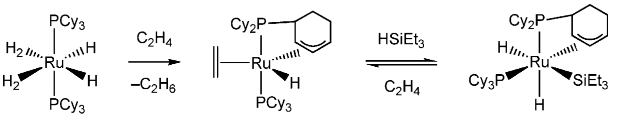
The complex $IrH_2Cl\ (P^iPr_3)_2$ behaves in a different manner to scheme 12 and *heterolytically activates* the H_2 ligand (Section 2.3) to form HCl and $IrH_3(P^iPr_3)_2$, where the known H_2 complex [69] is identified as an intermediate (equation 15) [70].

$$IrH_2Cl(P^iPr_3)_2IrH_2Cl(H_2)(PPr_3)_2\ {}^{-HCl}\,IrH_3(P^iPr_3)_2 \qquad (15)$$

The unsaturated trihydride then catalyzes hydrogenation of benzylideneacetone to 4-phenylbutan-2-one in isopropanol at 60 °C.

Several precious-metal H_2 complexes are alkene hydrogenation catalysts including $OsHCl(H_2)(CO)(P^iPr_3)_2$ which converts styrene to ethylbenzene under 1 atm of H_2 at 60 °C in isopropanol [46,47]. $[Ir(H_2)H_2(PMe_2Ph)_3]^+$ catalyzes room temperature hydrogenation of ethylene [67], and $RuH_2(H_2)(PPh_3)_3$ is a versatile catalyst for a variety of processes [48–53], including hydrogenation of 9-methylanthracene and unactivated ketones. In all cases, facile H_2 loss from the complex is crucial, particularly for dehydrogenation of ethanol to acetaldehyde in ethanol/NaOH solution at 150 °C catalyzed by $RuH_2(H_2)(PPh_3)_3$ [50]. The catalyst precursor is actually $Ru(N_2)H_2(PPh_3)_3$ which is rapidly converted to the H_2 complex. The versatile bis-H_2 complex $RuH_2(H_2)_2(PCy_3)_2$ (**9**), the chemistry of which has been reviewed [55], catalyzes a variety of reactions, e.g. hydrogenation of arenes and the activated alkene, dimethylfumarate [71]. Reaction of **9** with ethylene leads to dehydrogenation of a Cy group on the phosphine to give **10** containing a cyclohexenyl group (scheme 13) [72].

This unusual species is a highly efficient catalyst for selective dehydrogenative silylation of ethylene into the



(9) **(10)** **(11)**

vinylsilane $CH_2=CHSiEt_3$. **9** catalyzes room temperature addition of ethylene to acetophenone and benzophenone to give mono and di-addition products, e.g. 2,2′-diethylbenzophenone (Murai reaction) [73,74]. **9** also catalyzes silylation of ethylene [75] and hydrogenation of arenes, where surprisingly increasing the H_2 pressure lowers conversion [76]. Apparently there is reduced accessibility of catalytic sites due to increased stabilization of **9**, i.e. lower lability of the H_2 ligands. Lastly, **9** is an effective catalyst precursor for hydrogenation of thiophene to tetetrahydrothiophene under mild conditions (80 °C, 3 bar H_2) [77]. Dibenzothiophene is not reduced due to formation of the *S*-coordinated H_2 complex $[RuH_2(\eta^2\text{-}H_2)\{\eta^1(S)\text{–}C_{12}H_8S\}(PCy_3)_2$.

Complex **9** can be used to prepare ruthenium carbenes used in ring-opening metathesis polymerization (ROMP) [78]. ROMP followed by hydrogenation to give polyolefins inaccessible by other means has been studied by Fogg [79]. The Grubbs-type catalyst here, $RuCl_2(=CHPh)(PCy_3)_2$, readily transforms into potentially interconvertible dihydride, dihydrogen, and hydridochloro species under hydrogen. Small variations in reaction conditions lead to dramatic changes in hydrogenation activity.

$OsHCl(H_2)(CO)(P^iPr_3)_2$ is a very active, selective catalyst for silylation of acetylenes (equation 16) [47].

$$HSiEt_3 + PhC \equiv CH \overset{60\,C}{\rightarrow} PhHC = CH(SiEt_3) \times (\textit{trans}\text{ and }\textit{cis}\text{ isomers}) \qquad (16)$$

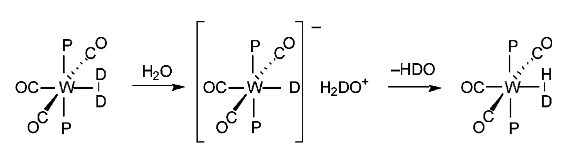
η^2–H_2 and/or η^2-Si–H complexes could be relevant here, and the isolable complex $Os(SiEt_3)Cl(H_2)(CO)(P^iPr_3)_2$ proposed as an intermediate contains η^2-H_2, which is favored over the $OsH(\eta^2\text{-}HSiEt_3)$ isomeric structure in theoretical studies.

2.5. Catalysis of isotopic exchange by H_2 complexes

Hydrogen-containing systems readily lend themselves to isotopic substitution or labeling by deuterium and tritium. Scrambling of H_2 and D_2 to form HD is often facile and can even occur over 18e H_2 complexes such as $W(CO)_3(PR_3)_2(H_2)$ (equation 17) [80–84].

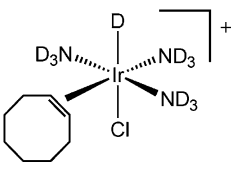
$$D_2 + W(H_2)(CO)_3L_2HD + W(HD)(CO)_3L_2H_2 + W(D_2)(CO)_3L_2 \qquad (17)$$

The exchange is not rapid, but complete isotopic equilibration occurs *even in the solid state* within days at 1 atm. This is highly enigmatic because there appears to be only one labile coordination site in these systems (isotopic exchange in complexes with multiple H_2/hydride ligands or two labile sites can be rationalized mechanistically). Dissociation of CO or phosphine to allow D_2 into the coordination sphere followed by isotopic exchange as in equation 17 seems unlikely, especially in the solid. Possible mechanisms could involve 7- or 8-coordinate 20e intermediates such as a $(H_2)(D_2)$ complex or species such as $WH_2(D_2)(CO)_3(PR_3)_2$, but no evidence exists for these. Trace quantities of adventitious water may lead to exchange since isotopic scrambling of $W(CO)_3(PR_3)_2(D_2)$ with H_2O occurs in solution within days [85] or less for other D_2 complexes [86–92]. A reasonable exchange mechanism for complexes with one open coordination site is deprotonation of η^2-H_2 by the weak base water followed by reprotonation with H_2DO^+.

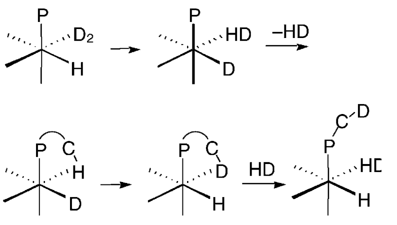


However, much stronger bases than H_2O such as alkoxides [93] are required to deprotonate the W complex. Also the rate of H_2/D_2 exchange is much faster than H_2O/D_2 exchange, which is unlikely to occur as above in the solid state and is not seen for solid $W(CO)_3(P\text{-}i\text{-}Pr_3)_2(D_2)$ plus H_2O. This pathway could operate in solution for systems with more acidic η^2-H_2, but another explanation is needed for isotopic scrambling in group 6 complexes. Systems that heterolytically cleave H_2 intramolecularly (Section 1.2) commonly catalyze D_2/H_2O exchange, often *via* an unobserved or transient D_2 complex. This is well exemplified by Sellmann's Ni, Fe, and Ru complexes containing multidentate sulfur ligands that cleave D_2 to give D–M–SD species that undergo proton exchange with water [94]. These and related systems model dihydrogen cleavage and isotopic exchange reactions observed in biological enzymes such as hydrogenases and nitrogenases [9].

Several other novel intramolecular exchanges have been observed. An Ir complex in THF slowly exchanges the deuterium in both Ir–D and N–D bonds with protons from a cyclooctene ligand, which becomes deuterated [95].



Another remarkable reaction that occurs even in the solid involves incorporation of deuterium into the PMe_3 ligands of $[Fe(D_2)H(PMe_3)_4]^+$, which may involve agostic interactions in which associative (σ-bond metathesis as in equation 2) or dissociative C–H bond activation occurs [96].



In solution, isotopic incorporation of deuterium from deuterated solvents into metal-bound hydrogen is common, e.g. reaction of acetone-d_6 and $[RuCl(dppe)_2(H_2)]^+$ or $[OsH(H_2)(PP_3)]^+$ gives the HD isotopomer in 20 min and the fully deuterated complexes in a few hours [87,97].

Complexes with both hydride and H_2 ligands such as $[Ir(H_2)H(bq)(PPh_3)_2]^+$ or unsaturated hydrides such as $IrClH_2(P^iPr_3)_2$ are advantageous for isotopic exchange because of facile exchange of the bound H_2 with D_2 and substrates with exchangeable protons combined with low barriers to intramolecular exchange with the hydride ligand. The complexes can even undergo H/D scrambling with toluene-d_8, which must bind to Ir by adding as a sixth ligand or displacing H_2 [98,99]. The cationic Ir species is an excellent catalyst for deuterium incorporation into alcohols for example (equation 18) [86].

$$\mathrm{ROH + D_2 \xrightleftharpoons[R=Me,Et,{}^tBu]{[Ir(H_2)H(bq)(PPh_3)_2]^+} ROD + HD} \qquad (18)$$

3. Relevance of dihydrogen binding on surfaces and in heterogeneous catalysis

Observation of molecular binding of H_2 to solid materials and catalysts such as metal surfaces and small metal clusters is rare since formation of metal hydrides is generally favored. Molecular H_2 is however observed by electron energy loss spectroscopy (EELS) to be bound on a stepped Ni(510) surface containing coordinatively unsaturated sites (figure 8) [100]. No such chemisorption is observed on the flat Ni(100) surface which lack the residual unfilled *d* states at the step sites that bind the H_2. Undoubtedly H_2 coordination as in figure 8 is the first step in the dissociation of H_2 on metal surfaces to form hydrides and is followed by rapid splitting of H–H analogous to oxidative addition in homogeneous solution activation of H_2. Other surfaces binding H_2 include Ni(1 1 1), Ni(1 0 0), Ni(1 1 0), and Pd(2 1 0) as evidenced by high-resolution electron energy-loss spectroscopy (HREELS) [101]. Evidence for H_2 ligation in small clusters such as $Cu_2H_2(H_2)_x$ ($x = 1,2$) and $Cu_3(H_2)$ in Ar matrices also exists [102], and H_2 binds to other $M_x(H_2)_y$ and $M_xH_y(H_2)_z$ species (M = Fe, Co, Ni, Pd) at low T [1a]. Monometallic species of these types have also been studied in great detail experimentally and calculationally by Andrews for many of the transition metals, including gold [103].

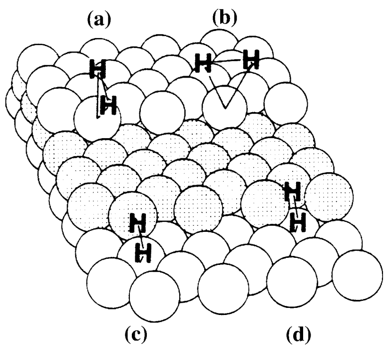
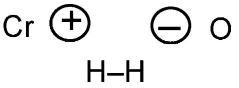
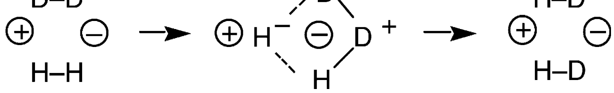


Figure 8. Model of the Ni(5 1 0) surface, showing some different adsorption sites (a)–(d). Case (a) is consistent with molecular H_2 binding as evidenced by EELS showing vibrational bands similar to those for organometallic H_2 complexes.

Transition metal oxides, sulfides, and zeolitic materials are vital heterogeneous catalysts and/or supports in many processes involving H_2 such as hydrotreatment of crude oils. Coordinatively unsaturated sites (cus) are crucial in these and other heterogeneous catalysts. Dehydroxylated chromia (Cr_2O_3) had been proposed by Burwell to contain cus in 1969, and the Cr^{3+}(cus) and O^{2-}(cus) ion pairs physisorb H_2 non-dissociatively below −130 °C, most probably at Cr *via* polarization adsorption at the ion pairs [104].



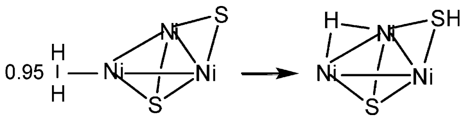
Pulses of D_2 at −196 °C completely and rapidly displaced adsorbed H_2 without formation of HD, although above −163 °C substantial HD is formed. This is consistent with molecular binding of H_2 to the metal at −196 °C, with *heterolytic H_2 splitting* taking place on $Cr^{3+}\ldots O^{2-}$ at higher temperatures. A proposed mechanism for scrambling of H_2 + D_2 to HD involved a transient containing H^- associated with the Cr^{3+} and HD_2^+ with O^{2-}(scheme 14).



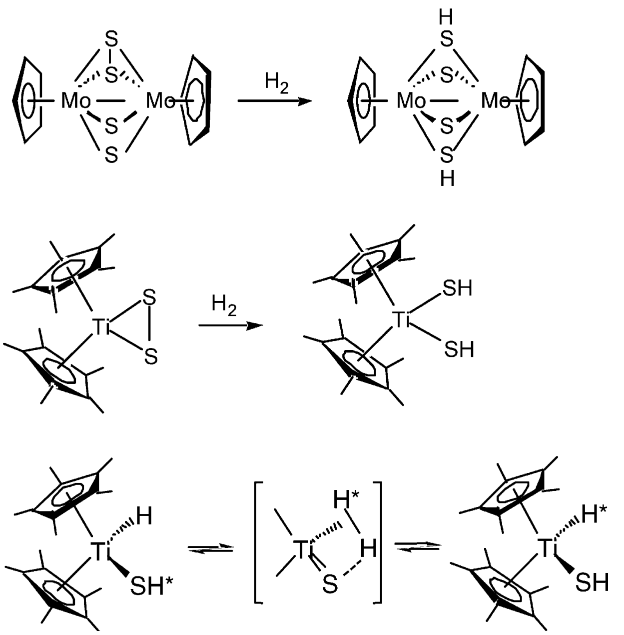
Burwell pointed out that many other oxides adsorb and activate H_2 at low temperatures, including Co_3O_4, V_2O_3, MnO, and even main group oxides such as MgO. Various different types of adsorbed hydrogen have been observed on ZnO, an important catalyst, and alumina even at 25 °C, some of which could be molecular. Chromium dioxide dihydrogen and bis-dihydrogen complexes: $(\eta^2\text{-}H_2)CrO_2$ and $(\eta^2\text{-}H_2)_2CrO_2$ have indeed been prepared by cocondensation of the CrO_2 molecules generated from laser ablation of CrO_3 with H_2 in excess argon at 11 K [105]. Broad-band photolysis of $(\eta^2\text{-}H_2)CrO_2$ induced a photoisomerization to produce the HCrO(OH) molecule, ostensibly *via* heterolytic cleavage of the bound H_2. Density functional theoretical calculations supported assignments of the aforementioned species, and $(\eta^2\text{-}H_2)CrO_2$ was predicted to have a $^3B_1$ ground state with pseudotetrahedral C_{2v} symmetry. The binding energy with respect to CrO_2 ($^3B_1$) + H_2 was computationally estimated to be 8.6 kcal/mol. The $(\eta^2\text{-}H_2)_2CrO_2$ complex has a $^1A_1$ ground state and H_2 is more strongly bound (18.0 kcal/mol per H_2) than the former due to large donation and back-donation. Other interactions of H_2 with oxides have been studied theoretically [106] and include hematite (Fe_2O_3), modeled as a simple $Fe(\mu\text{-}O)_3$ Fe cluster with H_2 binding to an apical Fe with $d_{HH} = 0.80$ Å [106a], and MgO(111) surface [106b]. A recent review addresses computational versus experimental studies of metal oxide surfaces relevant to heterogeneous catalysis [107].

The coordinatively unsaturated sites proposed above many years ago have now been *visually* identified on a ruthenium oxide surface: RuO_2(1 1 0) can be seen to bind CO to Ru ^{cus} by scanning tunneling microscopy [108]. Remarkably this same Ru^{cus} catalytic site has recently been found to also bind H_2 non-dissociatively at 85 K, as evidenced by HREELS and theory [109]. A weak peak at 2960 cm^{-1} is attributed to the H–H stretch of adsorbed H_2 (cf 2950 cm^{-1} in $Mo(CO)_3(PCy_3)_2(H_2)$ [80]). Calculations indicate that the H–H bond length is 0.81 Å and that the H_2 is 1.85 Å from the Ru^{cus} atoms (cf 0.82 Å and 1.81 Å respectively in the neutron structure of *trans*-$RuH(H_2)(Ph_2PC_2H_4PPh_2)_2$ [110]). These closely matching data suggest that, as for H_2 on Ni surfaces, the binding of H_2 to Ru^{cus} is quite similar to that in organometallic complexes. The binding site on RuO_2(1 1 0) is crucial: H_2 interacts dissociatively on the O^{bridge} atom site to form a metastable dihydride (water-like) complex, which transforms into a stable monohydride when heated further.

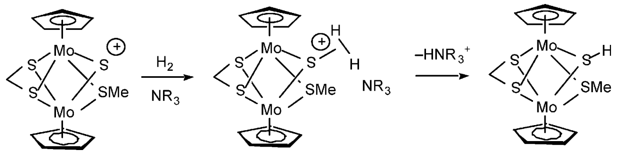
The activation of H_2 and other small molecules on transition metal sulfur compounds has been reviewed [111]. Hydrodesulfurization (HDS) catalysts vital to the petroleum industry contain metal sulfides, typically MoS_2 and RuS_2 based, often with Co promoters [111d]. Heterolysis of H_2 to form M–H and M–SH groups can be modeled on a Ni_3S_2 cluster, and a transient Ni–H_2 species is calculated to be stable by ~16 kcal/mol and energetically capable of transferring one H to S (scheme 15) [112].



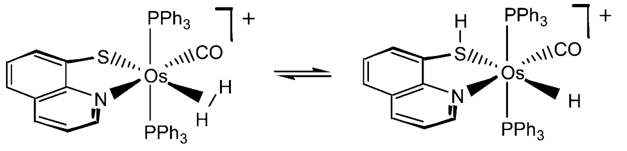
H_2 also readily reacts with a select few organometallic sulfides to give SH complexes that can show exchange behavior (scheme 16) [113–116].



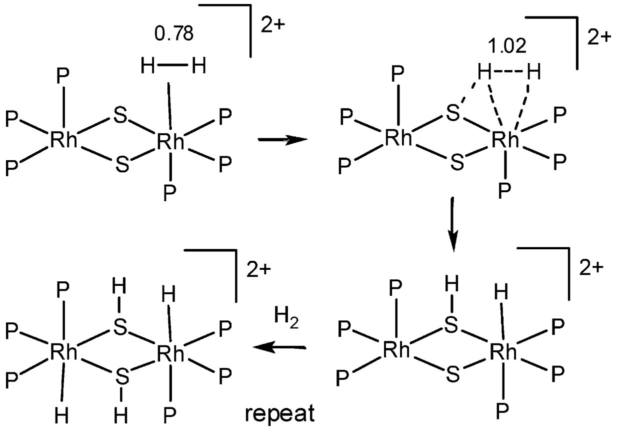
Although the mechanism of the Mo reaction is unknown [113,116], a 4-center S_2H_2 transition state or a reduction coupled with proton transfer as in metalloenzymes can be envisioned. The titanium system represents the first example of H_2 addition to a nonbridging disulfide complex [114]. An undetected H_2 complex may explain NMR evidence for H/H*-atom exchange on Ti, which also involves the protons in dissolved H_2 gas. A related Mo–S system shows reaction of H_2 with saturated cationic sulfide-bridged complexes in the presence of a base, which may be explainable by direct attack of H_2 on sulfur to form a 3c–2e S–H_2 interaction, followed by base-assisted heterolytic cleavage of H_2 (scheme 17) [113,116].



Although this type of reaction is quite rare, the possibility that activation of H_2 could be *sulfide ligand-based* in certain biological and industrial catalyst systems must be considered. η^2-H_2 ligands are known to react intramolecularly with thiolate ligands *via* heterolytic cleavage, which is an equilibrium process here (scheme 18) [117].



In this case hydrogen is activated at the metal *via* a H_2 complex, and calculations indicate this occurs for activation of two H_2 molecules on the electrophilic dinuclear sulfido complex, $[(triphos)Rh(\mu\text{-}S)_2Rh(triphos)]^{2+}$ to form $[(triphos)(H)Rh(\mu\text{-}SH)_2Rh(H)(triphos)]^{2+}$ (scheme 19).



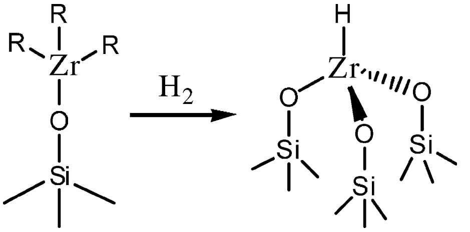
The process involves double heterolytic cleavage of a metal-bound H_2 intermediate, which could not be detected experimentally. A transition state with a long H···H distance and close approach of one H to S was identified in the calculations (this could also occur on H_2 addition to metal sulfides as in scheme 15). NMR experiments confirmed that the addition is stepwise since the half-hydrogenated complex could be observed.

Zeolitic materials are also well utilized in catalysis and are also capable of binding H_2 molecularly [118]. Fe-containing zeolites have for example recently attracted attention because of their promising catalytic activity in oxidation of benzene to phenol, selective oxidation of methane, NO_x reduction, and N_2O decomposition. Adsorption of H_2 onto the extraframework iron species in Fe-ZSM5 obtained by sublimation of $FeCl_3$ has been found to occur at 110 K [118a]. The $H_2$is strongly bound to iron centers much as in dihydrogen complexes such as $FeH_2(H_2)(PEtPh_2)_3$ [119]. Inelastic neutron scattering (INS) studies, a vital diagnostic for molecular H_2 interactions with materials, show evidence for at least two distinguishable adsorption sites related to the iron cluster. Dihydrogen also adsorbs within nonmetal containing zeolites. The hindered rotations and vibrations of molecular H_2 adsorbed into partially and fully Ca ion exchanged Na-A zeolites have also been studied at low temperatures with the use of INS [118b]. Despite a loading of one molecule per supercage to avoid multiple site occupancies, the INS spectra of the rotational transitions of H_2, HD, and D_2 clearly show that physical adsorption occurs on several different sites. The principal adsorption site in CaNa-A is in the vicinity of the Ca^{2+}cation where H_2 experiences a rotational barrier of about 1 kcal/mol (versus 2–10 kcal/mol in transition metal H_2 complexes).

3.1. *Systems at the interface between heterogeneous and homogeneous catalysis*

It may be concluded from the above discussion that there is much opportunity for *research at the interface between heterogeneous and homogeneous catalysis employing H_2 interactions* that can for example act as probes to catalytic binding sites in both regimes. There are a number of convenient structural and spectroscopic diagnostics available (crystallography, vibrational, NMR, and inelastic neutron scattering spectroscopies) and well-established computational methodologies. Several good example of such research have been reported [120]. One is Bianchini's heterogenization of the Rh(I) catalysts (sulfos)Rh(cod) and (sulfos)Rh$(CO)_2$[sulfos = $-O_3S(C_6H_4)CH_2C(CH_2PPh_2)_3$; cod = cycloocta-1,5-diene] *via* controlled adsorption on partially dehydroxylated high surface area silica [120a]. The grafted catalyst (sulfos)Rh(cod)/SiO_2 is active for the hydrogenation and hydroformylation of alkenes. Although an H_2 complex is not directly proven to be involved in the mechanisms, catalyst poisoning may occur *via* a dihydride(H_2) complex. Another example of bridging the gap between homogeneous and heterogeneous catalysis has very recently been reported by Matthes *et al.* [120b]. Using the example of Vaska's catalyst $Ir(CO)Cl(PPh_3)_2$, it was shown that complexes that catalyze the chemical ortho–para nuclear spin conversion of dihydrogen, the associated isotopic scrambling reaction of dihydrogen isotopomers, and the hydrogenation of unsaturated compounds *in organic solvents can do so also in the solid state* (as crystallites). The findings shed new light on the mechanisms of these reactions, which can involve dihydrogen complexes as intermediates.

Silica-supported zirconium hydride species have been the subject of numerous investigations and have been identified as highly active olefin polymerization catalysts.

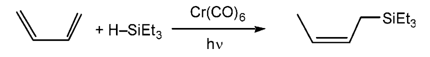


These materials also catalyze hydrogenolysis of alkanes by activating C–H bonds under relatively mild conditions. Several H/D exchange processes have been studied to obtain mechanistic information [120c]. The rate and temperature dependence of H/D exchange between H_2 and D_2 and between CH_4 and D_2 was determined utilizing a glass recycle reactor in which reactants and products were repeatedly passed over the catalyst. A sequential, single-atom exchange process was observed for both exchange processes, and H_2/D_2 exchange to an equilibrium distribution was instantaneous even at 77 K. An upper bound for the activation energy was estimated to be about ~2 kcal/mol. The exchange kinetics between CH_4 and D_2 were characterized by a high negative entropy of activation

(-27 ± 3 eu) and relatively low energy of activation ($\sim7\pm1$ kcal/mol), consistent with a σ-bond metathesis pathway (equation 2). Such pathways would be expected to be quite widespread in both heterogeneous and homogeneous catalytic systems involving this type of reactivity.

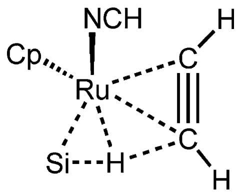
4. Catalysis involving Si–H and C–H sigma complexes

The reactions of hydrosilanes have been well reviewed [121] and only the major points concerning the involvement of σ-silane complexes in catalysis will be addressed in this Section. Dynamics and reactivity have not been as extensively studied as those for H_2 complexes, but are remarkably similar, e.g. hydrosilylation is well known *via* Chalk–Harrod type mechanisms [3] that involve oxidative Si–H addition to the metal analogous to most homogeneous hydrogenation mechanisms. Alkene insertion into a M–Si bond is quite common also, and dienes can be photocatalytically hydrosilylated in the presence of $Cr(CO)_6$ (equation 19) [122].

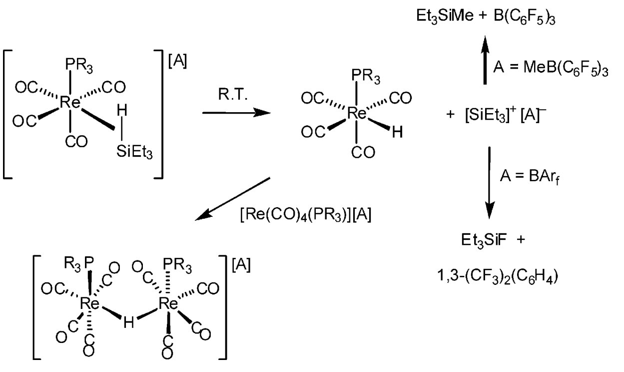


(19)

The mechanism is proposed to involve photolytically promoted displacement of three meridonal CO by the diene and silane, followed by OA of η^2-silane and transfer of hydride and silyl groups to diene. As for η^2-H_2, direct reaction of η^2-silane with a substrate is not well established but is conceivable in equation 19 and in other reactions. Indeed unusual regiochemistry (Markovnikov products) has been observed for hydrosilylation of alkynes catalyzed by cationic ruthenium complexes, e.g. $[CpRu(MeCN)_3]^+$ and theoretical studies indicate that a Chalk–Harrod mechanism cannot occur here [123]. Computations suggest a mechanism where Ru orchestrates *direct addition* of silane to the alkyne *via* initial silane coordination through Si–H followed by insertion of H into bound alkyne. The latter is calculated to occur *via* a five-membered transition state reminiscent of the σ-bond-metathesis-like structure in equation 9 for H–H addition.



Heterolytic Si–H cleavage is very facile in cationic σ-silane complexes, which are normally stable only in solution at low temperature and rarely isolatable [124], and, as for heterolysis of η^2-H_2, may be a key step in catalytic reactions. Heterolysis of Et_3SiH in the electrophilic complex *cis*-$Re(CO)_4(PR_3)(\eta^2\text{-}HSiEt_3)][A]$ (R = Ph, Cy) occurs (scheme 20) [20c] much like that in analogous H_2 heterolysis (equation 4 and scheme 5) where a hydride-bridged dimer also results, once again emphasizing the close relationship between H–H and Si–H bond activation.

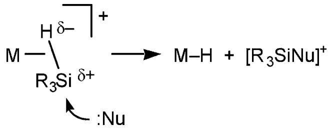


4.1. Silane alcoholysis and other silylations

The alcoholysis of hydrosilanes (equation 20) has important applications in the synthesis of silyl ethers and in protection of reactive OH groups in organic synthesis [122c].

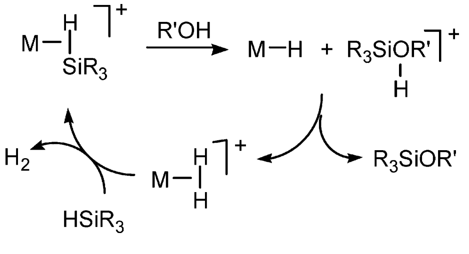
$$R'_3SiH + ROH \rightarrow R'_3SiOR + H_2 \qquad (20)$$

Luo and Crabtree had found that when heterolytic cleavage reactions of silanes were carried out in the presence of alcohols, homogeneous catalysis of silane alcoholysis occurs with high efficiency and selectivity according to equation 20 [124]. Importantly, direct nucleophilic attack by ROH on a η^2-Si–H bond as in equation 21 occurred rather than initial OA.



(21)

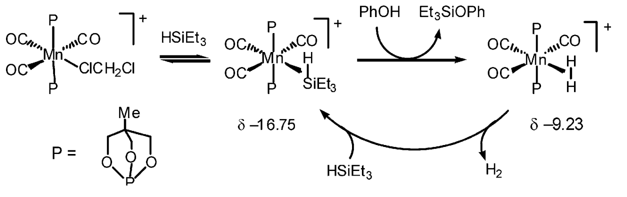
Subsequent kinetic, mechanistic, and computational studies on two different catalytic iron and manganese systems indicate that this is the key step. Brookhart and coworkers found that the cationic σ-silane complex $[CpFe(CO)(PR_3)(HSiEt_3)][BAr_F]$ catalyzed silane alcoholysis [125]. Although rapid deactivation of the catalyst occurred with ethanol as substrate, phenol reacted



continuously with turnover numbers up to 80 min^{-1}. It was proposed (scheme 21) that attack of the alcohol on bound silicon would give a protonated silyl ether that could rapidly protonate M–H to form a dihydrogen complex $[M–H_2]^+$ (the known complex $[CpFe(CO)(PR_3)(H_2)]^+$).

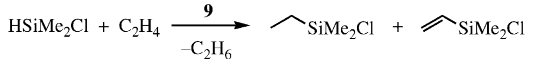
The silane substrate would then displace H_2 to give back the starting silane complex for further alcoholysis, and this was determined to be the rate-limiting step. These are all known reactions, and this mechanism and rate-determining step were recently supported by theoretical calculations that showed the heterolysis to be a highly concerted process, i.e. transformation of the σ-silane complex to the H_2 complex could even take place in a single step, thus circumventing the transient hydride complex [126]. It is noteworthy that the mechanism of this reaction involves *two different σ-complexes*: M(η^2-Si–H) and M(η^2-H_2).

The cationic dichloromethane complex, $[Mn(CO)_3(P)_2(CH_2Cl_2)][BAr_F]$, which contains tied-back phosphites, also catalyzes reaction of phenol with triethylsilane, presumably by a mechanism similar to that proposed for the above Fe system (scheme 22) [127].



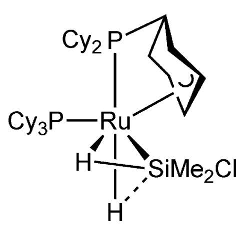
The ratio of silane to the catalyst was about 24:1, and a slight deficiency of phenol was added at −78 °C in an NMR tube reaction. ^1H NMR spectra recorded from −80 to 25 °C all showed a broad signal at −9.23 ppm presumably due to the H_2 complex formed as an intermediate. Upon exposure of the solution in the NMR tube to a He atmosphere after reaction was complete, the ^1H NMR spectrum showed a triplet at −16.75 ppm corresponding to the known silane σ-complex. The latter would be expected to be present according to scheme 22 since unreacted silane remained in the system and is a stronger ligand than either H_2 or CH_2Cl_2. The expected product of silane alcoholysis, $PhOSiEt_3$, was isolated in ca. 50% yield, demonstrating that the reaction is catalytic. Manganese carbonyl species such as $Mn(CO)_5(CH_3)$ and $[Mn(CO)_4Br]_2$ are also effective precatalysts for alcoholysis of silanes [128] and may operate *via* a similar pathway, i.e. the true catalyst is an electrophilic unsaturated Mn fragment that heterolytically cleaves an intermediate silane σ-complex. Neither electrophilic cationic complexes nor organometallic catalysts are required for catalysis of silane alcoholysis [129]. Neutral transition metal complexes as well as heterogeneous systems containing Pd(0) also function well [129a], as does a Ni(II) complex with N, S, O donor atoms [129b].

Vinylsilanes are useful reagents in organic chemistry and chlorovinylsilanes are important monomers for polyorganosiloxane and ceramic production. Dehydrogenative silylation of olefins catalyzed by transition metal complexes is one of the various methods available for their preparation that can compete favorably with hydrosilylation. An efficient synthesis of triethylvinylsilane has been reported [72] by using as catalyst precursor the versatile bis(dihydrogen) complex $RuH_2(H_2)_2(PCy_3)_2$ (**9** in scheme 13) [55]. The scope of the system was extended to disilane activation where a more complicated system is obtained and the selectivity and activity are highly dependent on the chain length *n* of the disilane $HSiR_2(CH_2)_nSiR_2H$ [75]. The system has an unexpected tolerance for chlorosilane activation by ethylene. Mechanistic studies allowed the identification of new σ-chlorosilane and chlorosilyl complexes that generate different catalytic cycles [130]. The findings demonstrate a competition between Si–H and Si–Cl bond activation. The catalytic experiments were performed at room temperature with ethylene pressure in the range 1.5–20 bar and **9** or related species were tested as catalyst precursors (equation 22).



(22)

Surprisingly the vinylsilane product was favored by a low pressure of ethylene in contrast to previous results on triethylsilane activation (scheme 13), prompting a mechanistic investigation. The mechanism was consistent with initial reaction of **9** with C_2H_4 to form **10** (as in scheme 13) which reacted with $HSiMe_2Cl$ to form the vinylsilane, ethane, and a new complex RuH(η^2-H–$SiMe_2Cl$)(η^3-C_6H_8)PCy_2 (PCy_3) (**12**) which was characterized by X-ray to contain a σ-bonded silane.



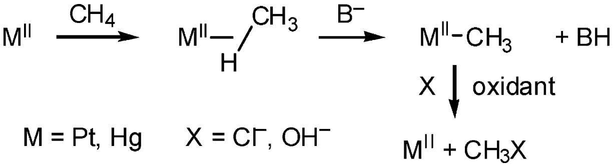
(**12**)

12 shows novel features, including coordination of a dehydrogenated Cy ring from a PCy_3 ligand, which was also seen in **10**. Of particular importance is the coordination of the bulky phosphines in a *cis* position, which favors the formation of a σ-complex that contains a stabilizing SISHA interaction (Secondary Interactions between Silicon and Hydrogen Atoms) with the hydride ligand (denoted above by H—Si). The latter is related to cis interactions for dihydrogen ligands and is especially favored here by the well-known tendency of Si to become hypervalent. The σ coordinated H–Si distance in **12** is 1.91(2) Å, at the higher limit for σ-Si–H bonds [121]. The SISHA interaction H–Si has a distance of 1.99(2) Å.

Remarkably, **12** is stable under ethylene whereas the analogue with $HSiMe_3$, which is a *dihydrido(silyl)* species (**11**in scheme 13) regenerates **10** and eliminates ethyl and vinylsilane. Thus **12** generates another catalytic cycle as seen by NMR monitoring after mixing **12** and $HSiMe_2Cl$ under C_2H_4 atmosphere: formation of vinylsilane was observed, **12** remaining the only detected organometallic species. The reaction occurs at a much lower rate compared to the system with **11**. **11** and **12** present similar overall structures, but **12** contains a more electropositive Si atom (versus the oxidatively added silane in **11**), which might be one of the factors responsible for the difference of activity and selectivity between $HSiMe_2Cl$ and $HSiEt_3$. It is significant that σ-Si–H and SISHA interactions in **12** play a major role in the processes. **12** can be considered as an intermediate between arrested Ru(II) and Ru(IV) structures that are normally invoked in the elementary step of oxidative addition of a silane in catalysis.

4.2. Relevance of alkane sigma complexes in catalysis and methane conversion

Aside from the noble gases and perfluorocarbons, alkanes are the poorest ligands because of their strong nonpolar C–H bonds, and a stable complex has not been prepared. The enthalpy of binding of alkanes to metal centers is only 10–15 kcal/mol. Nonetheless alkane complexes have been detected spectroscopically at low temperatures and are well-established intermediates in C–H cleavage as described in reviews of alkane binding and activation [131–133]. Adsorptions of alkanes are even identifiable on *metal surfaces* by techniques such as reflection-absorption IR, HREELS, and Auger electron spectroscopies [134]. Below 170 K, cyclohexane binds weakly to Pt(1 1 1) *via* direct axial hydrogen/Pt interactions and begins to undergo dehydrogenation to C_6H_{11} species at 200 K, possibly *via* σ-bond metathesis [134b, c]. Isotopic exchange between CH_4 and D_2 on silica-supported zirconium hydride species is also consistent with a σ-bond metathesis pathway. Highly acidic sites such as that in the zeolite HZSM-5 can also bind and activate alkanes. Isobutane recently has been found to form a specific adsorption complex (carbonium ion-like) with the Bronsted acid site proton in HZSM-5 and not simply undergo physical adsorption [135]. Alkanes are extremely poor acids, but on analogy with H_2 binding to metal complexes, coordination to highly electrophilic metal centers greatly enhances the acidity of the C–H bond and promotes heterolytic cleavage. This has been demonstrated in electrophilic C–H activation involving H/D exchange between acidic protons in rhodium complexes containing ηC,H *agostic* interactions and bases such as water and methanol [136]. Soft electrophiles such as Pt(II) and Hg(II) are ideal because they bind CH_4 and other alkanes transiently even in aqueous solution. Thus superacid catalysis in a conventional acid medium is possible, a very important potential route to alkane oxidation. Such metal centers can stabilize the product of cleavage in the form of an alkyl ligand for conversion to e.g. alcohols (scheme 23).

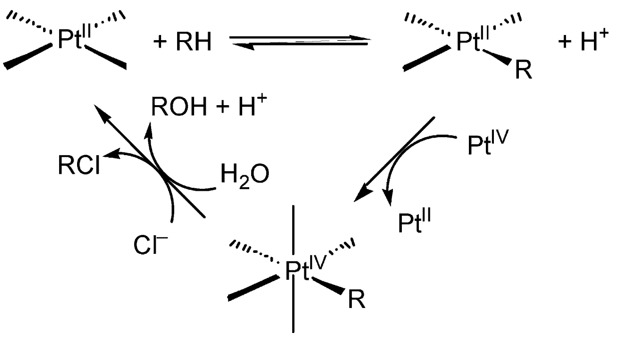


In 1969 Shilov and co-workers observed the incorporation of deuterium into alkanes in solutions of $K_2[PtCl_4]$ in D_2O/acetic acid-d_1 and subsequently reported that addition of $H_2[PtCl_6]$ to the reaction mixture generated oxidized alkane products RCl and ROH (equation 23) [132].

$$CH_4 + [PtCl_6]^{2-} + H_2O(Cl^-) \xrightarrow[H_2O,120\,^\circ C]{[PtCl_4]^{2-}} CH_3OH(CH_3Cl) + [PtCl_4]^{2-} + 2HCl \quad (23)$$

This system is remarkably robust, and it is surprising that alkane binding and activation can take place in aqueous solution where H_2O is a much stronger ligand than alkanes. The complex $PtCl_2(H_2O)_2$ has been proposed as the active catalyst, and the observed selectivity patterns reflect those of other organometallic activation systems, namely, primary > secondary > tertiary C–H. This and related chemistry has been well reviewed [132,133] and only aspects dealing with evidence for σ-complexes will be discussed.

In 1983 Shilov *et al.* proposed a mechanism for Pt-catalyzed alkane oxidation consisting of three basic transformations (scheme 24): a) activation of the alkane by Pt^{II} to generate an alkyl Pt^{II} intermediate, b) two-electron oxidation of the alkyl Pt^{II} intermediate to generate an alkyl Pt^{IV} species, and c) reductive elimination of RX (X = Cl or OH) to give back the Pt^{II} catalyst.

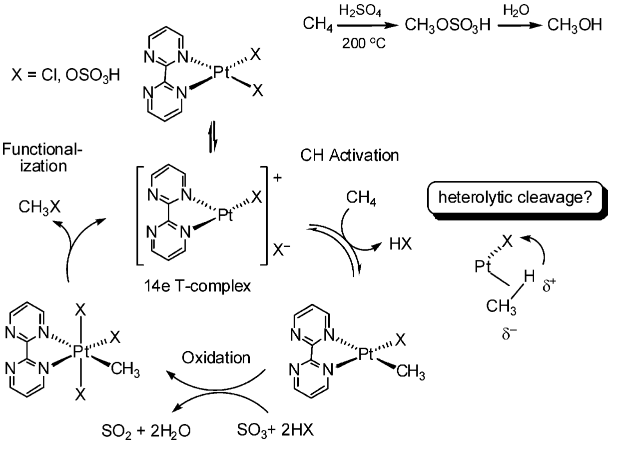


Many features of the individual steps have only recently been identified, particularly through the work of Bercaw and Labinger [133], and each of the three steps can potentially proceed by at least two different pathways not discussed in detail here. However, the first step determines both the rate and selectivity of the oxidation and is the most interesting in terms of σ-complex participation, but it is the most difficult to study. The reaction stoichiometry involves electrophilic displacement of a proton on the alkane by Pt^{II}, which essentially represents heterolytic cleavage of C–H. Once again two different mechanisms have been considered: (1) deprotonation of an intermediate Pt^{II}-alkane σ-complex by a base as in scheme 23, or (2) OA of the C–H bond at Pt^{II} producing an alkyl(hydrido)Pt^{IV} complex that is subsequently deprotonated. Considerable evidence has been obtained supporting both paths. Studies of model $[Pt(CH_3)(NC_5F_5)(tmeda)][BAr_F]$ complexes by Bercaw and Labinger show deuterium incorporation into the methyl ligand on prolonged heating (85 °C) in benzene-d_6 (methane isotopomers CH_3D, CH_2D_2, CHD_3, were observed) [133c]. This requires an intermediate with significant lifetime such as a σ-complex as shown in scheme 23, and logical extension to Shilov and related systems suggests that either an alkane σ-complex or $Pt^{IV}(R)(H)$ species are transients in alkane conversion processes. Theoretical studies indicate the mechanism of C–H activation could include σ-bond metathesis pathways (similar to equation 2), although oxidative addition pathways are generally favored for Pt^{II} systems. In a related system, $TpPtMe(H)_2$ (Tp = hydridotris(pyrazolyl)borate) undergoes H/D scrambling in methanol-d_4 without concomitant liberation of either methane or dihydrogen ($k_H/k_D = 0.76$, 55 C) [137]. Although this complex has a very high energy barrier for the liberation of methane, it readily forms a σ-CH_4 Pt(II) complex, whose existence is strongly indicated by the observed inverse kinetic isotope effect in the H/D exchange reaction.

Related systems have been intensely investigated, and mechanistic studies by Sen and co-workers indicate that Zeise's salt, $[PtCl_3(C_2H_4)]^-$, is an intermediate in the oxidation of both ethane and ethanol [138]. This is significant because direct oxidation of ethane to ethylene glycol is a very attractive alternative to the oxidation of ethylene. Considerable attention has been directed toward alkane oxidation by electrophilic metal ions in strong acid media using other metals in their highest stable oxidation state such as Hg^{2+}. Hg^{II} and subsequent Pt^{II} mediated systems discovered by Periana and coworkers represent a major advance for the direct, selective oxidation of CH_4 [139,140]. For example, the reaction in equation 24 can be carried out at 180 °C in fuming sulfuric acid (!) and is catalytic in Hg^{II}, generating methyl bisulfate (CH_3OSO_3H) in 43% yield (85% selectivity at 50% conversion).

$$CH_4 + 2H_2SO_4 \xrightarrow[180\,^\circ C]{Hg} CH_3OSO_3H + 2H_2O + SO_2 \quad (24)$$

The high selectivity suggests that CH_4 is about 100 times as reactive as CH_3OSO_3H. Many of the features of this reaction are consistent with simple electrophilic substitution, i.e. deprotonation of a transient Hg^{II}-CH_4 σ-complex. Catalysis is observed with Pd or Pt salts, with Pt being the more efficient as shown in scheme 25 for a bipyrimidine (bpym) complex of Pt^{II} [140].



At 200 °C in fuming sulfuric acid, methyl bisulfate can be obtained in 70% one-pass yield based on CH_4 (90% conversion, 81% selectivity) when X is HSO_4. The mechanism appears to be closely related to scheme 23, and H/D exchange and other experiments show that the C–H activation step must be faster than either the oxidation step or the functionalization step. The process is believed to occur *via* a 14e, cationic T-shaped complex (scheme 25) that may promote very rapid heterolytic cleavage of the C–H bond on contact of CH_4 with the Lewis acidic vacant Pt site. Intramolecular transfer of the proton to either the cis X or the anion X is possible, as for heterolysis of H_2. Multiple D incorporation into the methanes produced upon reaction of (bpym)Pt(CH_3)(Cl) with D_2SO_4 at 25 °C supports the 4-coordinate methyl complex in scheme 25 as a key intermediate. A single C–H activation can lead to multiple H/D exchange, again most likely *via* a CH_4 σ-complex before CH_4 loss or oxidation of Pt–CH_3 to methyl bisulfate occurs, similar to the above findings of Bercaw and others. DFT calculations on model systems support a σ-complex intermediate that either undergoes OA or heterolytic cleavage [141]. Regardless of mechanism, the experimental results are very encouraging since catalytic alkane oxidation in 40–70% yields is unprecedented. Periana has also reported conversion of methane to acetic acid in sulfuric acid using palladium sulfate as catalyst [142].

In order for the above systems to be practical, a cheap oxidant such as O_2 is needed. A recent report addresses this and also modification of the Pt catalyst system to be *heterogeneous* [143]. The homogeneous catalyst in scheme 25 was methylated and paired with a polyoxometalate anion to give $[Pt(Mebipym)Cl_2]^+[H_4PV_2Mo_{10}O_{40}]^-$ that was then supported on silica. Methane was oxidized under mild, aerobic (50–60 °C, 1–2 bar O_2) aqueous conditions to methanol and then partially further to acetaldehyde. The presence of the polyoxometalate in the hybrid catalyst is key in enabling mild aerobic oxidation of methane and possibly facilitates both oxidation of Pt(II) to Pt(IV) intermediates and the addition of methane to a Pt(II) center by providing a conduit for improved oxidation of intermediate hydride species. The mechanism was proposed to involve electrophilic cleavage of CH_4 as in scheme 24, and this system is a superb example of catalysis at the heterogeneous/homogeneous interface.

In summary, while OA of the C–H bond may be possible in the Pt^{II}-mediated reactions, this is not a viable pathway for other systems (e.g. Hg^{II}). In these highly electrophilic systems, a coordinated C–H bond is polarized towards $C^{\delta-}\cdots H^{\delta+}$, where the mobile H^+ can very rapidly split off and transfer to either a cis ligand or an anion as soon as the alkane contacts the metal. The metal center may thus be considered to be a superelectrophile isolobal with H^+, mimicking superacid-induced carbocation chemistry, i.e. a σ-complex such as M^+-CH_4 bears an electronic relationship to CH_5^+ and also a strong analogy to the isobutane-HZSM-5 complex [134] described above. A clear example of reversible, intramolecular heterolytic C–H cleavage at diazabutadiene ligands on iridium(III) has recently been reported [144]. Also, calculations support a heterolytic mechanism in scheme 12 over one based on C–H oxidative addition [141]. However other calculations favor OA pathways in methane activation on model complexes such as $M(CH_3)(HN{=}CHCH{=}NH)$ ($M = Pd^+, Pt^+, Rh^+, Ir^+$, Rh, Ir), the exceptions being Pd^+ and Rh^+ [145]. Thus for third-row metal centers, even if they are electrophilic, the two pathways are close in energy (and may even occur concurrently [135]), depending on factors such as ancillary ligand properties and reaction conditions.

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