Coordination Chemistry Reviews, 121 (1992) 155–284
Elsevier Science Publishers B.V., Amsterdam

Reactions of transition metal dihydrogen complexes

Philip G. Jessop and Robert H. Morris
Department of Chemistry, University of Toronto, 80 St George Street, Toronto, Ont. M5S 1A1 (Canada)

(Received 13 May 1992)

CONTENTS

Correspondence to: R.H. Morris, Department of Chemistry, University of Toronto, 80 St. George Street, Toronto, Ont. M5S 1A1, Canada.

0010-8545/92/$15.00 © 1992 Elsevier Science Publishers B.V. All rights reserved

ABBREVIATIONS

app	apparent
binap	2,2′-bis(diphenylphosphino)-1,1′-binaphthyl
BDE	bond dissociation energy
bq^-	cyclometalated benzoquinolato
$c\text{-}C_6H_{10}O$	cyclohexanone
cod	1,5-cyclo-octadiene
cot	1,3,5-cyclo-octatriene
Cp^-	cyclopentadienyl anion
Cp^{*-}	1,2,3,4,5-pentamethylcyclopentadienyl anion
Cy	cyclohexyl
Cyp	cyclopentyl
cyttp	$(Cy_2PCH_2CH_2CH_2)_2PPh$
dape	1,2-bis{di(*p*-methoxyphenyl)phosphino}ethane
dcpe	1,2-bis(dicyclohexylphosphino)ethane
DD-8	dodecahedral eight-coordinate
dedppe	1-(diethylphosphino)-2-(diphenylphosphino)ethane
depe	1,2-bis(diethylphosphino)ethane
diop	(*R*,*R*)-4,5-bis(diphenylphosphinomethyl)-2,2-dimethyl-1,3- dioxolane
$diphpyH_2$	2,6-diphenylpyridine
dmdppe	1-dimethylphosphino-2-diphenylphosphinoethane
dmgH	dimethylglyoxime
dmpe	1,2-bis(dimethylphosphino)ethane
dmso	dimethylsulfoxide
DNMR4	dynamic nuclear magnetic resonance simulation program, version 4
dpb	diporphyrinatobiphenylene tetra-anion
dpbp	2,2′-bis(diphenylphosphino)biphenyl
dppm	bis(diphenylphosphino)methane
dppe	1,2-bis(diphenylphosphino)ethane
dppp	1,3-bis(diphenylphosphino)propane
dppb	1,4-bis(diphenylphosphino)butane
dppf	1,1′-bis(diphenylphosphino)ferrocene
dtfpe	1,2-bis{bis(*p*-trifluoromethylphenyl)phosphino}ethane
dtpe	1,2-bis(di-*p*-tolylphosphino)ethane
E_{pa}	anodic peak potential
eqn	equation
eu	entropy units (cal mol^{-1} K^{-1})
Fc^+/Fc	ferrocinium/ferrocene electrochemical couple
$HB(3,5Me_2pz)_3^-$	tris-(3,5-dimethylpyrazolyl)hydroborato

HMQC	^{1}H-detected heteronuclear multiple-quantum coherence
HOTf	trifluoromethylsulfonic acid
Im	imidazole
IPR	isotopic perturbation of resonance
L	ligand
(L_2)	bidentate ligand, e.g. dmpe, depe, dppe, etc.
LUMO	lowest unoccupied molecular orbital
M	metal atom or metal complex fragment (ML_n)
MeIm	*N*-methylimidazole
meso-tet	meso-tetraphos-1, (*R*,*S*)-$Ph_2PCH_2CH_2PPhCH_2CH_2PPhCH_2CH_2PPh_2$
$M(H_2)$	spinning dihydrogen complex
$M(H)_2$	classical dihydride complex
$M(H\cdots H)$	elongated non-spinning dihydrogen complex
MO	molecular orbital
nbd	norbornadiene
NHE	normal hydrogen electrode
NMR	nuclear magnetic resonance
nOe	nuclear Overhauser effect
OC-6	octahedral six-coordinate
OCF-7	mono-face-capped octahedral seven-coordinate
oep^{2-}	octaethylporphyrin dianion
PB-7	pentagonal bipyramidal seven-coordinate
pnp^-	bis(2-diphenylphosphino-1-sila-1,1-dimethylethane)amide, $[N(SiMe_2CH_2PPh_2)_2]^-$
pp_3	tetraphos-2, $P(CH_2CH_2PPh_2)_3$
pp_3me	$P(CH_2CH_2CH_2PMe_2)_3$
py	pyridine
QEC	quantum mechanical exchange coupling
R	alkyl or aryl group
R-prophos	(*R*)-(+)-1,2-bis(diphenylphosphino)propane
rac-tet.	racemic-tetraphos-1, (*R*,*R*;*S*,*S*)-$\{Ph_2PCH_2CH_2PPhCH_2\}_2$
rot	rotational
$salen^{2-}$	*N*,*N*′-ethylene(bis(salicylidene-iminato) dianion
σ	sigma bond or mirror plane
SCE	saturated calomel electrode
SP-4	square planar four-coordinate
SP-5	square pyramidal five-coordinate
SPS-7	square-based-four-legged piano stool seven-coordinate
T	temperature
T_1	longitudinal relaxation time of nuclear spins
T_1(av)	T_1 of nuclei undergoing fast chemical exchange

T_1(eff)	effective T_1 (nuclear magnetization relaxation data fit to an exponential function with a time constant, T_1(eff), when a double exponential function should have been used)
T_1(min)	minimum T_1 observed
T_1(ne)	T_1 at temperatures below θ_1
T_2	transverse relaxation time of nuclear spins
TB-5	trigonal bipyramidal five-coordinate
thf	tetrahydrofuran
tmp^{2-}	tetramesitylporphyrin dianion
tot	total
TP-3	trigonal planar three-coordinate
triphos	$PhP(CH_2CH_2PPh_2)_2$
$\omega_{1/2}$	width of peak at half height
X	anionic ligand
θ	temperature
θ_1	temperature at the onset of slow exchange
θ_2	temperature of relaxation coalescence
θ_3	temperature of line-shape coalescence
?-7	seven-coordinate complex of unknown geometry

A. INTRODUCTION

The surprising report in 1984 by Kubas et al. [1] that the H—H bond can remain intact when coordinated in a metal complex uncapped a volcano of scientific activity that continues to this day. By 1988, there were 70 papers on the subject. About 40 different types of complexes of group 6 to group 10 metals* were known by 1988 and half of these could be isolated under ambient conditions. Review articles in that year by Kubas [2,3], Crabtree and Hamilton [4], and Henderson [5] summarized many of the important properties of the dihydrogen ligand. These reviews concentrated mainly on the methods for elucidating the structure and bonding of such complexes in the solid state and in solution. By this time, some types of reaction were emerging, namely oxidative addition, deprotonation, and elimination of the dihydrogen ligand (Sects. B, D and E of this review, respectively) as well as H atom exchange and fluxionality (Sect. C).

At the end of 1991, the number of papers has risen to more than 300. Now, about 90 structural types are known, 60 of which are stable at room temperature. Progress in the determination of the structures of dihydrogen complexes in the solid state has been slow because of the shortage in the world of neutron scattering and diffraction facilities. Only four single crystal neutron diffraction studies have been

* Each complex of a different metal and different stereochemical arrangement of donor atoms was counted but related complexes containing different substituents on the donor atoms were not counted.

reported; the complexes are $W(H_2)(CO)_3(P^iPr_3)_2$ (d(H–H) = 0.82(1) Å* [6]), $[Fe(H_2)H(dppe)_2]BPh_4$ (d(H–H) = 0.82(2) Å at 20 K [7], see Fig. 1 which shows the metal and donor atoms of the molecule), $Fe(H_2)(H)_2(PEtPh_2)_3$ (d(H–H) = 0.82(1) Å at 27 K [8]), and $Mo(H_2)(CO)(dppe)_2$ (d(H–H) = 0.80–0.85** Å [9]).

There is also a neutron diffraction study of the intriguing complex $Re(H\cdots H)(H)_5(P(p\text{-tol})_3)_2$, with a very elongated dihydrogen unit (d(H–H) = 1.357(7) Å at 20 K [10]). Hydrogen atoms in H_2 ligands have been located in certain X-ray single crystal structure determinations but the results are less reliable [11–16]. Some of these will be discussed in Sect. B.

(i) The scope of the review

This review covers the reactions of dihydrogen complexes in the liquid and solid phase. It includes most reactions since the discovery of the dihydrogen ligand (ca. 1980 by Kubas [17]) as well as some reactions from the 1960s and 1970s which are of relevance to this chemistry. In particular, there have been great advances in the reaction of dihydrogen complexes over the past four years. Examples of each of the four reaction categories covered in Sects. B–E increased greatly in number and

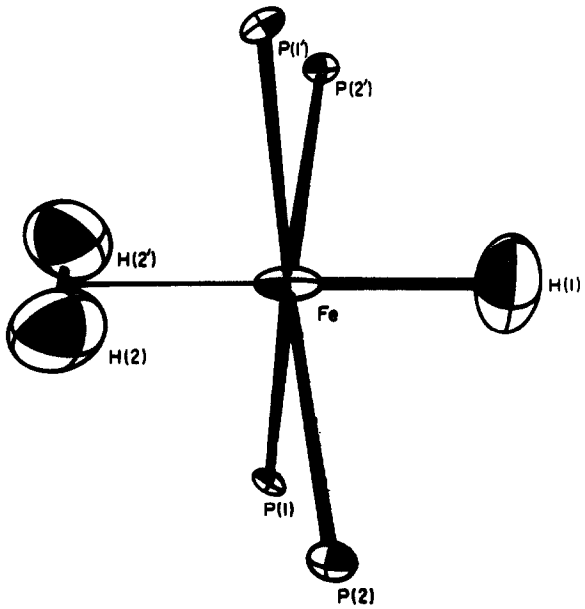


Fig. 1. The core of the cation $[Fe(H_2)H(dppe)_2]^+$ as determined by a single-crystal neutron diffraction study. Reproduced with permission from ref. 7.

* Disorder of the alkyl groups of one phosphine ligand prevented publication of the neutron structure [6(b)].

** Libration motion of the H_2 resulted in uncertainty in the H–H distance.

in diversity. New sub-categories have emerged: the intermolecular homolytic cleavage of dihydrogen (Sect. B) and reactions of very acidic dihydrogen complexes (Sects. D and F.(ii)). Added to these are new classes of reaction involving redox chemistry (Sect. F) and reactions where the H_2 ligand is retained (Sect. G). Some dihydrogen complexes are active homogeneous catalysts (Sect. H). There is only brief coverage of the preparation of dihydrogen complexes (see below) and reactions that occur after the loss of the H_2 ligand (Sects. E and H) when these have little to do with the nature of the dihydrogen complex. (Discussion of binary complexes such as $Pd(H_2)$ are not included in this review [18–24].)

The discovery of dihydrogen complexes has caused much excitement in the theoretical community. Burdett et al. [25], Tsipis [26], Bertran et al. [27(a)] and Ginzburg and Bagatur'yants [27(b)] have recently reviewed calculations on dihydrogen complexes. Empirical and ab initio theories which have been developed to rationalize some of the reactions will be discussed only briefly in the present review.

How does the reactivity of dihydrogen complexes differ from that of hydride complexes? Some significant differences will be pointed out. Most of the structures, reactions and catalytic cycles of transition metal hydrides still need to be re-examined in the new light of the dihydrogen ligand era. This has only been partially accomplished in this review.

Since 1988, there has been significant progress in the interpretation of solution NMR data for dihydrogen complexes. Section B outlines under which conditions a dihydrogen ligand, (H_2), can be distinguished from a dihydride structural unit, $(H)_2$, in a complex. This field is still developing rapidly and cannot be adequately covered in this review article. Recent papers by Desrosiers et al. [28], Earl et al. [29], and Luo et al. [30] describe the current status of H–H distance determinations from the measurement of spin–lattice relaxation times, T_1, of the hydrogen nuclei. Kubas briefly reviewed methods of distinguishing $M(H_2)L_n$ and $M(H)_2L_n$ complexes in the solid state and solution in a recent article [31]. There are some cases where the solid and solution structures can differ [3]. The methods of inelastic neutron scattering [32(a)] and solid state NMR [32(b)] are powerful techniques in the study of dihydrogen complexes in the solid state. The rotational and quantum mechanical tunneling dynamics of the H_2 ligand probed by these methods are beyond the scope of this review.

(ii) The preparation of dihydrogen complexes

Two general methods of making dihydrogen complexes are reactions of coordinatively unsaturated complexes with hydrogen gas or protonation of metal hydride species. The preparations can be viewed as reactions of dihydrogen complexes in reverse; the first is the reverse of H_2 elimination reactions described in Sect. E and the second is the reverse of the heterolytic splitting of dihydrogen as described in Sect. D.

(a) Preparation from dihydrogen gas

A common method of preparation is the reaction of hydrogen gas with a coordinatively unsaturated complex, ML_n (eqn. (1), L not necessarily all the same and not necessarily neutral), or with a complex with a displaceable neutral ligand L′ (eqn. (2)) or an anionic ligand, X^- (eqn. (3)).

$$L_nM + H_2 \rightleftarrows L_nM(H_2) \quad (1)$$

$$L_nML' + H_2 \rightleftarrows L_nM(H_2) + L' \quad (2)$$

$$L_nMX + H_2 \rightleftarrows [L_nM(H_2)]^+ + X^- \quad (3)$$

Some complexes prepared via eqn. (1) include $M(H_2)(CO)_3(PCy_3)_2$, M = Cr, Mo, W [1,6,33]; $Mo(H_2)(CO)(dppe)_2$ [34]; $M(H_2)Cl(H)(CO)(P^iPr_3)_2$, M = Ru, Os [35,36]; $(H_2)(dppb)Ru(Cl)_3RuCl(dppb)$ [37]; $[Ru(H_2)H(dppe)_2]^+$ [14]; $[Ru(H_2)Cl(dcpe)_2]^+$ [38]; $[Rh(H_2)(pp_3)]^+$ [39]; $M(H_2)H(Cl)_2(P^iPr_3)_2$, M = Rh, Ir [40,41]; $Ir(H_2)Cl(H)_2(P^iPr_3)_2$ [42] and $Eu(H_2)Cp^*_2$ [43]. Reaction (2) usually requires the assistance of UV or visible light when L′ is carbon monoxide. The following complexes have been prepared by displacement of CO: $M(H_2)Cp(CO)_3$, M = V, Nb [44]; $M(H_2)(CO)_5$, M = Cr, Mo, W [45–49]; $M(H_2)$(cyclooctene)$(CO)_4$, M = Cr, Mo, W [50]; $M(H_2)(nbd)(CO)_3$, M = Cr, Mo [51]; $M(H_2)H(Cp)(CO)_2$, M = Mo, W [52]; $Mn(H_2)Cp(CO)_2$ [53]; $Fe(H_2)(CO)(NO)_2$ and $Co(H_2)(CO)_2(NO)$ [54]; $Co(H_2)CH_3(CO)_3$ [55]; and $Ni(H_2)(CO)_3$ [56]. Low-temperature Ar matrices (in the work of Sweany) or Xe(l) solutions (used by the group of Poliakoff and Turner) have provided the best conditions for observing these dihydrogen species. Other ligands L′ which have been displaced are N_2 [57] and NH_3 [58]. Often a group 1 metal ion or Tl^+ is present in reaction (3) to precipitate with the anion. Complexes prepared as in eqn. (3) are $[Re(H_2)Cp^*(CO)NO]^+$ [59], $[M(H_2)H(depe)_2]^+$, M = Fe, Ru, Os [60], $[M(H_2)Cl(depe)_2]^+$, M = Ru, Os [61] and $[Ru(H_2)H(dcpe)_2]^+$ [38].

The synthesis of polyhydride complexes which are thought to contain a dihydrogen ligand, such as $RuH_4(PPh_3)_3$, are usually made via eqn. (4) [62], a more complex version of eqn. (1).

$$L_nMX_m + mH^- + H_2 \rightarrow L_nM(H_2)H_m + mX^- \quad (4)$$

Common sources of hydride in eqn. (4) are NaH, $NaBH_4$, $LiAlH_4$, or H_2 gas in the presence of a base, such as NEt_3 or OR^-. The anion, X^-, is usually chloride or bromide. Complexes made according to eqn. (4) are $ReH_7(PR_3)_2$ [63]; $[Fe(H_2)H(pp_3)]^+$ [64]; $M(H_2)H_2(PR_3)_3$, M = Fe, Ru [8,28,65]; $Ru(H_2)H_2$(cyttp) [66]; $[M(H_2)H(L_2)_2]^+$, M = Fe, Ru, Os [61]; and $Rh(H_2)H_2(HB(3,5\text{-}Mc_2pz)_3)$ [67].

(b) Protonation of a hydride complex

Another common method of preparation is the addition of H^+ to a hydride (or polyhydride) complex to produce a dihydrogen complex via eqn. (5).

$$L_nMH + H^+ \rightleftarrows [L_nM(H_2)]^+ \quad (5)$$

Complexes prepared as in eqn. (5) are $[Re(H_2)H_2(CO)(PMe_2Ph)_3]^+$ [68]; $[Re(H_2)(CO)_2(PMe_2Ph)_3]^+$ [69]; $[Re(H_2)H_4(cyttp)]^+$ [16]; $[ReH_8(PCy_3)_2]^+$ [70]; $[Fe(H_2)H(L_2)_2]^+$, L_2 = dppe, dmpe [60,71], $(L_2)_2$ = meso-tet, pp_3me [72,73]; $[M(H_2)H(PPh(OEt)_2)_4]^+$, M = Fe, Ru, Os [74–76]; $[Ru(H_2)H(L_2)_2]^+$, L_2 = dppe, dppp, dppb, binap, diop [60,77–80], $(L_2)_2 = pp_3$ [81]; $[M(H_2)Cl(L_2)_2]^+$, M = Ru, Os, L_2 = depe, dcpe [38–61]; $[Ru(H_2)(Cp$ or $Cp^*)(L)(L')]^+$ [82–85]; $[Os(H_2)(OAc)(PPh_3)_3]^+$ [86]; $[OsH_5(PMe_2Ph)_3]^+$ [87]; $[Os(H_2)(oep)(thf)]^+$ [88]; $[Co(H_2)(pp_3)]^+$ [89]; $[Ir(H_2)H_2(PMe_2Ph)_3]^+$ [90]; $[Ir(H_2)H(bq)(PPh_3)_2]^+$ and $[Ir(H_2)_2H_2(PCy_3)_2]^+$ [91].

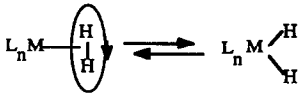
(c) Other methods of preparation

Some less common preparations have been reported. The reduction of complexes of Re(V) or Os(III) in the presence of a source of protons and electrons (H^+ and Mg or Na) produces the complexes $ReH_2Cl(PMePh_2)_4$ [92] and $[OsH_2(NH_3)_5]^{2+}$ [93], respectively. Oxidation of the latter complex with $[FeCp_2]PF_6$ gives $[OsH_2(NH_3)_5]^{3+}$. The reaction of Ru(cod)(cot) with PCy_3 and H_2 gives $RuH_6(PCy_3)_2$ [94]. Some complexes which are prepared by modifying existing dihydrogen complexes will be discussed in Sect. G.

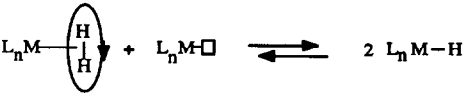
B. HOMOLYTIC SPLITTING OF COORDINATED DIHYDROGEN

(i) Introduction

There are two common classes of reaction in which the H–H bond of a dihydrogen ligand cleaves in a homolytic fashion: intramolecular (eqn. (6)) and intermolecular (eqn. (7)).



(6)



(7)

The first class is formally a two-electron oxidative addition reaction; the oxidation state of the metal increases by two. The electron density at the metal is usually assumed to be less in the dihydride tautomeric form (see, for example, refs. 53 and 95). However, the addition of dihydrogen to certain Ir(I) complexes to give Ir(III) dihydrides can be reductive with respect to the metal [96]. Therefore it is better to refer to eqn. (6) as a homolytic splitting in preference to an oxidative addition.

Reaction (6) is of direct importance to the mechanism of many homogeneous hydrogenation catalysts, including Wilkinson's catalyst, $RhCl(PPh_3)_3$, where the unobserved dihydrogen ligand in a Rh(I) intermediate rapidly splits to give the dihydride intermediate responsible for the hydrogenation of an unsaturated compound. The η^2-dihydrogen/dihydride equilibrium has direct parallels to the equilibria between η^2-alkane and alkylhydride species [97], η^2-silane and silylhydride species [98–103] and between η^2-stannane and stannylhydride complexes [104,105]. These equilibria are important in catalytic hydrosilylation and hydrostannylation reactions and potentially important in C–H bond functionalization, but are beyond the scope of this review.

There is only one well-characterized example to date of the intermolecular splitting of a dihydrogen ligand as shown in eqn. (7). This involves the dihydrogen complex $Ir(H_2)HCl_2(P^iPr_3)_2$ [106,107], as will be discussed below. However, there are several mechanisms of homogeneous catalysis which involve the reaction of dihydrogen with two metal centers to give two monohydrides and these will also be considered. The formal oxidation state of each of the two metals increases by one electron when the dihydrogen splits according to eqn. (7).

(ii) Observing the dihydrogen–dihydride equilibrium (6)

The chemistry of such an equilibrium is complicated by the variable structural and spectroscopic properties of species thought to be dihydrogen complexes and those thought to be dihydrides. The definition of dihydrogen complexes is still evolving because there appears to be a range of H–H distances possible, and research has still not found the borderline distance between $M(H_2)$ and $M(H)_2$ structures. This review defines dihydrogen complexes as having the characteristics listed in Table 1. The H–H distance should fall in the range 0.8–1.0 Å. This range appears suitable to include complexes with a rapidly spinning H_2 unit whose properties are perturbed little from those of free H_2 gas (d(H–H) = 0.74 Å, ν(H–H) = 4400 cm^{-1}, J(HD) = 43.5 Hz). This also includes those with an H_2 ligand which has internal motion (probably spinning like a propeller) which is much faster than the tumbling of the molecule in solution and yet has physical properties associated with a longer H–H distance (d(H–H) $\leqslant$ 1.0 Å, ν(H–H) = 3100–2400 cm^{-1}, J(HD) > 25 Hz, T_1(min) < 22 ms at 200 MHz (see structure **1**, Fig. 2).

Complexes with structure **1** have been referred to as non-classical dihydrides, molecular hydrogen complexes, and η^2-dihydrogen complexes. They will be referred to here as dihydrogen complexes, $M(H_2)$, or spinning dihydrogen complexes. The T_1(min) time quoted here is for the case where the ^1H NMR measurement is made at 200 MHz on a complex where only dipolar relaxation between the two hydrogen nuclei is important and where the dihydrogen ligand has a correlation time which is much shorter than that of the rest of the molecule. Equations have been proposed to calculate d(H–H) from T_1(min) for the case of rapid internal motion of the H_2

TABLE 1

Some characteristics of dihydrogen, dihydride and intermediate H ··· H structures

	$M(H_2)L_n$ (1)	$M(H \cdots H)L_n$ (2)	$M(H)_2L_n$ (3)	$M(HD)L_n$	$M(H \cdots D)L_n$	$M(H)(D)L_n$	Ref.
Structural							
d(H–H) (Å)	0.8–1.0	1.0–1.6	>1.6				29
Vibrational							
ν(H–H) (cm^{-1})	3100–2400	–	–				3,32(a)
ν(M–H) (cm^{-1})	–		1500–2200				304
ν_s(M–H_2) (cm^{-1})	850–950	–	–				32(a)
rot. tunneling ν (cm^{-1})	0.7–6.4	–	–				32(a)
NMR							
T_1 (min., 200 MHz)[a] (ms)	5–22	6 to 90	>90				28,29
J(HP) (Hz) (L = PR_3)	0–6		>10 usually				
J(HD) Hz				34–25	25–4	<5	29

[a]Corrected by factoring out other sources of relaxation (see Sect. B.(ii)).

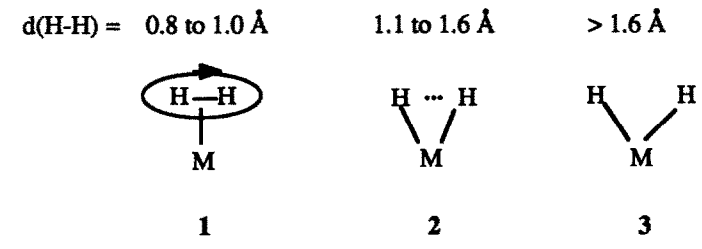


Fig. 2. Structures **1**, $M(H_2)$, **2**, $M(H \cdots H)$, and **3**, $M(H)_2$.

ligand; distances are found to be a factor of 0.793 shorter than the case of the H_2 ligand having the same correlation time as the molecule as a whole [29]. Values obtained at other observation frequencies are directly proportional and are readily converted to the 200 MHz scale: e.g. T_1(min, 200 MHz) = T_1(min, 400 MHz)/2. Other sources of relaxation such as metal–hydrogen dipole–dipole and ancillary ligand hydrogen–dihydrogen dipole–dipole interactions have to be factored out to obtain a T_1(min) value which represents only the H—H dipole–dipole relaxation in the dihydrogen ligand [28]. The effects on T_1 measurements of chemical exchange between dihydrogen and a hydride species must also be considered (see Sect. C and ref. 108). There is also the concern that quantum mechanical effects have been neglected when trying to relate T_1(min) to d(H—H) quantitatively via equations based on relaxation theories which assume classical molecular dynamics [109]. If there are phosphorus donor ligands in the complex, then the J(HP) coupling between ($^1H_2$) and ^{31}P nuclei will be less than 6 Hz and usually near to zero Hz. Inelastic neutron scattering experiments reveal the existence of a rotational tunneling transition in the far-IR and show that there is often a small barrier (< 3 kcal mol^{-1}) to rotational tunneling in dihydrogen complexes of structure **1** in the solid state [32(a)].

All equilibria (6) which have been studied are solution phase and the techniques of observation are IR and NMR spectroscopy. The dihydrogen mode ν(H—H) is weak and is not usually observed for complexes in solution by the IR method; an exception is studies employing Xe(l) as a solvent [44]. The best proof for the existence of a dihydrogen complex in solution is the observation by use of NMR of both a short minimum T_1 time and also a large H—D coupling for the corresponding HD complex.

Dihydrides have distances d(H—H) expected for two ligands which occupy the usual stereochemical positions in coordination polyhedra (1.8–2.5 Å, structure **3**, Fig. 2). Such distances usually result in little communication between the nuclei: a long minimum T_1 time (> 90 ms at 200 MHz) and a very small J(HD) coupling constant (< 5 Hz, see Table 1) for the M(H)(D) complex. A class of trihydrides of formulae $[IrH_3CpL]^+$, RuH_3CpL, and NbH_3Cp_2 with hydrides which are separated by approximately 1.7 Å exhibit quantum mechanical exchange coupling [110–114] (see also Sect. C.(ii)). Simultaneous quantum mechanical tunneling of two protons

through a vibrational potential surface accounts for this phenomenon; covalent bonding between the hydrogens is not necessarily needed [109]. The metal–hydride stretch of hydride complexes in solution is often intense enough to be observed in IR spectra. Typically, these can range in frequency from 1500 cm^{-1} for early 3d transition metals such as Cr to up to 2300 cm^1 for late 5d transition metals such as Pt. Dihydrides have also been called classical dihydrides and will be printed as $M(H)_2$ in complex formulae in this review.

In polyhydride complexes, two hydride ligands are known from single-crystal neutron diffraction studies to approach as closely as 1.6 Å in $OsH_6(P^iPr_3)_2$ [115] and even 1.36(1) Å in $ReH_7(P(p\text{-tolyl})_3)_2$ [10]. The latter complex enters a region of as yet incompletely defined H–H interaction or elongated dihydrogen structure, denoted in this review as H···H, structure **2**. X-ray diffraction studies of $[ReH_6(cyttp)]^+$ [16], $Re(H_2)(Cl)(PMePh_2)_4$ [12], $RuH_3I(PCy_3)_2$ [11] and $[RuH_2Cp(dppm)]^+$ [13] suggest that H–H distances of 1.08(5), 1.17(13), 1.03(7) and 1.0(1) are present, respectively. Complexes $[RuH_2Cp(CO)(PCy_3)]^+$ and $[RuH_2Cp(dmpe)]^+$ have d(H–H) values of 0.97 and 1.02 Å, respectively, according to solid state NMR measurements [109]. These complexes also appear to contain ligands with undefined H···H interactions. Neutron diffraction studies are still needed for these. Both of the complexes $[Ru(HD)Cp(dppm)]^+$ and $[Ru(HD)Cp(dmpe)]^+$ have couplings, J(HD), of 22 Hz but it is not known whether these are temperature-dependent [83,84]. Complexes $M(H\cdots D)L_n$ with H–D distances which are thought to be in the range 1.0–1.6 Å exhibit J(HD) couplings of intermediate size (4–25 Hz; see Table 1) in ^1H or ^2H NMR spectra. The T_1(min) value of the H···H nuclei should be corrected to remove sources of relaxation other than the H···H dipole–dipole interaction [28,30,116]. Rotational motion of the elongated H···H structure is assumed to be restricted (but this has not been proven) so that d(H–H) is calculated from the T_1(min) without the factor of 0.793 used in the case of rapid motion [29]; T_1(min) values which correspond to 1.0 and 1.6 Å are 6 and 90 ms at 200 MHz (see Table 1). This assumes that the potential energy versus H–H distance plot for such a complex has one minimum at the equilibrium H–H distance (Case I, Fig. 3). Case I is actually drawn with three minima to account for the possible existence of less stable dihydrogen and dihydride forms. In other words, this is a case of arrested homolytic cleavage of H_2, similar to the case of the arrested splitting of agostic C–H bonds [117]. However, the properties of a complex $M(H\cdots H)L_n$ might also be explained by the averaging of the properties of a dihydride complex, **3**, and a complex with a rotating dihydrogen ligand, **1**, caused by a low energy bond-splitting/bond-forming process; in such a case, a potential surface with a double well must be drawn (Case II, Fig. 3) [29]. Possible examples of such a rapid, reversible homolytic cleavage process are described below. Theory suggests that hydride–hydride overlap is always positive even when the H···H distance is as long as 2 Å, so that there is no electronic reason for the barrier of Case II [118]. Nevertheless, several examples are introduced below where there is a

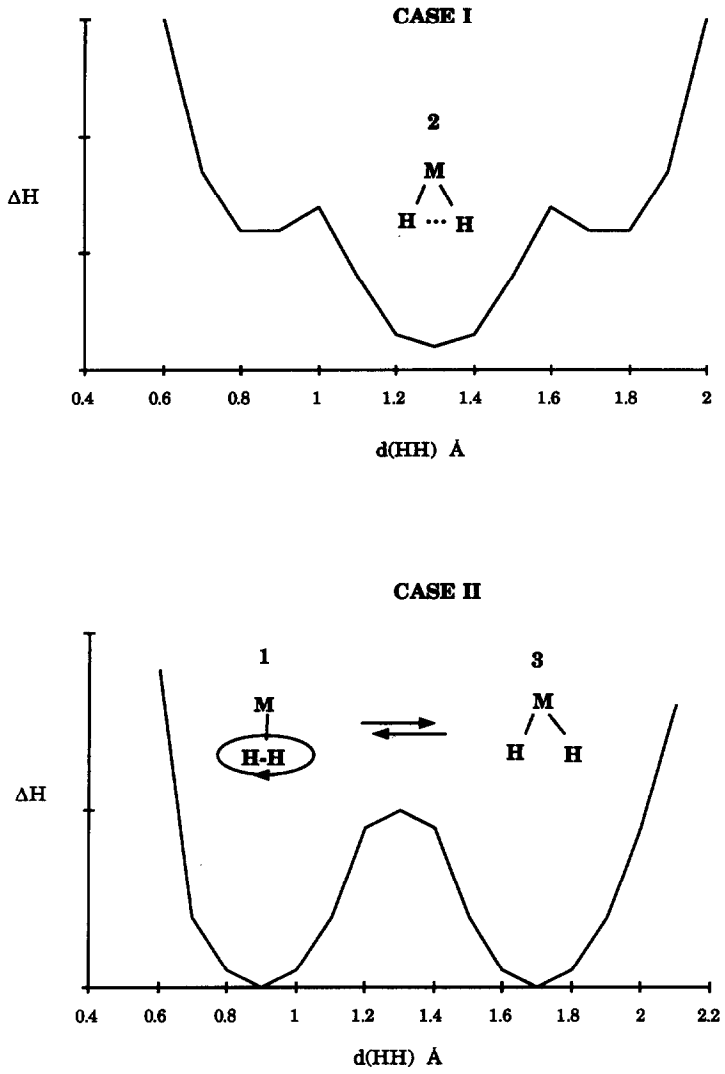


Fig. 3. Case I. Arrested homolytic cleavage of dihydrogen. Case II. Rapid reversible homolytic cleavage of dihydrogen.

sizable energy barrier between dihydrogen and dihydride tautomers. Future single-crystal neutron diffraction structural studies could help to resolve the mysteries of $M(H \cdots H)L_n$ complexes.

Several indirect methods for distinguishing dihydrogen from dihydride are summarized in Table 2. Polyhydrides with formulae $[ReH_8(PR_3)_2]^+$ [70] and $[MoH_6(dppe)_2]^{2+}$ [119] must contain at least one H–H bond so as not to exceed the maximum oxidation state of the metal. Bianchini et al. [120] propose that gold

TABLE 2
Indirect ways which have been proposed to distinguish dihydrogen and dihydride structures

	$M(H_2)L_n$ (1)	$M(H)_2L_n$ (3)	Ref.
$MH_xL_n^{z+}$ oxidation state	$x+z$ exceeds group number of metal		5,70
Reaction with $ClAuPR_3$	Gives $MClL_n^- + H_2$ or $ML_n(\mu\text{-H})AuP + HCl$	No reaction or gives $MHL_n(\mu\text{-H})AuP^+$	120
Reaction with $AuPR_3^+$	Gives $M(PR_3)L_n + Au + 2H^+$	No reaction or gives $MHL_n(\mu\text{-H})AuP^+$	120
$E_{1/2}$(ox)	Less positive	More positive	95
H_2 lability	More labile	Less labile	2,87
ν(CO) (cm^{-1})[a]	Similar to ν(CO) of $M(N_2)L_n$[a]	Higher than ν(CO) of $M(N_2)L_n$[a]	44,51,53, 103,299

[a] When a CO ligand is one of the ancillary ligands L_n.

reagents react with dihydrogen complexes of Co(I) and Rh(I) in a different fashion than with similar dihydride complexes of Ir(III). Notably, the dihydrogen complexes reduce $AuPR_3^+$ to Au(0) whereas the dihydrides do not. This is consistent with Zanello's proposal that dihydrogen complexes are more reducing than tautomeric dihydride complexes and that this difference can be detected by electrochemical measurements [95]. This may not always be the case. Both dihydrogen complex $[Os(H_2)H(dppe)_2]^+$ and complex $[Os(H\cdots H)H(depe)_2]^+$ have very similar potentials for their oxidation [29]. Intuitively, it would be expected that dihydrogen complexes should evolve H_2 more easily and quickly than comparable dihydride complexes. In fact, it was on this basis that Ashworth and Singleton proposed in 1976 that $[Ru(H_2)H(dppe)_2]^+$ contained a coordinated dihydrogen molecule [77] long before the existence of the dihydrogen ligand was reported in 1984 by Kubas et al. [1], and before its existence in this Ru complex was proved by Morris et al. in 1985 [14]. However, Halpern et al. pointed out that there is the same difference in lability between the two non-classical complexes $[RuH_5(PPh_3)_3]^+$ and $[OsH_5(P(p\text{-tol})_3)_3]^+$ and between the non-classical $RuH_4(PPh_3)_3$ and the classical $OsH_4(P(p\text{-tol})_3)_3$ [121] so that high dihydrogen evolution rates might not be definitive proof of a dihydrogen versus dihydride formulation (see Sect. E for further discussion of this point).

The final entry in Table 2 indicates that the frequency, ν(CO), of a $MH_2(CO)L_n$ complex provides evidence for the existence of a dihydrogen ligand if the ν(CO) of the corresponding dinitrogen complex, $MN_2(CO)L_n$ is comparable. If ν(CO) for $MH_2(CO)L_n$ is much higher than that of the dinitrogen complex, then a dihydride is present. Note that this criterion supports the view that dihydrogen complexes are more reducing, and hence more strongly backbonding, than tautomeric dihydride complexes. We find that this criterion fails to distinguish between the complexes

trans-$Mo(H_2)(CO)(dppe)_2$, $\nu(CO) = 1815$ and $Mo(H)_2(CO)(depe)_2$, $\nu(CO) = 1790\ cm^{-1}$; the corresponding complexes $Mo(N_2)(CO)(L_2)_2$ have $\nu(CO) = 1799$ and $1776\ cm^{-1}$, respectively [34]. Of the methods of Table 2, only the measurement of $\nu(CO)$ is likely to signal the simultaneous existence of dihydrogen and dihydride forms in equilibrium by showing distinct $\nu(CO)$ absorptions for each. For example, an equilibrium between $Nb(H_2)Cp(CO)_3$ and $Nb(H)_2Cp(CO)_3$ in Xe(l) was detected by IR spectroscopy [44]. The observation of distinct electrochemistry for $M(H_2)$ and $M(H)_2$ forms might be possible under special circumstances.

(iii) Factors influencing the dihydrogen–dihydride equilibrium (6)

Some factors which are known to stabilize either a dihydrogen complex (the left-hand side of eqn. (6)) or dihydride complexes (the right-hand side) are listed in Table 3. These factors also relate to other addition reactions, such as the well-studied homolytic cleavage of carbon–hydrogen bonds [122–128]. Strong metal–hydride bonds will push equilibrium (6) to the right. The trend down a column of the periodic table is thought to be an increase in the M–H bond strength as M changes from a 3d to 4d to 5d transition metal. This explains why $V(H_2)Cp(CO)_3$ is a dihydrogen complex whereas $Ta(H)_2Cp(CO)_3$ is a dihydride; consistent with the trend is the observation that $Nb(H_2)Cp(CO)_3$ and $Nb(H)_2Cp(CO)_3$ co-exist in equilibrium [44]. This is also why $Ru(H\cdots H)H_2(PPh_3)_3$ probably has an elongated dihydrogen ligand (see below) whereas $OsH_4(PPh_3)_3$ is a tetrahydride [65]. The reason for this trend is thought to be a relativistic contraction of orbitals which improves $d(M)–\sigma(H^-)$ overlap. The 5d metals also give the most stable dihydrogen complexes with respect to H_2 loss. As a result, equilibrium (6) is possible for a variety of 5d metal complexes (see below).

Making the metal very π-basic will destabilize the dihydrogen complex because of excessive $d(M)\rightarrow\sigma^*(H_2)$ backbonding and force the equilibrium to the right. Factors that make a metal π-basic in a complex $[MH_2L_xX_y]^{z+}$ (L = neutral ligand, X = anionic ligand) are high-energy d electrons and good M–H_2 orbital overlap. Metal-based electrons are more energetic (reducing) in a complex of an early transition metal (e.g. group 6 > group 9) with a charge, z, as negative as possible, and with electron-donating ligands, as indicated in Table 3. Conversely, dihydrogen complexes are stabilized by weakly π-basic metal centers produced by later transition metals in positive oxidation states with the correct mix of σ donor and π acceptor ligands to provide the critical amount of backbonding to the H_2 ligand. A nice example of the electronic effect of the ligand is the observation by Kubas et al. [34] that $Mo(H_2)(CO)(dppe)_2$ is a dihydrogen complex whereas $Mo(H)_2(CO)(P^iBu_2CH_2CH_2P^iBu_2)_2$ is a dihydride complex with a chelating phosphine of the same size but more electron-donating than dppe. Another is the observation that $Ir(H_2)(H)_2Cl(P^iPr_3)_2$ is a dihydrogen complex whereas $Ir(H)_5(P^iPr_3)_2$ is a pentahydride [42]. Here, the replacement of electronegative chloride by hydride shifts eqn. (6)

TABLE 3

Factors that determine stability of dihydride complexes, dihydrogen complexes and coordinatively unsaturated complexes which have a low affinity for dihydrogen

Factor	Complex		
	Dihydride $M(H)_2L_xX_y^{z+}$	Dihydrogen $M(H_2)L_xX_y^{z+}$	Coordinatively unsaturated $ML_xX_y^{z+}$
Properties of M–H bond			
Bond energy	High	Medium	Low
Energy decrease with row of M	5d > 4d > 3d	5d > 3d > 4d	
orbital overlap	Good d(M)–σ(H^-)	Good d(M)–$\sigma^*(H_2)$	Poor overlap (nodes)
Properties of metal M			
π-basicity of M	Strong	Weak	Very weak
Favored group of M	Group 6 > group 9	Group 8	
Favored electron config.	d^6 when $x+y=4$	d^6 when $x+y=5$	
Charge $z+$	$<+2$	0 to $+3$	>0 best
Properties of ligands L			
Donor properties of L, X^-	Electron donating e.g. NH_3, PMe_3, depe, SR^-, OR^-, NR_2^-, H^-	Correct mix of σ donor and π-acid ligands	
Size of L, X^-	Small	Small or large	Ligand which shields the vacant site, possibly with a C–H···M bond
Polydentate L, X^-	Favor coord. number $x+y+2$ e.g. Cp^- in $CpRhH_2L$	Favor coord. number $x+y+1$ e.g. pp_3 in $[Co(H_2)(pp_3)]^+$	Favor coord. number $x+y$ e.g. pnp ligand in $Ir(pnp)(H)_2$
Nature of trans ligand	Strongly σ donating	π acid ligand in an electron-rich complex	High trans influence e.g. H^-, CO, PR_3, R^-

to the right. Some of these factors have been noted in reports of calculations on model complexes of the type $W(H_2)(CO)_3(PH_3)_2$ versus $W(H)_2(PH_3)_5$ [129] and $[Fe(H_2)(CO)_5]^{2+}$ versus $[Fe(H)_7]^{3-}$ [130,131]. These and related calculations have recently been reviewed by Burdett et al. [25] and Tsipis [26].

The corresponding dinitrogen complex $[M(N_2)L_xX_{5-x}]^{z+}$ can be used as an indicator of π-basicity of the d^6 binding site $[ML_xX_{5-x}]^{z+}$, where M is a metal from groups 6–9. It was proposed that when $\nu(N_2)$ is less than 2060 cm^{-1}, a dihydride $M(H)_2$ will form (equilibrium (6) will lie to the right) whereas when it is greater than 2060 cm^{-1}, the dihydrogen complex will be favored [132]. More recently, this approach has been refined to include limits on the electrochemical potentials of the dinitrogen complexes (Table 4, [133]). Dihydrogen complexes which have corresponding N_2 complexes with $E_{1/2}(d^5,d^6) < 0$ V versus NHE should undergo homolytic splitting. If the dihydrogen is trans to a σ-donor such as hydride and is on a 4d or 5d metal, splitting will occur at the more positive potential of 0.5 V. The strength of this method is that the potentials can be calculated from the structure of the complex by an additive ligand parameter method proposed by Lever [134,135]. In principle, the stability of a dihydrogen complex with any combination of d^6 metal and five ancillary ligands can be predicted on the basis of the guidelines of Table 4 and the additive parameter approach. Unfortunately, this only gives information about the stability of the dihydrogen complex on the left of eqn. (6); if the dihydride on the right side is made particularly stable by the stereochemistry of the ligands (see below), then homolytic splitting might occur even when $\nu(N_2)$ of the corresponding dinitrogen complex is greater than 2060 cm^{-1} and $E_{1/2}$ is greater than 0.5 V. Some examples of this will be described below.

Complexes of the type $[M(H_2)L_xX_y]^{z+}$ are particularly stable when the metal

TABLE 4

Properties of the corresponding dinitrogen complexes which indicate the stability of dihydride complexes, dihydrogen complexes and coordinatively unsaturated complexes when there are five ancillary ligands on the complex [133]

	Property of $[M(N_2)L_xX_{5-x}]^{z+}$		
	Too reducing	Correct energy of HOMO	Too oxidizing
N_2 trans to CO			
$E_{1/2}$ vs. NHE (V)	<0	$0 < E < 1$	>0.5 (3d metal) >1.0 (4d, 5d)
$\nu(N_2)$ (cm^{-1})	<2060	$2060 < \nu < 2160$	>2160
N_2 trans to σ-donor			
$E_{1/2}$ vs. NHE (V)	<0 (3d metal) <0.5 (4d, 5d metal)	$0 < E < 1.7$ (3d) $0.5 < E < 2.0$ (4d, 5d)	>1.7 (3d) >2.0 (4d, 5d)
$\nu(N_2)$ (cm^{-1})	<2060	$2060 < \nu < 2180$	>2180
Corresponding complex	Dihydride $[M(H)_2L_xX_{5-x}]^{z+}$	Dihydrogen $[M(H_2)L_xX_{5-x}]^{z+}$	Coordinatively unsaturated $[ML_xX_{5-x}]^{z+}$

has a d^6 configuration and the complex is octahedral so that the sum of neutral and anionic ligands, $x + y$, is five. The majority of known dihydrogen complexes are of this type. Dihydride complexes with the metal in the d^6 electron configuration are also very stable when the complex is octahedral; in this case the sum $x + y$ is four. Even electron-poor complexes such as $M(CO)_4(H)_2$, M = Fe, Ru, Os, exist as dihydrides with negligible H–H bonding. The dihydrogen complexes $M(CO)_4(H_2)$ are destabilized by a repulsion between a filled d orbital and the filled $\sigma(H_2)$ orbital and by poor backbonding from the low-energy d orbitals [136].

The stereochemistry of the ancillary ligands can influence equilibrium (6). The shift from left to right of eqn. (6) involves an increase by one in the coordination number of the metal. Small ligands will favor the dihydride tautomer. However, large ligands might also do the same by preventing a metal from adopting an octahedral geometry and therefore disallowing the favorable d^6 configuration. For example, the ligand 1,1'-bis(diphenylphosphino)ferrocene (dppf) has a large bite angle of 106°; this prevents octahedral coordination around Ru and causes the formation of a seven-coordinate trihydride complex, $[Ru(H)_3(dppf)_2]^+$, instead of the dihydrogen–hydride structure $[Ru(H_2)(H)(L_2)_2]^+$ which is found in all other cases where chelating phosphine ligands, L_2, are present [137]. Similarly, it has been proposed that $[OsH_3(PPh_3)_4]^+$ does not contain a dihydrogen ligand because interactions between the large PPh_3 ligands do not allow a regular octahedral structure to form [29]. Cyclopentadienyl ligands, which are assumed to occupy three coordination sites, strongly favor six-coordinate, d^6 complexes $M(H)_2CpL$, M = Co, Rh, Ir over five-coordinate complexes $M(H_2)CpL$ [136], whereas the tetradentate phosphine pp_3 appears to favor five-coordinate, d^8, dihydrogen complexes over six-coordinate, d^6 dihydride complexes for $[M(H_2)(pp_3)]^+$, M = Co(I) and possibly Rh(I) [89].

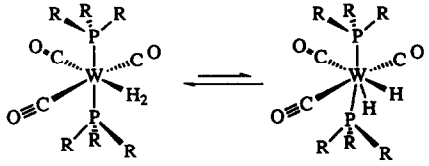
A UV photon is usually required to cause the elimination of dihydrogen from dihydrides like $Ir(H)_2CpL$ and $Fe(H)_2(dmpe)_2$ which lie far to the right of eqn. (6), probably by ΔH greater than 25 kcal mol^{-1} [136]. The photon excites an electron from a MO which is H–H antibonding (dihydride) to a MO which is H–H bonding and M–H antibonding (transient dihydrogen intermediate) [138,139]. The high-energy intermediates can sometimes insert into the C–H bonds of unreactive alkanes such as methane [140–142].

The ligand trans to dihydrogen in an octahedral complex is crucial to the stabilization of the complex with respect to H_2 loss. Electron-poor complexes require a good σ-donor trans to the dihydrogen whereas more electron-rich complexes require a good π acid such as CO [132]. A good σ-donor like a hydride when trans to dihydrogen in an electron-rich complex will cause a shift to the right in eqn. (6). The trans influences of hydride versus phosphine on dihydrogen coordination has recently been explored in an ab initio study of complexes *trans*-$[Fe(H_2)H(PH_3)_4]^+$ and $[Fe(H_2)(PH_3)_5]^{2+}$ [143]. The first complex was calculated to be much more stable with respect to H_2 loss than the second, despite the high trans influence of hydride; we note that the second complex is probably too electron deficient to be stable.

(iv) Thermodynamics of the dihydrogen–dihydride equilibrium (6)

Table 5 lists free energy changes in equilibria between well-characterized dihydrogen complexes and their dihydride tautomers. Only examples where both species are directly observed (by NMR or IR) are included. In the usual case, the ratio of concentrations of the two species must be between 1:50 and 50:1 to be detectable reliably by NMR. They are organized by stereochemical change and then by metal group number. The stereochemical notation is the one suggested by Sloan [144]: octahedral, OC-6, etc. Some enthalpy and entropy changes are also listed in Table 5. Activation energies for some of these reactions will be discussed in Sect. B.(v) below.

All of the complexes except two in Table 5 involve octahedral, d^6 dihydrogen complexes and seven-coordinate, d^4 dihydrides. Kubas et al. [6,145,146] reported the first examples of such an equilibrium between the complexes $W(H_2)(CO)_3(PR_3)_2$ and their dihydride isomers which are thought to have a mono-face-capped octahedral geometry (OCF-7) (eqn. (8)).



(8)

The geometry of the dihydrogen complex was established by neutron diffraction while the structure of the product follows from the NMR observations that the two hydride and two phosphorus nuclei become inequivalent when fluxional exchange processes of the seven-coordinate complex are frozen out at 200 K. IR spectra showed ν(CO) peaks due to both tautomers. The ^{1}H NMR spectra of the HD complexes revealed a 1:1:1 triplet for the W(HD) species with a coupling of 33.5 Hz but only a 1:2:1 triplet with J(HP) coupling and no resolvable J(HD) coupling for the W(H)(D) species as expected. Quantitative data for the equilibria were obtained by use of ^{31}P and ^{1}H NMR. The $W(H_2)$ form is slightly more stable than the $W(H)_2$ form at room temperature but, unlike the other examples in Table 5, it becomes less favored as the temperature increases (ΔS has the positive value of 1.2 or 2.4 e.u. for the two complexes examined). If the loss of rotational freedom of the H_2 ligand on going to the dihydride was the major contribution to ΔS, then a negative ΔS would have been expected. More ancillary ligand disorder in the seven-coordinate $W(H)_2$ form must override the loss of entropy of the H_2 ligand. For these tungsten complexes the movement of the large, flexible phosphine substituents could be freer in the seven-coordinate isomer.

Several examples of d^6 complexes containing Cp or Cp* (C_5Me_5) ligands are represented in Table 5. They all involve the same stereochemical change from three-

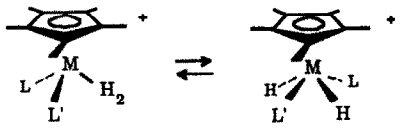
TABLE 5

Stereochemical and thermodynamic data for the equilibrium $M(H_2)L_n \rightleftharpoons M(H)_2L_n$, where both the dihydrogen and dihydride complexes have been directly observed[a]

Stereochemical change	Change in d configuration	Dihydrogen complex	Temp. (K)	ΔG (kcal mol^{-1})	ΔH (kcal mol^{-1})	ΔS (e.u.)	J(HD) (Hz)	Ref.
OC-6 ⇄ OCF-7	$d^6 \rightleftharpoons d^4$	$W(H_2)(CO)_3(P^iPr_3)_2$	298	0.80	1.2	1.2	33.5	146
		$W(H_2)(CO)_3(PCyp_3)_2$	298	0.78	1.5	2.4		146
OC-6 ⇄ SPS-7	$d^6 \rightleftharpoons d^4$	$[Re(H_2)Cp^*(CO)(NO)]^+$	195	1.0			27	59
		$[Ru(H_2)Cp(CO)(PCy_3)]^+$	298	2			28.5	205
		$[Ru(H_2)Cp(dtfpe)]^+$	295	−0.3			25.3	85
		$[Ru(H_2)Cp(dppe)]^+$	295	−0.4			24.9	83,85
		$[Ru(H_2)Cp(dape)]^+$	295	−0.6			24.3	85
		$[Ru(H\cdots H)Cp(dmdppe)]^+$	298	0.2	−0.92	−4.5	23.8	84
		$[Ru(H\cdots H)Cp(dmpe)]^+$	298	1.0			22	84
		$[Ru(H\cdots H)Cp^*(dppm)]^+$	295	0.4			20.9	84
OC-6 ⇄ ?-7	$d^6 \rightleftharpoons d^4$	$[Re(H_2)(CO)_2(PMe_2Ph)_3]^+$	200	−0.1	−1.7	−8	31	69
		$Ru(H_2)(OCOCF_3)_2(PCy_3)_2$	243	−1				252
		$Os(H_2)Cl(CO)SiEt_3(P^iPr_3)_2$	298	>1				298
PB-7 ⇄ DD-8	$d^4 \rightleftharpoons d^2$	$[Re(H_2)(H)_2(CO)(PMe_2Ph)_3]^+$	213	−0.6	−1.1	−2.4	34	68
SPS-7 ⇄ ?-8	$d^4 \rightleftharpoons d^2$	$Nb(H_2)Cp(CO)_3$	228		0.8			44

[a] OC-6 = octahedral; OCF-7 = mono-face capped octahedral; SPS-7 = transoid square-based-four-legged piano stool; PB-7 = pentagonal bipyramidal; DD-8 = dodecahedral.

legged piano stool (octahedral) dihydrogen complex to transoid-square-based-four-legged piano stool (SPS-7) dihydride (eqn. (9)).



(9)

The Re dihydrogen complex is the least stable of these complexes with respect to H_2 loss because the strong π-acid ligands, CO and NO^+, inhibit backbonding to the H_2 ligand. Nevertheless the J(HD) coupling of 27 Hz for the Re(HD) complex suggests a reasonably strong M—HD π interaction. Both the $Re(H_2)$ and $Re(H)_2$ forms are observed at 190 K by ^1H NMR, with the $Re(H_2)$ form in slightly greater concentration [59]. The strong Re—H bonds and the small size of the ligands are favorable factors for dihydride formation. The Cp* ligand also appears to play a role in making the SPS-7 geometry quite favorable.

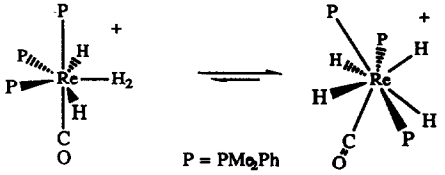
Steric interactions between the phosphine ligands and the Cp or Cp* ring are very important in determining the position of equilibria for the ruthenium cyclopentadienyl complexes of Table 5. The substituents on phosphorus are brought closer to the C_5 ring in the $Ru(H_2)$ complex than in the transoid dihydride complex so that larger phosphines and Cp* versus Cp favor the $Ru(H)_2$ form. This is illustrated by the decrease in ΔG values in the series $[RuH_2CpL_2]^+$, as L_2 increases in size from dmpe to dmdppe to dppe. Note that, if electronic effects dominated, the reverse would have been expected (see below). Similarly, $[Ru(H_2)Cp(dppm)]^+$ is completely in the dihydrogen form [83] whereas $[RuH_2Cp^*(dppm)]^+$ has $\Delta G = 0.4$ for eqn. (6) [84]. In the series $[RuH_2CpL_2]^+$, $L_2 = P(C_6H_4\text{-}4\text{-}R)_2CH_2CH_2P(C_6H_4\text{-}4\text{-}R)_2$, R = CF_3 (dtfpe), H (dppe) and OMe (dape), steric effects are kept constant while electron-donating capacity increases. Here, ΔG for eqn. (6) becomes more negative and the dihydride form becomes more favorable on going from $R = CF_3$ to R = OMe [85]. A more electron-donating ligand should favor the $Ru(H)_2$ form, as observed. The elongated dihydrogen tautomer, $[Ru(H \cdots H)Cp(dmdppe)]^+$ becomes more stable than the dihydride form as the temperature is raised ($\Delta S = -4.5$ e.u.). It was argued that this was due to the higher entropy of the spinning H_2 ligand [84]. Actually, it is not clear whether the H_2 ligand is spinning rapidly since the J(HD) couplings for most of these CpRu complexes are 25 Hz or less, indicative of elongated, non-spinning or slowly spinning H ··· H units (structure **2**, Fig. 2).

There are three other equilibria involving d^6 dihydrogen complexes and seven-coordinate dihydrides with undefined stereochemistry in Table 5. The best characterized is the Re complex of Luo et al.[69]. NMR studies (^1H and ^{31}P) indicate that a thermally unstable dihydrogen complex with H_2 trans to CO is in equilibrium with a dihydride according to the equation

$$[Re(H_2)(CO)_2(PMe_2Ph)_3]^+ \rightleftarrows [Re(H)_2(CO)_2(PMe_2Ph)_3]^+ \quad (10)$$

In the corresponding HD complexes, the Re(HD) complex has $J(HD) = 31$ Hz whereas the Re(H)(D) complex has no resolvable $J(HD)$ coupling. Again, it is the dihydrogen complex which is strongly favored by an increase in temperature. Luo et al. comment that ΔS reflects, in part, the large rotational entropy of the H_2 ligand and they propose that dihydrogen/dihydride equilibria (Fig. 3, Case II) are likely to be much more common than elongated H · · · H structures **2** (Case I). The other two $d^6 \rightleftarrows d^4$ entries in Table 5 are less well established because $J(HD)$ couplings for the (HD) isomers have not been determined. The complex $Ru(H_2)(\eta^1\text{-}OCOCF_3)(\eta^2\text{-}OCOCF_3)(PCy_3)_2$ is thought to have trans PCy_3 ligands and one monodentate and one chelating trifluoroacetate ligand. It is present in a small amount relative to the fluxional seven-coordinate dihydride $Ru(H)_2(\eta^1\text{-}OCOCF_3)(\eta^2\text{-}OCOCF_3)(PCy_3)_2$ and its presence is indicated by a small broad singlet in the ^1H and ^{31}P NMR spectra. The second complex, $Os(H_2)Cl(CO)(SiEt_3)(P^iPr_3)_2$ has unknown stereochemistry; a broad singlet in the high field region of the ^1H NMR spectrum was assigned to the dihydrogen tautomer whereas a small triplet was attributed to the less abundant dihydride form.

The complex $[ReH_4(CO)(PMe_2Ph)_3]^+$ discovered by Luo and Crabtree has several unique and fascinating features [68]. It is the only example of a pentagonal bipyramidal (PB-7) dihydrogendihydride complex in equilibrium with a dodecahedral (DD-8) tetrahydride complex (eqn. (11)).



(11)

The geometries are assigned on the basis of ^1H, ^{31}P and $\nu(CO)$ data and comparisons with complexes of known PB−7 and DD-8 structures. Other structures might also be possible. The complexes decomposed above 280 K, but below this temperature ^1H NMR signals for both species were evident. Thermodynamic parameters were obtained from ^1H NMR studies. The dihydrogen form is in lower concentration, $[Re(H_2)]$, than that of the dihydride, $[Re(H)_2]$, but $[Re(H_2)]$ increases at the expense of $[Re(H)_2]$ as the temperature increases (positive ΔS). The positive ΔS was attributed to the rotation of the dihydrogen ligand. The study provided the first evidence that eqn. (6) shifts to the left upon isotopic substitution of the complexes. That is, in the complex $[ReH_4(CO)(PMe_2Ph)_3]^+$, the equilibrium constant, K, for eqn. (11) is $1/0.18 = 5.6$ at 193 K whereas the K for the $ReHD_3^+$ complexes is $1/0.25 = 4$ [68].

The equilibrium between the complexes $Nb(H_2)Cp(CO)_3$ and $Nb(H)_2Cp(CO)_3$ in Xe(l) was studied by IR and time-resolved IR spectroscopy by Haward et al. [44]. The dihydrogen complex is thought to have a square-based-piano-stool geometry (SPS-7); the geometry of the formally eight-coordinate dihydride is unknown. The

changes in ν(CO) absorbances of the two species at equilibrium were monitored over the temperature range 163–228 K. A ΔH value of 0.8 ± 0.1 kcal mol^{-1} indicated that the dihydrogen complex was slightly more stable than the dihydride. When the experiments were repeated with a $Nb(D_2)/Nb(D)_2$ equilibrium mixture, the ΔH value increased to 1.3 ± 0.1 kcal mol^{-1}. This shift in eqn. (6) to the left with deuterium substitution was ascribed by Haward et al. to a small net change in zero point energy. This work supports the emerging theme that deuterium prefers to occupy the non-classical bonding sites in molecules.

We have calculated, using the additive ligand approach [133], the $E_{1/2}$ potentials for the dinitrogen complexes of selected complexes of Table 5. All are above the 0 V limit for homolytic splitting suggested by the data in Table 4: $W(N_2)(CO)_3(P^iPr_3)_2$ (0.5 V), $[Re(N_2)(CO)_2(PMe_2Ph)_3]^+$ (1.8 V), $[Re(N_2)Cp^*(CO)(NO)]^+$ (2.1 V), $[Ru(N_2)Cp(dmpe)]^+$ (1.3 V) and $Ru(N_2)(\eta^1\text{-}OCOCF_3)(\eta^1\text{-}OCOCF_3)(PCy_3)_2$ (1.1 V). They should be above this limit for the dihydrogen form to exist. One would have thought that the complexes should be near to the 0.5 V limit indicated in Table 4 so that the dihydride could also exist. In fact, it is the stereochemistry of the ancillary ligands which stabilizes the dihydride and pushes eqn. (6) to an equilibrium position.

In summary, dihydrogen complexes associated with a range of J(HD) coupling constants have dihydride tautomeric forms close in energy. The metals in the complexes have a range of electronic and stereochemical environments; however, all are sufficiently electron-deficient to have an observable dihydrogen form ($E_{1/2}(M(N_2)) > 0.5$ V). One definite trend is that if the stereochemical requirements of the ancillary ligands are held constant, then more electron-donating ligands will push eqn. (6) to the right. Bulky ligands favor the dihydride form in complexes $[RuH_2CpL_2]^+$. Dueterium substitution in complexes $[ReH_4(CO)(PMe_2Ph)_3]^+$ favors the non-classical form. The ΔS value for eqn. (6) can be negative or positive depending on the ancillary ligands in the complex. Complexes $M(H \cdots H)L_n$ (structure **2**) have equilibria which exhibit thermodynamic properties similar to those of dihydrogen complexes $M(H_2)L_n$ (structure **1**). There are no well-characterized examples of equilibrium (6) for 3d transition metal complexes. Factors against such an equilibrium are the steric difficulties of forming seven-coordinate complexes on a small 3d metal and the weakness of the M–H bonds in the dihydride form under the electron-deficient conditions necessary for stabilization of the dihydrogen form.

(v) Kinetics of the dihydrogen–dihydride equilibrium (1)

Dynamic NMR methods of spin saturation transfer and line shape analysis have been used to examine the rates of H atom exchange of certain of the well-defined equilibria of Table 5. The activation parameters for the forward reaction of these equilibria, i.e. the splitting of the dihydrogen ligand, are listed in Table 6.

The forward rate of eqn. (8), $PR_3 = P^iPr_3$, was studied by saturating the ^{31}P resonance of the dihydride complex, $W(H)_2(CO)_3(P^iPr_3)_2$, and monitoring the

TABLE 6

Activation parameters for the homolytic splitting of the dihydrogen ligand to give two hydride ligands

Stereochemical change	Change in d configuration	Dihydrogen complex	Temp. (K)	$\Delta G^{\ddagger}$ (kcal mol^{-1})	$\Delta H^{\ddagger}$ (kcal mol^{-1})	$\Delta S^{\ddagger}$ (e.u.)	Ref.
OC-6 → OCF-7	$d^6 \rightarrow d^4$	$W(H_2)(CO)_3(P^iPr_3)_2$	298	16.0	10.1	−19.9	146
OC-6 → SPS-7	$d^6 \rightarrow d^4$	$[Re(H_2)Cp^*(CO)(NO)]^+$	195	11.2			59
		$[Ru(H_2)Cp(dmdppe)]^+$	302	19.5	18.5	−3.3	84
		$[Ru(H_2)Cp(dmpe)]^+$	298	20.2			84
		$[Ru(H_2)Cp(PPh_3)_2]^+$	220	16.7	16.1	−2.8	84
		$[Ru(H_2)Cp^*(PPh_3)_2]^+$	253	18.9			84
OC-6 → ?-7	$d^6 \rightarrow d^4$	$[Re(H_2)(CO)_2(PMe_2Ph)_2]^+$	213	>11.5			69
PB-7 → DD-8	$d^4 \rightarrow d^2$	$[Re(H_2)(H)_2(CO)(PMe_2Ph)_3]^+$	213	11.6			68

decrease in magnetization of the ^{31}P peak of the dihydrogen complex [146]. The dihydride peak appears as a shoulder on a ^{183}W satellite peak of the $W(H_2)$ species. Above 310 K, this shoulder became too broad due to fast ^{31}P site exchange according to eqn. (8); below 288 K, the shoulder broadened as the two phosphorus ligands on the dihydride became inequivalent [6]. Rate constants ranging from 6 to 23 s^{-1} were found over a temperature range of 288–310 K. Obtaining rate constants for the reverse reaction was not possible due to poor signal-to-noise ratios, and obtaining rates by saturating ^1H resonances was hindered by the rapid relaxation of the dihydrogen nuclei. This study serves to illustrate some of the difficulties encountered in studying the NMR properties of dihydrogen complexes which undergo such diverse dynamic processes.

The reaction coordinate diagram for eqn. (8) is shown in Fig. 4. The activation enthalpy for dihydrogen ligand homolysis is 10.1 kcal mol^{-1}. The $\Delta S^{\ddagger}$ of -20 e.u. suggests a well-ordered, late transition state where the H_2 ligand has lost rotational freedom.

The rate constant of the reverse reaction of eqn. (8), $PR_3 = PCy_3$, was determined by use of the stopped-flow (UV detection) method [147]. Equation (8) was treated as a pre-equilibrium to a second-order substitution reaction of the dihydrogen complex by pyridine. The $\Delta H^{\ddagger}$ value of 14.4 kcal mol^{-1} for this pre-equilibrium step (dihydride to dihydrogen) should be compared with the reverse reaction of eqn. (8), $PR_3 = P^iPr_3$, where $\Delta H^{\ddagger} = 8.9$ kcal mol^{-1} (Fig. 4). The values differ because of the different ligands in the two studies and also because of the large errors in the $\Delta H^{\ddagger}$ values resulting from the small temperature ranges of the studies (30°). Zhang et al. found no isotope effect (1.08 ± 0.04) for the reaction of $W(D)_2(CO)_3(PCy_3)_2$ to give $W(D_2)(CO)_3(PCy_3)_2$. This is perhaps surprising considering that an H–H (D–D) bond is being created.

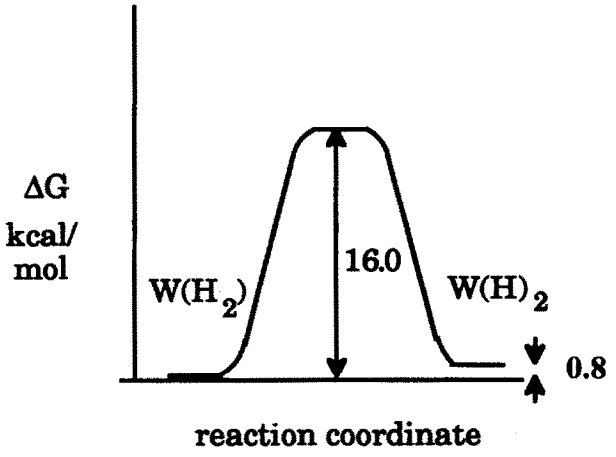
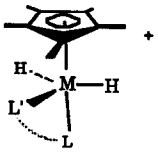


Fig. 4. Reaction coordinate diagram for $W(H_2)(CO)_3(P^iPr_3)_2 \rightleftharpoons W(H)_2(CO)_3(P^iPr_3)_2$.

Chinn et al. [59] observed that the piano stool complex $[Re(H_2)Cp^*(CO)(NO)]^+$ and its transoid dihydride tautomer were interconverting via eqn. (9) at 195 K. The kinetics of this reaction were studied by saturating the methyl resonance of the dihydride tautomer and observing spin transfer to the methyl in the $Re(H_2)$ complex. Calculations provided a rate constant of 2.5 s^{-1} and a $\Delta G^{\ddagger}$ barrier to the reaction of approximately 11 kcal mol^{-1}, lower than the tungsten complexes discussed above.

Studies of spin transfer from cyclopentadienyl protons on the $[CpRu(H \cdots H)L_2]^+$ complex to the transoid-$[CpRu(H)_2L_2]^+$ complex and vice versa provided rate constants at a variety of temperatures for ligands, L_2 = dmpe and dmdppe [84]. The latter complex was the more thoroughly studied of the two. Rate constants in the range 5×10^{-3} to 0.1 s^{-1} were obtained over a temperature range of 289–328 K. The $\Delta G^{\ddagger}$ of 19.5 kcal mol^{-1} for $[CpRu(H \cdots H)dmdppe]^+$ is higher than that of $W(H_2)(CO)_3(P^iPr_3)_2$ (see above and Fig. 4). The $\Delta S^{\ddagger}$ value of -3 e.u. indicates a less ordered transition state than that of the tungsten complex. Structure **4** is the proposed transition state for the isomerization reaction of the complexes with L_2 = dmpe and dmdppe.



4

Related complexes $[Ru(H_2)(Cp \text{ or } Cp^*)(PPh_3)_2]^+$, once formed, are unstable and irreversibly isomerize to the dihydride isomer. The decay of the Cp or Cp* peak was monitored by ^1H NMR to obtain first-order rate constants at suitable temperatures (212–231 K for Cp; only 253 K for Cp*). The rate constants were unaffected by the presence of added PPh_3 during the reaction. The $\Delta G^{\ddagger}$ value for the Cp* complex is much greater than that of the Cp complex at 253 K. The reason might be that the latter has a higher energy transition state for reaction (9) (see structure **4**) than the former due to steric repulsions.

Jia et al. [148] found that the complex $[Ru(H \cdots H)Cp^*(dppp)]^+$ irreversibly isomerized to the transoid-dihydride form at a first-order rate constant of 4.0×10^{-4} s^{-1} at 293 K. The related complex $[Ru(H \cdots H)Cp^*(dppm)]^+$ exists as a mixture of elongated dihydrogen and dihydride forms which interconvert above 210 K, as indicated by averaging of the T_1 times of the hydrogens on the ruthenium. The acidic dihydrogen complex, $[Ru(H_2)(Cp)(CO)(PMe_3)]^+$, is thought to be irreversibly converted to the dihydride tautomer [149]. First deprotonation of the H_2 ligand promoted by the solvent (e.g. CH_3CN) is thought to produce RuH(Cp)-$CO(PMe_3)$ in low concentration. This complex is then probably reprotonated

between the CO and PMe_3 ligands to give the dihydride tautomer, $[Ru(H)_2(Cp)(CO)(PMe_3)]^+$. In other words, heterolytic cleavage of dihydrogen ultimately results in its homolytic cleavage! This mechanism would only be reversible when protonation at the metal versus reprotonation at the hydride are competitive processes. The other Ru complexes discussed in this section are not sufficiently acidic for this mechanism to be important. However, the complex $[Re(H_2)Cp^*(CO)NO)]^+$ is acidic enough and its mechanism of interconversion should be re-examined in light of this alternative mechanism.

The forward rate for eqn. (11), the conversion of $[Re(H_2)(H)_2(CO)(PMe_2Ph)_3]^+$ to the tetrahydride product, was obtained by saturation of the tetrahydride resonance and observing the decay of the resonance of the hydrides in the $Re(H_2)(H)_2$ tautomer [68]. This multiplet is distinct from the dihydrogen resonance in the ^1H NMR spectrum of these dihydrogen–dihydride species at 213 K. The $\Delta G^{\ddagger}$ is 11.6 kcal mol^{-1}, which is comparable with that of the $[Re(H_2)Cp^*(CO)(NO)]^+$ complex. Line shape analysis of the variable-temperature ^1H NMR spectra was not attempted because the dihydrogen resonance was found to be anomalously broad. However, the coalescence temperature for the dihydrogen-dihydride to tetrahydride tautomerism process (eqn. (6) or eqn. (11)) was observed to be 278 K; from $\Delta\nu = 309$ Hz and a population ratio of 1.0:0.46 for ReH_4:$Re(H_2)(H)_2$ a rate constant of 720 s^{-1} and hence a $\Delta G^{\ddagger}$ (278 K) of 12.6 kcal mol^{-1} was calculated.

In conclusion, these well-defined dihydrogen/dihydride equilibria have activation enthalpies which range from 10 to 20 kcal mol^{-1} and negative activation entropies. The loss of the H–H bond could be balanced by M–H bond making so that this may not be an important enthalpic contribution to the barrier. The $\Delta H^{\ddagger}$ probably arises because the complex has to change its coordination number and geometry and the ancillary ligands have to move in the process. Therefore steric contributions to the barrier are important. A loss of rotational freedom of the H_2 might explain why $\Delta S^{\ddagger}$ is negative. A conclusive study of activation barrier as a function of changing electronics at the metal remains to be done; steric interactions would have to remain constant throughout the reaction to observe a systematic trend. Difficulties in rate constant determinations in many of the studies discussed here stem from the instability of the complexes in certain cases, from the rapid relaxation of the dihydrogen nuclei and from other dynamic exchange processes which complicate the analysis.

(vi) Rapid dihydrogen–dihydride equilibrium (6) or elongated H ··· H ligand?

Section B.(ii) introduced the difficulties in determining the true nature of dihydrogen complexes with T_1(min, 200 MHz) in the range 6–90 ms and J(HD) couplings between 25 and 4 Hz. One possible model is that these observed properties are a result of an averaging of properties of a normal dihydrogen form, **1**, and a normal dihydride form, **3**, (as defined in Table 1) caused by rapid interconversion of the two forms via eqn. (6) (see case II, Fig. 3). The activation energy, $\Delta G^{\ddagger}$, would have to be less than 10 kcal mol^{-1} so that the separate species would not be observable, even

at temperatures which are low for solution NMR experiments (200 K). If the equilibria have a non-zero ΔS, then the chemical shift of the H_2 resonance and its coupling(s), J(HP) should change according to changes in the temperature-dependent relative populations of the $M(H_2)$ and $M(H)_2$ species. Similarly, δ(HD) and J(HD) should also change as the temperature changes. The lack of such changes was used as evidence that complexes $Re(H)_7L_2$ are not in rapid equilibrium with a dihydrogen form [150]. Similarly, the complex $[Re(H\cdots H)(H)_4(cyttp)]^+$ appears to have an elongated dihydrogen ligand in the solid state and in solution. The T_1(min) time of the H_2 nuclei of the complex in solution corresponds to a distance d(H—H) of 1.14 Å, [28] (if there is not rapid rotation of the H_2 unit), which is similar to the X-ray determined value (d(H—H) = 1.08(5) Å, [16]). However, temperature-dependent NMR parameters for the complex $[Os(H\cdots H)(H)(depe)_2]^+$ suggest that a rapid equilibrium is present [29] (see below).

Table 7 lists some candidates for this rapid equilibrium. The first complex $[RhH_2PP_3]^+$ is known by means of an X-ray diffraction study to be an octahedral dihydride in the solid state and also in solution below 183 K, according to the NMR spectra (^1H and ^{31}P) [39]. Above 183 K, the complex is thought to isomerize completely to a dihydrogen complex of C_{3v} symmetry (eqn. (12)) with couplings,

TABLE 7

Possible examples of rapid equilibria between dihydrogen, $M(H_2)L_n$, and dihydride, $M(H)_2L_n$, tautomers; alternatively there could be one $M(H\cdots H)L_n$ structure

Change in electron configuration	Complex	J(HD) (Hz)	T_1(min) (ms, 200 MHz)	J(HP) (Hz)	Ref.
$d^8 \rightleftharpoons d^6$	$[Rh(H{\cdot\cdot}H)(pp_3)]^+$	18	<425	67, 14	39
$d^6 \rightleftharpoons d^4$	$Re(H{\cdot\cdot}H)Cl(PMePh_2)_4$		25(33[a])	19	12
	$Ru(H{\cdot\cdot}H)(H)_2(PPh_3)_3$	16 ± 4	20 ± 4(23[b])	6[c]	28,63,153
	$[Ru(H{\cdot\cdot}H)Cp^*(dppm)]^+$	21	12	<3	148
	$[Os(H{\cdot\cdot}H)H(dedppe)_2]^+$	19	~30	<5	188
	$[Os(H{\cdot\cdot}H)H(depe)_2]^+$	10–12	35–40	5.5	29
	$[Ru(H{\cdot\cdot}H)Cl(depe)_2]^+$		14	7.2[c]	61
	$[Os(H{\cdot\cdot}H)Cl(depe)_2]^+$		30	11.8[c]	61
	t-$[Os(H{\cdot\cdot}H)(L)(NH_3)_4]^{2+}$ [d]	20–4[d]	39–19[d]		290
	$[Os(H{\cdot\cdot}H)(PPh_3)_3(\eta^2\text{-}OAc)]^+$	13.7	20	9.5[c]	86
	$Os(H{\cdot\cdot}H)(thf)(oep)$	12	54		88

[a] T_1(min) corrected to remove Re—H and H—H($PMePh_2$) relaxation contributions according to the method of Desrosiers et al. [28].

[b] T_1(min) corrected to remove averaging with terminal hydride T_1 and for H—H(PPh_3) relaxation contributions according to the method of Desrosiers et al. [28].

[c] Averaged J(PH) value due to fluxionality.

[d] J(HD) and T_1(min) depend on L. J(HD) decreases as $L = CH_3CN > py > Im > NH_3 > I^- > Cl^- > D_2O > Me_2CO > Br^-$. T_1(min), when observed, decreases in the opposite order.

(12)

J(HP), to the axial ^{31}P atom of 67 Hz and to the three equatorial ^{31}P of 14 Hz. These couplings are unusually large for a dihydrogen complex. They do not appear to change with temperature. The T_1 of the dihydrogen resonance at 303 K was 170 ms at 80 MHz or 425 ms at 200 MHz. This is much too long for a dihydrogen complex; the closely related dihydrogen complex $[Ru(H_2)H(pp_3)]^+$ has a T_1 value of 25 ms at 340 K and 300 MHz [81]. The evidence against this being a fluxional dihydride is the observation of a multiplet for the HD complex, the analysis of which revealed a coupling, J(HD), of 18 Hz. The observation of a Rh(I)-based oxidation of the complex [151] also supports the dihydrogen formulation. It is not known whether this coupling is temperature-dependent. Perhaps a rapid equilibrium (12) lying quite far to the right can harmonize all of these facts. It is interesting that the C_{3v} complex $[Rh(H_2)(PH_3)_4]^+$ was calculated ab initio to be 31 kcal mol^{-1} less stable than the C_{2v} complex $[Rh(H)_2(PH_3)_4]^+$ [27,152].

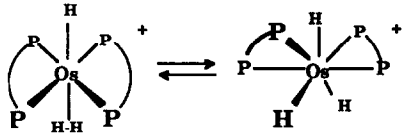
The complex *trans*-Re(H $\cdots$ H)Cl$(PMePh_2)_4$ has a minimum T_1 time of 33 ms (corrected for Re–H dipole–dipole and ligand–H relaxation) that falls in the range assigned to ambiguous H_2 ligands. The J(HP) of 19 Hz is unusually large [12] and indicates Re-hydride character in the bonding. Again, these values could be the result of a rapid equilibrium.

A recent report by Gusev et al. [153] of an averaged J(HD) coupling of approximately 2.7 Hz for the RuH_2D_2 isotopomer of $RuH_4(PPh_3)_3$ places this complex in the ambiguous H $\cdots$ H region. The authors calculated that a 2.7 Hz average indicates an 8.5 Hz J(HD) for a static Ru(HD)(H)(D)P_3 complex. They suggest that this complex should be formulated as a tetrahydride with H–H distances averaging about 1.37 Å. They rule out an equilibrium between dihydrogendihydride and tetrahydride species on the basis of no change in chemical shifts with temperature and no broadening of the lines due to exchange. However, we calculate that a 2.7 Hz average represents about 16 Hz J(HD) (see Table 7 and Sect. C.(iii)(d)). The best interpretation at the present is to formulate this complex as Ru(H $\cdots$ H)$(H)_2(PPh_3)_3$ with a slowly rotating elongated dihydrogen with an H–H distance of about 1.1 Å [28]. Gusev et al. argued against this structure on the basis that representative cis-J(HP) couplings of 15–30 Hz and trans-J(HP) coupling of 75 Hz could not average to the observed J(PH) value of 6 Hz. However, they did not consider the possibility that these couplings probably have opposite signs.

There are several complexes $[Ru(HD)(Cp \text{ or } Cp^*)L_2]^+$ with J(HD) values between 25 and 20 Hz (see Tables 5 and 7) that fall in the ambiguous region. The T_1(min) times and small J(HP) couplings are consistent with a dihydrogen formula-

tion. It has been proposed that these complexes have elongated H_2 ligands (1.0–1.1 Å) which rotate slowly [148]. The alternative is that the J(HD) coupling is an average due to rapid interconversion of a Ru(HD) complex of structure **1** (Fig. 2) and a square piano stool complex of structure **3**, *cisoid*-[Ru(H)(D)(Cp or Cp*)L_2]$^+$ (as opposed to the slower conversion to the transoid structure as in eqn. (9)).

The complexes *trans*-[Os(H $\cdots$ H)(H)$(L_2)_2$]$^+$, L_2 = dedppe and depe, provide evidence for a rapid equilibrium. The J(HD) coupling for the latter complex in acetone-d_6 increases from 10.5 to 11.6 Hz as the temperature is raised from 220 to 325 K [29]. The couplings change when the solvent is CD_2Cl_2: J(HD) = 11.3 Hz at 220 K and 12.4 Hz at 311 K. The T_1(min) time is shorter in CD_2Cl_2 (35 ms) than in acetone-d_6 (40 ms). A shift in a rapid equilibrium (13) from $Os(H)_2H^+$ to $Os(H_2)H^+$ structures as the temperature increases and on going from acetone to CD_2Cl_2 can explain these and other changes in chemical shifts and couplings J(PH) of this complex. Equation (13) also shifts to the left when H atoms are replaced by D atoms. This is the second instance of deuterium favoring the non-classical structure (see above).



(13)

A variety of other ruthenium and osmium complexes have recently appeared with spectroscopic characteristics of ambiguous M(H $\cdots$ H) structures as listed in Table 7. Rapid equilibria could also be operating here.

The NMR properties of these complexes should be examined carefully for changes resulting from variations in temperature and solvent. These would signal the perturbation of a rapid equilibrium. Clearly, future crystallographic work is also required to resolve these structural ambiguities.

(vii) Other dihydrogen to dihydride reactions

Table 8 lists reactions where the homolysis of H_2 is postulated but only the reactant or the product is observed. The reactions are listed by stereochemical change with the lowest coordination number complexes coming first. The exchange of H atom positions in complexes *cis*-Pt$(H)_2L_2$, where L_2 is a bulky chelating phosphine ligand, was proposed to proceed via an unobserved dihydrogen intermediate [154]. The stereochemistry of the kinetic product obtained by the oxidative addition of dihydrogen to complexes $IrCl(CO)L_2$ has been rationalized in terms of the preferred orientation of a side-on bonded H_2 ligand [155,156]. Similarly, the interconversion of isomeric *cis*-dihydrides of Ir(III), IrH_2XL_3 or [$IrH_2(L{-}L')_2$]$^+$, might involve an Ir(I) dihydrogen complex [157].

TABLE 8

Other postulated dihydrogen–dihydride interconversions where only one of the species is directly observed. The postulated species are between quotation marks

Stereochemical change	Complexes	Ref.
SP-4⇌TP-3	*cis*-$Pt(H)_2L_2$⇌"$Pt(H_2)L_2$"	
	$L_2 = PCy_2(CH_2)_nPCy_2$, $n = 3, 4$	154
SP-5→OC-6	"$Ir(H_2)Cl(CO)L_2$"→$Ir(H)_2Cl(CO)L_2$	
	$L = PPh_3$	156
	"$Ir(H_2)Cl(CO)L_2$"→$Ir(H)_2Cl(CO)L_2$	
	L_2 = dppe	155
OC-6⇌TB-5	*cis*-$Ir(H)_2XL_3$⇌"$Ir(H_2)XL_3$"	157
OC-6⇌PB-7	$[M(H_2)(H)(L_2)_2]^+$⇌"$[M(H)_3(L_2)_2]^+$"	
	M = Fe, Ru, Os, L_2 = dppe, depe	60
OC-6 $\xrightarrow{h\nu}$?-7	$Ir(H_2)(H)Cl_2L_2 \xrightarrow{h\nu}$ "$IrH_3Cl_2L_2$"	
	$L = P^iPr_3$	107
SPS-7 $\xrightarrow{h\nu}$?-8	$WCp(H_2)(CO)_2H \xrightarrow{h\nu}$ "$WCp(H)_3(CO)_2$"	160
9⇌8	$[WH_3Cp_2]^+$⇌"$[W(H_2)HCp_2]^+$"	161,162

The exchange of H atoms between dihydrogen and hydride sites in the complexes $[M(H_2)H(L_2)_2]^+$, L_2 = dppe, depe, has been postulated to proceed via homolysis of the H_2 ligand to give an unobserved trihydride intermediate [60]. The activation parameters for the process involving the Fe and Os complexes ($\Delta H^\ddagger = 9$–12 kcal mol^{-1} and $\Delta S^\ddagger = -13$ to -2 e.u) are similar to the parameters obtained for well-defined homolytic splitting reactions (Table 6). The trend that the depe ligand causes faster exchange than the dppe ligand for a given metal is explained by the fact that the more basic depe ligand would favor the formation of the trihydride intermediate. This is discussed further in Sect. C.

There are two reports of the possible photoinduced homolysis of a dihydrogen complex to give a dihydride. The first is the conversion of a mixture of postulated dihydrogen complexes $Ir(H_2)HCl_2(P^iPr_3)_2$ (see below) to a possible trihydride species $Ir(H)_3Cl_2(P^iPr_3)_2$ upon UV irradiation of a hydrogen purged CH_2Cl_2 solution [107]. The trihydride has ν(Ir–H) at 2000 cm^{-1} and produces a triplet at -12.6 ppm (J(PH) 7.3 Hz). A T_1 measurement was not made to confirm the structural assignment. Gusev et al. [158] first suggested, on the basis of NMR work, that this is not a trihydride but instead is an HCl adduct of $IrH_2Cl(P^iPr_3)_2$; however, these authors have now withdrawn this suggestion [159]. The second report involves the photolysis of $WCp(H)(CO)_3$ in an Ar matrix in the presence of some H_2 to give products which were identified on the basis of IR spectra to be $W(H_2)Cp(H)(CO)_2$ and possibly $W(H)_2Cp(H)(CO)_2$ (footnote 9 of ref. 160).

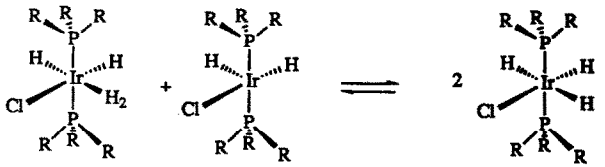
The homolysis of a non-spinning HD ligand intermediate might explain why,

nine times out of ten, addition of D^+ occurs between the two hydrides of $W(H)_2Cp_2^*$ to give the trihydride $[W(H)(D)(H)Cp_2^*]^+$ [161,162]. Parkin and Bercaw propose that D^+ adds to a W–H bond and not to the metal to give an HD complex with the D end oriented between the two hydrogens. An alternative mechanism which they favored was the direct formation of a (H–D–H) ligand which fragments into the preferred product; there is no definitive example yet of such a ligand.

(viii) Intermolecular homolytic cleavage of a dihydrogen ligand

There are several examples of complexes which split hydrogen gas in an intermolecular homolytic fashion to give monohydride products. These include the reactions of H_2 with $Co_2(CO)_8$ or $Co(CN)_5^{3-}$ to give $CoH(CO)_4$ or $CoH(CN)_5^{3-}$, respectively [163]. The former reaction is of considerable importance in the catalytic hydroformylation of olefins [164]. Dihydrogen intermediates have not been detected in such reactions. Therefore it is interesting to note the observation of a possible dihydrogen complex in such a process as described below.

The paramagnetic Ir(IV) dihydride complexes *trans,trans*-$Ir(H)_2(Cl)_2(PR_3)_2$, $R = {}^iPr$, Cy, when dissolved in $CDCl_3$ give diamagnetic species which were studied by ^1H and ^{31}P NMR [106]. Spectra suggest the presence of a monohydride species (e.g. ^1H NMR, −47.9 ppm, t, $J(PH) = 11$ Hz; ^{31}P NMR, 35.8 ppm, s, when $PR_3 = PCy_3$) and a dihydrogen species (−0.4 ppm, broad, $T_1 < 10$ ms). Traces of the Ir(IV) complex caused all the hydride and phosphorus nuclei to relax rapidly and the peaks broadened and shifted as the temperature was lowered to 200 K. The equilibrium (14) was shifted by bubbling H_2 gas through the solution and the resonance at −0.4 ppm disappeared, presumably because of rapid exchange with free dihydrogen. The complex with $PR_3 = P^iPr_3$ has a broad resonance in the ^1H NMR spectrum at +2.5 ppm, which increases in intensity when dihydrogen is introduced. This behavior seems consistent with a closely related, well-defined dihydrogen complex $Ir(H_2)(H)_2Cl(P^iPr_3)_2$, which also loses and re-coordinates dihydrogen reversibly [42]. Equation (14), proposed by Mura et al. [106], provides a reasonable explanation of this complex system. Here, an octahedral d^6 dihydrogen complex reacts with a five-coordinate d^6 complex to give two octahedral d^5 hydride species in a formal intermolecular one-electron oxidative addition (eqn. (7)). A related reaction in which an end-on oriented, bridging dihydrogen ligand appears only in the transition state is



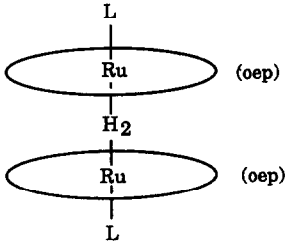
(14)

the addition of H_2 to the d^7 tetramesitylporphyrin complex Rh(tmp) to give d^6 RhH(tmp) [165].

There is a variety of reactions where monohydrides react in an intermolecular fashion to eliminate dihydrogen. This is the reverse of eqn. (7) where the dihydrogen intermediate is not observed or is assumed to be the transition state structure. The closest system to eqn. (7) is the reported intermolecular elimination of dihydrogen from two d^5 octaethylporphyrin complexes RuH(oep)(THF) to give two d^6 Ru(oep)-$(THF)_2$ complexes and free H_2 (eqn. (15)) [166].

$$2RuH(oep)(thf) \rightarrow \mathbf{5} \rightarrow 2Ru(oep)(thf)_2 + H_2 \quad (15)$$

This reaction is proposed to proceed via a bridging dihydrogen intermediate, **5**. The precedent for structure **5** is the diamagnetic complex $Ru_2(\mu\text{-}H \cdots H)(dpb)(L)_2$, dpb = biphenylene-bridged diporphyrin, L = 1-*tert*-butyl-5-phenylimidazole, which has a minimum T_1 time of 66 ms at 200 MHz [88(b),166] (see Sect. E.(i)). The analogous $H \cdots D$ complex has $J(HD) = 15$ Hz. The special bridging ligand dpb, which consists of two ruthenium porphyrins held cofacial with $d(Ru{-}Ru) = 3.8$ Å by a biphenylene spacer, traps the dihydrogen ligand and stabilizes it with respect to elimination as in eqn. (15). A further example of dihydrogen elimination is the conversion of d^6 *trans*-$CoH(dmgH)_2(PR_3)$ to d^5 $Co(H_2O)(dmgH)_2(PR_3)$ via a postulated linear Co–H–H–Co transition state [167].



5

The production of paramagnetic hydrides from dihydrogen complexes (eqn. (14)) is fascinating and deserves further study. It will be interesting to see how common is this intermolecular splitting of coordinated dihydrogen.

C. EXCHANGE OF H ATOMS BETWEEN DIHYDROGEN AND OTHER HYDROGEN-DONOR LIGANDS

(i) Introduction

The interchange of H atoms between dihydrogen and hydride ligands was reported soon after the identification of dihydrogen complexes. Crabtree and Lavin reported in 1985 that the ^1H NMR signals of the dihydrogen and hydride ligands which are situated cis in $[Ir(H_2)H(bq)(PPh_3)_2]^+$ coalesce at 240 K because of such

an exchange [168]. At about the same time, Morris et al. [14] showed that the hydride trans to the dihydrogen in $[Fe(H_2)H(dppe)_2]^+$ exchanges positions with H atoms of the H_2 ligand. Since then many such examples have appeared from several research groups. Exchange between dihydrogen and one hydride, the simplest case, will be considered first. Many other more complex systems involving four or more H-donor ligands (especially polyhydride complexes) display fluxional processes that may involve such an exchange. Usually, less is known about these; they will be discussed in Sect. C.(iii) below.

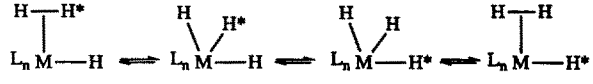
Before the era of dihydrogen ligands, the fluxionality of polyhydrides [62,169] could have been viewed as the traveling of hard spheres of hydrogen over the surface of a metal atom in the complex. Clearly, mechanisms that involve the association of hydrogen atoms as an intermediate step must now be considered as well. The brilliant line-shape analysis of the ^1H NMR spectra of complexes ML_4H, M = Co, Rh, Ir, ML_4H_2, M = Fe, Ru, Os and ML_4H_4, M = Mo, W, L = PR_3 or L_2 = dppe by Meakin et al. [169] revealed that barriers to intramolecular rearrangement were relatively insensitive to ligand variation, whereas there is a definite trend to higher barriers for higher atomic numbers of the central atom. These complexes do not contain H–H interactions. Nevertheless, it is interesting that an intermediate for the hydride site exchange that looks like *trans*-$M(H_2)_2L_4$, M = Mo, W, (see Fig. 5 of ref. 169) could not be ruled out.

(ii) Intramolecular H atom exchange for a three-hydrogen system M(H₂)H

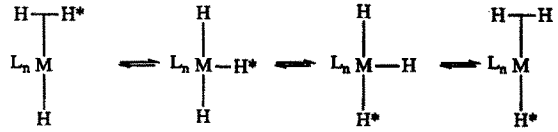
(a) Mechanisms of H atom exchange

Two general types of mechanism can be envisaged. The first is *dissociative* and involves homolysis of the H–H bond (eqn. (6)) to produce a fluxional trihydride intermediate which allows the intramolecular exchange of H atoms between H_2 and H ligands. The dissociative category can be broken into two groups, those where (H_2) and H are adjacent (eqn. (16)) and those where they are not (eqn. (17)).

Dissociative H–H



(16)



(17)

Equations (16) and (17) are governed by the same factors that influence the kinetics of homolytic splitting of H_2 (see Sect. B.(v)).

The second general mechanism is *associative* and would implicate a trihydrogen intermediate or transition state (eqn. 18).

(a)

(b)

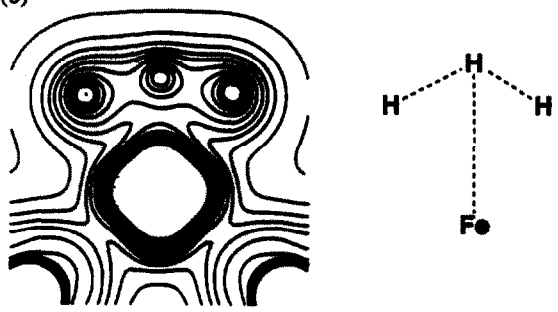
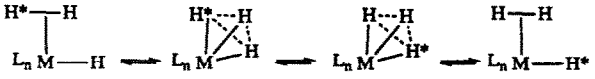


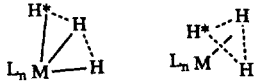
Fig. 5. Electron isodensity contour maps for the transition states of the hydrogen transfer reactions in (a) $[ScHCl_2] + H_2$ and (b) $[Fe(H_2)H(PH_3)_4]^+ + H_2$. Reproduced with permission from ref. 170.

Associative H–H



(18)

The trihydrogen ligand of the intermediates in mechanism (18) rotate to allow exchange. Calculations suggest that a trihydrogen transition state or intermediate is more stable in the open goemetry, **6**, than in a closed, triangular geometry, **7** [170,171].

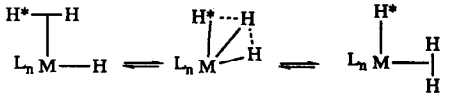


6 **7**

Maseras et al. [170] calculate that $[Fe(H_3)(PH_3)_4]^+$ with an open H_3 grouping (**6**) is the transition state for H atom exchange in *cis*-$[Fe(H_2)H(PH_3)_4]^+$ (see below in this section). The NMR study of the complex $[Re(H_2)(H)_2(PMe_2Ph)_3(CO)]^+$ by

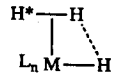
Luo and Crabtree [68] makes the most convincing case that the associative mechanism (18) can be distinguished from the dissociative one of eqn. (16) (see below).

Mechanism (19) is a special case of associative exchange which involves dihydrogen complexes of two different stereochemistries (**8** and **10**) unless the trihydrogen transition state or intermediate, **9**, has a symmetry element (σ or C_2) containing the central H and the metal which make the two outer hydrogens equivalent.



8 **9** **10** (19)

There is some evidence that a cis interaction between H_2 and H (**11**) can be regarded as the incipient formation of the H_3 ligand of **9** in *cis*-$M(H_2)(H)$ complexes $Fe(H_2)(H)_2(PEtPh_2)_3$ [8] and $Ru(H_2)H(PCy_3)_2X$, X = Cl, I [11] and that this is linked to high fluxionality of the complexes.

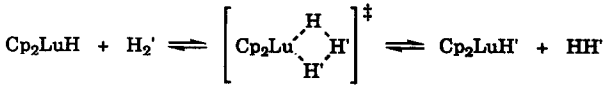


11

Eisenstein describes this cis effect on the basis of extended Hückel calculations as partial bond formation caused by the donation of hydride electron density into the σ^* orbital of the H_2 ligand [8,11,25]. Bertran et al. [27], on the basis of ab initio studies, propose that, instead of a covalent interaction, this is an electrostatic attraction between positively polarized H_2 and negatively polarized H^- ligands. Both of these views support the proposal of Crabtree et al. that eqn. (19) involves an acidic dihydrogen ligand transfering a proton to an adjacent hydride base [91].

Technically, all four equations (16)–(19) result in σ bond metathesis [172] (M–H and H–H* going to M–H* and H–H σ bonds) although only eqn. (19) shows the transition state with two H–H interactions which must be invoked in the case of d^0 metal complexes [171]. The term σ bond metathesis should probably be reserved for d^0 metal systems where π bonding is not important. For the other metals, we prefer the expression "four-center transition state mechanism".

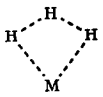
Extended Hückel calculations by Rabaa et al. [171] showed that a four-center transition state mechanism is energetically preferred over the oxidative addition mechanism for eqn. (20).



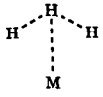
(20)

The calculated overlap population between Lu and the central H was less than a fourth of that between Lu and the outer H atoms. This is consistent with the

traditional representation of bonding in a four center transition state mechanism activated complex (**12**).



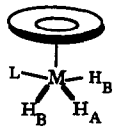
12



13

The same bonding arrangement (**12**) is predicted for the activated complex $[ScH_3Cl_2]^{\ddagger}$ from the electron density contours generated by the ab initio MO calculations of Maseras et al. [170] (Fig. 5(a)). A similar contour map showed an open trihydrogen ligand bound by the center hydrogen for the transition state $[Fe(H_3)(PH_3)_4]^{+\ddagger}$ (structure **13**, Fig. 5(b), eqn. (19)). If the iron complex is representative of late transition metals, then there is a significant difference in the bonding in the transition state of late transition metals compared with that of early transition metals. Maseras et al. used the expression "open direct transfer" to describe the four-center transition state mechanism with this open trihydrogen type of transition state (**13**).

Some complexes, $[IrH_3CpL]^+$, L = PMe_3, PPh_3, $AsPh_3$ [173], RuH_3Cp^*L, L = PMe_3, PPh_3, P^iPr_3, PCy_3, and $NbH_3(C_5H_4SiMe_3)_2$ [174], were initially suspected of containing the trihydrogen structure **9** on the basis of huge, temperature-dependent, J(HH) couplings in the ^{1}H NMR. These couplings were measured from second-order spectra with spin systems AB_2 as might result from an open $H_BH_AH_B$ ligand. However, it soon became apparent that these were not ordinary J(HH) couplings when values greater than the coupling in free H_2 gas (280 Hz) were observed [110]. Also, the spectra had strange temperature-dependent features: the couplings increased with temperature and then disappeared (above 200 K for the Ru and Ir complexes and above 320 K for the Nb complexes) giving spectra with A_3 ^{1}H spin systems which were typical of a trihydride undergoing fast intramolecular rearrangement. Interaction of the ruthenium complex with CuCl gave an asymmetric complex $Ru(H_2)HCp^*(PCy_3)\cdot CuCl$ according to the ^{1}H NMR spectra [175]. This suggested that $Ru(H_2)HCp^*(PCy_3)$ was a dihydrogen hydride. In fact the research group of Heinekey has demonstrated that the Ir complexes [111,112], the Ru complexes [113] and the Nb complexes [114] are trihydrides containing angular H–H–H geometries, **14**, (ring is Cp-type ligand, L = monodentate ligand for Ir and Ru complexes, L = $C_5H_4SiMe_3$ for Nb) with two fairly close H–H distances of about 1.7 Å and with shallow M–H vibrational potential wells that allow the phenomenon of quantum-mechanical exchange coupling (QEC) [109,112,176,177] to occur. This phenomenon explains the origin of the large J(HH) couplings. Ab initio calculations on the Nb system suggest that this quantum-mechanical effect may arise under conditions which also favor dihydrogen–hydride structures as thermally accessible higher energy isomers of the trihydrides [178]. The exchange coupling phenomenon does not cause an averaging of chemical shifts. Line-shape coalescence in the high temperature



14

spectra occurs when the exchange coupling constant, J(HH), greatly exceeds the chemical shift separation of the inequivalent hydrides; under these conditions an AB (or AB_2) spectrum is indistinguishable from an A_2 (or A_3) spectrum [177]. An important characteristic of the QEC phenomenon is that the exchanging particles must have the same mass and spin. If one is ^{1}H and the other is ^{2}D or ^{3}T, then there is negligible quantum mechanical tunnelling and there is no large exchange coupling contribution to the usual scalar J(HD) or J(HT) coupling. For example, Ir(D)(H)(D)Cp(PPh_3) has no resolvable J(HD) coupling even though the all protio complex, $IrH_3Cp(PPh_3)$, has a H–H QEC value of 397 Hz at 196 K [111]. Thus, a study involving isotopic substitution of D for H in complexes MH_3L_n is crucial in revealing whether QEC is present.

We note that the T_1 values (these may not be minimum values) of all the trihydrides that display QEC are consistent with trihydride as opposed to dihydrogen/hydride structures (200 ms at 193 K, 500 MHz for $Ir(H)_3Cp(AsPh_3)$ [173]; 100 ms at 193 K, 250 MHz for $Ru(H)_3Cp^*(P^iPr_3)$ [179]; 55 ms at 200 K, 200 MHz for $Nb(H)_3(C_5H_4SiMe_3)_2$ [174]; accounting for the significant effect of the Nb–H dipole–dipole relaxation gives a corrected T_1(H–H) of about 100 ms for this complex (see also Sect. B.(ii)).

Further complexes should be examined for QEC effects. The complexes $[Os(H)_3(C_6Me_3H_3)(PMe_3)]^+$ [180] and $[Ru(H)_3(C_6Me_6)PMe_3]^+$ [181] do not appear to display QEC at the temperatures at which they were examined; however, Heinekey and Harper have reported that complexes $[Os(C_6H_6)L(H)_3]^+$ do exhibit QEC [182].

(b) Observing H atom exchange for a three-hydrogen system $M(H_2)H$

Rates of H atom exchange can be determined quantitatively by line-shape analysis, by observing T_1 averaging, by spin saturation transfer studies, or by 2D NMR methods. Rates can also be estimated qualitatively by use of isotopic labelling studies. All of these methods, apart from 2D experiments, have been applied to dihydrogen complexes. For the three-hydrogen system, the objective is to obtain the rate constants k^{H_2} and k^H (equal to $2k^{H_2}$) in eqn. (21).

$$M(HH^*)(H)L_n \underset{k^H}{\overset{k^{H_2}}{\rightleftharpoons}} M(H_2)(H^*)L_n \qquad (21)$$

Complete line-shape analysis is the preferred method for obtaining rate versus temperature data, and it will be considered first.

(c) Complete line-shape analysis

It is useful to look at an example of a variable-temperature ^{1}H NMR study of such a system. The ^{1}H NMR spectra in the high field region as a function of temperature for the complex $[Fe(H_2)H(depe)_2]BPh_4$ in acetone-d_6 [60] is found in Fig. 6. Below the temperature defining the onset of slow exchange ($\theta_1 \approx 200$ K), there is a broad dihydrogen resonance, H_2, of intensity 2 downfield from a quintet of intensity 1 for the hydride ligand H (Fig. 6, 200 K). As the temperature is raised above θ_1, the hydride peak broadens and the dihydrogen peak sharpens a little as the relaxation rates of these nuclei start to average; the chemical shifts remain at

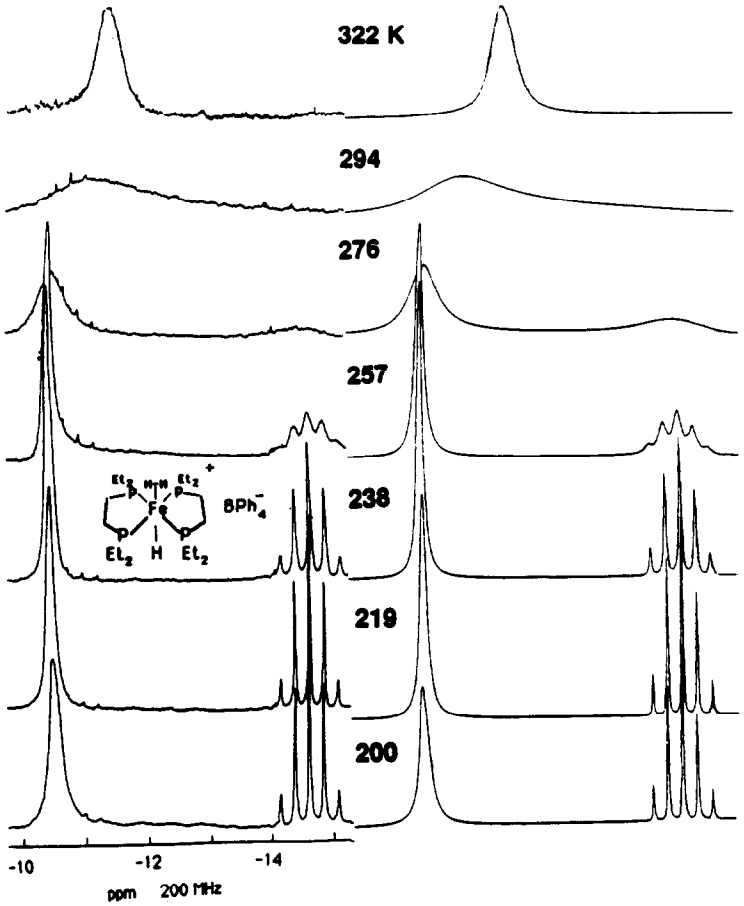


Fig. 6. 200 HMz NMR spectra (left) and simulated spectra (right) of $[Fe(H_2)H(depe)_2]^+$ in acetone-d_6; the temperatures (K) and rate constants (k^{H_2}, s^{-1}) are as follows: 200, 0.02; 219, 0.35; 238, 3.9; 257, 29; 276, 165; 294, 800; 322 K, 4500 s^{-1}.

their no-exchange values. At the relaxation coalescence temperature ($\theta_2 \approx 250$ K) the two peaks have the same, averaged $1/T_1$ values (average weighted 2:1, see Table 9). At a higher temperature, $\theta_3 \approx 294$ K, the peaks coalesce (line shape coalescence). At the highest temperature of the series of spectra in Fig. 6, the nuclei are near the fast exchange limit; a quintet of intensity 3 should be observed in this case as three hydrogen, made equivalent by exchange, couple to four equivalent ^{31}P nuclei. In the present case, the line width is too broad to resolve this coupling because of the short T_2 of the protons. By the use of a different solvent, ethanol-d_6, it is possible to resolve the quintet.

The program DNMR4 was used for the simulation of the spectra. This program allows nuclei at different sites to have different T_2 values; this is the case for the dihydrogen and hydride nuclei. Since hydride and dihydrogen nuclei have a negligible H–H coupling between themselves (see below), the case of two interconverting "conformations" was used to simplify the calculations. One confirmation has an $H_2^A P_4^X$ spin system with a very short T_2 for H^A nuclei (the H_2 ligand) and with four equivalent phosphorus nuclei P^X of the depe ligands and the other has an $H^B P_4^X$ system, H^B being the hydride ligand with a long T_2. A complete line-shape analysis of the no-exchange spectrum (200 K, Fig. 6) requires a knowledge of the T_2 at a no-exchange temperature ($\theta < \theta_1$) for each site ($T_2^{H_2}$ and T_2^H), as well as the coupling constants $J(H_2,H)$, $J(H_2,P)$ and $J(H,P)$. Unfortunately, in this case the first two couplings could not be observed directly and phosphorus decoupling was not available. However, the complete temperature dependence of T_1 was determined for each site, and from the temperature-dependent correlation time equation, the value of $T_2^{H_2}$ could be calculated [183]. $J(H_2,H)$ is known to be close to zero (<2 Hz). Iterative fitting of the dihydrogen resonance with changing $J(H_2,P)$ gave a value of -5 Hz for $J(H_2,P)$. A better value (-2 Hz) was obtained from a spectrum of the sample in ethanol-d_6 at the fast exchange limit at 293 K, where an averaged coupling of -17 Hz results from the averaging (1:2) of the terminal hydride coupling of -47 Hz and the $J(H_2,P)$ of -2 Hz. The fast exchange spectrum, a quintet, was not obtained in experiments with the complex in acetone-d_6 (Fig. 6). The T_2^H value can be obtained from the width of the peaks in the quintet in the no-exchange spectrum.

Once the no-exchange spectrum has been simulated, it is necessary to obtain the temperature-dependent values of $T_2(\theta)$ for the two sites and values for the chemical shifts $\delta^{H_2}(\theta)$ and $\delta^H(\theta)$, if they are temperature-dependent. The T_2 values can be measured from singlets in the spectrum or calculated from T_1 data as long as H–H dipolar relaxation is dominant. The temperature dependence of the chemical shifts can be checked in the no-exchange and slow-exchange regions. For an H_2/H exchanging system, the averaged chemical shift in a fast exchange spectrum should be $\delta^{H_2} \times \frac{2}{3} + \delta^H \times \frac{1}{3}$ (see Table 9); a change from this value must also be accounted for by the temperature dependence of δ values. It is very important to check the temperature indicated by the VT unit of a commercial spectrometer, by use of the methanol calibration method. Only in this case is a comparison of kinetic data

TABLE 9

Expressions for the chemical shift (δ) and spin-lattice relaxation time (T_1) for the dihydrogen and hydride ligands in complexes $M(H_2)HL_n$ as a function of temperature (θ) and also expressions for the rate of exchange of H atoms (k^{H_2}, $k^H = 2k^{H_2}$) for various exchange regimes

Exchange regime	$\delta^{H_2}(\theta)$ (ppm)	$1/T^{H_2}(\theta)$ (s^{-1})	$k^{H_2}(\theta)$ (s^{-1})	$\delta^{H}(\theta)$ (ppm)	$1/T_1^{H}$(obs) (s^{-1})
No exchange $\theta \leqslant \theta_1$	$\delta^{H_2}(\theta)$	$1/T_1^{H_2}(\theta)$	0	$\delta^{H}(\theta)$	$1/T_1^{H}(\theta)$
Slow exchange $\theta_2 > \theta > \theta_1$	$\delta^{H_2}(\theta)$	$1/f(T_I, T_{II})$ or $1/T_1^{H_2}$(eff.)	$1/T_1^{H}(\theta) < k(\theta) < 1/T_1^{H_2}(\theta)$ or $\pi\omega_{1/2}^{H_2} - 1/T_2^{H_2}(\theta)$	$\delta^{H}(\theta)$	$1/f(T_I, T_{II})$ or $1/T_1^{H}$(eff.)
Relaxation coalescence at θ_2 $\theta = \theta_2$	$\delta^{H_2}(\theta_2)$	$0.666/T_1^{H_2}(\theta_2) + 0.333/T_1^{H}(\theta_2)$	$\sim 1/T_1^{H_2}(\theta_2)$	$\delta^{H}(\theta_2)$	$0.666/T_1^{H_2}(\theta_2) + 0.333/T_1^{H}(\theta_2)$
Line shape coalescence at θ_3 $\theta = \theta_3$	$2\delta^{H_2}(\theta_3)/3 + \delta^{H}(\theta_3)/3$	$0.666/T_1^{H_2}(\theta_3) + 0.333/T_1^{H}(\theta_3)$	$\nu_0\{\delta^{H_2}(\theta_3) - \delta^{H}(\theta_3)\}$	$2\delta^{H_2}(\theta_3)/3 + \delta^{H}(\theta_3)/3$	$0.666/T_1^{H_2}(\theta_3) + 0.333/T_1^{H}(\theta_3)$
Fast exchange $\theta \gg \theta_3$	$2\delta^{H_2}(\theta)/3 + \delta^{H}(\theta)/3$	$0.666/T_1^{H_2}(\theta) + 0.333/T_1^{H}(\theta)$	$\gg k(\theta_3)$	$2\delta^{H_2}(\theta)/3 + \delta^{H}(\theta)/3$	$0.666/T_1^{H_2}(\theta) + 0.333/T_1^{H}(\theta)$

obtained by use of different spectrometers by different research groups valid. Frequently, temperatures of uncalibrated NMR probes can be too high or too low by 20° at 200 K, and this can result in large errors in the calculated activation energies.

Rates of exchange in the slow exchange and line-shape coalescence regions can be estimated as described below. The iterative procedure of varying the rate constant, calculating a spectrum and comparing it with the one observed leads to the best estimates of the rate constants.

(d) Activation parameters from complete line-shape studies

The activation parameters are calculated by use of the Eyring equation (with a transmission coefficient of 1). Published values are listed in Table 10. This table includes results from two line-shape studies [81,184] of ^{31}P NMR spectra of complexes $[M(H_2)H(pp_3)]^+$, M = Fe, Ru which also show H_2/H exchange in the ^1H NMR (the ^1H NMR spectra were not simulated). In the coordinated ligand $P^A(CH_2CH_2P^MPh_2)_2(CH_2CH_2P^XPh_2)$ in these complexes there are two equivalent terminal nuclei P_2^M which can exchange positions with one terminal nucleus P^X. The central phosphorus P^A cannot exchange with the others. The $P^AP_2^MP^X$ spectra were simulated in this case with equal T_2 values for all phosphorus nuclei.

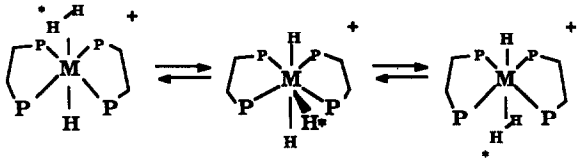
If the last ruthenium complex is ignored, the enthalpies of activation listed in Table 10 are in the range of 9–12 kcal mol^{-1}. The entropies of activation vary depending on the ligand system and are small and negative in most cases. These parameters fall in the same ranges as those for the intramolecular homolytic splitting of dihydrogen (see Table 6). Therefore an H–H dissociative mechanism (eqn. (17)) could explain these exchange processes. In isostructural complexes, *trans*-$[M(H_2)H(L_2)_2]^+$, the 5d metal, Os, favors exchange compared with the 3d metal, Fe, and the more electron-donating and smaller ligand depe favors exchange compared with the less basic, larger ligand dppe (Table 10). Both of these factors are

TABLE 10

Activation parameters for the exchange of H atoms between dihydrogen and hydride sites in the complexes $[M(H_2)HL_4]^+$. These were obtained from complete line-shape analyses

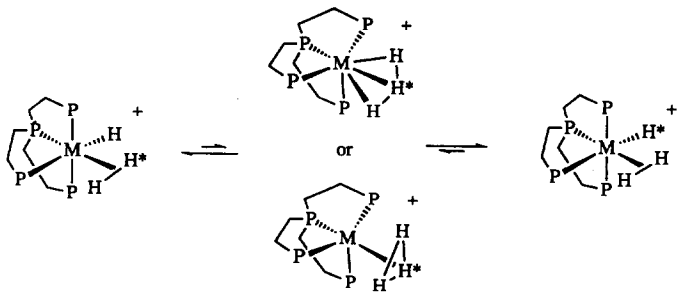
Complex	Sets of exchanging nuclei	Temp. range (K)	$\Delta H^\ddagger$ (kcal mol^{-1})	$\Delta S^\ddagger$ (e.u.)	$\Delta G^\ddagger$ (300 K) (kcal mol^{-1})	Ref.
$[Fe(H_2)H(depe)_2]^+$	t-2H/H	200–320	12.2	−2.5	13.0 ± 0.2	60
$[Fe(H_2)H(dppe)_2]^+$	t-2H/H	213–329	11.0	−10.0	14.0 ± 0.3	60
$[Os(H\cdots H)H(depe)_2]^+$	t-2H/H	200–312	9.1	−12.9	12.9 ± 0.2	29
$[Os(H_2)H(dppe)_2]^+$	t-2H/H	200–294	9.9	−11.5	13.3 ± 0.3	29
$[Os(H_2)H(dedppe)_2]^+$	t-2H/H	200–313	8.8	17.5	13.9 ± 0.4	188,305
$[Fe(H_2)H(pp_3)]^+$	2P/P	188–318	9.7	−9	13 ± 1	184
$[Ru(H_2)H(pp_3)]^+$	2P/P	203–302	24.0	44	12 ± 1	81

consistent with the homolysis of the H–H bond (see Table 3). Thus a fluxional trihydride intermediate (see eqn. (17) or eqn. (22)) could explain the exchange in this case. In fact a very fluxional trihydride $[Ru(H)_3(dppf)_2]^+$ which can be considered as a model of this intermediate has recently been characterized [137].



(22)

An associative H–H mechanism was postulated for exchange in the complexes $[M(H_2)H(pp_3)]^+$ (eqn. (23)) [81,184]. A trigonal bipyramidal structure with an open or closed H_3 ligand (see structures **6** and **7** above) was suggested to be the intermediate. Such intermediates were postulated because the simple associative H–H mechanisms depicted in eqns. (18) and (19) cannot explain how the terminal phosphorus atoms of the pp_3 ligand become equivalent. However, the activation parameters are equally consistent with a dissociative mechanism with a trihydride intermediate, at least for the iron complex. It is possible that the H_2/H and P_2^M/P^X exchange processes for the complex $[Ru(H_2)H(pp_3)]^+$ are not related to each other or that a different mechanism of H atom exchange is involved in this case. This will have to be determined by simulating the ^1H NMR spectra.



(23)

(e) Slow exchange with incomplete T_1 averaging

The T_1 times of the (H_2) and H^- nuclei have been measured as a function of temperature for a variety of dihydrogen complexes. In several cases H_2/H exchange has been detected by the convergence of T_1 values of the H_2 and H^- nuclei to an averaged value as the temperature is raised. However, no rate constants were derived from this data. The complete averaging of T_1 values (relaxation coalescence) [185] takes place at exchange rates corresponding to temperatures at or above the relaxation coalescence temperature, θ_2. This temperature is below that of the temperature, θ_3, where line-shape coalescence is attained. At temperatures ($\theta \geqslant \theta_2$) above the

relaxation coalescence point, the H_2 and H resonances have the same T_1(obs) value. Here, $1/T_1$(obs) is given by the average of $1/T_1^{H_2}$ and $1/T_1^{H}$ weighted $\frac{2}{3}$:$\frac{1}{3}$ (see Table 9).

Relaxation time constants T_1 have been reported for $M(H_2)H$ complexes listed in Table 11 in the region of slow exchange at temperatures θ (see Table 9) which are below the temperature, θ_2, of relaxation coalescence where $1/T_1$ values average and well below the temperature, θ_3, of line-shape coalescence. The measured effective T_1 time T_1(eff) of the hydride is usually much shorter than the T_1(ne) (ne = no-exchange) value expected, while that of the dihydrogen is close to the short T_1(ne) value expected (see Table 11). In actual fact, the T_1(eff) value for the hydride is false because a single exponential analysis of the inversion recovery data is employed. In this slow exchange region, the change in magnetization is described by a double exponential expression with time constants T_I and T_{II} which are complicated functions of the lifetimes of the H_2 and H sites and the relaxation times $T_1^{H_2}$(ne) and T_1^{H}(ne). Fortunately, the case where $T_1^A = 10T_1^B$ (A = H, B = H_2 here) has been analyzed in detail by Strehlow and Frahm [186]. Future studies of T_1 in exchanging systems of this type should take advantage of this analysis to obtain rate constants and true T_1 values. Nevertheless, if partial T_1 averaging is observed, then the rate constant k^{H_2} must fall in the fairly narrow range of values between $1/T_1^{H_2}$(ne) and $1/T_1^{H}$(ne) (see Table 9). This allows us to estimate the rate constant k^{H_2} (Table 11) and $\Delta G^{\ddagger}$ (Table 12) reasonably accurately

TABLE 11

Estimation of rate constants for H_2 to H site exchange from T_1(eff) data (from the literature) which were obtained below the region of relaxation coalescence. The T_1(ne) are the expected no-exchange values

Complex	MHz	θ (K)	H_2		H		k[a] (s^{-1})	Ref.
			T_1(eff) (ms)	T_1(ne) (ms)	T_1(eff) (ms)	T_1(ne) (ms)		
$[Fe(H_2)H(dmpe)_2]^+$	400	242	20	~18	49	~400	30	71
$[Fe(H_2)H(depe)_2]^+$	400	213	31	19	391	428	0.5	60
	400	230	31	25	145	600	8	60
$[Fe(H_2)H(dppe)_2]^+$	200	244	11	12	116	169	5	60,183
$[Fe(H_2)H(dtfpe)_2]^+$	400	293	21	20	21	287	>50[b] <500[b]	306
$[Ru(H_2)H(depe)_2]^+$	400	273	56	57	885	1457	1	60
	400	295	70	83	241	2132	10	60
$[Ru(H_2)H(dppe)_2]^+$	200	285	29	26	294	357	2	60
$[Ru(H_2)H(dppp)_2]^+$	400	303	14	~10	14	~400	>100[b] <1000[b]	80
$[Ir(H_2)H(bq)(PPh_3)_2]^+$	250	220	8	8	37	200	~50	63

[a] Estimate by Morris and Jessop (this work).

[b] Near relaxation coalescence but below line shape coalescence.

TABLE 12

Activation free energies, $\Delta G^{\ddagger}$, for the rate of H atom exchange from dihydrogen to hydride in the complexes $M(H_2)HL_4$. These are calculated from peak coalescence data (when $\Delta\nu$ is reported) or relaxation coalescence data (from Table 11). Literature values of $\Delta G^{\ddagger}$ are given in parentheses

Complex	Sets of exchanging nuclei	$T(\theta)$ (K)	$\Delta\nu$ (Hz)	$\Delta G^{\ddagger}$ (kcal mol^{-1})	Ref.
$[Ru(H_2)H(dppb)_2]^+$	t-2H/H	243	1920	10.4	80
$[Fe(H_2)H(pp_3Me)]^+$	2P/P	280	1442	12.2	73
$[Fe(HD)D(pp_3Me)]^+$	c-HD/D	200	308	9.2(9.1)	73
$[Ir(H_2)H(bq)(PPh_3)_2]^+$	c-2H/H	240	3075	10.1	91
	c-2H/H	220		11.0	Table 11
$[Ir(H_2)H(bq)(PCy_3)_2]^+$	c-2H/H	258	3215	10.8	91
$[Ru(H_2)H(dpbp)_2]^+$	t-2H/H	250–270	1440	10.9–11.8	78
	2P/2P	243	1328	10.3	78
$[Fe(H_2)H(PPh(OEt)_2)_4]^+$	t-2H/H	243	251	11.4	74
$[Ru(H_2)H(diop)_2]^+$	t-2H/H	280	2080	12.0	289
$[Fe(H_2)H(pp_3)]^+$	c-2H/H	290	1578	12.6(12.1)	64
	2P/P	273	669	12.3(12.4)	184
$[Fe(H_2)H(dmpe)_2]^+$	t-2H/H	242		12.4	Table 11
	t-2H/H	293	2108	12.6	71
$[Os(H_2)H(depe)_2]^+$	t-2H/H	240	45	12.1(12.1)	29
$[Ru(H_2)H(pp_3)]^+$	c-2H/H	303	1818	13.2	81
	2P/P	269	330	12.5(12)	81
$[Os(H_2)H(dppe)_2]^+$	t-2H/H	280	440	12.9(13.1)	29
$[Fe(H_2)H(depe)_2]^+$	t-2H/H	294	820	13.2(12.9)	60
$[Os(H_2)H(dedppe)_2]^+$	t-2H/H	290	200	13.8(13.9)	188
$[Os(H_2)H(PPh(OEt)_2)_4]^+$	2H/H	273	40	13.9	76
$[Fe(H_2)H(dppe)_2]^+$	t-2H/H	310	940	13.9(14.1)	60
$[Ru(H_2)H(dppp)_2]^+$	t-2H/H	303		14.0–15.0	Table 11
$Os(H_2)H(CO)Cl(P^iPr_3)_2$	t-2H/H	313	528	14.4	36
$[Fe(H_2)H(dtfpe)_2]^+$	t-2H/H	293		15	Table 11
$[Fe(H_2)H(dedppe)_2]^+$	t-2H/H	>323	880	>15	188
$[Fe(H_2)H(dppm)_2]^+$	t-2H/H	340	640	15.5	307
$[Ru(H_2)H(depe)_2]^+$	t-2H/H	295		15.9	Table 11
$[Ru(H_2)H(PPh(OEt)_2)_4]^+$	2H/H	343	366	16.1	76
$[Ru(H_2)H(dppe)_2]^+$	t-2H/H	285		16.3	Table 11
$[Ru(H_2)H(binap)_2]^+$	t-2H/H	>303		>16	79
$[Fe(H_2)H(meso\text{-}tet)]^+$	t-2H/H	>303		>18	72
$[Os(H_2)H(meso\text{-}tet)]^+$	t-2H/H	>303		>18	72

for cases where incomplete averaging of T_1 values has been reported. Trends in these $\Delta G^{\ddagger}$ values as well as those obtained from line-shape coalescence studies will be discussed below.

Since minimum values of $T_1^{H_2}$ are used to calculate H—H distances in dihydro-

gen complexes [63,183], it is important that no-exchange values T_1(ne) and not effective ones T_1(eff) are measured. We note that T_1(eff) values instead of minimum values of $T_1^{H_2}$(ne) are expected for the complex $[Fe(H_2)H(depe)_2]^+$ when measured at 400 MHz, 213 K, and the complex $[Ir(H_2)(bq)H(PPh_3)_2]^+$ when measured at 250 MHz, 200 K (Table 11). These are about the temperatures at which slow exchange is occurring and at which minimum T_1 values are expected. In a different process, where $Cr(H_2)(CO)_3(PCy_3)_2$ is exchanging its dihydrogen ligand with free H_2 gas with a rate constant of 62.5 s^{-1}, the effective T_1 of the H_2 ligand is 17.3 ms whereas the T_1(ne) of the H_2 ligand is 9 ms at 300 MHz [108].

Table 9 also indicates that rate constants for systems in the slow exchange regime can be obtained from line widths at half-height ($\omega_{1/2}$) if the value of T_2 is known and if there is no spin-spin coupling. However, this approach has not yet been used.

(f) Line-shape coalescence

A typical coalescence ^{1}H NMR spectrum for an $M(H_2)(H)$ system is shown in Fig. 6 when the temperature is 294 K. This is the temperature at which the "valley" between the H_2 and H peaks just disappears as the temperature of the solution is raised. Shanan-Atidi and Bar-Eli [187] have provided a simple analysis of this case. In fact, the rate constant, k^{H_2}, at the coalescence temperature, θ_3, is just the separation of the two no-exchange chemical shifts in Hz (see also Table 9)

$$k^{H_2} = \Delta\nu = |\nu_0(\delta^{H_2} - \delta^{H})| \tag{17}$$

where ν_0 is the spectrometer frequency.

The coalescence temperatures of many exchanging systems have been reported (Table 12) but corresponding activation energies $\Delta G^{\ddagger}$ were not calculated. We have calculated these values (Table 12) and compared them with those obtained by line-shape analysis and incomplete T_1 averaging. The agreement is good in all cases where the coalescence temperature was accurately observed. In certain cases, the phosphorus nuclei are also exchanging in a 2:1 site population ratio; the rate constants at coalescence are again just the chemical shift separation of non-exchanging nuclei in Hz.

The complexes of Table 12 are listed in order of increasing $\Delta G^{\ddagger}$ values. Since $\Delta S^{\ddagger}$ values for these intramolecular processes are small (see Table 10) the ordering of $\Delta H^{\ddagger}$ values will not be too different from the order of $\Delta G^{\ddagger}$ values in Table 12. Complexes with *cis*-$M(H_2)(H)$ geometries tend to have low $\Delta G^{\ddagger}$ values (see also Sect. C.(ii)(g), below). This might be explained by the ease of the "least motion" associative pathway, eqn. (19). The energies calculated ab initio for transition states of H-atom exchange in *cis*-$[Fe(H_2)(H)(PH_3)_4]^+$ are 3 kcal mol^{-1} for an open H_3 ligand complex, 69 kcal mol^{-1} for a closed, triangular H_3 ligand complex and very high for a trihydride complex [170]. However, a complex with a *cis*-$(H_2)(H)$ configuration can have a fairly high $\Delta G^{\ddagger}$ (e.g. $[Ru(H_2)H(pp_3)]^+$) and a complex with a

trans-$(H_2)(H)$ geometry can have a low $\Delta G^{\ddagger}$ (e.g. $[Ru(H_2)H(dppb)_2]^+$). Thus, eqn. (19) for $[Ru(H_2)H(pp_3)]^+$ may not have as low a $\Delta G^{\ddagger}$ as expected because the pp_3 ligand must also move or perhaps this complex exchanges via a dissociative H–H mechanism. The low $\Delta G^{\ddagger}$ of the dppb complex has been attributed to the flexibility of the seven-membered chelate ring [78,80]. Note that $\Delta G^{\ddagger}$ decreases for the complexes *trans*-$[Ru(H_2)H(L_2)_2]^+$ on going from L_2 = dppe (RuL_2 five-membered ring) to dppp (six-membered ring) to diop, dpbp, and dppb (seven-membered rings). Not only does the flexibility of the ligand increase in this order, but the bite angle and effective cone angle also increase. Larger size ligands will destabilize the ground state octahedral geometry and favor the trihydride intermediate in the exchange process (eqn. (22)). As mentioned above, a trihydride transition state was calculated to be unfavorable for exchange in a *cis*-$(H_2)H$ complex [170]; however, the trihydride intermediate appears to be the best explanation for the exchange in the *trans*-$(H_2)H$ complexes. The very rigid *meso*-tetraphos ligand complexes of Fe and Os do not exhibit H_2/H exchange; this ligand forces the H_2 and H ligands to remain trans to each other [72].

It was stated in Sect. C.(ii)(c) that more basic ligands favor exchange in complexes *trans*-$[M(H_2)H(L_2)_2]^+$ because they stabilize the trihydride intermediate of eqn. (22). Table 12 provides more evidence for this. When M is Fe, Ru, or Os, $\Delta G^{\ddagger}$ decreases when L_2 is changed from dppe to depe [29,60]. Similarly, $\Delta G^{\ddagger}$ decreases when L_2 in the iron complexes changes from electron-withdrawing dtfpe to dppe; in this case, both ligands have the same size. The J(HD) couplings of the complexes *trans*-$[M(HD)D(L_2)_2]^+$ always decrease when a more electron-donating ligand L_2 is present [60]. This trend is expected on the basis that a more electron-rich metal will back-bond more strongly to the HD ligand and weaken the H–D bond. This relationship only holds for a series of similar complexes. There is no overall trend between J(HD) and $\Delta G^{\ddagger}$ for the complexes in Table 12. The complexes with the dedppe ligand are anomalous in that they have higher $\Delta G^{\ddagger}$ values than those with either the dppe or depe ligands [188]. This is the case despite the fact that the dedppe ligand should be intermediate in electron-donor ability. A special steric interaction must destabilize the trihydride intermediate containing the dedppe ligand.

A further trend is that, for isostructural complexes, $\Delta G^{\ddagger}$ decreases as the metal changes from Ru to Fe to Os [60]. This can be seen in the complexes $[M(H_2)H(L_2)_2]^+$, L_2 = dppe, depe and dedppe, with the *trans*-$M(H_2)H$ geometry and in the complexes $[M(H_2)H(pp_3)]^+$ with the *cis*-$M(H_2)H$ geometry. The $PPh(OEt)_2$ complexes have undefined stereochemistry but still show this trend. The Ru > Fe > Os trend can be explained by stabilization of the trihydride intermediate which favors exchange for Os with its strong Os–H bonds and stabilization of the ground state dihydrogen complex with a strong H–H bond which hinders exchange for Ru. The order of J(HD) couplings for the dppe and depe complexes Ru > Fe > Os supports this idea [60]. The J(HD) values for the pp_3 complexes also decrease as Ru > Fe [64,81].

(g) No line-shape decoalescence

Table 13 lists complexes $M(H_2)HL_n$ which remain at the fast exchange limit at low temperatures. This must be caused by a small $\Delta G^{\ddagger}$, a small chemical shift difference, a low observation frequency (ν_0) or a combination of these factors. As mentioned in Sect. C.(ii)(a), the ruthenium complexes in this table are thought to have a *cis*-(H_2)—H interaction which facilitates H atom exchange. The PCy_3 complexes in this table have elongated dihydrogen ligands (H ··· H) (see Table 1, Sect. B.(ii)) which might also lower $\Delta G^{\ddagger}$. The stereochemistries of the $P(OEt)_3$ complexes of Table 13 are unknown but might be cis. The fairly long minimum T_1 time for the rac-tetraphos complex indicates that it may also have an elongated dihydrogen ligand (H ··· H) which is cis to a hydride. However, the chemical shift difference and hence $\Delta G^{\ddagger}$, is not known for any of these complexes.

(h) Intramolecular exchange of isotopes

Usually, dihydrogen ligands labelled with deuterium can be introduced readily by exchange of H_2 in dihydrogen complexes with HD or D_2 gas (e.g. see representative equations (25)–(29) and Sect. E) or by addition of a source of D^+ to a hydride complex (see Sect. D).

$$M(H_2)(H)L_n \underset{H_2}{\overset{D_2}{\rightleftharpoons}} M(D_2)(H)L_n \tag{25}$$

$$M(D_2)(H)L_n \rightleftharpoons M(HD)(D)L_n \tag{26}$$

$$M(HD)(D)L_n \underset{HD}{\overset{D_2}{\rightleftharpoons}} M(DD)(D)L_n \tag{27}$$

$$M(H_2)(H)L_n \underset{H_2}{\overset{HD}{\rightleftharpoons}} M(HD)(H)L_n \tag{28}$$

TABLE 13

Complexes $M(H_2)HL_n$ whose NMR properties are averaged by rapid exchange of H atoms between dihydrogen and hydride at low temperature

Complex	Sets of exchanging nuclei	T (K)	T_1(av) (ms)	MHz	Ref.
$Ru(H_2)H(OCOCF_3)(PCy_3)_2$	c-2H/H	193	72	250	252
$Ru(H \cdots H)H(I)(PCy_3)_2$	c-2H/H	193	72	200	11
$Ru(H \cdots H)H(Cl)(PCy_3)_2$	c-2H/H	193	75	200	11
$[Fe(H_2)H(P(OEt)_3)_4]^+$	2H/H	188	4	80	74
$[Os(H_2)H(P(OEt)_3)_4]^+$	2H/H	188	40	80	76
$[Os(H \cdots H)H(rac\text{-}tet)]^+$	c-2H/H	252	160	400	72
		<180	[a]	400	72

[a] No T_1 available, but fast exchange spectrum observed.

$$M(HD)(H)L_n \rightleftharpoons M(H_2)(D)L_n \quad (29)$$

Intramolecular H/D exchange produces a close to statistical mixture of isotopomers [60]. It will not be completely statistical because deuterium probably prefers to be in the (HD) or (DD) site (see also Sects. B.(iv), B.(vi), and C.(iii)(d)). Isotopomers can be detected in solution by NMR methods or, in a low-temperature matrix, by IR spectroscopy.

The presence of isotopomers in solution is usually verified by ^1H or ^2H NMR or by an isotope effect on the NMR of the nucleus (e.g. ^{31}P) of an ancillary ligand. Separate resonances for dihydrogen site and hydride site isotopes are observed in the spectra of complexes at the no intramolecular exchange limit. In this exchange regime, the isotopomers with (HD) ligands should give a typical $J(HD)$ coupling of magnitude 25–35 Hz for dihydrogen complexes $M(H_2)L_n$ and 5–25 Hz for $M(H \cdots H)L_n$ (see Table 1). However, in cases where reaction (26) is fast, only averaged chemical shifts and $J(HD)$ coupling constants are observed. The $J(HD)_{av}$ coupling at the fast exchange limit for either a complex MH_2DL_n or MHD_2L_n is approximately $J(HD)/3$, where $J(HD)$ is the no-exchange coupling of the (HD) ligand [29]. For example, the no-exchange $J(HD)$ for $[Os(H \cdots D)(D)(depe)_2]^+$ is about 12 Hz, whereas the fast exchange, averaged $J(HD)_{av}$ is about 4 Hz [29]. Small deviations of $J(HD)_{av}$ from the value $J(HD)/3$ are expected because of the preference of deuterium to be in the non-classical site. The ^1H NMR pattern of the fast exchange spectrum should be a 1:1:1 triplet for MH_2DL_n and a 1:2:3:2:1 quintet for MHD_2L_n [29,73]; there may be additional splitting caused by ^{31}P nuclei. The $J(HD)_{av}$ coupling of 10 Hz for the isotopomers of $[Fe(H_2)(H)\{P(CH_2CH_2CH_2PMe_2)_3\}]^+$ (ref. 73, Fig. 7) was attributed to a no-exchange coupling of 30 Hz [30].

Luo and Crabtree [68] have pointed out that isotopic perturbation of chemical shift (also known as IPR [189]) should be observed in the fast exchange ^1H NMR spectra of isotopomers of non-classical polyhydrides. Each isotopomer will show a distinct hydride resonance if M—H and $M(H_2)$ sites have significantly different chemical shifts and if there is a substantial deuterium fractionation between the two sites. The isotopomers of the iron complex $[Fe(H_2)H\{P(CH_2CH_2CH_2PMe_2)_3\}]^+$ give an IPR shift of approximately -0.020 at 298 K (see Fig. 7(a)).

Intramolecular isotope exchange reactions in isotopomers of $M(H_2)HL_n$ complexes are reviewed below in the order of decreasing d electron count at the metal (from d^8 to d^0). The sole d^8 system to be reported is the postulated complex $Co(D_2)(H)(CO)_4$, which is presumed to mediate the photochemical conversion of $CoH(CO)_4$ to $CoD(CO)_4$ in a low-temperature Ar/D_2 matrix [55].

There are several qualitative studies of intramolecular exchange between isotopomers of $M(d^6)$ complexes *trans*-$[M(H_2)HL_4]^+$, M = Fe, Ru or Os. The intramolecular exchange rates of isotopomers $[MH_xD_{3-x}(L_2)_2]^+$ appear to be qualitatively similar to rates for the *trans*-$[M(H_2)(H)(L_2)_2]^+$ complexes, M = Fe, Ru, Os, L_2 = dppe, depe (see Tables 10–12) [60]. Thus, lifetimes of the species $[MHD_2(depe)_2]^+$

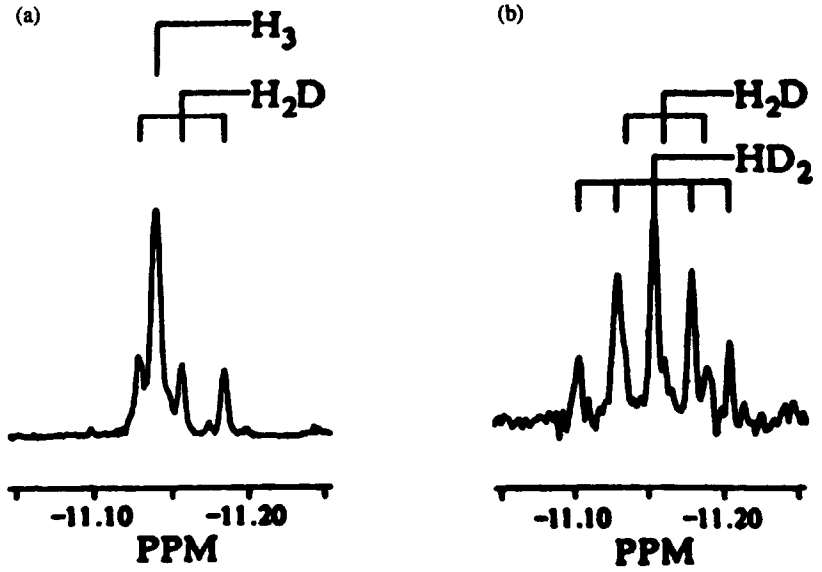


Fig. 7. ^{1}H NMR spectra (^{31}P decoupled) of isotopomers. $[FeH_xD_{3-x}\{P(CH_2CH_2CH_2PMe_2)_3\}]^+$ in acetone-d_6 (298 K) with increasing deuteration: (a) 60% deuteration according to ref. 73 but we calculate 20%; (b) 90% deuteration. Reproduced with permission from ref. 73.

undergoing exchange at 300 K according to eqn. (26) would be approximately 0.1 s for Ru and 0.005 s for Fe and Os. This can be compared with the times for replacement of half of the hydrogens at the metal with deuteriums by reaction with D_2 gas (1 atm) according to eqns. (25–29) of less than 5 min for Ru, 2 h for Fe and 180 h for Os [60]. Thus, the intramolecular exchange rate is qualitatively faster than the intermolecular exchange of D_2 with $M(H_2)$ under these conditions. Mixtures of isotopomers produced according to eqns. (26) and (29) have also been observed in this series of complexes with M = Fe, Ru or Os, L_2 = dppe [60] and L_2 = dedppe, M = Fe, Os [188]. Earl et al. [29] made use of an inversion-recovery pulse sequence first introduced by Kubas et al. [6] to observe the (HD) resonance of the dppe complex $[Os(HD)H(dppe)_2]^+$, which was buried under the broad (H_2) resonance of the isotopomer $[Os(H_2)D(dppe)_2]^+$. Half of the metal-bonded hydrogens in the complexes $[Fe(H_2)(H)L_4]^+$, L = $P(OEt)_3$ and $PPh(OEt)_2$ are replaced by D in 3.5 h, presumably via reactions (25)–(29) [74]. There is no evidence for intramolecular H/D exchange in the complexes *trans*-[M(HD)(H)(*meso*-tetraphos)]$^+$, M = Fe, Os, where the tetraphos ligand holds the octahedron in a rigid configuration [72]. In the complex $Ir(HD)Cl_2(H)(P^iPr_3)_2$ the hydride and HD ligands are thought to be trans to each other and do not exchange [41]. The other *trans*-$[M(H_2)(H)L_4]^+$ complexes of Tables 10 and 12 must exhibit intramolecular isotope exchange.

Of the compounds *cis*-$M(H_2)(H)L_n$ with d^6 metal ions of Tables 12 and 13, intramolecular isotope exchange has been reported for two but must occur for all.

The complex $[Ir(H_2)H(bq)(PPh_3)_2]^+$ exchanges H_2 with D_2 readily and also has a low barrier to intramolecular exchange (eqns. (26) and (29)) [91]. These properties contribute to making this complex an excellent catalyst for deuterium exchange into alcohols (eqn. (30)) [190].

$$ROH + D_2 \underset{R = Me, Et, {}^tBu}{\overset{[Ir(H_2)H(bq)(PPh_3)_2]^+}{\rightleftharpoons}} ROD + HD \tag{30}$$

The separate ^1H resonances for the isotopomers *cis*-$[Fe(HD)D(L_4)]^+$ and *cis*-$[Fe(D_2)H(L_4)]^+$, $L_4 = P(CH_2CH_2CH_2PMe_2)_3$, were observed at 180 K. At 200 K the resonances coalesced. This gives a $\Delta G^{\ddagger}$ value of 9.1 kcal mol^{-1} (see Table 12) [73].

Complexes $M(D_2)HL_n$ have been postulated as intermediates or transition state structures in a variety of reactions of D_2 with d^4–d^0 metal hydride complexes to give deuterides.

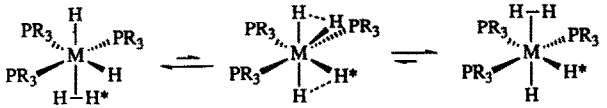
$$MHL_n + D_2 \rightleftharpoons M(D_2)HL_n \rightleftharpoons M(HD)DL_n \rightleftharpoons MDL_n + HD \tag{31}$$

The Mo(d^4) complex $Mo(D_2)H(CO)_2Cp$ is presumed to mediate the photochemical conversion of $MoH(CO)_3Cp$ to $MoD(CO)_3Cp$ in a low-temperature Ar/D_2 matrix [160]. The Mo(d^2) complex $MoH(SC_6H_2{}^iPr_3)_3(PEtPh_2)$ is converted to deuteride $MoD(SC_6H_2{}^iPr_3)_3(PEtPh_2)$, possibly via eqn. (31) [191]. These reactions may be of relevance to the formation of HD from D_2 by nitrogenase which might have dihydrogen and/or hydride at the active site [119]. An acid/base exchange mechanism might also account for the nitrogenase isotope exchange reaction; see Sect. D. The unstable W(d^2) complex $[W(HD)H(Cp)_2]^+$ might explain why D^+ adds preferentially between the hydrides of $W(H)_2Cp_2$ [161]. Gell et al. [192] postulated the existence of the unstable Zr(d^0) complex $Zr(H_2)D(R)Cp_2$, $R = CH_2C_6H_{10}D$, to account for the formation of $ZrH(R)Cp_2$ from $ZrD(R)Cp_2$ and H_2 gas. The proposed scheme was an associative exchange mechanism, eqn. (19), which is also a sigma bond metathesis reaction.

(iii) Intramolecular H atom exchange for dihydrogenpolyhydride systems $M(H_2)H_x$

(a) Mechanisms

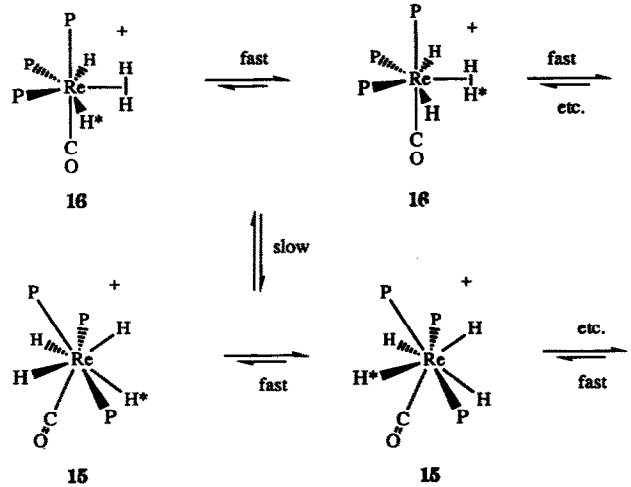
Many more pathways for H atom exchange are available to dihydrogen complexes which also contain two or more hydride ligands. The mechanisms would probably be composites of various dissociative (eqns. (16) or (17)) or associative (eqn. (19)) $(H_2)/H$ processes. In addition, associative processes involving tetrahydrogen intermediates might be possible [193,194]. Concerted processes are also a possibility. For example, simultaneous oxidative addition of dihydrogen and reductive coupling of an adjacent dihydride set in complexes mer-$M(H_2)H_2L_n$, could be a favorable, low-energy pathway (see eqn. (32)).



(32)

(b) Line-shape coalescence

The complex $[Re(H_2)(H)_2(PMe_2Ph)_3(CO)]^+$ is a well-characterized dihydrogen complex with a corresponding J(HD) coupling of 34 Hz [68]. The NMR study of this compound by Luo and Crabtree provides the first, and so far only, evidence for an associative mechanism (eqn. (18) or eqn. (19)) which involves a rotating trihydrogen intermediate. The argument is based on the fact that two tautomers, a dodecahedral tetrahydride complex, $[Re(H)_4L_3(CO)]^+$, **15**, and a pentagonal bipyramidal dihydrogen/dihydride complex, $[Re(H_2)(H)_2L_3(CO)]^+$, **16**, coexist in similar concentrations and are in "slow" equilibrium ($\Delta G^{\ddagger}$ 11.6 kcal mol^{-1} at 213 K, see Table 6). Yet each tautomer undergoes "fast" intramolecular site-exchange processes which are independent of each other (Scheme 1). The barrier to H-atom exchange within the dihydrogen tautomer, **16**, is $\Delta G^{\ddagger} = 9.9 \pm 0.2$ kcal mol^{-1} at 213 K (Table 14) on the basis of coalescence of the resonances of (H_2) and $(H)_2$ species of equal population. The barrier to exchange within eight-coordinate **15** is assumed to be very low. Since the site exchange in **16** occurs faster than the conversion of **16** to **15**, the tetrahydride must be ruled out as a possible intermediate for the former process [68]. This in turn suggests that the dissociative mechanism (eqn. (17)) is not involved in the site exchange within the dihydrogen complex **16**. A possible intermediate *trans*,mer-$[Re(H_2)_2(PMe_2Ph)_3(CO)]^+$ was ruled out on the basis of the observation



Scheme 1.

TABLE 14

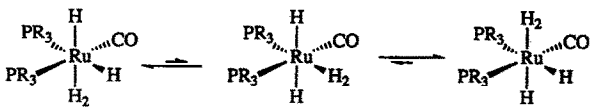
Activation free energies, $\Delta G^{\ddagger}$, calculated from peak coalescence data for the complexes $M(H_2)H_xL_n$. Literature values of $\Delta G^{\ddagger}$ are given in parentheses

Complex	Sets of exchanging nuclei	$T(\theta)$ (K)	$\Delta\nu$ (Hz)	$\Delta G^{\ddagger}$ (kcal mol^{-1})	Ref.
$[Re(H_2)H_2(CO)(PMePh_2)_3]^+$	2H/2H	213	125	9.9(9.9)	68
$Ru(H_2)H_2(CO)(P^iPr_3)_2$	H/H	175	132	8.1	35
	2H/2H	181	992	7.6	35
$Ru(H\cdots H)H_2(PPh_3)_3$	2P/P	210	891	9.3(5.9)	153
mer-$Ru(H_2)H_2$(cyttp)	2H/2H	245	750	10.6	195
$[Ir(H_2)_2H_2(PCy_3)_2]^+$	4H/2H	200	2538	8.4	91

of diastereotopic methyl groups on the PMe_2Ph ligands at the fast exchange temperature (263 K).

A pseudo-octahedral structure $[Re(H_3)(H)(PMe_2Ph)_3(CO)]^+$ (Scheme 1) was proposed as the intermediate or transition state of the exchange reaction within complex **16** (see also eqn. (19)). The $\Delta G^{\ddagger}$ of 9.9 kcal mol^{-1} is the lowest measured (see Table 12) and is consistent with a facile associative process. Luo and Crabtree noted that this (H_3) intermediate would be no more than 10 kcal mol^{-1} less stable than the dihydrogendihydride structure, making a ground-state (H_3) ligand a reasonable goal for future work [68].

The variable-temperature ^1H NMR spectra reported for $Ru(H_2)(H)_2(CO)(P^iPr_3)_2$ [35] show two coalescences of peaks which are apparently related to the same site exchange process. First the broad peaks due to inequivalent hydrides coalesce at 175 K (denoted H/H exchange in Table 14). Then at 181 K, this coalesced peak merges with the broad dihydrogen resonance (2H/2H exchange). We calculate the $\Delta G^{\ddagger}$ values for both processes to be near 8 kcal mol^{-1}. An associative exchange mechanism (eqn. 19)) may be operating here as well. Hydrogen atoms can be imagined to be travelling easily from one mer position to the other (eqn. (33)). However, the concerted mechanism of eqn. (32) cannot be ruled out.

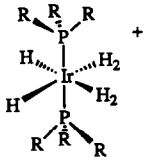


(33)

The mechanisms of eqn. (32) or eqn. (33) might also apply to the complexes mer-$Ru(H_2)(H)_2L_3$, $L_3 = (PPh_3)_3$ or cyttp and mer-$Fe(H_2)(H)_2(PEtPh_2)_3$. Peak coalescence in the ^{31}P NMR spectra is observed for the first complex [153] and in the ^1H NMR spectra of the cyttp complex [195]. No decoalescence of peaks is

observed for the Fe complex at low temperature [8]. The $\Delta G^{\ddagger}$ values are low in the first two cases in accord with the facile process suggested by eqn. (32) or eqn. (33).

The complex $[IrH_6(PCy_3)_2]^+$ has been formulated as the bis dihydrogen complex $[Ir(H_2)_2H_2(PCy_3)_2]^+$ **17** [91].



17

Separate ^1H NMR resonances for the hydride and dihydrogen ligands (ratio 1:2) are observed at 188 K. These peaks coalesce at 200 K. We calculate the $\Delta G^{\ddagger}$ at this temperature to be 8.4 kcal mol^{-1}. Again, a very low barrier is obtained for this polyhydride with dihydrogen and hydride ligands situated cis to each other around the equatorial plane of the complex.

(c) No line-shape decoalescence

The dihydrogenpolyhydride complexes of Table 15 have ^1H nuclei which remain equivalent in the ^1H NMR spectra to low temperatures. All the M–H resonances have short T_1 times at low temperature, which are suggestive of averaging of short T_1 times of dihydrogen ligands with long T_1 times of hydrides (see also Table 1).

TABLE 15

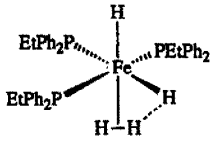
Complexes $M(H_2)H_xL_n$ whose NMR properties are averaged by rapid exchange of H atoms between dihydrogen and hydride at low temperature

Complex	Sets of exchanging nuclei	T (K)	T_1(av) (ms)	MHz	Ref.
$[ReH_8L_2]^+$, L = PCy_3	$(H_2)H_6$?	173	30	400	70
L = PPh_3	$(H_2)H_6$?	173	20	400	70
$[Re(H\cdots H)H_4(cyttp)]^+$	$(H_2)H_4$	183	68	250	16
$Fe(H_2)H_2(PEtPh_2)_3$	$(H_2)H_2$	205	24	250	65
		<173	[a]	250	8
$RuH_6(PCy_3)_2$	$(H_2)_2H_2$?	203	28	200	94
$[OsH_5(PMePh_2)_3]^+$	$(H_2)H_3$?	203	68	360	87
$Rh(H_2)H_2(HB(3,5\text{-}Me_2Pz)_3)$	c-$(H_2)H_2$	166	42	400	67
$Ir(H_2)H_2(Cl)(PCy_3)_2$	$(H_2)H_2$	190	73	200	41
$Ir(H_2)H_2(Cl)(P^iPr_3)_2$	$(H_2)H_2$	<190	[a]	200	41
$[Ir(H_2)H_2(PMe_2Ph)_3]^+$	$(H_2)H_2$	203	20	360	90

[a] No T_1 available, but fast exchange spectrum observed.

All the metal ions could be in the d^6 configuration, except perhaps the Re complexes. The complex $[ReH_8L_2]^+$ may be $[Re(d^0)(H_2)H_6L_2]^+$, $[Re(d^2)(H_2)_2H_4L_2]^+$ or $[Re(d^4)(H_2)_3H_2L_2]^+$. Hydrogen atoms are mobile in these complexes because there is at least one hydride cis to a dihydrogen ligand in each complex. The bulky phosphine ligands, L, will remain approximately trans so that the hydrogen ligands occupy sites around the equator. The presence of more than one H_2 ligand is supported by the short T_1 times of these complexes, even after the Re–H dipole–dipole contribution is subtracted out (see Sect. B.(ii)). The eight-coordinate cyttp complex $[Re(H\cdots H)H_4(cyttp)]^+$ has an elongated dihydrogen ligand as discussed in Sect. B.(ii). The hydrogen ligands are situated in a meridional band around the metal. The 250 MHz ^1H NMR spectrum of the complex in solution at 183 K shows three separate Re–H resonances with integrals 1:4:1; the dihydrogen resonance is coalesced with or is overlapping a hydride resonance to give the peak which has the intensity of four protons.

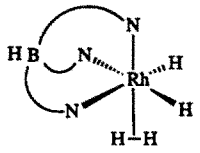
A neutron diffraction study of the complex mer-$Fe(H_2)H_2(PEtPh_2)_3$, **18**, revealed that the dihydrogen ligand has an interaction with the hydride which is located cis [8]. This nascent $H–H_2$ bonding is proposed to facilitate the hydride/dihydrogen fluxionality according to an associative process such as eqn. (19) in an overall exchange process resembling eqn. (33).



18

The Ru and Os complexes of Table 15 could have two, one or no dihydrogen ligands. The Ru complex is formulated as $Ru(d^6)(H_2)_2H_2(PCy_3)_2$ on the basis of the proposed structure of $[Ir(d^6)(H_2)_2H_2(PCy_3)_2]^+$, **17**. The Os complex could be $[Os(d^2)(H)_5(PMe_2Ph)_3]^+$, $[Os(d^4)(H_2)H_3(PMe_2Ph)_3]^+$ or $[Os(d^6)(H_2)_2H(PMe_2Ph)_3]^+$. Desrosiers et al. point out that there are several possible structures for these Ru and Os complexes which are consistent with the T_1 values [28].

The group 9 metal complexes of Table 15 are all thought to be d^6. In the complex $Rh(H_2)H_2(HB(3,5\text{-}Me_2Pz)_3)$, **19**, the presence of one dihydrogen ligand which is cis to two hydrides has been established by isotope substitution studies (see Sect. C.(iii)(d) below). There is fast exchange at low temperature. The bulky phosphines, L, in complexes $Ir(H_2)H_2(Cl)L_2$ are trans and the hydrogen ligands are mer, making for ready exchange by the mechanism of eqn. (32) or eqn. (33). The complex $[Ir(H_2)H_2(PMe_2Ph)_3]^+$ likely has a similar structure to the iron complex **18** with a mer arrangement of H-bonded ligands.



19

(d) Intramolecular exchange of isotopes

The main use of deuterium labelling of these very fluxional dihydrogenpolyhydride complexes is to establish the existence of H–H (H–D) bonding. This is achieved by the observation of an averaged $J(HD)_{av}$ coupling or of a perturbation of chemical shift (see discussion of IPR is Sect. C.(ii)(h) above).

Of the complexes of Table 14, the isotopomers of the Re complex $[ReH_xD_{4-x}(CO)(PMe_2Ph)_3]^+$ have been the most thoroughly studied by Luo and Crabtree [68]. The ^1H NMR spectrum of the isotopomer $Re(HD)D_2$ in CD_2Cl_2 at 193 K includes a 1:1:1 triplet with $J(HD) = 34$ Hz. No net IPR was observed for this complex. Luo and Crabtree point out that, since there are two tautomeric forms of this complex, $Re(H)_4$, **15** and $Re(H_2)(H)_2$, **16** (Scheme 1), there will be two contributions to the IPR shift of the fast average ^1H NMR spectra of the isotopomers and that these contributions tend to cancel each other. An upfield shift contribution comes from the isotope effect on the equilibrium between the two tautomers; deuteration increases the relative concentration of **16** whose ReH resonances are upfield of that of **15**. A downfield shift contribution is expected because deuterium prefers to occupy the non-classical site, which is upfield from the hydride site in this case.

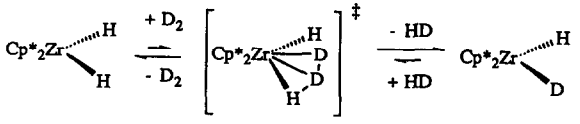
The averaged coupling, $J(HD)_{av}$, of approximately 2.7 Hz for the RuH_2D_2 isotopomer of $RuH_4(PPh_3)_3$ suggests that this complex contains an elongated dihydrogen ligand as discussed in Sect. B.(vi). The 2.7 Hz value was observed indirectly by Gusev et al. [153] by simulating couplings in a $RuH_2D_2P_3$ spin system to fit a proton-coupled ^2H NMR broad resonance at the fast exchange limit (at 278 K). Subsequent proton decoupling verified that $J(HD)$ was contributing to the line width. There is a large uncertainty in this procedure because it is difficult to ensure that only $RuH_2D_2P_3$ is present; $RuHD_3P_3$ and RuH_3DP_3 could also be formed in significant amounts and these would give different coupling patterns in the ^2H NMR spectrum. Gusev et al. calculated that a 2.7 Hz average indicates an 8.5 Hz $J(HD)$ for a static $Ru(HD)(H)(D)P_3$ complex. However, we calculate that a 2.7 Hz average represents about 16 Hz $J(HD)$: one must average couplings in Ru(HD)(D)(H) $\{(^1J(HD) + 3\,^2J(HD))/4 = 16/4\}$, Ru(HH)$(D)_2$ $\{^2J(HD) = 0\}$ and Ru(DD)$(H)_2$ $\{^2J(HD) = 0\}$ according to the statistical weightings of approximately $\frac{2}{3}:\frac{1}{6}:\frac{1}{6}$, respectively. The statistical weights will have some error because of the preference of deuterium to be in the (HD) ligand over the terminal hydride position. (See ref. 29 for a similar treatment.)

The complex $Ru(H \cdots H)H_2(PPh_3)_3$ is an efficient catalyst in solution for $H_2/HD/D_2$ isotope equilibration [196,197]. This is explained by the ease of exchange of the H_2 ligand with D_2 gas and the ease of intramolecular exchange of isotopes on Ru.

Nanz et al. [198] report that a 2D-(^1H,^{103}Rh)-HMQC experiment reveals $J(HD)_{av}$ values of 4.7 Hz for isotopomers $Rh(HD)(D)_2L$ and $Rh(HD)H(D)L$, L = ($HB(3,5\text{-}Me_2Pz)_3$), which are in the fast exchange limit (see Table 15). We calculate a no-exchange $J(HD)$ of 28 Hz for this complex by use of the method which we used for the case of the complex $Ru(H \cdots H)H_2(PPh_3)_3$ (see above). These authors also note two opposite contributions to the averaged chemical shift of the isotopomers. The first is a downfield shift contribution because deuterium prefers to occupy the non-classical site, $Rh(HD)H_2$, over the classical ones, $Rh(H_2)HD$. The non-classical site is thought to be upfield from the hydride sites in this case (see also the IPR of the Re complex above). The second is "a normal isotope effect", which is an upfield shift.

The complexes $[OsD_5(PMe_2Ph)_3]^+$ [87] and $[IrD_4(PMe_2Ph)_3]^+$ [199] were prepared by reacting the parent dihydrogen complexes in solution with D_2 (see Table 15). The properties of other isotopomers were not reported.

Reactions with deuterium gas can give evidence for unstable, fluxional dihydrogen intermediates. Before the dihydrogen molecule was a recognized ligand, Brintzinger in 1979 [200] proposed that the transient $Zr(d^0)$ complex $Zr(D_2)(H)_2Cp^*_2$, mediated H/D exchange via the associative transition state species $[Zr(H)(DDH)Cp^*_2]^‡$ to give $Zr(D)(H)Cp^*_2$ according to the equation



(34)

(iv) H/D exchange in the reaction of $M(H_2)L_n$ with D_2

The previous sections have demonstrated that dihydrogen complexes with additional hydride ligands, $M(H_2)H_xL_n$, are often efficient catalysts for $H_2/HD/D_2$ isotope equilibration of the gases. However, a few coordinatively saturated dihydrogen complexes with no hydrides also catalyze this reaction.

The unstable complex $Cr(D_2)_2(CO)_4$ in liquid Xe at $-70°C$ causes $D_2/HD/H_2$ isotope exchange [46]. This was demonstrated indirectly by reacting a mixture of $Cr(D_2)_2(CO)_4$ and the more stable $Cr(D_2)(CO)_5$ with H_2 and observing by IR spectroscopy the formation of $Cr(HD)(CO)_5$. Similarly, there was evidence that $Cr(HD)_2(CO)_4$ under HD gas gives coordinated H_2 and D_2 species.

$$Cr(HD)_2(CO)_4 \rightleftharpoons Cr(H_2)(D_2)(CO)_4 \tag{35}$$

However, complex $Cr(H_2)(CO)_5$ reacts with D_2 gas under pressure to give $Cr(D_2)(CO)_5$ but not $Cr(HD)(CO)_5$. Therefore it appears that two coordinated molecules XY (X, Y = H, D) are required for H/D exchange.

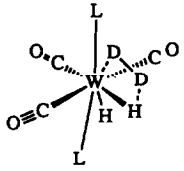
Several mechanisms, supported by semi-empirical or ab initio calculations, have been proposed for exchange reaction (35) [25,201,202]. It is generally agreed that a coordinated square or tetrahedron of hydrogen isotopes all bonded together would be too high in energy to be an transition state for this reaction. Likewise, the Cr(IV) tetrahydride $Cr(H)_4(CO)_4$ and the complex $Cr(H_3)H(CO)_4$ with a closed, triangular H_3 ligand (structure **7** above) would be too unstable. The likely structures for the transition state(s) or intermediate(s) of eqn. (35) are isotopomers of $Cr(H_2)(H)_2(CO)_4$ and/or $Cr(HHHH)(CO)_4$ with an open H_4 ligand (four H bonded in a chain) or $Cr(H_3)H(CO)_4$ with an open H_3 ligand (structure **9**).

Curious reactions, first reported by Kubas et al. [6], are the isotope scrambling reactions of eqns. (36) and (37), L = PCy_3 or P^iPr_3.

$$D_2 + W(H_2)(CO)_3L_2 \rightleftharpoons HD + W(HD)(CO)_3L_2 \rightleftharpoons H_2 + W(D_2)(CO)_3L_2 \quad (36)$$

$$2W(HD)(CO)_3L_2 \rightleftharpoons W(H_2)(CO)_3L_2 + W(D_2)(CO)_3L_2 \quad (37)$$

Starting with equimolar amounts of D_2 gas and H_2 complex, isotope equilibration takes place according to reaction (36) for the complexes in toluene over a period of days at 20°C and 1 atm. Surprisingly, this equilibration also takes place with the microcrystalline H_2 complex over a period of nine days. Prior loss of CO or phosphine ligand L to allow D_2 coordination, formation of $W(H_2)(D_2)(CO)_3L$ or $W(H_2)(D_2)(CO)_2L_2$, and exchange as an eqn. (36) appears to be an unlikely mechanism because ligand loss would be a high-energy process, especially in the solid state. These tungsten complexes are thought to undergo substitution reactions via an associative mechanism [203]; for example, the 20-electron transition state $W(CO)_3L(L\text{-}CH)(py)$, with a phosphine ligand L coordinated via P and a C–H bond to W is the favored intermediate in the substitution of $W(CO)_3L_2(py)$ by $P(OMe)_3$. Perhaps a 20-electron intermediate such as the dihydride $W(H)_2(D_2)(CO)_3L_2$, **20**, could account for this slow isotope exchange process.



20

As suggested in Sect. C.(iii) above, such dihydrogen/dihydride species undergo rapid intramolecular H atom exchange and thus would catalyze isotope equilibration. Pacchioni suggests that $Cr(H_2)(CO)_5$ does not exchange with D_2 to give HD because

the dihydride $Cr(H)_2(CO)_5$ is calculated to be too high in energy [202]; the tungsten complexes, on the other hand, are in equilibrium with dihydride tautomers which may be responsible for the associative exchange reaction. Although the isotope scrambling of $W(D_2)(CO)_3L_2$ does occur over a period of days with H_2O, H^+/D^+ exchange by traces of water is not thought to be responsible for exchange reaction (37) [204]. Equation (37) could be explained by the loss of HD from one tungsten center (a low-energy process) and then attack of free HD on another tungsten, as in eqn. (36), to give isotope scrambling.

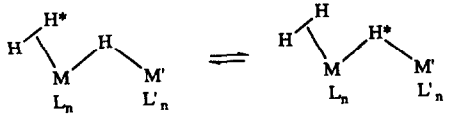
The ^1H NMR spectrum of a product isolated from the reaction of $[Ru(H_2)Cp(PPh_3)CN^tBu]^+$ in CH_2Cl_2 with D_2 revealed the presence of $[Ru(HD)Cp(PPh_3)CN^tBu]^+$ [82]. The intermediate for exchange was postulated to be $[Ru(H)_2(D_2)Cp(CN^tBu)]^+$. More recently, Chinn and Heinekey [205] have proposed that, since this dihydrogen complex is quite acidic, a catalytic amount of base could account for the H/D scrambling between $Ru(H_2)$ and $Ru(D_2)$ complexes.

Another complex which displays exchange of this sort is *trans*-$Re(H\cdots H)Cl(PMePh_2)_4$ [12,92]. Reaction of the complex in solution with D_2 gives the HD complex and deuterium incorporation into the ortho protons of the phosphine ligand. No mechanism was discussed.

Bianchini et al. [39] suggest that simultaneous coordination of H_2 and D_2 is required for H/D exchange in $M(H_2)L_n$ complexes. On this basis, they were not surprised when $[Rh(H\cdots H)pp_3]^+$ did not react with D_2 to give the Rh(HD) complex. More research is needed in this interesting area.

(v) Intramolecular H atom exchange in bimetallic systems

Exchange of H atoms between dihydrogen and a hydride which is bridging between metals is observed in all cases where the two groups are cis to each other (eqn. (38)).



(38)

Such a reaction has been reported for the Ru_2 complex $(L_2)(H_2)Ru(\mu\text{-}H)(\mu\text{-}Cl)_2RuH(PPh_3)_2$, $L_2 = FeCp(1,2\text{-}C_5H_3(CHMeNMe_2)(P^iPr_2))$ [15]. We calculate from the rate data reported here the parameters $\Delta G^{\ddagger}(293\ K) = 11.8$, $\Delta H^{\ddagger} = 15.3$ kcal mol^{-1} and $\Delta S = 12$ cal mol^{-1} K^{-1}. The $\Delta H^{\ddagger}$ value is higher than those observed for mononuclear complexes (see Table 10). Jackson and Eisenstein [206] point out that this binuclear complex has a cis H_2/H interaction (see Sect. C.(ii)) which might assist the exchange process. However, we note that the energy for exchange is not especially low for this complex. Perhaps the energy is high because a hydride must move from its very stable bridging position. The RuRe complex

$[(PPh_3)_2(H_2)Ru(\mu\text{-}H)_3(\mu\text{-}CO)ReH(PPh_3)_2]^+$ [207] also exchanges via eqn. (38). In both the RuRu and RuRe complexes, the terminal hydride exchange positions with the bridging hydride at a much slower rate. Significantly, the related complex $[(PPh_3)_2(H_2)Ru(\mu\text{-}Cl)_2(\mu\text{-}H)(\mu\text{-}CO)ReH(PPh_3)_2]^+$, which probably does not have adjacent H_2 and μ-H groups, does not show this intramolecular H atom exchange reaction.

The complexes $(P(p\text{-}tol)_3)_2(H_2)Ru(\mu\text{-}H)(\mu\text{-}Cl)_2RuH(P(p\text{-}tol)_3)_2$ [208] and $(PCy_3)_2(H_2)Ru(\mu\text{-}H)_3RuH(PCy_3)_2$ [94] are particularly fluxional with exchange occurring between all hydrogen donor ligands. A simultaneous oxidative addition of H_2 to give $(H)Ru(\mu\text{-}H)$ and reductive elimination of $(\mu\text{-}H)Ru(H^*)$ to give $Ru(HH^*)$ (eqn. (39)) can be proposed based on a related mechanism proposed by Dekleva et al. [209].

$$(H_2)Ru(\mu\text{-}H)Ru(H^*) \rightleftharpoons (H)Ru(\mu\text{-}H)Ru(HH^*) \tag{39}$$

Note the similarity to the concerted mechanism of eqn. (32).

A complex formulated as a mixture of $Cp^*(PCy_3)Ru(\mu\text{-}H_2)(\mu\text{-}H)CuCl$ and $Cp^*(PCy_3)Ru(\mu\text{-}H)_3CuCl$ was proposed to undergo H atom exchange [175]. However, the ^1H NMR spectra are equally consistent with the presence of one dynamic trihydride species with bridging and terminal hydrides which are coupled by quantum mechanical exchange (see Sect. C.(ii)(a)).

Finally, the complex $Ru_2(\mu\text{-}H_2)(dpb)L_2$, which contains a dihydrogen bridging in some manner between two Ru(porphyrin) moieties, exchanges the H_2 for D_2 [166]. However, no intramolecular exchange to give an HD ligand is observed.

D. HETEROLYTIC CLEAVAGE OF THE DIHYDROGEN LIGAND

(i) Introduction to intermolecular heterolytic cleavage

Intermolecular heterolytic cleavage of a dihydrogen ligand produces a hydride and the conjugate acid of the external base.

$$M(H_2)L_x + B \rightleftharpoons [M(H)L_x]^- + BH^+ \tag{40}$$

Intramolecular heterolytic cleavage is the protonation of a coordinated ligand by a dihydrogen ligand (eqn. (41)), and will be discussed in Sect. D.(iv).

$$M(H_2)L_x \rightleftharpoons M(HL)(H)L_{x-1} \tag{41}$$

The most dramatic example of intermolecular heterolytic cleavage is the protonation of diethyl ether solvent by an extremely acidic dihydrogen complex [59].

$$[Re(H_2)Cp^*(CO)(NO)]^+ + Et_2O \rightleftharpoons ReHCp^*(CO)(NO) + Et_2OH^+ \rightarrow \text{dimer} \tag{42}$$

In addition to simple stoichiometric reactions such as eqn. (42), intermolecular heterolytic cleavage is observed or postulated in several general mechanisms.

(a) Base-assisted hydride donation by H_2

A combination of a base and free H_2 can be an effective hydride-donating mixture for the synthesis of metal hydrides, via a presumed intermediate dihydrogen complex 2, e.g. [88]

$$Ru(oep)(thf)_2 + KOD + H_2 \rightarrow [RuH(oep)(thf)]^- + (HOD + K^+) \quad (43)$$

In this case, the presumed intermediate $Ru(H_2)(oep)(thf)$ is not observed, but the dinitrogen analogue $Ru(N_2)(oep)(thf)$ has a $\nu(NN)$ frequency of 2110 cm^{-1} [210], within the range expected for analogues of stable dihydrogen complexes [132], and $Os(H \cdots H)(oep)(thf)$ is known [88].

(b) Exchange of protons between a hydride and an acid

Two of the possible mechanisms for this exchange involve dihydrogen complexes.

$$M(H) + DA \rightleftharpoons [M(HD)]^+ + A^- \rightleftharpoons M(D) + HA \quad (44)$$

$$M(H) + DA \rightleftharpoons M(H)(DA) \rightleftharpoons M(HD)(A) \rightleftharpoons M(D)(HA) \rightleftharpoons M(D) + HA \quad (45)$$

Examples of the first mechanism are eqn. (46) [211] and possibly eqn. (47) (M = Cr, W, [212]).

$$Fe(H)_2(dmpe)_2 + DCCPh \rightleftharpoons FeH(D)(dmpe)_2 + HCCPh \quad (46)$$

$$[MH(CO)_5]^- + MeOD \rightarrow [MD(CO)_5]^- + MeOH \quad (47)$$

The intermediate dihydrogen complexes $[FeH(H_2)(dmpe)_2]^+$ [213] and $M(HD)(CO)_5$ [45,48,214] are known but are not observed in these reactions. A proposed example of the second mechanism (eqn. (45)) is the deuteration of the hydride ligand of $[IrH(H_2O)(bq)(L_2)]^+$ ($L = PPh_3$, PCy_3) by addition of D_2O [91].

(c) Exchange of protons between a dihydrogen complex and alcohol or water

The first step is protonation, by the dihydrogen complex, of alcohol (eqn. (48)), alkoxide ion (eqns. (49) and (50)), or a metal alkoxide.

$$M(H_2) + DOR \rightleftharpoons [M(H)]^- + HDOR^+ \rightleftharpoons M(HD) + HOR \quad (48)$$

$$M(H_2) + OR^- \rightleftharpoons [M(H)]^- + HOR \quad (49)$$

$$[M(H)]^- + DOR \rightleftharpoons M(HD) + OR^- \quad (50)$$

The synthesis of η^2-HD complexes can be achieved by the addition of D_2O or ROD to a dihydrogen complex [71,84] or the addition of H_2O or ROH to a dideuterium complex [204].

(d) Catalytic H/D exchange between D_2 and alcohol or water

Dihydrogen complexes must be labile and acidic to be catalytically active for this process.

$$M + D_2 + H_2O \rightleftharpoons M(D_2) + H_2O \rightleftharpoons M(DH) + HOD \rightleftharpoons M + DH + HOD \quad (51)$$

The proton exchange step may proceed by any of the intermolecular mechanisms described above for isotope exchange between $M(H_2)$ and ROD; i.e. protonation by the dihydrogen complex of either ROH (eqn. (48)) or OR^- (eqns. (49) and (50)). Protonation of OD^- is proposed as the mechanism for this step during the catalysis of exchange between D_2O and H_2 by Ru(oep)(thf)$_2$ in the presence of KOD; in the absence of base, the catalysis did not occur [88]. Protonation of ROH is proposed for the catalysis of exchange between ^{t}BuOH and D_2 by $[Ir(H_2)H(bq)(PPh_3)_2]SbF_6$ [190]. Intramolecular exchange processes are also possible (see Sect. D.(iv)). For example, the complexes $[Ir(MeOH)(D)(bq)(PPh_3)_2]^+$ and $[Ir(MeOD)(H)(bq)(PPh_3)_2]^+$ are suggested as two of the intermediates in the isotope exchange reaction between D_2 and MeOH [190]. An unusual intramolecular example (Scheme 2) will be described in Sect. D.(iv). If nitrogenase contains an η^2-H_2 ligand, then reaction (51) may be involved in the catalysis by nitrogenase [119] of H/D exchange between H_2O and D_2.

(e) Other catalytic cycles involving deprotonation of dihydrogen complexes

These include the catalytic production of H_2 from alcohols by $RuH_2(H_2)(PPh_3)_3$ (Sect. H) and possibly the cycle of nickel hydrogenase [215].

$$\underset{\uparrow \quad\quad\quad\quad\quad\quad\quad\quad \downarrow}{Ni(H_2) \xrightarrow{-H^+} NiH^- \xrightarrow{-H^+,2e^-} Ni} \qquad (52)$$
$$\underset{H_2}{\longleftarrow}$$

If nitrogenase contains an acidic dihydrogen ligand (see above), then protonation by that ligand of an η^1-N_2 moiety (see ref. 216 and references cited therein) could be part of the catalytic cycle of the enzyme. A model for this reaction has been reported [217].

$$W(N_2)_2(dppe)_2 + 2[RuH_2Cp(dtfpe)]BF_4 \rightarrow$$
$$[WF(NNH_2)(dppe)_2]BF_4 + 2RuHCp(dtfpe) + BF_3 \cdot thf + N_2 \quad (53)$$

(f) Dimerization of dihydrogen complexes

Deprotonation of a dihydrogen complex could be the first step in the formation of a dinuclear complex with hydride bridges, e.g. [218]

$$2[Ru\text{–}H_2]^+ \xrightarrow{-H^+} Ru\text{–}H + [Ru\text{–}H_2]^+ \xrightarrow{-H_2} [Ru\text{–}H\text{–}Ru]^+ \quad (54)$$

where $Ru^+ = [RuCp(PPh_3)(CN^tBu)]^+$.

Evaluation of proposed mechanisms involving heterolytic cleavage of H_2 ligands requires a knowledge of the thermodynamic and kinetic acidities of molecular hydrogen complexes. These subjects will be discussed in the following sections.

(ii) Thermodynamic acidity

Although the pK_a values of dihydrogen complexes are not normally measured in aqueous solution, all of the values discussed in this review will be on the aqueous scale, for ease of comparison. Acetonitrile has been suggested [219] as a better scale and solvent for pK_a measurements of hydride complexes, but it suffers from the drawback that it is too strongly coordinating for dihydrogen complexes (see Table 20, Sect. E). The pK_a values of hydride complexes have been extrapolated to the aqueous scale [220]. For acidic transition metal hydrides, and presumably dihydrogen complexes, the scales can be interconverted by eqn. (55) [220].

$$pK_a(H_2O) = pK_a(MeCN) - 7.5 \quad (55)$$

The pK_a values of dihydrogen complexes are usually determined by measuring the concentrations of species in an equilibrium (eqn. (40)) with an external base such as a phosphine [148,217], an amine [205], a metal hydride [85,148,221], or an alkoxide [198]. The bases which have been used are listed in Table 16, with the pK_a values (aqueous scale) of the conjugate acids. The concentrations are calculated from the ^1H or ^{31}P NMR spectra of the solutions at equilibrium. The pK_a ranges of alcohols (10–20) and protonated phosphines (0–11) are complimentary, although the use of phosphines and alkoxides have disadvantages. Ion-pairing may occur between alkoxides and cationic dihydrogen complexes or between protonated phosphines and the anionic conjugate bases of neutral dihydrogen complexes. If proton-decoupled ^{31}P NMR spectroscopy is used for studies involving phosphines, gated decoupling and very long delay times between pulses are required, the former to suppress the nOe effect, and the latter to allow full relaxation of the magnetization. The longitudinal relaxation of free phosphines is very slow; typical T_1 values are 15 s for P^nPr_3 (field strength not reported [222]) and 26 s for PPh_3 (at 5.9 Tesla) [223] in solution at ambient temperature. This problem can be avoided if the concentrations of PR_3 and $[HPR_3]^+$ are calculated from the original concentrations of added PR_3 and the ratio of $[M(H_2)^+]/[M(H)]$, which in turn is calculated from ^{31}P or preferably ^1H NMR spectral data. Phosphines used as external bases need to be bulky to prevent substitution of the dihydrogen ligand.

The solvent of choice for pK_a measurements is thf because CD_2Cl_2 and CD_3CN can be too reactive. Most of the reported measurements (Table 17) have been made in thf, although CD_2Cl_2 is sometimes used because of solubility problems and the high cost of thf-d_8.

TABLE 16

Selected bases and the pK_a values (aqueous scale) of the conjugate acids

Base	$pK_a(BH^+)$	Ref.
H^-	35	224
$^tBuO^-$	19.2	308
EtO^-	15.9	308
HO^-	15.7	309
MeO^-	15	308
$RuHCp^*(PMe_2Ph)_2$	14.3	148
Proton sponge	12.3	310
P^tBu_3	11.4	311
NEt_3	10.8	312
PhO^-	10.0	308
PCy_3	9.7	312
P^nBu_3	8.4	312
$RuHCp(PPh_3)_2$	8.0	85,313
RuHCp(dppm)	7.5	85,313
PMe_2Ph	6.5	312
$MeCOO^-$	4.7	308
$PMePh_2$	4.6	314
$P(C_6H_4\text{-}p\text{-}Me)_3$	3.8	311
$HCOO^-$	3.7	308
PPh_3	2.7	312
$P(C_6H_4\text{-}p\text{-}Cl)_3$	1.0	311
PPh_2H	0.0	312

The pK_a of the dihydrogen complex is determined from the K_{eq} of eqn. (40) by the equation

$$pK_a = pK_{eq} + pK_{BH^+} \tag{56}$$

where pK_a and pK_{BH^+} are on the same acidity scale.

The pK_a values of interconverting dihydrogen and dihydride tautomers (eqn. (57)) are related by eqn. (58).

$$M(H_2) \overset{K}{\rightleftharpoons} M(H)_2 \tag{57}$$

$$pK_a(M(H_2)) = pK_a(M(H)_2) - \log K \tag{58}$$

The major tautomer is always the weaker acid. If the minor tautomer is observable (i.e. >1% of the mixture), then the difference between the pK_a values of the tautomers will be less than 2 units.

Because K (eqn. (57)) for dideuterium complexes is smaller than that for η^2-H_2 complexes, (Sect. B.(iv), [68]), the acidity of the classical tautomer will be increased by deuteration, at the expense of the non-classical form.

TABLE 17

Reported pK_a values (aqueous scale) of dihydrogen and hydride complexes

Complex	pK_a	Solvent	Ref.
Group 7			
$[Re(H_2)Cp^*(CO)(NO)]^+$	−2	Et_2O	59
Group 8			
$[Fe(H_2)H(dmpe)_2]^+$	~16	EtOH	71,257
$[Fe(H_2)H(dtpe)_2]^+$	16	thf	306
$[Fe(H_2)H(dppe)_2]^+$	~12	thf	315
$[Fe(H_2)H(dtfpe)_2]^+$	7.8	thf	221
$Ru(H\cdots H)H_2(PPh_3)_3$	17	thf	133,196
$[Ru(H_2)H(dppe)_2]^+$	14.1	thf	231
$[Ru(H_2)H(dtfpe)_2]^+$	9.1	thf	221
$[Ru(H)_2Cp^*(PMe_3)_2]^+$	16.3 ± 0.7	thf	148
$[Ru(H)_2Cp^*(PMe_2Ph)_2]^+$	14.3 ± 0.5	thf	148
$[Ru(H)_2Cp^*(PMePh_2)_2]^+$	12.2 ± 0.4	thf	148
$[Ru(H)_2Cp^*(PPh_3)_2]^+$	11.1 ± 0.2	thf	148
$[Ru(H)_2Cp^*(dppp)]^+$	10.4 ± 0.5	thf	148
$[Ru(H_2)Cp^*(dppm)]^+$	9.2	thf	85
$[Ru(H)_2Cp^*(dppm)]^+$	8.8	thf	85
$[Ru(H_2)Cp(dmpe)]^+$	10.1[a]	MeCN	205
$[Ru(H)_2Cp(dmpe)]^+$	9.3[a]	MeCN	205,220
$[Ru(H)_2Cp(dape)]^+$	9.0	thf	85
$[Ru(H_2)Cp(dape)]^+$	8.6	thf	85
$[Ru(H)_2Cp(dppp)]^+$	8.6	thf	85,313
$[Ru(H)_2Cp(PPh_3)_2]^+$	8.0	thf	85,313
$[Ru(H_2)Cp(dppm)]^+$	7.5	thf	85,313
$[Ru(H)_2Cp(dppe)]^+$	7.5	thf	85
$[Ru(H_2)Cp(dppe)]^+$	7.2	thf	85
$[Ru(H)_2Cp(dtfpe)]^+$	4.9	thf	85,217
$[Ru(H_2)Cp(dtfpe)]^+$	4.6	thf	85,217
$[Os(H_2)H(depe)_2]^+$	~16	EtOH	133
$[Os(H_2)H(dppe)_2]^+$	12.6	thf	231
$[Os(H_2)H(dtfpe)_2]^+$	8.4	thf	221

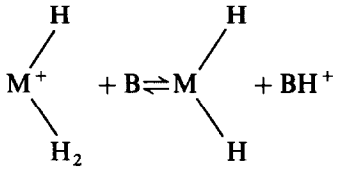
[a] Converted [220] from acetonitrile scale using $pK_a(\text{aqueous}) = pK_a(\text{MeCN}) - 7.5$.

The apparent pK_a of rapidly interconverting tautomers is greater than the pK_a of either tautomer alone (eqn. (59), [220]).

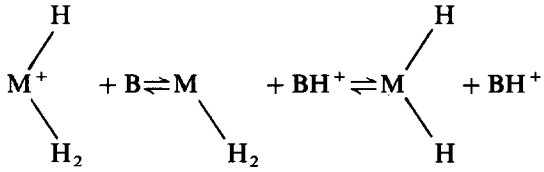
$$K_a^{app} = \left\{\frac{1}{1+K}\right\} K_a(M(H_2)) = \left\{\frac{K}{1+K}\right\} K_a(M(H)_2) \quad (59)$$

The thermodynamic acidities of hydride and dihydrogen ligands in a hydrido(di-

hydrogen) complex (e.g. $[IrH(H_2)(bq)(PPh_3)_2]^+$ are identical because deprotonation from either site results in the same thermodynamic product (eqns. (60) and (61)).



(60)



(61)

Selective deprotonation of the dihydrogen ligand, which has been observed (Sect. D.(iii)), is evidence of greater kinetic rather than thermodynamic acidity of the dihydrogen ligand. Only if the second step of reaction (61) is prevented by rigidity of the ancillary ligands could the hydride and dihydrogen ligands have differing thermodynamic acidities. The dihydrogen product of deprotonation at the hydride site is likely to be unstable with respect to oxidative addition because of the increased basicity of the metal. If oxidative addition is not possible, then the dihydrogen ligand in the original complex will be more acidic than the hydride ligand.

How are the acidities of di- or poly-hydrides related to the degree of H_2 activation? Free hydrogen has a pK_a of 35 [224], while most hydrides have pK_a values below 20 on the aqueous scale [220,225]. One might expect, therefore, that acidity increases with H–H bond weakening. However, we have seen that dihydrides are not necessarily more acidic than their dihydrogen tautomers. The increase in acidity caused by weakening of the H–H bond is countered by a strengthening of the M–H bond, which decreases the acidity. The sum of these bond strengths, as expressed by ΔH_{BDE} (defined in eqn. (62), [133]), is a major factor in determining the pK_a.

$$\Delta H_{BDE}\{M(H_2)\} = \Delta H_f\{H\cdot\} + \Delta H_f\{MH\cdot\} - \Delta H_f\{M(H_2)\} \quad (62)$$

If ΔH_{BDC} were the only factor, one would expect that electron-deficient labile dihydrogen complexes, with their strong H–H bonds and high ΔH_{BDE} values, would be the least acidic dihydrogen complexes. Early indications are that the reverse is true [133]. Electron-deficient dihydrogen complexes are both labile and acidic. Examples are the labile and very acidic complexes $[Ru(H_2)Cp^*(CO)_2]BF_4$ and $[Re(H_2)Cp^*(CO)(NO)]OSO_2CF_3$ [59]. The acidity of both dihydrides and dihydrogen complexes is increased by a decrease in the electron density caused by oxidation or ancillary ligand substitution. For example, $[Os(H_2)(NH_3)_5]^{3+}$ is more

acidic than $[Os(H\cdots H)(NH_3)_5]^{2+}$ [93(a)] and $[ReH_4(CO)(PMe_2Ph)_3]^+$ is more acidic than $[ReH_4(PMe_2Ph)_4]^+$ [68].

The electrochemical potential $E_{1/2}$ for d^5/d^6 couples is an indicator of the electron density of the d^6 metal; a low $E_{1/2}$ value indicates an electron-rich metal center. The pK_a of a dihydride $[M(H)_2L_5]^+$ or dihydrogen complex $[M(H_2)L_5]^+$ has been linked to the electrochemical potential of the conjugate base (MHL_5) by a thermochemical cycle and resulting equation (eqn. (66), $T = 300$ K, [85]) modified from those of Tilset and Parker for hydrides [226].

$$[M(H_2)L_5]^+ \rightarrow MHL_5 + H^+ \qquad \Delta G = 2.301RTpK_a = 1.37pK_a \tag{63}$$

$$MHL_5 \rightarrow [MHL_5]^+ + e^- \qquad \Delta G = FE^0_{ox}(MH) = 23.1E^0(MH^+/MH) \tag{64}$$

$$H^+ + e^- \rightarrow H\cdot \qquad \Delta G = \text{constant} \tag{65}$$

$$[M(H_2)L_5]^+ \rightarrow [MHL_5]^+ + H\cdot \qquad \Delta G_{BDE} = 1.37pK_a + 23.1E^0 + \text{constant} \tag{66}$$

Equation (66) can be transformed by rearrangement, conversion to enthalpies rather than free energies (using the assumptions of Tilset and Parker [226]), and substitution of an empirically derived constant, to a more useful form [133]

$$pK_a = (0.730\ \text{kcal}^{-1}\ \text{mol})\Delta H_{BDE} - (16.9\ V^{-1})E_{1/2} - 43 \tag{67}$$

where $E_{1/2}$ is the reduction potential for the MH/MH^- (d^5/d^6) pair with reference to the $FeCp_2^+/FeCp_2$ potential. The constant (−43) is based on a small data set [133] and needs to be refined as more data become available.

The ΔH_{BDE} value is difficult to measure or estimate. Typical hydride ΔH_{BDE} values of 58–68 kcal mol^{-1} (3d metals), 65–70 kcal mol^{-1} (4d metals), and 70–75 kcal mol^{-1} (5d metals) [226] (note the published correction [227]). If tautomerism is observed (minor tautomer > 1%), then the ΔH_{BDE} of the dihydrogen complex must be within 3 kcal mol^{-1} of that of the dihydride. The major tautomer has the greater ΔH_{BDE}.

If tautomerism is not observed and the complex has $E_{1/2}$ or ν(NN) values far from the borderline with dihydrides, then the ΔH_{BDE} could range as high as 104 kcal mol^{-1}, the ΔH_{BDE} of free H_2 [228], although more likely values for labile dihydrogen complexes would be on the order of 80 kcal mol^{-1}. The gas phase ΔH_{BDE} of $[Mn(H_2)(CO)_5]^+$ is 83.5 kcal mol^{-1} (p. 679 of ref. 229), much higher than typical Mn–H ΔH_{BDE} values of ~60 kcal mol^{-1} [226].

It is likely that ΔH_{BDE} varies with $E_{1/2}$; possible evidence of this was presented by Jia and Morris [85]. They simplified eqn. (67) by assuming that ΔH_{BDE} was constant for complexes $[Ru(H_2)Cp(\text{diphosphine})]^+$ (eqn. 68)).

$$pK_a = -(16.9\ V^{-1})E_{1/2} + C' \tag{68}$$

where $C' = (0.730\ \text{kcal}^{-1}\ \text{mol})\Delta H_{BDE} - 43$.

The observed slope of the plot of pK_a vs. $E_{1/2}$ was $-10.7\ V^{-1}$ instead of the

theoretical 16.9 V^{-1} [85]. This difference could have been due to a variable ΔH_{BDE} or a systematic error in converting between acidity scales.

The uncertainty in ΔH_{BDE} creates difficulties in using eqn. (67) to predict pK_a values of observed or postulated dihydrogen complexes. A possible range of 60–85 kcal mol^{-1} in ΔH_{BDE} translates into a range of 18 units for the predicted pK_a. Substituting 60 kcal mol^{-1} for the ΔH_{BDE} gives a lower limit on the pK_a of the dihydrogen complex (eqn. (69) [133]).

$$pK_a(\text{lower limit}) = 11 - (16.9\ V^{-1})E_{1/2}(MH/MH^+) \quad (69)$$

The upper limit of the pK_a can be obtained by adding 18 units to the lower limit; this corresponds to a ΔH_{BDE} of 85 kcal mol^{-1}. The $E_{1/2}$ value can be measured or it can be estimated from Lever's additivity parameters [133–135]. Despite the uncertainty in predicted pK_a values (± 9), the usefulness of eqns. (67)–(69) has been demonstrated [149,230].

The above discussion describes the factors which determine acidity and the methods for predicting or determining the pK_a of dihydrogen complexes. The pK_a values for several dihydrogen complexes have been reported (Table 17), while limits can be placed on the possible pK_a values for many more such complexes (Table 18). The latter data are available from the reported reactions or non-reactions of dihydrogen complexes with external bases (Table 16).

The qualitative trend predicted in eqns. (67) and (69), that greater electron density at the metal (lower $E_{1/2}$ value) corresponds to lower acidity, is consistent with the observed trends in pK_a with respect to choice of ligand. For the classical or non-classical complexes $[RuH_2Cp(L_2)]^+$, the trend in acidity with varying L_2 is dmpe < dape < dppp < $2PPh_3$ < dppe = dppm < dtfpe. The trend for $[RuH_2Cp^*(L_2)]^+$ complexes is $2PMe_3 < 2PMe_2Ph < 2PMePh_2 < 2PPh_3$ < dppp < dppm. The $[RuH_2Cp^*(L_2)]^+$ complexes have pK_a values 2 or 3 units higher than the corresponding Cp complexes.

Similar trends have been reported for classical hydrides. Substitution of CO by phosphine or Cp by Cp* results in higher pK_a values for monohydride complexes [220]. Basic ligands decrease the acidity of both hydrides and dihydrogen complexes.

For isostructural monohydrides, acidity decreases down the group because of the increasing M–H bond strength [220,226], although there is some evidence that the 4d complex is the most acidic in the series $[MH(P(OMe)_3)_4]^+$ (M is of group 10) and $MH(CO)_4$ (M is of group 9) [220].

For dihydrogen complexes on the borderline with dihydrides, is there the same trend in acidity with respect to the metal? The only complete series of complexes with reported pK_a values is the group 8 series *trans*-$[M(H_2)H(dtfpe)_2]BF_4$ [221], for which the trend in acidity is 3d > 5d > 4d. The 4d metals may be the least acidic because they have the least hydride character or weakest $M–H_2$ interaction and strongest H–H bond (Sect. E.(ii)). An opposing factor is the high E_{pa} value for the Ru complex compared with the Fe and Os complexes. Other factors may be involved

TABLE 18

Reactions of dihydrogen complexes with external bases in organic solvents, and ranges of possible pK_a values (aqueous scale) for the complexes

Complex	Strong bases[a]	Weak bases[b]	$pK_a(M(H_2))$	Ref.
Group 6				
$M(H_2)(CO)_5$ (M = Cr, Mo, W)	HCO_3^-?	–	<7?	133
$W(H_2)(CO)_3(PCy_3)_2$	O^tBu^-	–	<19	316
$W(H_2)(CO)_3(P^iPr_3)_2$	O^tBu^-, KH	PCy_3, NEt_3	11–19	6,204,316
$W(H_2)(CO)_3(Pcyp_3)_2$	O^tBu^-	–	<19	316
$W(H_2)(CO)_3(P^iPrCy_2)_2$	O^tBu^-	–	<19	316
Group 7				
$[ReH_8L_2]^+$ (L = PPh_3, PCy_3, P^tBu_2Me)	NEt_3	–	<11	70
$[Re(H_2)H_4(cyttp)]^+$	NEt_3, $HCOO^-$ PMe_3,$MeCOO^-$	–	<4	16
$[Re(H_2)H_2(CO)(PMe_2Ph)_3]^+$	NEt_3	–	<11	68,317
$[ReH_6(triphos)]^+$	NEt_3	–	<11	318
$[Re(H_2)(CO)_2(PMe_2Ph)_3]^+$	NEt_3	–	<11	69
Group 8				
$[Fe(H_2)H(P(OEt)_3)_4]^+$	NEt_3	–	<11	74
$[Fe(H_2)H(PPh(OEt)_2)_4]^+$	NEt_3	–	<11	74
$Fe(H_2)H_2(PEtPh_2)_3$	O^tBu^-	–	<19	316
$[Ru(H_2)H(pp_3)]^+$	O^tBu^-	–	<19	81
$[Ru(H_2)H(dcpe)_2]^+$	OEt^-	–	<16	38
$[Ru(H_2)H(PPh(OEt)_2)_4]^+$	NEt_3	–	<11	76
$[Ru(H_2)H(P(OEt)_3)_4]^+$	NEt_3	–	<11	76
$[Ru(H_2)H(P(OMe)_3)_4]^+$	NEt_3	–	<11	76
$[Ru(H_2)Cp^*(CO)_2]^+$	Et_2O	–	<0?	59
$[L_2HReH_3(CO)Ru(H_2)L_2]^+$[c]	NEt_3	–	<11	207
$[L_2HReHCl_2(CO)Ru(H_2)L_2]^+$[c]	NEt_3	–	<11	207
$[OsH_5(PMe_2Ph)_3]^+$	NEt_3	–	<11	284
$[Os(H_2)H(PPh(OEt)_2)_4]^+$	NEt_3	–	<11	76
$[Os(H_2)H(P(OEt)_3)_4]^+$	NEt_3	–	<11	76
Os(H ··· H)(oep)(thf)	$N^iPr_2^-$	–	–	88
$[Os(H \cdots H)(NH_3)_5]^{2+}$	–	OMe^-	>15	93(a)
Group 9				
$[Ir(H_2)_2H_2(PCy_3)_2]^+$	NEt_3	–	<11	91,253
$[Ir(H_2)H_2(PMe_2Ph)_3]^+$	NEt_3	–	<11	199
$[Ir(H_2)H(bq)(PPh_3)_2]^+$	Me^-, Bu^-	–	–	91,168

[a] Bases strong enough to deprotonate the dihydrogen complex.

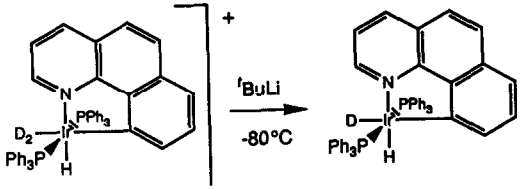
[b] Bases not strong enough to deprotonate the dihydrogen complex.

[c] L = PPh_3.

[231]. The scarcity of pK_a data for other series of dihydrogen complexes prevents us from determining whether the above trend in acidity is a general phenomenon.

(iii) Kinetic acidity

For reasons discussed in the previous section, the hydride and dihydrogen ligands in $[IrH(H_2)(bq)(PPh_3)_2]^+$ have equal Brønsted acidity. However, reactions with partially deuterated analogues of this complex (e.g. eqn. (70) [91]) show that the dihydrogen ligand is selectively deprotonated.



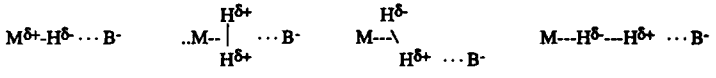
(70)

Another hydrido(dihydrogen) complex, *trans*-$[Ru(H_2)H(dppe)_2]^+$, was investigated by Bautista et al. [60]. At −80°C, BuLi deprotonated the dihydrogen ligand selectively, giving *trans*-$RuH_2(dppe)_2$, which isomerizes to the cis complex at higher temperatures. These two studies show that there is a kinetic selectivity for deprotonation of the dihydrogen ligand rather than the terminal hydride. In other words, the dihydrogen ligand has a greater kinetic acidity.

Other evidence suggests that the kinetic acidity of a dihydrogen complex is greater than that of its dihydride tautomer. This evidence includes the selective deprotonation of the dihydrogen tautomer in dihydrogen/dihydride pairs. For example, the reaction of NaOEt with a mixture of $[Ru(H_2)CpL]^+$ and $[Ru(H)_2CpL]^+$ (L = dtfpe, dppe, dape) at −60°C in acetone-d_6 results in rapid deprotonation of the dihydrogen complex, followed by slow deprotonation of the dihydride [148]. Chinn and Heinekey [205] reported the observation of rapid proton exchange between $[Ru(H_2)Cp(dmpe)]^+$ and RuHCp(dmpe) but not between $[Ru(H)_2Cp(dmpe)]^+$ and RuHCp(dmpe). This is evidence for a kinetic acidity difference, not a thermodynamic acidity difference, as had been suggested [2,61,205]. In fact, the dihydride $[Ru(H)_2Cp(dmpe)]^+$ is more acidic than the dihydrogen tautomer [220].

Why should dihydrogen complexes have greater kinetic acidity than classical hydrides of similar structure? The activation barrier for deprotonation of hydrides is primarily a result of the structural and electronic rearrangement [220]. Deprotonation of a dihydrogen complex requires very little rearrangement because there is no change in coordination number [148]. Formation of a hydrogen bonded pair between a hydride and an external base (**21**) is not normally possible because of the partial negative charge on the hydride [220]. A hydrogen-bonded pair could be formed as a transition state or even an unstable intermediate for a dihydrogen complex (**22**)

because of the lower electron density at the hydrogen atoms compared with classical hydrides, or because of distortion of the dihydrogen ligand to an unsymmetrical (**23**) or even η^1-bonded configuration (**24**).



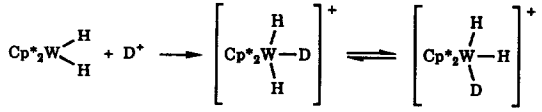
21 **22** **23** **24**

Further kinetic study is required to determine whether or not this type of hydrogen bonding occurs.

If the kinetic acidity of dihydrogen complexes is greater than that of classical hydrides, then application of the principle of microscopic reversibility requires that protonation of a metal hydride at the hydride, rather than at the metal, is the mechanism for the protonation reactions of at least some hydrides. There is evidence for this; in an equilibrium mixture of $[Ru(H_2)Cp(dmpe)]^+$, $[Ru(H)_2Cp(dmpe)]^+$ and RuHCp(dmpe), saturation of the ^1H NMR signal of the Cp protons of the neutral complex results in saturation transfer to the dihydrogen complex only [84]. Protonation of $RuHL(PPh_3)_2$ (L = Cp, Cp*) at 195 K produces $[Ru(H_2)L(PPh_3)_2]^+$ exclusively, which is converted upon warming to $[Ru(H)_2L(PPh_3)_2]^+$ [84]. Similar results were obtained with the complexes RuHCp*(dppp) [148], FeHCp*(dppe) [232] and $RuHCpL_2$ (L_2 = dppe, dtfpe, dape [148], depe, dmdppe, and R-prophos [84]); in some of these cases, the thermodynamic product is a mixture of the two tautomers.

A counter-example is the case of $RuHCp^*(PMePh_2)_2$, which, when protonated at −60°C, produces $[Ru(H)_2Cp^*(PMePh_2)_2]^+$. Similarly, protonation of RuHCp*(dppm) produces a mixture of the tautomers [148]. It is possible that $[Ru(H_2)Cp^*L_2]^+$ is the kinetic product even in these two cases, and that the homolytic cleavage reaction is rapid (not likely at this temperature) or that an error in the experiment caused a temporary warming of the solution, a possibility suggested in the report [148].

A dihydrogen complex can be inferred as the intermediate in the protonation of $W(H)_2Cp^*_2$ because of the results of labelling studies (eqn. (71) [162]).



(71)

The observed kinetic product is $[W(H)(D)(H)Cp^*_2]^+$, which partially isomerizes to $[W(H)(H)(D)Cp^*_2]^+$. Because the lone pair, which corresponds to the HOMO of $WH_2Cp^*_2$, is lateral to the two hydrides, protonation by D^+ at the metal would be expected to produce $[W(H)(H)(D)Cp^*_2]^+$. Therefore, protonation at either one or both hydrides is indicated, giving either $[W(H)(\eta^2\text{-}DH)Cp^*_2]^+$ or

$[W(\eta^3\text{-HDH})Cp^*_2]^+$ as the intermediate [162]. There is as yet no precedent for an η^3-H_3 ligand, although there has been considerable speculation (Sect. C.(ii)).

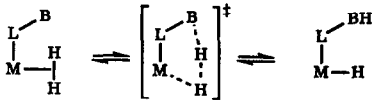
There is therefore evidence for protonation of hydrides at the hydride rather than at the metal for several systems. This may be a favorable mechanism, particularly if the product of protonation is a dihydrogen complex or a classical polyhydride close in energy to its non-classical tautomer. This is a necessary conclusion from the observation of the greater kinetic acidity of dihydrogen ligands compared to terminal hydrides.

(iv) Mechanisms of intramolecular heterolytic cleavage: protonation of ligand lone pairs

Intramolecular heterolytic cleavage of a dihydrogen ligand (eqn. (41)) results in protonation of a basic ligand, either at the metal–ligand bond or at a ligand lone pair. Oxidative addition of H_2 gas or an η^2-H_2 ligand to a metal center could be viewed as a protonation by η^2-H_2 of a metal lone pair [192]. Mechanisms of protonation of a ligand lone pair are the following.

(a) Direct proton transfer

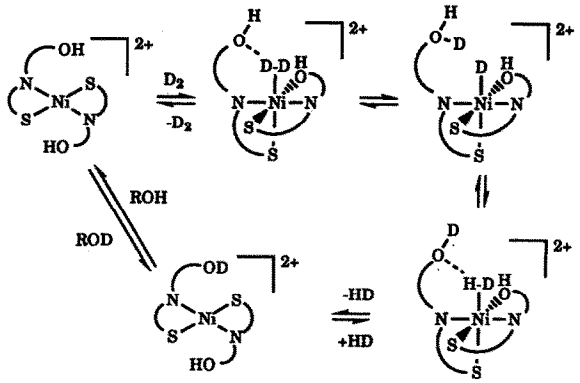
If the basic site on the ancillary ligand is near to the dihydrogen ligand (i.e. a lone pair on the metal-bound atom or on another atom proximate to the dihydrogen ligand), then the mechanism could be direct intramolecular proton transfer



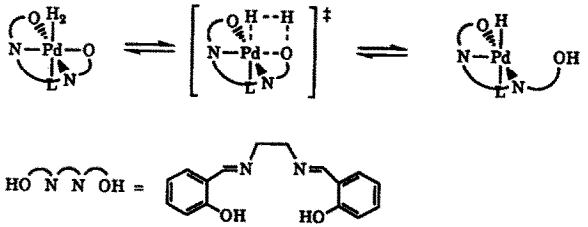
(72)

where B is a basic site on ligand L. Such a reaction could be a step in the catalysis of H/D exchange between D_2 and ethanol by the square planar Ni complex $[NiL_2]Cl_2$ ($L = o\text{-}C_6H_4(OH)CH{=}N{-}NHCSNH_2$) (Scheme 2). Zimmer et al. [233] proposed intramolecular exchange between a D_2 ligand and the dangling OH group as a step in the mechanism. We show a possible complete cycle for this catalysis (Scheme 2). The last step, exchange of the dangling OD group with free alcohol, could be acid-catalyzed; Zimmer et al. reported that the exchange was promoted by added acid.

Before the advent of known dihydrogen complexes, Brothers [234] proposed a dihydrogen complex as a step in the catalytic hydrogenation of olefins by Pd(salen). This step provides the empty site cis to hydride required before olefin coordination and insertion.



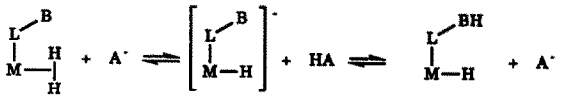
Scheme 2.



(73)

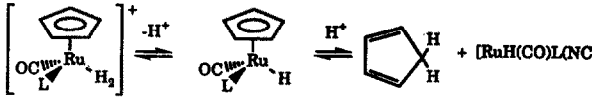
(b) External base catalysis

The second mechanism for protonation at a ligand lone pair is external base catalysis (eqn. (74), B = basic site, A^- = external base), which allows protonation at any lone pair, regardless of its distance from the dihydrogen ligand. It is also a viable mechanism for protonation of the metal–ligand bond or the metal center itself. Although it may be difficult to determine which site on the complex is protonated, it is easy to prove that the mechanism is operating; the rate should increase in basic solution.



(74)

Ryan et al. [149,235] report an example. The rate of loss of cyclopentadiene from $[Ru(H_2)Cp(CO)L]^+$ (L = PPh_3 or PMe_3, eqn. (75)) was increased by addition of an external base such as the conjugate base RuHCp(CO)L, and decreased by addition of excess $HBF_4 \cdot Et_2O$. The immediate product of protonation of RuHCp(CO)L is not known, but could be the trans dihydride $[Ru(H)_2Cp(CO)L]^+$ (protonation at the metal), or $[RuH(C_5H_6)(CO)L(MeCN)]^+$ (protonation at the ring). There is little precedent for the latter. The dihydride intermediate could lose C_5H_6 by ring slippage



(75)

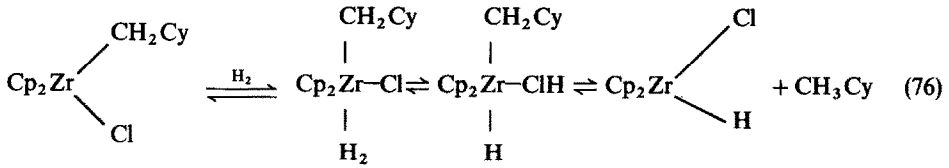
to $[Ru(H)_2(\eta^1\text{-}C_5H_5)(CO)L(MeCN)_2]^+$ followed by reductive elimination, or by proton transfer to the ring from one of the hydrides.

(v) Mechanisms of intramolecular heterolytic cleavage: protonation of the metal–ligand bond

Ancillary ligands with no lone pairs, such as hydride, alkyl or silyl groups, can be protonated at the metal–ligand bond. Possible mechanisms include external base catalysis, internal base catalysis, oxidative addition, and σ bond metathesis. Aspects of these mechanisms have already been discussed in the section on H atom exchange (Sect. C). Each of these mechanisms will be defined and discussed in the section below, with the exception of external-base catalysis, which was described in Sect. D.(iv) above. The examples shown below are from η^2-H_2 chemistry as well as studies of hydrogenolysis of M–X bonds, whether or not there are indications of an η^2-H_2 type intermediate. The hydrogenolysis examples are included for two reasons: further study may show that some of them do, in fact, involve η^2-H_2 intermediates, and the nature of and effects on the activated complexes for heterolytic cleavage may be independent of the prior formation of an η^2-H_2 intermediate. However, a comprehensive review of hydrogenolysis is not within the scope of this review.

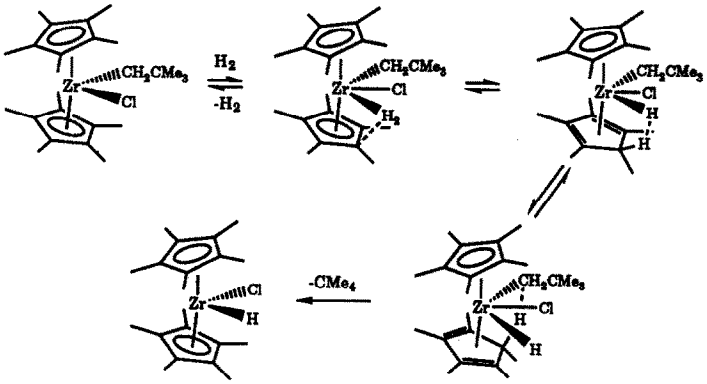
(a) Internal base catalysis mechanism

This mechanism consists of two or more sequential intramolecular heterolytic cleavage steps. For example, the postulated mechanism for hydrogenolysis of $ZrCp_2Cl(CH_2Cy)$ involves protonation of the chloride, which in turn protonates the alkyl ligand [192].



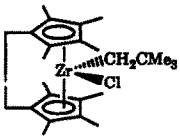
(76)

Wochner and Brintzinger [236] showed that the rate of hydrogenolysis of $ZrCp^*_2Cl(CH_2CMe_3)$ was 24 times faster than the Cp derivative, and suggested that the greater Brønsted basicity of pentamethylcyclopentadienyl ligands allowed rapid hydrogenolysis by a ring-mediated internal base catalysis mechanism (eqn. (77)). Strong supporting evidence is the lack of reaction in the ethylene-bridged analogue



(77)

$Zr\{C_2H_4(C_5Me_4)_2\}Cl(CH_2CMe_3)$ (**25**), due to the prevention by the bridge of the ring-rotation step in the above mechanism.



25

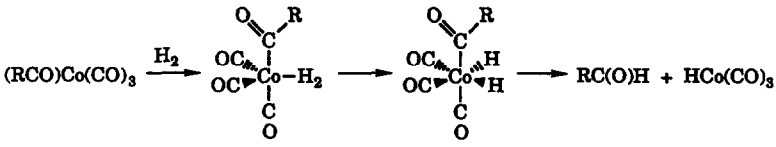
The hydrogenolysis of $ZrCp^*_2Cl(CH_2CMe_3)$ (eqn. (76)) exhibited an inverse isotope effect of $k_{H_2}/k_{D_2} = 0.85$. This effect could result from a preequilibrium which favors the η^2-D_2 intermediate (η^2-D_2 coordination is favored over η^2-H_2 coordination at some temperatures (Sect. E.(ii)). The inverse isotope effect is not evidence for or against the internal base catalysis mechanism.

(b) The oxidative addition mechanism

This mechanism (eqn. (78)) requires an oxidizable electron-rich metal center, making it impossible for d^0 metals and unlikely for metals in high oxidation states [234], and many of the lanthanides and actinides [237]. Oxidative addition is favored by a basic metal center or basic ancillary ligands. Heterolytic cleavage of H_2 is not involved in the mechanism, but the overall reaction involves formal heterolytic cleavage. Therefore the products (and possibly the kinetics) are indistinguishable from those of other mechanisms for heterolytic cleavage.

$$\begin{array}{cccccc} & H & & H & & H \\ & | & & | & & | \\ M{-}H_2 & \rightleftharpoons & M{-}H & \rightleftharpoons & M & \rightleftharpoons & M + RH \\ | & & | & & | & & \\ R & & R & & RH & & \end{array} \qquad (78)$$

This mechanism was suggested by Orchin and Rupilius [164], well before the discovery of stable η^2-H_2 complexes, for the hydrogenolysis of acyl cobalt carbonyls (eqn. (79)) during hydroformylation of olefins.



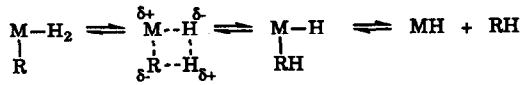
(79)

Heck and Breslow [238] had earlier suggested the same mechanism but without the dihydrogen intermediate. The approximate density functional calculations of Versluis and Ziegler [239] supported the suggestion that the more stable product of H_2 addition to $Co(CO)_3(C(O)R)$ is the η^2-H_2 complex, rather than the dihydride, and compared the oxidative addition (eqns. (78) and (79)) and four-center transition state (eqn. (80), below) mechanisms. The result showed that the two mechanisms have similar energies of activation although the oxidative addition reaction might be favored if the electron density at the metal center were increased by substitution of a carbonyl by a phosphine.

The kinetic isotope effect (k_{H_2}/k_{D_2}) of oxidative addition of H_2 to *trans*-IrCl(CO)$(PPh_3)_2$ in toluene is 1.06 to 1.22 [156,240]. The isotope effect for the oxidative addition mechanism may be comparable. As will be discussed below, this is also within the range possible for a four-center transition state mechanism.

(c) Four-center transition state mechanism

The expression "σ bond metathesis" was coined by Thompson et al. [172] to refer to a concerted mechanism with a four-center activated complex involving cleavage of H–H or C–H bonds (e.g. eqn. (80)). The mechanism is analogous to that of olefin metathesis.



(80)

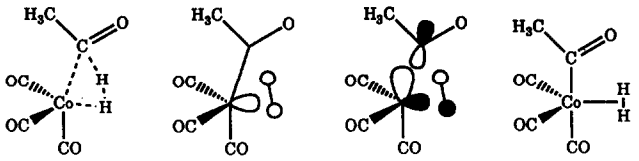
The term σ bond metathesis should properly be reserved for d^0 metals with alkyl, hydride, or related σ bonding ligands. For the other metals, we prefer the expression "four-center transition state mechanism". Obviously, a cis arrangement of the H_2 and X ligands is required. The structure of the four-center transition state has been discussed in Sect. C.(ii).

Brothers [234] suggests that the four-center transition state mechanism would be favored in a polar solvent because the activated complex involves charge separation (as shown in eqn. (80)). Increased rates in polar solvents were interpreted by Lin and Marks [237] as support for a four-center transition state mechanism for hydro-

genolysis of $UCp^*_2(Me)(OCH^tBu_2)$, although they note that oxidative addition of H_2 to *trans*-$IrCl(CO)(PPh_3)_2$ [240] is also faster in polar solvents. Thompson [172] suggests that there may be little charge separation in the four-center transition state.

A kinetic isotope effect is observed (e.g. k_{H_2}/k_{D_2} of 1.64 and 2.5 for hydrogenolysis of *n*-octyllithium [241] and $ThCp^*_2(CH_2{}^tBu)(O^tBu)$ [237], respectively). These values are greater than 1, possibly because there may be greater H–H bond stretching in the four-center transition state [237]. Folga et al. [242] calculated by approximate density functional theory that the kinetic isotope effect k_{HH}/k_{HD} of the model reaction of Cl_2LuH with H_2 or HD (cf. eqn. (82), below, M = Lu) is less than 1 at lower temperatures and greater than 1 at higher temperatures. The reasons are $\Delta S^{\ddagger}(HH) > \Delta S^{\ddagger}(HD)$ because of the greater rotational entropy of free HD compared with H_2, and $\Delta H^{\ddagger}(HH) > \Delta H^{\ddagger}(HD)$ because the zero-point energy in $[Cl_2LuH_2D]^{\ddagger}$ is lower than that in the non-deuterated analogue.

Both of the bonding interactions in an η^2-H_2 complex ($M \leftarrow H_2$ σ donation and $M \rightarrow H_2$ π backdonation) lower the energy of the η^2-H_2 intermediate or transient which precedes the four-center transition state. If similar σ and π bonding is present in the transition state, then the electronic and steric factors which influence the strengths of η^2-H_2 bonding would be expected to affect the energy of the transition state similarly. However, while the $M \leftarrow H_2$ σ donation is the same in the transition state, the $M \rightarrow H_2$ π backdonation is not. The calculations of Versluis and Ziegler [239] show that the four-center transition state for the hydrogenolysis of $Co(CO)_3(C(O)CH_3)$ (structure **26**, see eqn. (79)) has both an $M(\sigma, LUMO) \leftarrow H_2$ σ donation (**27**) and an $M \rightarrow H_2(\sigma^*)$ π backdonation (**28**). Note that the π backbonding orbital on the metal is not the $d_{x^2-y^2}$ orbital which was responsible for the π backdonation in the dihydrogen complex (**29**) but rather the metal-acyl bonding MO.

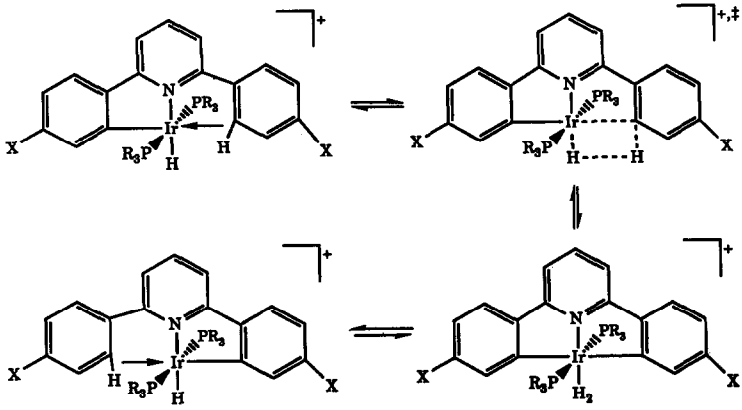


26 **27** **28** **29**

Electronic and steric factors inhibiting the $M(\sigma, LUMO) \leftarrow H_2$ σ donation may be responsible for the different rates of hydrogenolysis of the Zr–R bond in $Cp_2Zr(R)(X)$ complexes. The slower rate observed for X = Cl compared with H may result from partial donation of electron density from Cl to the LUMO by pπ overlap. The failure of the complex with X = η^2-acyl to react is attributed to occupation of the vacant site at the LUMO by the carbonyl oxygen [192]. The rate of hydrogenolysis of these compounds also depends on the energy of the LUMO; if it is too high, the donation from the H_2 is weakened and the activation energy is too high for rapid hydrogenolysis [243]. The LUMO must be sterically accessible (ref. 243 and

references cited therein). The location of the LUMO can determine the site of H_2 attack [200].

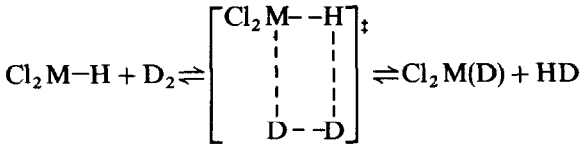
The strength of the π backbonding interaction is also expected to affect the activation barrier. Increased electron density in the M–R σ bonding MO (e.g. in eqn. (80) or structure **28**) should strengthen this interaction. Therefore σ donating ancillary ligands could lower the activation barrier and increase the rate of the four-center transition state mechanism, although we suggest that the increase in the strength of the M–X bond could actually raise the activation barrier. There is little evidence either way [243]. A possible example is the dynamic equilibrium observed by Albeniz et al. [244] and shown in eqn. (81) as a four-center transition state mechanism, although other mechanisms were not ruled out and there was no direct evidence of a dihydrogen intermediate. They observed that the equilibrium with X = H is faster if $L = P^nBu_3$ or PPh_2Me than if $L = P(Aryl)_3$. This could be an example of a four-center transition state of lowered energy because of stronger σ basic ancillary ligands.



(81)

For the case of $L = PPh_3$ and $X = CH_3$, the $\Delta G^{\ddagger}$ value for eqn. (81) was 12.3 kcal mol^{-1} at 257 K.

Steigerwald and Goddard [245] showed by Hartree–Fock gradient optimization of the geometry and bonding for the transition state of the equation



(82)

where M = Ti(III), Sc(III) or $[Ti(IV)]^+$ that the principal MOs of the transition state were two orthogonal delocalized three-center bonds (one H–M–D and the other H–D–D), which can only be formed from d orbitals. They suggest therefore that

M–R (eqn. (80)) bonds with low d character would not have this delocalization in the transition state and therefore would be less easily metathesized because of the greater activation energy. For example, the greatest rate for eqn. (82) was observed for $[TiHCl_2]^+$, which they attributed to the high d character of the Ti–H bond in this complex (~90%) compared with the Sc(III) and Ti(III) complexes (50–70%). Other factors which lowered the energy of the $[TiH_3Cl_2]^+$ transition state compared with the isoelectronic ScH_3Cl_2 were the greater electronegativity of Ti, which encouraged a greater donation from H_2 to the $[TiHCl_2]^+$ fragment in the transition state, and a weaker M–H bond in $[TiHCl_2]^+$ compared with ScH_3Cl_2.

As mentioned previously, hydrogenolysis of metal alkyl complexes can occur with or without an η^2-H_2 intermediate. For example, Lin and Marks [237] used chemical shift methods to show that $UCp^*_2(Me)(OCH^tBu_2)$ does not coordinate H_2 to any significant extent (<0.001%). With the support of theoretical calculations, they proposed a four-center transition state mechanism without an η^2-H_2 intermediate for the hydrogenolysis of the U–OR bond.

(vi) Thermodynamics of intramolecular heterolytic cleavage

In the vast majority of cases, protonation by an η^2-H_2 ligand of a metal–ligand (M–L) bonding pair or a lone pair on a metal-bound atom is followed by elimination of HL. The free acid is often a thermodynamic sink: the reaction is irreversible. There are no stoichiometric examples of the reverse reaction, the synthesis of an η^2-H_2 complex by intramolecular protonation of a hydride by a bound acid.

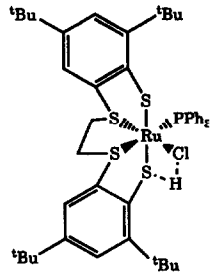
If protonation of a ligand does not result in elimination of the protonated ligand, the equilibrium between the two tautomers

$$M(H_2)(L) \rightleftharpoons M(H)(HL) \tag{83}$$

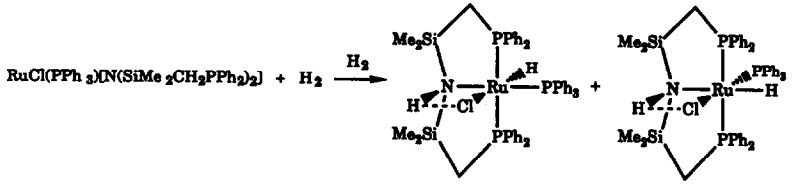
depends on the relative acidities of the ligands H_2 and HL. We have seen that prediction of η^2-H_2 acidities is difficult. Even less is known about the pK_a values of bound acids (HL) other than water. The pK_a is usually decreased rather than increased upon coordination because the M–L bonding is primarily M ← L σ donation. The decrease will be lessened if (a) there are one or more atoms between the metal and the acidic proton (e.g. eqn. (72)), (b) there is significant M → L backbonding, or (c) if the proton on the ligand is hydrogen bonded to neighbouring basic ligands (e.g. complex **30** [246]). A clear example of such a complex, which results directly from protonation by an η^2-H_2 ligand, is lacking. Gusev et al. [158] proposed

$$IrH(H_2)Cl_2(P^iPr_3)_2 \rightleftharpoons IrH_2Cl(HCl)(P^iPr_3)_2 \tag{84}$$

with hydrogen bonding between the HCl and Cl ligands, but later unpublished results showed that the structure assignment of the product was incorrect [159]. Fryzuk et al. [247] have a stronger case for their suggestion that intramolecular hydrogen bonding is the driving force for reaction (85).



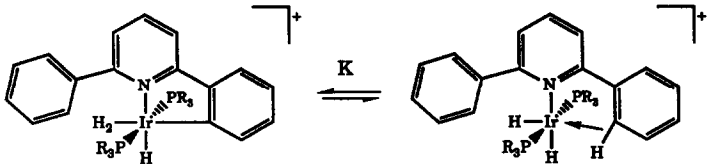
30



(85)

There is no direct evidence for a dihydrogen intermediate in eqn. (85). The proposal for hydrogen bonding in the product stems from an analogy to the crystallographically characterized orthometallated complex $RuCl(C_6H_4PPh_2)[NH(SiMe_2CH_2PPh_2)_2]$, which has an H—Cl separation of 2.55 Å.

Albeniz et al. [244] observed that equilibrium (86) depends on the choice of phosphine.



(86)

The equilibrium lies to the left for basic phosphines (P^nBu_3 and PPh_2Me) but to the right for acidic phosphines ($PArYl_3$). Albeniz et al. suggested that this trend results from the preference of the basic metal in the P^nBu_3 complex for oxidative addition of the more electron-withdrawing aryl group. For the $P(C_6H_4\text{-}p\text{-}CH_3)_3$ complex, the ΔH and ΔS were 1.6 ± 0.4 kcal mol^{-1} and 8 ± 2 kcal mol^{-1} K^{-1}. The positive entropy was attributed to "the greater freedom of motion of the agostic acyl group (in the product) compared to the Ir—Aryl bond (of the reactant)" [244]. The small ΔH indicates that the agostic and dihydrogen ligands have similar binding strengths.

Equilibria of the type shown in eqn. (83) are steps in the postulated mechanism for H/D exchange between D_2 gas and the NH_3 ligands of $IrH(Cl)(NH_3)_2$-

$(PEt_3)_2]PF_6$ (eqn. (87) [248]) and between D_2O and the hydride ligand of $[IrH(H_2O)(bq)L_2]^+$ (L = PCy_3, PPh_3, eqn. (88) [91]).

$$Ir(H)(NH_3) \rightleftharpoons Ir(H_2)(NH_2) \overset{D_2}{\rightleftharpoons} Ir(D_2)(NH_2) \rightleftharpoons Ir(D)(NH_2D) \quad (87)$$

$$Ir(H)(H_2O) \overset{D_2O}{\rightleftharpoons} Ir(H)(D_2O) \rightleftharpoons Ir(HD)(OD) \rightleftharpoons Ir(D)(HOD) \quad (88)$$

E. LOSS OR SUBSTITUTION OF THE DIHYDROGEN LIGAND

(i) Types of reaction

By far the largest number of observed reactions of dihydrogen complexes involve elimination of H_2 because of the weak binding of the H_2 ligand to the metal. Types of reaction in this class are simple elimination, substitution, substitution followed by insertion, ligand exchange, and elimination followed by dimerization. These are discussed below, with examples.

(a) Elimination

Simple elimination from dihydrogen complexes is the first step in most of these reactions, but the immediate product is only observed in the absence of other potentially coordinating reagents (e.g. eqn. (89) [249]).

$$Mo(H_2)(CO)_3(PCy_3)_2 \rightleftharpoons Mo(CO)_3(PCy_3)_2 + H_2 \quad (89)$$

The stability of dihydrogen complexes with respect to this reaction (Table 19; entries are listed by metal, and then by decreasing number of hydride ligands per metal) depends on the number of factors which will be discussed in Sect. E.(ii). A few examples of photochemical dissociation of H_2 from dihydrogen complexes have been reported. These involve complexes $Mo(H_2)HCp(CO)_2$ [52], $Cr(H_2)(CO)_5$ [214], and $Ni(H_2)(CO)_3$ [56]. Veillard suggests that, for the last two complexes, dissociation occurs by donation of an electron into the $M(H_2)$ antibonding orbital, creating a dissociative low-lying excited state [139].

(b) Substitution

Table 20 lists the dihydrogen complexes which have been observed to react by substitution. The most common strongly binding ligands used are CO, phosphines, amines and nitriles. Other ligands include N_2, O_2, D_2, water, alkenes and alkynes (e.g. eqn. (90) [250]).

$$[Fe(H_2)H(pp_3)]^+ + N_2 \rightleftharpoons [Fe(N_2)H(pp_3)]^+ + H_2 \quad (90)$$

where $pp_3 = P(CH_2CH_2PPh_2)_3$.

Whether or not N_2 is a more strongly binding ligand than H_2 depends on the

TABLE 19
Stability of dihydrogen complexes

Complex	ν(NN)	J(HD)	Solid state stability[a]			Solution stability[a]		Ref.
			Argon	Vacuum	Air	Heat	Argon	
Group 6								
$Cr(H_2)(CO)_3(PCy_3)_2$	2128	–	sw	un	un	un	un	33,108,268
$Mo(H_2)(CO)(dppe)_2$	2120	34	sw	un	un	un	un	34,145,319
$Mo(H_2)(CO)_3(PCy_3)_2$	2159	–	sw	un	un	un	un	1,17,33,6,146,249
$Mo(H_2)(CO)_3(PCy_2{}^iPr)_2$	–	–	sw	un	un	un	un	146,249
$W(H_2)(CO)_3(PCy_3)_2$	2113	–	sw	un	un	un	un	1,17,33,6,146,249
$W(H_2)(CO)_3(PCy_2{}^iPr)_2$	–	–	sw	un	un	un	un	6,146,249
$W(H_2)(CO)_3(P^iPr_3)_2$	–	33.5	sw	un	un	un	un	1,6,146,249
$W(H_2)(CO)_3(PCyp_3)_2$	–	–	sw	un	un	un	un	146
Group 7								
$[Re(H_2)H_4(cyttp)]^+$	–	–	st	st	st	un	–	16,264
$[Re(H_2)H_2(CO)(PMe_2Ph)_3]^+$	–	34	–	–	–	un	un	68,317
$[Re(H_2)(CO)_2(PMe_2Ph)_3]^+$	–	31	–	–	–	un	un	69
Group 8								
$Fe(H_2)H_2(PEtPh_2)_3$	2043	–	–	–	un	–	un	8,320
$[Fe(H_2)H(PhP(OEt)_2)_4]^+$	–	–	st	–	st	sw	st	74,270
$[Fe(H_2)H(pp_3)]^+$	2100	28.3	st	st	st	st	st	64,184,321
$[Fe(H_2)H(meso\text{-}tetraphos)]^+$	2130	32.3	–	–	–	–	un	72,322
$[Fe(H_2)H(P(OEt)_3)_4]^+$	–	–	st	–	–	sw	st	74
$[Fe(H_2)H(dmpe)_2]^+$	2094	31	–	–	un	un?	–	71,255,257
$[Fe(H_2)H(depe)_2]^+$	2090	29.5	st	st	un	un	st	60,275,321
$[Fe(H_2)H(dppe)_2]^+$	2120	30	st	st	un	st	st	14,60
$[Fe(H_2)Cl(depe)_2]^+$	–	–	–	–	–	–	un	61

TABLE 19 (*continued*)

Complex	ν(NN)	J(HD)	Solid state stability[a]			Solution stability[a]		Ref.
			Argon	Vacuum	Air	Heat	Argon	
$Ru(H_2)_2H_2(PCy_3)_2$	–	–	–	–	–	un	–	94
$Ru(H_2)H_2(cyttp)$	2100	–	st	st	–	–	–	195
$Ru(H_2)H_2(PPh_3)_3$	2147	~16	–	–	–	un	un	323,324
$[Ru(H_2)H(dcpe)_2]^+$	–	31.5	un	un	–	un	un	38
$[Ru(H_2)H(pp_3)]^+$	2182	29.7	st	st	–	–	–	81
$[Ru(H_2)H(PPh(OEt)_2)_4]^+$	–	32	st	–	st	sw	st	76,270
$[Ru(H_2)H(P(OMe)_3)_4]^+$	–	31	un	–	–	–	–	76
$[Ru(H_2)H(P(OEt)_3)_4]^+$	–	–	un	–	–	–	–	76
$[Ru(H_2)H(binap)_2]^+$	–	30	un	un	–	–	–	79
$[Ru(H_2)H(dppe)_2]^+$	2194	32	un	un	un	un	un	14,60
$[Ru(H_2)H(depe)_2]^+$	2163	32	st	–	un	un	st	60,275,321
$[Ru(H_2)Cl(depe)_2]^+$	–	–	–	–	–	–	sw	61
$[Ru(H_2)Cp(PPh_3)(CNtBu)]^+$	–	28.6	–	–	–	–	sw	82
$[Ru(H_2)Cp(CO)(PCy_3)]^+$	–	–	–	–	–	–	un	190
$[Ru(H_2)Cp(CO)(PPh_3)]^+$	–	–	–	–	–	un	un	84
$[Ru(H_2)Cp(CO)(PMe_3)]^+$	–	28.5	–	–	–	un	un	84
$[Ru(H_2)Cp(CO)(PMe_2Ph)]^+$	–	–	–	–	–	un	un	84
$[Ru(H_2)Cp(dmpe)]^+$	–	22.1	st	st	–	–	st	84,205
$Ru_2(\mu H_2)(dpb)(L)$	–	15	–	–	–	un	–	166
$Ru_2(H_2)(dppb)_2(\mu Cl)_3Cl$	2175	29.4	–	–	–	–	un	37
$Ru_2H_4Cl_2(Ptol_3)_4$	–	–	–	–	–	–	un	208
$[Os(H_2)H_3(PMe_2Ph)_3]^+$[b]	–	–	–	–	–	–	st	121,284
$[Os(H\cdots H)H(depe)_2]^+$	2136	11	st	st	st	st	st	60,275,321
$[Os(H_2)H(dppe)_2]^+$	–	26	st	st	sw	st	st	60

$[Os(H_2)H(PPh(OEt)_2)_4]^+$	–	–	st	–	st	sw	st	76,270
$[Os(H_2)H(P(OEt)_3)_4]^+$	–	–	st	–	–	st	st	76
$Os(H_2)H(Cl)(CO)(P^iPr_3)_2$	–	–	–	–	–	–	un	36
$[Os(H\cdots H)Cl(depe)_2]^+$	–	–	st	–	–	–	sw	325
$[Os(H\cdots H)Cl(dppe)_2]^+$	–	–	st	–	sw	–	sw	61,325
Group 9								
$[Co(H_2)(P(CH_2CH_2PPh_2)_3)$	2125	27.8	st	–	–	–	st	89
$Rh(H_2)H_2(HB(3,5\text{-}Me_2pz)_3)$	–	28[c]	st	–	–	–	sw	67
$[Rh(H_2)(P(CH_2CH_2PPh_2)_3)]^+$	–	18	–	–	–	–	un	39
$[Ir(H_2)_2H_2(PCy_3)_2]^+$	–	–	un	–	–	–	–	253
$Ir(H_2)H_2Cl(P^iPr_3)_2$	–	–	un	–		–	un	42
$[Ir(H_2)H(PPh_3)_2(diphpyH)]^+$	–	–	–	–	–	–	un	244

[a] st = stable, un = unstable, sw = slow loss or decomposition.

[b] Could be $[Os(H)_5L_3]^+$.

[c] Calculated for the case of no-exchange; see Sect. C.(iii)(d).

TABLE 20
Substitution reactions of dihydrogen complexes

Complex	Reagent	Ref.
Group 6		
$Cr(H_2)(CO)_5$	N_2, CO, D_2	46,214
$Cr(H_2)(CO)_3(PCy_3)_2$	N_2	57
$Cr(H_2)_2(CO)_4$	N_2, CO	46
$Cr(H_2)(CO)_4$(t-cyclooctene)	N_2	50
$Cr(H_2)(CO)_2(C_6H_5Me)$	CO	103
$Mo(H_2)(CO)(dppe)_2$	N_2	34
fac-$Mo(H_2)(CO)_3$(nbd)	N_2	51
$W(H_2)(CO)_3$(t-cyclooctene)$_2$	N_2	50
$W(H_2)(CO)_3(PCy_3)_2$	py	147
$W(H_2)(CO)_3(P^iPr_3)_2$	H_2O, N_2	204,269
$W(H_2)(CO)_3(PCyp_3)_2$	N_2	146
Group 7		
$Mn(H_2)Cp(CO)_2$	N_2	53,103
$Re(H\cdots H)Cl(PMePh_2)_4$	N_2, CO, HD	92
$[Re(H_2)Cp^*(CO)(NO)]^+$	$OSO_2CF_3^-$	59
Group 8		
$Fe(H_2)H_2(PEt_2Ph)_3$	N_2	65,320
$Fe(H_2)H_2(PEtPh_2)_3$	N_2	65
$[Fe(H_2)H(PhP(OEt)_2)_4]^+$	D_2, CO, RCN, RNC, PR_3	74,270
$[Fe(H_2)H(depe)_2]^+$	N_2, D_2	60,275
$[Fe(H_2)H(P(OEt)_3)_4]^+$	D_2, CO, RCN, RNC, PR_3	74
$[Fe(H_2)H(pp_3)]^+$	N_2, MeCN	64,184
$[Fe(H_2)H(dppe)_2]^+$	N_2, CO, MeCN	14
$[Fe(H_2)H(dmpe)_2]^+$	N_2, CO, MeNC, C_2H_4, $CCPh^-$, PR_3, Cl^-, SR^-	71,211,213,257,326
$Fe(H_2)(CO)_2(C_4H_4)$	CO	103
$Fe(H_2)(CO)(NO)_2$	D_2	54
$Ru(H\cdots H)H_2(PPh_3)_3$	N_2, D_2, CO, PR_3, RC(O)R	196,296,324
$Ru(H_2)H_2$(Cyttp)	N_2, D_2, CO, CNR, $P(OR)_3$	195,327
$Ru(H_2)HI(PCy_3)_2$	D_2	11
$[Ru(H_2)H(PPh(OEt)_2)_4]^+$	CO, CNR, RCN, PR_3	76,270
$[Ru(H_2)H(P(OMe)_3)_4]^+$	D_2, CO, CNR, PR_3	76
$[Ru(H_2)H(dppe)_2]^+$	D_2, CO, MeCN	14,60
$[Ru(H_2)H(depe)_2]^+$	D_2	60
$[Ru(H_2)H(pp_3)]^+$	D_2, CO, MeCN, PR_3, SO_2, dmso	81
$[Ru(H_2)H(P(OEt)_3)_4]^+$	D_2	76
$[Ru(H_2)Cl(dcpe)_2]^+$	CO	38
$Ru(H_2)$(oep)(thf)	thf	88
$[Ru(H_2)Cp(dmpe)]^+$	MeCN	205

TABLE 20 (*continued*)

Complex	Reagent	Ref.
$[Ru(H_2)Cp(PPh_3)(CN^tBu)]^+$	CO, RI	82,328
$Ru_2(H_2)(dpb)L_2$[a]	D_2, N_2, 2py	88(b),166
$Ru_2(H_2)(H)_4(PCy_3)_4$	N_2	94
$Ru_2(H_2)Cl_4(dppb)_2$	N_2	37
$Ru_2(H_2)(H)_4(PPh_3)_4$	N_2	94
$[OsH_5(PMe_2Ph)_3]^+$	D_2, CO, olefins	87
$[Os(H_2)H(PPh(OEt)_2)_4]^+$	CO, CNR, RCN, PR_3	76,270
$[Os(H_2)H(P(OEt)_3)_4]^+$	CO, CNR, PR_3	76
$[Os(H\cdots H)H(dppe)_2]^+$	CO, RCN, PR_3, $P(OR)_3$, Cl^-, SR^-, MeIm	29,325
$[Os(H\cdots H)H(depe)_2]^+$	D_2, CO, Cl^-, RCN	29,60,325
$Os(H_2)H(Cl)(CO)(P^iPr_3)_2$	O_2	36
Group 9		
$Co(H_2)(CO)_2(NO)$	N_2, D_2	54
$[Co(H_2)(pp_3)]^+$	Cl^-, PR_3[b]	120
$[Rh(H_2)(pp_3)]^+$	D_2, C_2H_4, PR_3, thf	39,120
$[Ir(H_2)_2H_2(PCy_3)_2]^+$	MeCN	91,253
$[Ir(H_2)H_2(PMe_2Ph)_3]^+$	D_2, CO, MeCN, thf, C_2H_4, MeCCMe	90,199,295
$Ir(H_2)HCl_2(P^iPr_3)_2$	CO, MeCN, py	107
$[Ir(H_2)H(bq)(PPh_3)_2]^+$	D_2, H_2O, ROH	168,190
Group 10		
$Ni(H_2)(CO)_3$	CO	56

[a] L = 1-*tert*-butyl-5-phenylimidazole.
[b] By treatment with $[Au(PEt_3)]^+$ or $Au(PEt_3)Cl$, respectively.

complex and the temperature. For $M(X_2)(CO)_3(PCy_3)_2$, H_2 binding is weaker than N_2 binding for M = Mo or W, but the opposite is true for the Cr complex [33]. In general, $M(H_2)$ binding will be stronger than $M(N_2)$ binding at higher temperatures because of the lower entropy of free H_2 compared with N_2 (Sect. E.(ii)).

Dioxygen is not expected to bind strongly to a vacated η^2-H_2 site because the electron-deficient metal centers of dihydrogen complexes are usually not easily oxidized. The only example of substitution by O_2 is the irreversible reaction of $Os(H_2)HCl(CO)(P^iPr_3)_2$ with O_2 to produce $Os(O_2)HCl(CO)(P^iPr_3)_2$ [36]. Substitution of H_2 by D_2 may occur with or without H/D scrambling (Sect. C).

Dihydrogen complexes with potentially chelating ligands are unstable with respect to H_2 loss because the dangling end of the ligand may occupy the site liberated by H_2 elimination [251].

$$Ir(D_2)(H)_2(\eta^1\text{-}OCOCF_3)(PPh_3)_2 \rightleftharpoons Ir(H)_2(\eta^2\text{-}OCOCF_3)(PPh_3)_2 + D_2 \quad (91)$$

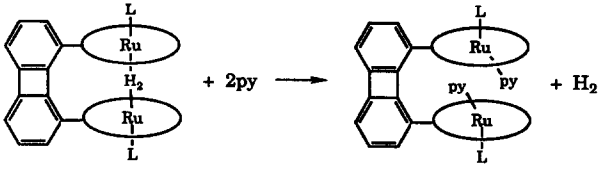
Some counterions [39,59,190,252] may substitute the H_2 ligand [39].

$$[Rh(H_2)(pp_3)]SO_3CF_3 \rightarrow Rh(pp_3)(SO_3CF_3) + H_2 \quad (92)$$

Stepwise substitution reactions are thought to occur with bis(dihydrogen) complexes such as *cis*-$Cr(H_2)_2(CO)_4$ (eqn. (93) [46]) and $[Ir(H_2)_2H_2(PCy_3)_2]^+$ [253].

$$Cr(H_2)_2(CO)_4 \overset{N_2}{\rightleftharpoons} Cr(H_2)(N_2)(CO)_4 \overset{N_2}{\rightleftharpoons} Cr(N_2)_2(CO)_4 \quad (93)$$

The bridging dihydrogen ligand in $Ru_2(H_2)(dpb)L_2$ (dpb = diporphyrinatobiphenylene tetraanion, L = 1-*t*-butyl-5-phenylimidazole) is replaced by two pyridine molecules [166].



(94)

Substitution reactions of proven or proposed dihydrogen complexes are invoked in the mechanisms of many reactions involving transition metal hydrides. For example, a number of reports propose the following mechanism for substitution reactions of hydrides by pseudohalides.

$$MHL_n + HX \rightarrow [M(H_2)L_n]^+ + X^- \rightarrow MXL_x + H_2 \quad (95)$$

where $X^- = SR^-$ [213,230], OR^- [254], Cl^- [119], $CF_3CO_2^-$ [252], or $CCPh^-$ [211].

If the predicted pK_a [133] of the dihydrogen intermediate is much lower than that of HX, then this type of reaction is unlikely to occur because the first step is energetically unfavorable [230]. There is some evidence that more steps are involved for the reaction with RCCH [255] (see Sect. H.(iii)).

Dihydrogen is such a weak ligand that its complexes are often useful catalyst precursors; H_2 elimination or substitution produces the catalytically active species. On the other hand, dihydrogen complexes appear within several proposed catalytic cycles. The subject of dihydrogen complexes in catalysis is covered in Sect. H.

(c) Substitution followed by intramolecular reaction

The substitution reactions of hydrido(dihydrogen) complexes with unsaturated reagents (alkenes [90,256], alkynes [184,250,257–259], RNN^+ [76], CO_2 [195,257,260,261], and CS_2 [257,260]) are often followed by insertion of the unsaturate into the M–H bond [257].

$$trans\text{-}[Fe(H_2)H(dmpe)_2]^+ + CX_2 \rightarrow [Fe(X_2CH)(dmpe)_2]^+ + H_2 \quad (96)$$

where X = O, S. The hydrido intermediate formed by the substitution step is rarely observed. This sequence of reactions is important in the catalytic cycle of the hydrogenation of unsaturates such as alkynes [75] or ketones [262]. However, Bianchini et al. [263] have proposed the insertion of an alkyne into the M–H bond of $[Fe(H_2)H(pp_3)]^+$ after substitution by alkyne of an arm of the phosphine rather than the H_2 ligand (Sect. H).

Substitution of the dihydrogen ligands can be followed by other kinds of intramolecular reaction. If the intermediates are not observed, it may be difficult to deduce the mechanism. For example, the reactions of $Ru(H_2)_2(H)_2(PCy_3)_2$ with PhI and CF_3CO_2H may start by simple substitution of the dihydrogen ligand (eqns. (97) and (98), [11,252]).

$$Ru(H_2)_2(H)_2(PCy_3)_2 + PhI \rightarrow Ru(H_2)(H)I(PCy_3)_2 + PhH + (H_2) \quad (97)$$

$$Ru(H_2)_2(H)_2(PCy_3)_2 + CF_3CO_2H \rightarrow Ru(H_2)(H)(OCOCF_3)(PCy_3)_2 + (2H_2) \quad (98)$$

The reaction of $[Re(H_2)H_4(cyttp)]^+$ with acetone (eqn. (99) [264]) is another unusual reaction that may proceed via substitution of the dihydrogen ligand and subsequent intramolecular reactions.

$$[Re(H_2)H_4(cyttp)]^+ \xrightarrow{Me_2CO} Re(=O)(H)_2(cyttp)]^+ \quad (99)$$

(d) Ligand exchange

Exchange of ligands between a dihydrogen complex and another complex is rare, but an example (eqn. (100) [265]) has been reported.

$$2[Fe(H_2)H(dmpe)_2]^+ + Mo(N_2)_2(dppe)_2 \rightarrow 2[Fe(N_2)H(dmpe)_2]^+ + MoH_4(dppe)_2 \quad (100)$$

The resulting Mo hydride is classical.

(e) Elimination followed by dimerization

Hydride ligands can occupy bridging positions in order to fill empty sites liberated by elimination of H_2 ligands from non-classical polyhydrides such as $Ru(H_2)_2H_2(PCy_3)_2$ (eqn. (101) [94]), $[Ru(H_2)Cp^*(CO)_2]BF_4$ [59], and $[Ru(H_2)Cp(CO)L]BF_4$ [84] (eqn. (102), L = PPh_3, PMe_2Ph, PMe_3).

$$2Ru(H_2)_2H_2(PCy_3)_2 \rightarrow (PCy_3)_2HRu(\mu\text{-}H)_3Ru(H_2)(PCy_3)_2 + 3H_2 \quad (101)$$

$$2[Ru(H_2)Cp(CO)L]BF_4 \rightarrow \{[RuCp(CO)L]_2(\mu\text{-}H)\}BF_4 + H_2 + (HBF_4) \quad (102)$$

(ii) Stability of dihydrogen complexes and the thermodynamics of H_2 elimination

Although dihydrogen complexes are usually unstable with respect to H_2 loss (eqn. (103)), a few are remarkably stable.

$$M(H_2)L_x \rightleftharpoons ML_x + H_2 \quad (103)$$

Several factors influencing the observed stability are summarized in Table 3; these include thermodynamic factors such as $M-H_2$ bond strength and stabilization of the unsaturated product complex, and kinetic factors such as the trans effect. The kinetics of H_2 elimination will be discussed in Sect. E.(iii). Because very few measurements of thermodynamic data for eqn. (103) have been reported (Table 21), this discussion will be focussed primarily on qualitative trends in dihydrogen complex stability. The quantitative thermodynamic data will be referred to where appropriate.

Trends in the stability of η^2-H_2 complexes can be reasoned in terms of the molecular orbital description of η^2-H_2 binding to metal centers. Two bonding interactions occur, $H_2(\sigma) \rightarrow M(\sigma)$ donation and $M(\pi) \rightarrow H_2(\sigma^*)$ back-donation [164] both of which weaken the H–H bond. The latter interaction is very sensitive to electron density at the metal center. If the metal is too electron-rich, the strong back-donation and resulting population of the $\sigma^*(H_2)$ orbital will give a classical dihydride. In an electron-poor complex, insufficient back-donation will result in a very weakly bound H_2 ligand. The optimum electron density for dihydrogen complexes exists if the dinitrogen analogues have ν(NN) frequencies between 2060 and 2150 cm^{-1} [132].

Prediction of the stability of a d^6 octahedral $ML_5(H_2)$ complex is possible using a ligand additivity approach [133] based on Lever's electrochemical parameters [134,135]. Such a complex is predicted to be stable if the calculated $E_{1/2}(d^5/d^6)$ potential of the corresponding dinitrogen complex $ML_5(N_2)$ falls within a certain range. High $E_{1/2}$ values indicate an electron-poor complex which will easily lose H_2.

TABLE 21

Thermodynamic data for the loss of H_2 or N_2 from dihydrogen or dinitrogen complexes

$M(H_2)L_x$	ΔH (kcal mol^{-1})	ΔS (e.u.)	ΔG^a (kcal mol^{-1})	$\nu(N_2)$ (cm^{-1})	Ref.
$Cr(H_2)(CO)_3(PCy_3)_2$	7.3 ± 0.1	25.6 ± 1.7	-0.3	–	57,108
$Cr(N_2)(CO)_3(PCy_3)_2$	9.3 ± 0.2	35.4 ± 2.3	-1.3	2128	33,57
$Mo(H_2)(CO)_3(PCy_3)_2$	6.5 ± 0.2	23.8 ± 2.1	-0.6	–	57
$Mo(N_2)(CO)_3(PCy_3)_2$	9.0 ± 0.6	32.1 ± 3.2	-0.6	2159	17,57
$W(H_2)(CO)_3(PCy_3)_2$	10.0 ± 1.0	–	–	–	57
$W(N_2)(CO)_3(PCy_3)_2$	13.5 ± 1.0	–	–	2113	33,57
$Ru(H_2)HCl(CO)(P^iPr_3)_2$	7.7 ± 0.2	23.2 ± 1	$+0.8$	–	35
$[Ir(H_2)H(bq)(PPh_3)_2]^+$	-3.16	-2.3	-2.43	–	91

[a] Calculated for 298 K from published data.

The method is particularly useful for explaining trends in stability and evaluating the likelihood of non-classical structures for di- or poly-hydrides.

Complexes which have significant hydridic character (i.e. with weak or non-existent H–H bonds) are generally more stable to H_2 loss. Classical dihydrides and $M(H \cdots H)$ complexes react by H_2 elimination or substitution often, but not always, more slowly or under more severe conditions. This is partly due to greater kinetic stability, rather than thermodynamic stability. The kinetic differences will be discussed in Sect. E.(iii). Of course, dihydrogen complexes are more thermodynamically stable than their dihydride tautomers if the equilibrium between them lies in favor of the dihydrogen complex. Some classical hydrides or elongated dihydrogen complexes are unstable to loss of H_2; an example is $ReH_5(H \cdots H)(PR_3)_2$ ($R = C_6H_5$ or C_6H_4-*p*-Me, [30]) which decomposes in benzene by loss of H_2 [266].

Because the dihydrogen H–H distance, d(H–H), is rarely known directly (e.g. from X-ray or neutron diffraction studies), it has to be estimated from observables such as vibrational frequencies $\nu(H_2)$ [2], $\nu(MH_2)$ [32(a)], or NMR data (T_1 or J(HD)). The use of such values as indicators of relative stability of dihydrogen complexes is suspect if not applied to isostructural complexes.

High $\nu_s(MH_2)$ or $\nu_{as}(MH_2)$ frequencies and low $\nu(H_2)$ frequencies indicate strong M–H_2 interactions, although for most complexes, these data are not available. For the complexes $M(H_2)(CO)_3(PCy_3)_2$ [2,32(a)], the trends in $\nu_s(MH_2)$ and $\nu_{as}(MH_2)$ frequencies is $5d \geq 3d > 4d$ and the trend in $\nu(H_2)$ frequency is $5d < 4d$. These trends match those of their thermodynamic stabilities ($5d > 3d > 4d$, see below).

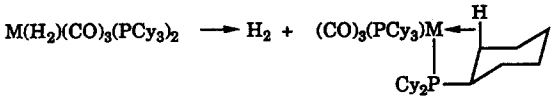
Another indicator frequently referred to is the ν(NN) frequency of the corresponding dinitrogen complex. As mentioned above, Morris [132] suggested that, if the ν(NN) frequency was greater than 2150 cm^{-1}, the dihydrogen complex would be unstable with respect to H_2 elimination. However, observed ν(NN) frequencies which correspond to stable dihydrogen complexes (in solution under argon) in Table 19 are as high as 2163 cm^{-1}, while those for unstable dihydrogen complexes are as low as 2043 cm^{-1}, well below the 2150 cm^{-1} limit. Within a series, the correlation of instability and ν(NN) frequency is quite good, as will be described below.

The chemical shift of the dihydrogen ligand may be another indicator, as suggested by Nanz et al. [198]. A complex with a chemical shift of the dihydrogen ligand at higher field than that of a hydride ligand in a similar environment (on the same complex or a related classical hydride complex) should have greater hydridic character and therefore small J(HD) values and slow rates of H_2/D_2 exchange [198]. For example, the H_2 signal is upfield of the H signal in $[Os(H \cdots H)H(depe)_2]^+$ but not in $[Os(H_2)H(dppe)_2]^+$ [29]. In practice, this is probably not a reliable indicator because of the large number of factors which influence the chemical shifts of hydride ligands. A counterexample to the rule is the classical complex $ReH_3(PMePh_2)_4$ which has a 2H signal 1 ppm *downfield* of the H signal at −105°C [267].

Within a series of complexes, those with larger J(HD) values are expected to

have more unstable H_2 ligands. For example, the J(HD) values for the series *trans*-$[M(HD)D(depe)_2]^+$ increases in the order Os < Fe < Ru, while the stability with respect to H_2 loss increases in the reverse order.

One might expect the ΔH value for H_2 loss, being a quantitative measure of the stability of the complex with respect to eqn. (103), to correlate with J(HD), ν(NN), or d(H–H) data. However, ΔH depends strongly on the nature and enthalpy of the product of H_2 loss. In the case of the Kubas-type complexes, the products $M(CO)_3(PCy_3)_2$ contain agostic interactions for all three metals (eqn. (104), M = Cr [268], Mo, W [269]).



(104)

If the enthalpies of these agostic complexes are similar, then the ΔH of H_2 loss should be indicative of H_2 activation (i.e. large ΔH indicates hydridic character) and therefore have the opposite of the trend in ν(NN) frequencies. The data (Table 21) support this conclusion; the dihydrogen complex which has the lowest ΔH (Mo) has the dinitrogen analogue with the highest ν(NN) frequency.

Note, as an aside, that the thermodynamic data for $[Ir(H_2)H(bq)(PPh_3)_2]^+$ [91] contrasts sharply with the other data in Table 21; a negative ΔS value is not expected for a dissociative process. The error in the data is probably very large because measurements were made at only two temperatures.

The choice of metal and ligands affects the stability of dihydrogen complexes. The qualitative stability of several isostructural series of dihydrogen complexes of groups 6 and 8 metals decreases in the order 5d > 3d > 4d. Specifically, the stability trends observed for group 6 complexes were 5d > 3d > 4d for $M(H_2)(CO)_5$ [46] and 3d > 4d for *fac*-$M(D_2)(CO)_3$(nbd) [51]. The stability trends observed for group 8 complexes were 5d > 3d, 4d for $[M(H_2)H(PPh(OEt)_2)_4]^+$ [270] and $MH_4(PPh_3)_3$ [65], and 5d > 3d > 4d for $[M(H_2)H(dppe)_2]^+$ and $[M(H_2)H(depe)_2]^+$ [60]. The only quantitative thermodynamic data for a complete series of complexes is that for the Kubas complexes $M(H_2)(CO)_3(PR_3)_2$ (M = group 6) and it supports the same trend; i.e. ΔH for eqn. (103) decreases in the order 5d > 3d > 4d (Table 21, not all of the ΔG values are available). There are two series of complexes for which the qualitative stability trend is 5d > 4d > 3d, the poorly characterized series $[M(H_2)Cl(depe)_2]^+$ (M = group 8) [61] and, ironically, the Kubas-type complexes. In toluene, $Cr(H_2)(CO)_3(PR_3)_2$ completely and instantaneously eliminates H_2, while the Mo complex partially dissociates H_2 [268]. The reason for the difference between the qualitative and quantitative trends for these complexes may be kinetic in origin. If the activation barrier for H_2 loss from the Mo complex were higher than from the Cr complex, the discrepancy would be explained. These data are not available.

The overall trend in stability for dihydrogen complexes is a function of the two bonding interactions; they will be dealt with separately.

(a) $M \leftarrow (H_2)$ σ donation

Bautista et al. [60] suggest that the strength of the $M \leftarrow (H_2)$ σ donation should increase down the group, as observed for hydrides and other σ ligands [226]. For example, M–L heats of binding in $M(L)(CO)_3(PCy_3)_2$ (M = group 6, [203]) increase down the group for L = py (a σ donor) but not for N_2 or H_2 (both of which have a π backbonding component). There is some indication, however, that M–H σ bonds do not always increase in strength down the group; calculated strengths of chemisorption of hydrogen on groups 7–10 metal surfaces are lowest for 4d metals [271]. Whatever the trend in M–H σ bond strengths, it is not clear that the same trend can be expected for $M \leftarrow H_2$ σ bond strengths. Jean et al. [130], using extended Hückel calculations, found that the σ donation in $M(H_2)L_5$ (L = H or CO) is stronger for Cr than for W because the lower-energy metal hybrid orbitals of the 3d Cr atom favor $M \leftarrow (H_2)$ dative bonding. "The lowering of the metal hybrid orbital (σ symmetry orbital of Cr) decreases the energy gap between interacting MOs but also corresponds to a smaller overlap with σ_{H_2} (less diffuse metal orbitals). At distances inferior to 1.7 Å, the energy factor is dominant" [130]. At this point, it is not possible to make any general conclusion.

(b) $M \rightarrow (H_2)$ π back-donation

It is also difficult to predict the trend in the strengths of the back-donation. Using the ligand additivity approach mentioned above, one can estimate the $E_{1/2}$ (d^5/d^6) reduction potentials for pseudo-octahedral dihydrogen complexes $ML_5(H_2)$ [133]. For any combination of ligands which would give an $E_{1/2}$ value in the range for stable dihydrogen complexes, the trend in $E_{1/2}$ values is $3d \leqslant 5d < 4d$ for group 6 and $5d \leqslant 3d < 4d$ for group 8. If the $E_{1/2}$ values are taken as indicators of the electron deficiency at the metal center, then the 4d metals have the least electron density to backdonate to the H_2 ligand. The barrier to rotation of the ligand is an empirical indicator of the strength of the π backbonding. A neutron scattering study showed that the barrier is lower for rotation of the H_2 ligand in $[Ru(H_2)H(pp_3)]BPh_4$ than in $[Fe(H_2)H(pp_3)]BPh_4$ [272], which is consistent with a weaker π back-donation in the Ru complex. However, for the complexes $M(H_2)(CO)_3(P^iPr_3)_2$, this barrier increases in the order Cr < Mo < W [268,273]. This contrasts with the trend predicted by the ligand additivity approach (4d < 5d ⩽ 3d) but is consistent with the calculations of Jean et al. [130] who calculated that, for $ML_5(H_2)$, the π electron donating ability of W (5d) is greater than Cr (3d) if L = H (σ donor), or roughly the same if L = CO (π acceptor).

Orbital overlap varies depending on the metal binding site. Bickelhaupt et al. [274] calculated that a major reason for the failure of H_2 to bond in an η^2 fashion to $PtCl_4^{2-}$ is the poor π overlap of the metal orbitals with the σ* H_2 orbitals due to

nodes in the former. Bautista et al. [60] suggest that the Os member of the series $[M(H_2)H(depe)_2]^+$ has greater π (and σ) overlap because of relativistic contraction of the Os orbitals.

In summary, our understanding of the factors involved is not yet at a level where we can explain or predict the trend down the group, beyond the statement that 5d dihydrogen complexes are observed to be the most stable with respect to H_2 loss and have the longest H—H distances (calculated from T_1 data). It appears that the relative stabilities of the 3d and 4d metals depend on the ligand set.

The choice of ancillary ligands would be expected to affect both the thermodynamic and kinetic stability of the complexes. If the ancillary ligands are strong σ donors, the $M \leftarrow (H_2)$ σ donation is expected to be weakened. Electron-withdrawing ligands decrease the back-donation to the H_2 ligand and thereby decrease stability. Complexes $[Ru(H_2)H(R_2PCH_2CH_2PR_2)_2]^+$ [60] and $MoH_2(CO)(R_2PCH_2CH_2PR_2)_2$ [34] lose H_2 far more readily if R = Ph than if R = Et. The H—H bond is entirely cleaved in the Mo complex (R = Et) because of the strong back-donation. The complex $[Ru(H_2)HL_4]BF_4$ is far more stable [76] if L = $PPh(OEt)_2$ than if L = $P(OEt)_3$, presumably because the latter ligand is a stronger π acid. However, *cis*-$Cr(H_2)(CO)_4L$ is more stable if L = CO than if L = alkene [50]. This cannot be explained in terms of the π backbonding. The alternative is a weakening of the $M \leftarrow (H_2)$ σ donation by the higher electron density in the alkene complex. Obviously, the electronic effects of ligands on the stability of the dihydrogen complex are still difficult to predict or explain, given the present level of understanding.

The trans ligand in particular affects the stability of the dihydrogen complex; this is both a kinetic and a thermodynamic effect. For example, the complex *trans*-$[Ru(H_2)H(dcpe)_2]^+$ (dcpe = $Cy_2PCH_2CH_2PCy_2$) [38] is more unstable than *trans*-$[Ru(H_2)Cl(dcpe)_2]^+$. However, complexes *trans*-$[M(H_2)H(depe)_2]^+$ (M = Fe, Ru) are more stable than their chloro analogues [61,275]. Trans ligands which compete effectively with H_2 for π electron density are expected to weaken the back-donation. For example, Maseras et al. [143] calculated that the replacement of the terminal hydride in *trans*-$[Fe(H_2)H(PH_3)_4]^+$ with PH_3, a stronger π acid, in $[Fe(H_2)(PH_3)_5]^{2+}$ or *cis*-$[Fe(H_2)H(PH_3)_4]^+$ results in weaker H_2 binding. Dinitrogen will replace D_2 in fac-$Mo(D_2)(\eta^2\text{-nbd})(CO)_3$ (D_2 trans to CO) but not in the mer isomer (D_2 trans to olefin) [51], presumably because CO is a stronger π acid and has a stronger trans influence than the olefin.

The range of $E_{1/2}$ values needed for a stable d^6 dihydrogen complex remains constant from group 6 through group 9. In order to maintain $E_{1/2}$ values within this range, increasingly electron-donating ligand sets are required for the late transition metals [133]. For this reason, many group 6 dihydrogen complexes contain carbonyl ligands, while carbonyl(dihydrogen) complexes of the later metals would be unstable to H_2 elimination unless the π acid effect of the carbonyl is balanced by strong basicity in the other ligands. Ziegler et al. [136] reported another reason for the

instability of the theoretical adduct $M(H_2)(CO)_4$ (M = Ru, Os); it is destabilized by a two-orbital four-electron repulsion $H_2(\sigma) \rightarrow M(1a_1$, occupied), which occurs in addition to the favorable $H_2(\sigma) \rightarrow M(2a_1$, unoccupied) interaction.

The coordinatively unsaturated complexes produced by H_2 loss from dihydrogen complexes are often themselves unstable. Equilibrium (103) can be driven to the right if the product complex is trapped or stabilized in one of the following ways:

(a) reaction with a reagent which coordinates more strongly than H_2,

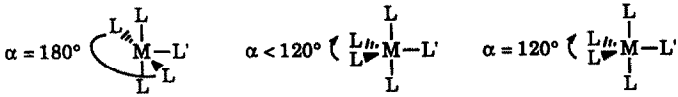
(b) dimerization (e.g. eqn. (101)),

(c) shielding of the empty site by a bulky ligand, or

(d) a chelation (e.g. eqn. (91)) or an agostic interaction with an ancillary ligand (e.g. eqn. (104)).

Because considerable rearrangement is required in eqn. (104), this agostic interaction is more difficult to achieve in the solid state. As a result, the dihydrogen complex $Cr(H_2)(CO)_3(PCy_3)_2$ is considerably more stable in that state [268]. Agostic interactions often involve a C–H of an ethyl or phenyl phosphine. An unusual case is a suspected agostic interaction with a methylene C–H bond in one of the dppb ligands of $[RuH(dppb)_2]^+$ [276]. Dihydrogen complexes which do not contain ligands capable of agostic interactions could be more stable as a result.

The five-coordinate product of H_2 elimination from an octahedral d^6 dihydrogen complex can have any of the possible structures:



31 32 33

Although the square pyramidal structure (**31**) has been assumed in theoretical calculations of interactions between ML_5 and H_2 (L = H^-, CO) [130], the Y structure (**32**) may actually occur in a large number of cases [277]. Extended Hückel calculations for IrH_5^{2-} show that structures **31** and **32** are local minima on a plot of potential energy versus α. The trigonal bipyramidal structure (**33**) is a local maximum for this ligand set. Structure **32** (the Y structure) is favored over structure **31** if the ligand L' is a weak σ donor (e.g. Cl^-) or a π donor (e.g. Cl^-, NH_2^-) or if the ligands subtending the acute angle do not have lone pairs or filled π systems [277,278]. Examples of all three structures being produced by dihydrogen loss are known or postulated. $Mo(H_2)(CO)(dppe)_2$ loses H_2 reversibly [34] to give square pyramidal $Mo(CO)(dppe)_2$ [279(a)]. Similarly, if the substitution reactions of $W(H_2)(CO)_5$ are dissociative, the transient would be $W(CO)_5$, a square pyramidal complex [279(b)]. Bianchini [151,184] reported that $[Fe(H_2)H(pp_3)]^+$ loses H_2 irreversibly to produce the paramagnetic trigonal bipyramidal complex $[FeH(pp_3)]^+$. The product of reaction (105)

[38] has a Y structure ($\alpha = 93°$ opposite the Cl), although it was originally described as a trigonal bipyramidal structure [280].

$$[Ru(H_2)Cl(dcpe)_2]^+ \rightarrow [RuCl(dcpe)_2]^+ + H_2 \quad (105)$$

Reaction (105) requires elevated temperatures. The dihydrogen complex can be synthesized by addition of H_2 to the five-coordinate complex [38]. The known dihydrogen complex *trans*-$[Fe(H_2)H(meso\text{-}tetraphos)]^+$ cannot be produced by H_2 addition to $[FeH(meso\text{-}tetraphos)]^+$ [72], which may also have a Y structure by analogy to $[FeBr(meso\text{-}tetraphos)]^+$ [281]. However, *trans*-$[Fe(H_2)H(meso\text{-}tetraphos)]^+$ is relatively stable in solution under argon, in contrast to the dihydrogen complex in eqn. (105). Particularly unstable five-coordinate complexes would be those with ligands which fit the electronic requirements for one of the possible structures (**31**–**33**) but for steric or ring-strain reasons cannot adopt that favored structure. The corresponding dihydrogen complexes would be expected to be relatively stable. Perhaps this suggests a strategy for the choice of ligands in the synthesis of stable dihydrogen complexes.

How do the thermodynamics of dihydrogen binding compare with those for other related ligands? For each group 6 metal, the ΔH value for N_2 loss from the dinitrogen complex is about 2–4 kcal mol^{-1} higher than for H_2 loss from the dihydrogen complex (Table 21). This enthalpic term favoring N_2 binding is counterbalanced by the lower ΔS of H_2 loss, which favors H_2 binding. The lower ΔS of H_2 loss results primarily [282] from the lower absolute entropy of H_2 compared with N_2 (31.2 vs. 45.8 cal mol^{-1} K^{-1} at 298.15 K [283]). The result is that H_2 is a stronger ligand than N_2 above a crossover temperature which depends on the exact values of ΔH and ΔS [176,282]. These temperatures for the equation

$$M(H_2)(CO)_3(PCy_3)_2 + N_2 \rightleftharpoons M(N_2)(CO)_3(PCy_3)_2 + H_2 \quad (106)$$

are -69, $+28$, and 46°C for Cr, Mo, and W, respectively [57]. Similarly, D_2 has a higher absolute entropy (34.6 cal mol^{-1} K^{-1}) than H_2 [283]. Consequently, the ΔS of elimination of D_2 (eqn. (103)) would be expected to be about 2–3 e.u. higher than that for elimination of H_2. If the ΔH value for loss of D_2 is higher than that for loss of H_2, then the equilibrium for eqn. (103) would lie further to the right for D_2 than for H_2 (i.e. $K_{D_2}/K_{H_2} > 1$) at temperatures higher than the crossover temperature. The ratio K_{D_2}/K_{H_2} for $IrH(H_2)Cl_2(PCy_3)_2$ is 0.5 at 260 K [41], which must be below the crossover temperature. Another result of this difference in entropies is that a competitive reaction between H_2 and D_2, similar to that in eqn. (106), would result in a higher proportion of the deuterated product at lower temperatures.

(iii) The kinetics of H_2 elimination or substitution

The conventional wisdom holds that dihydrogen complexes lose H_2 more readily than related dihydrides because $M(H_2)$ complexes are further along the

reaction pathway. This reputed difference has been used as a criterion for identifying non-classical dihydrides [29] or for suggesting the occurrence of an otherwise undetected dihydrogen complex [34]. For example, the rate of loss of H_2 from $[OsH_5(PMe_2Ph)_3]^+$ [87,284] is slow, with a rate ($k = 3 \times 10^{-4}\ s^{-1}$ in CH_2Cl_2 at 20°C) comparable with some dihydrides such as *cis*-$PtH_2(PMe_3)_2$ ($7.3 \times 10^{-4}\ s^{-1}$ in THF at 21°C) [285] and *cis,cis,trans*-$RuH_2(CO)_2(PPh_3)_2$ ($6.4 \times 10^{-4}\ s^{-1}$ in THF at 26°C) [230]; this would suggest that the osmium complex does not contain a dihydrogen ligand. However, the following objections to the generalization should be noted.

(a) Unstable dihydrides lose H_2 even more quickly; the complex $IrH_2Cl(PPh_3)_2$, which is most likely to be a classical dihydride, loses H_2 with a rate constant greater than $5 \times 10^5\ s^{-1}$ [286].

(b) If a dihydride/dihydrogen tautomeric pair is evolving H_2, then under some conditions the absolute rate of loss of the dihydride may be greater than that for the dihydrogen complex (see below).

(c) The rate-determining step of substitution reactions of $M(H_2)$ or $M(H)_2$ complexes is not necessarily H_2 elimination. The mechanism could be associative or could involve rate-determining prior dissociation of an ancillary ligand. An example of a related reaction having an associative mechanism is the elimination of pyridine from $W(py)(CO)_3(PCy_3)_2$ to form an agostic complex [203].

(d) Halpern et al. [121] note that the difference in the $\Delta H^{\ddagger}$ for H_2 elimination is 8 kcal mol^{-1} between $[RuH_5(PPh_3)_3]^+$ (8.8 kcal mol^{-1}, non-classical) and $[OsH_5\{P(p\text{-tol})_3\}_3]^+$ (16.8 kcal mol^{-1}, assumed to be non-classical) and approximately the same between $RuH_4(PPh_3)_3$ (17.9 kcal mol^{-1}, non-classical) and $OsH_4\{P(p\text{-tol})_3\}_3$ (25.2 kcal mol^{-1}, classical). If non-classical dihydrogen complexes react faster, then there should have been a much greater difference in the latter pair. Specifically, one would expect the $\Delta H^{\ddagger}$ barrier for $OsH_4\{P(p\text{-tol})_3\}_3$ to be more than 8 kcal mol^{-1} higher than $RuH_4(PPh_3)_3$ because the Os complex is classical. Their argument is weakened by our uncertainty as to the structures of $RuH_4(PPh_3)_3$ and $[OsH_5\{P(p\text{-tol})_3\}_3]^+$. Failure to observe a greater difference in $\Delta H^{\ddagger}$ could have been due to $RuH_4(PPh_3)_3$ being an elongated (M(H $\cdots$ H), see Sect. B), rather than rotating dihydrogen complex. The point is well taken, though, that dihydrogen complexes are not necessarily more labile than classical dihydrides and that, until more data are collected, H_2 lability should not be used as more than circumstantial evidence of non-classical character.

In a solution containing a pair of interconverting dihydride and dihydrogen tautomers, the concentration of each will decrease while dihydrogen is evolved. What are the relative rates of disappearance of the two tautomers? We consider this question with the proviso that the dihydride can only lose H_2 via the dihydrogen complex (the possibility of the dihydride losing H_2 by another route seems remote). Will the absolute rate of loss of the dihydrogen tautomer always be greater? Will the specific rate (meaning the rate per molar concentration of the complex) of loss

of the dihydrogen tautomer always be greater? There are two extreme cases one could consider; rapid tautomerism (k_2 is slow in eqn. (107)) and slow tautomerism (k_2 is fast).

$$M(H)_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} M(H_2) \xrightarrow{k_2} M + H_2 \tag{107}$$

If the tautomers are rapidly interconverting relative to the rate of loss of H_2 (i.e. $k_1, k_{-1} \gg k_2$), then they will remain at the equilibrium ratio of concentrations throughout the reactions. Therefore, they will be lost with the same specific rates. The absolute rate of loss of the major tautomer will be greater than that of the minor tautomer, by virtue of its greater concentration.

$$-\frac{d}{dt}[M(H_2)] = \left\{\frac{k_2K^2}{(1+K)^2}\right\}[MH_2]_{tot} = \left\{\frac{k_2K}{1+K}\right\}[M(H_2)] \tag{108}$$

$$-\frac{d}{dt}[M(H)_2] = \left\{\frac{k_2K}{(1+K)^2}\right\}[MH_2]_{tot} = \left\{\frac{k_2K}{1+K}\right\}[M(H)_2] \tag{109}$$

where $[MH_2]_{tot} = [M(H_2)] + [M(H)_2]$ and $K = k_1/k_{-1}$.

If the interconversion of the tautomers is very slow compared with k_2 (i.e. k_1, $k_{-1} \ll k_2$), then the concentration of the dihydrogen complex will rapidly approach steady state. Before it does so, it will be consumed at a greater rate than the dihydride. An example is the $W(H_2)(CO)_3(PCy_3)_2$ system, for which the values of k_1, k_{-1}, and k_2 are 37, 18 and 469 s^{-1}, respectively [147].

Intermediate cases are more difficult. There are some values of the rate constants that will cause the specific and absolute rates of loss of the dihydride to be greater than those of the dihydrogen complex, but only if one starts with a greater-than-equilibrium concentration of the dihydride (e.g. 1 M for each of $M(H_2)$ and $M(H)_2$, and $k_1, k_{-1}, k_2 = 4, 1, 2\ s^{-1}$).

In conclusion, the extreme cases show that the specific rate of loss of the dihydrogen complex will be equal to or greater than that of the dihydride tautomer. This may not be true in intermediate cases.

The lability of classical or non-classical polyhydride complexes increases with protonation. For example, the rate of elimination of H_2 from the ruthenium complexes in Table 22 increases in the order [121] $[RuH_3(PPh_3)_3]^- < RuH_4(PPh_3)_3 < [RuH_5(PPh_3)_3]^+$. Note that this is an effect of the decreasing $\Delta H^{\ddagger}$; the entropy of activation is negative for the charged complexes, because of solvation effects, and approximately zero for the neutral complex [121]. The extent of $M \rightarrow (H_2)$ π back-bonding in dihydrogen complexes is dependent on the electron density at the metal. Protonation of the complex will necessarily decrease the available electron density at the metal and therefore labilize H_2. Similar arguments could be used to explain the increase in lability of classical di- or poly-hydrides upon protonation: decreased electron density at the metal would stabilize a dihydrogen-like transition state.

TABLE 22

Kinetic data for the loss of H_2 or X_2 from dihydrogen and related complexes

$M(H_2)L_x$	k[a] (s^{-1})	$\Delta H^{\ddagger}$ (kcal mol^{-1})	$\Delta S^{\ddagger}$ (e.u.)	Ref.
$Cr(H_2)(CO)_3(PCy_3)_2$	2.9×10^{3}[c]	12.1 ± 1.0	-2.1 ± 4.5	108
$[Mo(H_2)H_4(dppe)_2]^{2+}$	1.3×10^{0}	–	–	119
$W(H_2)(CO)_3(PCy_3)_2$	4.7×10^{2}	16.9 ± 2.2	10.4[c]	147
$W(D_2)(CO)_3(PCy_3)_2$	2.7×10^{2}	16.2 ± 1.1	6.9[c]	147
$W(N_2)(CO)_3(PCy_3)_2$	7.5×10^{1}	17.8 ± 0.7	9.8[c]	147
$[Ru(H_2)H_3(PPh_3)_3]^{+}$[b]	3.6×10^{3}	8.8 ± 0.1	-12 ± 1	121
$Ru(H_2)H_2(PPh_3)_3$	2.1×10^{0}	17.9 ± 0.2	3 ± 1	121
$[RuH_3(PPh_3)_3]^{-}$	6.8×10^{-6}	21.8 ± 1.4	-9 ± 4	121
$[Os(H_2)H_3(P(p\text{-tol})_3)_3]^{+}$[b]	6.6×10^{-2}	16.8 ± 0.5	-9 ± 2	121
$[Os(H_2)H_3(PMe_2Ph)_3]^{+}$[b]	3×10^{-4}[d]	–	–	87,284
$OsH_4(PPh_3)_3$	6.1×10^{-7}	25.2 ± 1.3	-2 ± 4	121

[a] 298 K.
[b] Could be $[M(H)_5L_3]^{+}$.
[c] Calculated by Jessop and Morris from published data.
[d] 293 K.

The loss of D_2 from η^2-D_2 complexes is slower than the loss of H_2 from corresponding dihydrogen complexes. The isotope effect k_{H_2}/k_{D_2} is 1.7 for $W(H_2)(CO)_3(PCy_3)_2$ [147], 5 for $Cr(H_2)(CO)_5$ [45], and 6–7 for $Ir(H_2)HCl_2(PCy_3)_2$ [41]. The activation parameters (Table 22) for the W complex suggest that the reduced rate of D_2 elimination is due to the lower activation entropy, which could not have been anticipated from thermodynamic data; free D_2 has a higher entropy than H_2. The dramatic effect of the solvent on the $\Delta S^{\ddagger}$ for H_2 reductive elimination from a dihydride has been demonstrated [285]. Because of the high error (several cal mol^{-1} K^{-1}) in the $\Delta S^{\ddagger}$ values in Table 22, the unknown structure of the activated complex, and the unknown role of the solvent, it is unwise to interpret the observed activation entropies.

The reasons for the greater thermodynamic stability of $W(H_2)(CO)_3(PCy_3)_2$ compared with the Cr analogue were discussed in the previous section. The activation parameters show the W complex to be also kinetically more stable. The greater $\Delta H^{\ddagger}$ value is only partially offset by the greater $\Delta S^{\ddagger}$. The high $\Delta H^{\ddagger}$ is probably a direct consequence of the strength of the W–H_2 bond, which might be partially cleaved in the activated complex.

As discussed in the previous section, the effect of the trans ligand on dihydrogen complex stability could be kinetic rather than thermodynamic. Because accurate rate determinations are not available in most cases, separating the kinetic and thermodynamic factors is difficult or impossible. For this reason, most of the discussion of ligand effects on stability and lability of dihydrogen complexes has been put in

Sect. E.(ii). Comparison of quantitative rate data is possible between the complexes $[OsH_5(PPh_3)_3]^+$ [121] and $[OsH_5(PMe_2Ph)_3]^+$ [87,284]. The latter eliminates dihydrogen two orders of magnitude more slowly, because the PMe_2Ph ligands are stronger σ donors.

F. OXIDATION/REDUCTION CHEMISTRY OF DIHYDROGEN COMPLEXES

(i) Introduction

There are only a few studies of the electrochemistry of dihydrogen complexes, all involving cyclic voltammetry. The complexes undergo oxidation much more commonly than reduction, and the potentials for oxidation are usually more positive than the ferrocinium/ferrocene couple (Fc^+/Fc, Tables 23 and 24). Oxidation reactions would be expected because stable dihydrogen complexes have oxidizable d electrons which are used to back-bond to the H_2 ligand. Only two complexes, $Re(H\cdots H)Cl(PMePh_2)_4$ and $[Os(H\cdots H)(NH_3)_5]^{2+}$ display a reversible, one-electron oxidation (Table 23), whereas several undergo irreversible oxidations (Table 24). Non-coordinating dry solvents (thf or CH_2Cl_2) and electrolytes (NBu_4BF_4 or NBu_4PF_6) are usually needed to avoid side reactions in these studies. A variety of reference electrodes has been employed but most of the potentials can be referenced to the Fc^+/Fc couple; this has been done in the tables. The complexes are organized in the tables according to the group of the metal.

So far, two decomposition routes of oxidized dihydrogen complexes have been proposed. The first is H_2 evolution after oxidation (eqn. (110)) and the second is loss of a proton (eqn. (111)).

$$M(H_2)L_n \underset{+e^-}{\overset{-e^-}{\rightleftharpoons}} [M(H_2)L_n]^+ \rightarrow [ML_n]^+ + H_2 \quad (110)$$

$$[M(H_2)L_n]^+ \rightarrow MHL_n + H^+ \quad (111)$$

The $E_{1/2}$ values for oxidation of stable dihydrogen complexes, $M(H_2)L_n$, probably span a fairly small range (perhaps 2 V), as indicated by potentials of corresponding dinitrogen complexes (see Table 4). Decomposition via eqn. (110) might be expected

TABLE 23

Electrochemical potentials for the reversible oxidation of dihydrogen complexes

Complex	$E_{1/2}$ (V)	Reference	Solvent	$E_{1/2}$ (V vs. Fc^+/Fc)	Ref.
$Re(H\cdots H)Cl(PMePh_2)_4$	−0.07	AgCl/Ag	CH_2Cl_2	−0.59	267
$[Os(H\cdots H)(NH_3)_5]^{2+}$	0.58	NHE	CH_3CN	0.03	93(a)
	0.41	NHE	1 M HOTf		93(a)

TABLE 24

Anodic peak potentials (E_{pa}) for the irreversible oxidation of dihydrogen complexes

Complex[a]	E_{pa} (V)	Reference electrode	Solvent	E_{pa} (V vs. Fc^+/Fc)	Ref.
$Re(H\cdots H)H_5(PPh_3)_2$?	1.15	AgCl/Ag	CH_2Cl_2	0.68	287
$Re(H\cdots H)H_5(PMePh_2)_2$?	1.25	AgCl/Ag	CH_2Cl_2	0.78	287
$Re(H\cdots H)H_5(PMe_2Ph)_2$?	1.27	AgCl/Ag	CH_2Cl_2	0.80	287
$Re(H\cdots H)H_5(PCy_3)_2$?	1.10	AgCl/Ag	CH_2Cl_2	0.63	287
$Re(H\cdots H)H_5(dppe)$?	1.37	AgCl/Ag	CH_2Cl_2	0.90	287
$[Re(H\cdots H)H_4(PPh_3)_3]^+$?	1.64	AgCl/Ag	CH_2Cl_2	1.17	287
t-$[Fe(H_2)H(dppe)_2]^+$	0.8	Fc^+/Fc	thf	0.8	60
t-$[Fe(H_2)H(depe)_2]^+$	0.60	Fc^+/Fc	thf	0.60	60
c-$[Fe(H_2)H(pp_3)]^+$	0.70	SCE	thf	0.31	151
t-$[Ru(H_2)H(dppe)_2]^+$	>1	Fc^+/Fc	thf	>1	60
t-$[Ru(H_2)H(depe)_2]^+$	1.1	Fc^+/Fc	thf	1.1	60
c-$[Ru(H_2)H(pp_3)]^+$	0.41?	SCE	thf	0.02?	95
t-$[Os(H_2)H(dppe)_2]^+$	1.15	Fc^+/Fc	CH_2Cl_2	1.15	29
t-$[Os(H\cdots H)H(depe)_2]^+$	1.0	Fc^+/Fc	thf	1.0	29
$[Os(H\cdots H)(NH_3)_5]^{3+}$	1.3	NHE	CH_3CN	0.75	93(a)
$[Co(H_2)(pp_3)]^+$	0.45	SCE	thf	−0.11	151
$[Rh(H\cdots H)(pp_3)]^+$	0.73	SCE	thf	0.17	151

[a] c = cis, t = trans.

because the product dihydrogen complex $[M(H_2)L_n]^+$ would be about 1 V less reducing than the reactant, $M(H_2)L_n$ and this could place it beyond (more positive than) the limit of $E_{1/2}$ values which defines stable $M-H_2$ back-bonding. The observed difference between Os(IV)/(III) and Os(III)/(II) potentials for the complexes $[Os(H_2)(NH_3)_5]^{4+/3+/2+}$ in CH_3CN is 0.72 V, a little less than the 1 V change expected, although the first couple is irreversible [93(a)]. The pairs of complexes $[Os(H_2)(NH_3)_5]^{3+/2+}$ and $[Re(H_2)Cl(PMePh_2)_4]^{1+/0}$ (Table 23) are rare instances where the upper oxidation state complex is known to be stable to H_2 loss. This is probably because the lower oxidation state complex has an $E_{1/2}$ value near 0 V which is characteristic of complexes at the $M(H_2)/M(H)_2$ limit (see Table 4). Therefore the upper oxidation state complex has a sufficiently small, positive $E_{1/2}$ value to fall in the range of stability mentioned above. In addition, 5d metals are known to stabilize higher oxidation state complexes better than 3d or 4d metals and in particular stabilize dihydrogen complexes better with respect to loss of H_2 (see Table 3).

Oxidized dihydrogen complexes are expected to be about 17 pK_a units more acidic than the parent complexes and therefore are likely to decompose via eqn. (111). This is apparent from eqn. (67) described in Sect. D or its more general form for dihydrogen and dihydride complexes (eqn. (112)).

$$pK_a(MH_2L_n) = 0.73\Delta H_{BDE} - 16.9E_{1/2}(MHL_n/MHL_n^-) - 43 \quad (112)$$

If the $E_{1/2}(MHL_n^+/MHL_n)$ for the corresponding conjugate hydride of the oxidized dihydrogen complex, $[MH_2L_n]^+$, is about 1 V more positive than that for the unoxidized complex, then the oxidized dihydrogen complex should be about 17 pK_a units more acidic, assuming ΔH_{BDE} remains constant. The increase in acidity upon oxidation is clearly illustrated by the complexes $[Os(H_2)(NH_3)_5]^{3+/2+}$ in solution. The dication is stable in basic methanol whereas the trication is easily deprotonated by neutral water and is only stable in greater than 1 M HO_3SCF_3. Accordingly, the electrochemistry in aqueous acid is only reversible when the pH is 0 or less (Table 23) [93(a)].

The oxidation of $[Os(H_2)(NH_3)_5]^{2+}$ is irreversible in acetone because the product Os(III)(H_2) complex reduces acetone to isopropanol. This paradoxical reaction, where an oxidation turns the complex into a more potent reducing agent, is a further pathway to decomposition of oxidized dihydrogen complexes (see also Sect. H).

(ii) Irreversible oxidation of dihydrogen complexes

Most of the dihydrogen complexes show an anodic peak in the cyclic voltammogram corresponding to an irreversible oxidation process (Table 24). Specific details of this chemistry are described in this section and are organized according to the group of the metal. The two reversible oxidations of Table 23 were discussed in Sect. F(i). Table 25 lists the redox properties of some hydride complexes which are relevant to the work discussed here.

The complexes ReH_7L_2 and $[ReH_6L_3]^+$ are formally Re(VII) complexes with no easily ionizable d electrons. The observation that these complexes can be oxidized

TABLE 25

Electrochemical potentials for the oxidation of related hydride complexes. These are reversible except where noted

Complex	$E_{1/2}$ (V)	Reference	Solvent	$E_{1/2}$ (V vs. Fc^+/Fc)	Ref.
$ReH_5(PPh_3)_3$	0.29	AgCl/Ag	CH_2Cl_2	−0.18	287
$ReH_3(PMe_2Ph)_4$	−0.17[a]	AgCl/Ag	CH_2Cl_2	−0.69[a]	267
$ReH_3(dppe)_2$	−0.4[a]	Fc^+/Fc	THF	−0.4[a]	29
$Fe(Cl)H(dppe)_2$	−0.71	Fc^+/Fc	THF	−0.71	60
$Fe(H)_2(pp_3)$	−0.48	SCE	THF	−1.04	151
$Ru(Cl)H(dppe)_2$	−0.12	Fc^+/Fc	THF	−0.12	60
$Ru(H)_2(pp_3)$	0.08[a]	SCE	THF	−0.48[a]	151
$Os(Cl)H(dppe)_2$	−0.14	Fc^+/Fc	THF	−0.14	29
$Co(H)(pp_3)$	−0.48	SCE	THF	−1.04	151
$[Ir(H)_2(pp_3)]^+$	>1.4	SCE	THF	>0.9	151

[a] Anodic peak potential associated with irreversible oxidation.

(see Table 24) and then readily lose H_2 (cf. eqn. (110)) suggested to Costello et al. [287] that this is evidence for the existence of a dihydrogen ligand as proposed earlier by Hamilton and Crabtree [63]. These could be Re(V) complexes of the type $Re(H_2)H_5L_2$ and $[Re(H_2)H_4L_3]^+$ with an ionizable d electron pair. For example, the Re(V) complex $Re(H)_5(PPh_3)_3$ is easily oxidized (Table 25). The recent reports that $Re(H\cdots H)H_5(P(p\text{-tol})_3)_2$ [10] and $[Re(H\cdots H)H_4(cyttp)]^+$ [16] have elongated H–H bonds in the solid state supports this contention. However, the complex $Re(H)_7(dppe)$ has no short H–H distance in the solid state [288]. Solution NMR studies are ambiguous as to the existence of an elongated H–H bond [28,150]. The oxidation of these hydrides might just involve an electron in a HOMO with Re(VII)–H bond character and not involve a lower oxidation state of Re at all. Zanello argues that such Re–H oxidations are likely to be difficult because hydrides appear to remove more electron density from the metal than a dihydrogen ligand [95]. Interesting questions about these structures and reactions still remain to be answered.

The anodic peak potentials for the complexes $[M(H_2)H(L_2)_2]^+$ increase as $M = Fe < Os < Ru$ and $L_2 = depe < dppe$. This aperiodic ordering according to the metal is expected for d^6 octahedral complexes of group 8 metals [60] on the basis of electrochemical correlations suggested by Lever [134]. For example, it is observed for the reversible couples of the complexes $M(Cl)H(dppe)_2$ (Table 25). The ordering according to ligand is consistent with the depe ligand being more electron-donating than the dppe ligand. This electrochemical information along with spectroscopic data were used to support the argument that the π-basicity of the metal toward the H_2 ligand decreases as $Fe > Os > Ru$ [60]. The oxidized complexes, $[M(H_2)H(L_2)_2]^+$, were proposed to decompose by loss of H_2 or a proton (eqn. (110) or eqn. (111)). The trihydride $Re(H)_3(dppe)_2$ makes an interesting contrast to the isoelectronic complex $[Os(H_2)H(dppe)_2]^+$. It oxidizes at 1.5 V more negative than the Os complex (Table 25).

The complexes $[M(H_2)H(pp_3)]^+$, M = Fe, Ru, display complex voltammograms [95]. The iron complex has an irreversible oxidation at 0.3 V vs. Fc^+/Fc, a little more negative than the complexes $[Fe(H_2)H(L_2)_2]^+$. The oxidized complex $[Fe(H_2)H(pp_3)]^{2+}$ does not lose a proton (via eqn. (111)) because the reversible wave of the expected product, $[FeH_2(pp_3)]^+$ at -1.04 V, is not observed (see Table 25). The corresponding Ru complex decomposed rapidly in the electrochemical cell and so the assigned potential for this complex is tentative.

The oxidation of the unique complex $[Os(H_2)(NH_3)_5]^{3+}$, which is acidic and paramagnetic, is thought to proceed by initial loss of a proton [93(a)]:

$$\begin{aligned}&[Os(H_2)(NH_3)_5]^{3+} \rightleftharpoons [OsH(NH_3)_5]^{2+} + H^+\\ &[OsH(NH_3)_5]^{2+} \rightarrow [Os(CH_3CN)(NH_3)]^{3+} + 2e^- + H^+\end{aligned} \qquad (113)$$

The five coordinate, trigonal bipyramidal complexes $[M(H_2)(pp_3)]^+$, M =

Co(I), Rh(I) are the easiest complexes of those listed in Table 24 to oxidize. The rhodium complex might exist in rapid equilibrium with a Rh(III) dihydride form (see Sect. B.(vi)). The oxidized complexes decompose via loss of a proton (eqn. (114)) and the redox wave of the product is observed (e.g. a wave at −1.04 V for $[CoH(pp_3)]^{+1/0}$, see Table 25):

$$[M(H_2)(pp_3)]^+ \rightarrow [MH(pp_3)]^+ + e^- + H^+ \quad (114)$$

The dihydride, $[Ir(H)_2(pp_3)]^+$, in contrast to the Co(I) and Rh(I) dihydrogen complexes, is not oxidized at potentials as positive as 0.9 V vs. Fc^+/Fc.

(iii) Irreversible reduction of dihydrogen complexes

The only complex to be reduced electrochemically is $[Fe(H_2)H(pp_3)]^+$. The process is irreversible and the product identified is $Fe(H)_2(pp_3)$ [151]. The fate of the hydrogen atom in the reduction is unknown.

(iv) Ligand additivity method for estimating electrochemical potentials of dihydrogen complexes

Lever has shown that electrochemical potentials of complexes can be predicted based on a model involving additive ligand parameters E_L and linear equations for each metal oxidation and spin state [134,135]. Morris introduced a tentative E_L value of 0.8 V for the dihydrogen ligand [133]; this value may vary depending on the nature of the H_2 ligand (i.e. $M(H_2)$ vs. $M(H \cdots H)$). With this information, it is possible to calculate potentials, $E_{1/2}$(calc.), for six-coordinate dihydrogen complexes (see Table 26) and compare them with the observed values from Tables 23 and 24. In general, the agreement is good.

It is interesting that the electrochemical potential which we predict for the fictitious complex $Re(H_2)H(dppe)_2$ (−0.2 V) is similar to the observed potential for the trihydride $Re(H)_3(dppe)_2$ (−0.4 V). Therefore electrochemistry alone could not

TABLE 26

Observed potentials for the oxidation of dihydrogen complexes of d^6 metals and potentials calculated by use of Lever's additive ligand parameters, E_L

Complex	$E_{1/2}$(obs) (V vs. Fc^+/Fc)	ΣE_L	$E_{1/2}$(calc.) (V vs. Fc^+/Fc)
$Re(H_2)Cl(PMePh_2)_4$	−0.59	$0.8 - 0.24 + 4 \times 0.36 = 2.0$	−0.3
t-$[Fe(H_2)H(dppe)_2]^+$	0.8	$0.8 - 0.4 + 4 \times 0.36 = 1.84$	1.0
t-$[Ru(H_2)H(dppe)_2]^+$	>1	$0.8 - 0.4 + 4 \times 0.36 = 1.84$	1.2
t-$[Os(H_2)H(dppe)_2]^+$	1.15	$0.8 - 0.4 + 4 \times 0.36 = 1.84$	0.9
$[Os(H_2)(NH_3)_5]^{2+}$	0.03	$0.8 + 5 \times 0.07 = 1.15$	0.1

establish whether this was a trihydride or dihydrogen–hydride complex. In addition, it may not necessarily be the case that a dihydride complex, $M(H)_2L_n$, is more difficult to oxidize than a dihydrogen complex, $M(H_2)L_n$. Here, three hydrides in $Re^{III}(H)_3(dppe)_2$ are predicted to make the metal easier to oxidize than one dihydrogen and one dihydride ligand in "$Re^{I}(H_2)(H)(dppe)_2$".

G. REACTIONS IN WHICH THE DIHYDROGEN LIGAND IS RETAINED

The dihydrogen ligand is so unstable that almost all of the reactions of dihydrogen complexes involve the destruction of the dihydrogen ligand itself through H–H bond cleavage or H_2 elimination. Reactions of dihydrogen complexes which do not involve the destruction of the dihydrogen ligand are therefore very rare and deserve comment. They can also be used as synthetic methods for dihydrogen complexes. We have reviewed a few electrochemical reactions in which the dihydrogen ligand is preserved (Sect. F). There are also reactions of bis(dihydrogen) complexes in which one but not both dihydrogen ligands are destroyed (eqns. (93), (97), (98), and (101) of Sect. E). Other reactions in which a dihydrogen ligand is retained are described in the following sections.

(i) Substitution of ancillary ligands

Examples of simple substitution reactions of ancillary ligands include reactions (115) [6] and (116) [46].

$$W(H_2)(CO)_3(P^iPr_3)_2 + 2PCy_3 \rightarrow W(H_2)(CO)_3(PCy_3)_2 + 2P^iPr_3 \quad (115)$$

$$Cr(H_2)(CO)_5 + H_2 \underset{\Delta}{\overset{h\nu}{\rightleftharpoons}} \textit{cis}\text{-}Cr(H_2)_2(CO)_4 + CO \quad (116)$$

Li and Taube recently reported that the ligand trans to dihydrogen in the complexes $[Os(H\cdots H)(en)_2(L)]^{2+}$ can be substituted by donor groups of biologically important molecules [93(b)].

Bianchini et al. [263] proposed a mechanism for the catalysis of alkyne reduction by $[Fe(H_2)H(pp_3)]BPh_4$ which involved the dissociation of one of the branches of the tetradentate phosphine ligand, followed by coordination of an alkyne at the resulting free site (Scheme 4 in Sect. H). The dihydrogen ligand is, however, involved in the subsequent step, which is H_2 addition to the C≡C triple bond. A similar mechanism was proposed by Field et al. [255] for reaction (117) (eqn. (132) is Sect. H).

$$FeH_2(dmpe)_2 + 4PhC{\equiv}CH \rightarrow \textit{trans}\text{-}Fe(C{\equiv}CPh)_2(dmpe)_2 + 2CH_2{=}CHPh \quad (117)$$

(ii) Protonation of the dihydrogen complex

Halpern [121] reported the protonation of $RuH_2(H\cdots H)(PPh_3)_3$ (eqn. (118)). The number of dihydrogen ligands in the product is not known, but the T_1(min) of 18 ms at 500 MHz suggests that there is at least one.

$$RuH_2(H\cdots H)(PPh_3)_3 + CF_3SO_3H \rightarrow [RuH_5(PPh_3)_3]^+ + CF_3SO_3^- \quad (118)$$

Henderson [119] reported the reaction

$$MoH_4(dppe)_2 + 2HCl \rightarrow MoH_2Cl_2(dppe)_2 + 2H_2 \quad (119)$$

The suggested mechanism, the first steps of which are

$$MoH_4 \overset{H^+}{\rightleftharpoons} [MoH_5]^+ \rightleftharpoons [MoH_3(H_2)]^+ \overset{H^+}{\rightleftharpoons} [MoH_4(H_2)]^{2+} \xrightarrow{-H_2}$$

$$[MoH_4]^{2+} \xrightarrow{HCl} \longrightarrow MoH_2Cl_2 \quad (120)$$

is supported by kinetic results and the observation of the intermediate $[MoH_6(dppe)_2]^{2+}$, which must contain at least one dihydrogen ligand because Mo cannot reach the +7 oxidation state. For the same reason, a dihydrogen rather than dihydride tautomer of $[MoH_5(dppe)_2]^+$ is protonated. In a review, Henderson [5] suggested that, for polyhydridic complexes of transition metals in high oxidation states, protonation may depend on the ability of the complex to convert to a dihydrogen tautomer.

For the reaction of $MoH_4(dppe)_2$ with a variety of ligands in the presence of HBF_4, a similar mechanism (eqn. (121)) has been proposed [119] (L = NO, MeCN, CO, PhCCH, N_3^-, CO_2, SO_2, N_2).

$$MoH_4 \overset{H^+}{\rightleftharpoons} [MoH_5]^+ \rightleftharpoons [MoH_3(H_2)]^+ \overset{H^+}{\rightleftharpoons} [MoH_4(H_2)]^{2+} \xrightarrow{-H_2}$$

$$[MoH_4]^{2+} \xrightarrow{L} [MoH_4L]^{2+} \quad (121)$$

This is consistent with the general rule that the lability of a dihydrogen complex is increased upon protonation (Sect. E). Henderson suggests that this could be a model for the activation of nitrogenase given that "three electrons (and inferred protons) are consumed by the enzyme before dinitrogen binds, but dinitrogen displaces only one molecule of dihydrogen" [119].

(iii) Geometrical isomerization

The complex $[RuH(H_2)(diop)_2]^+$ undergoes rapid (on the NMR timescale) cis/trans isomerization above 303 K [289]. Saturation transfer is observed at 243 K but

not at 213 K. Other hydride(dihydrogen) complexes which undergo cis/trans isomerization include $[Fe(H_2)H\{PPh(OEt)_2\}_4]^+$ [74] and possibly $[Ru(H_2)H(dppb)_2]^+$ [80], although the ^{31}P NMR behavior of the latter could be explained by the existence of conformers (e.g. twist-chair and boat) of the chelate ring. The complexes *trans*-$[Os(H\cdots H)L(NH_3)_4]^{2+/1+}$ (L = py, I^-, Cl^-, MeCN, etc.) slowly isomerize to the cis isomer in acetone at room temperature [290]. Isomerization of $Ir(H_2)HCl_2(P^iPr_3)_2$ to a number of poorly characterized isomers has been reported [107].

(iv) Counterion exchange

The counterion can be exchanged, e.g. [7]

$$[Fe(H_2)H(dppe)_2]BF_4 + NaBPh_4 \rightarrow [Fe(H_2)H(dppe)_2]BPh_4 + NaBF_4 \quad (122)$$

(v) Insertion reactions of ancillary ligands

Insertion of an unsaturated molecule into a metal–hydride bond of a hydrido(dihydrogen) complex could occur

$$M(H_2)H + X{=}Y \rightleftharpoons M(H_2)(X{-}YH) \quad (123)$$

although there are no known examples. A proposed mechanism for eqn. (124) (L = $PPh(OEt)_2$, R = $-C_6H_4$-*p*-Me, $-C_6H_4$-*p*-OMe) invokes such a step (eqn. (125), [74]).

$$[Fe(H_2)HL_4]^+ + 2RN_2^+ \rightarrow [Fe(RN_2)_2L_3]^{2+} + H_2 + L + H^+ \quad (124)$$

$$[Fe(H_2)HL_4]^+ \xrightarrow{RN_2^+} [Fe(H_2)(RN{=}NH)L_4]^{2+}$$

$$\downarrow RN_2^+, -H_2$$

$$[Fe(RN_2)_2L_3]^{2+} \xleftarrow{-H^+, -L} [Fe(RN_2)(RN{=}NH)L_4]^{3+} \quad (125)$$

Given the lability of dihydrogen ligands, we suggest a more likely mechanism (126), which has precedence in the reactions of dihydrogen(hydride) complexes with unsaturates (Sect. E.(i)(c)).

$$[Fe(H_2)HL_4]^+ \xrightarrow{-H_2} [FeHL_4]^+ \xrightarrow{RN_2^+} [Fe(RN{=}NH)L_4]^{2+}$$

$$\downarrow RN_2^+$$

$$[Fe(RN_2)_2L_3]^{2+} \xleftarrow{-H^+, -L} [Fe(RN_2)(RN{=}NH)L_4]^{3+} \quad (126)$$

H. CATALYSIS AND RELATED REACTIONS

(i) Introduction

There are many well known processes of industrial and academic interest that involve the catalytic hydrogenation or dehydrogenation of compounds. Dihydrogen complexes can be considered as intermediates in all of these processes. Do dihydrogen complexes have unusual properties as catalysts? This question has not yet been answered. Table 27 lists the known catalytic reactions involving dihydrogen complexes as catalyst precursors. All of the transformations could be done, probably more efficiently, with other sorts of known homogeneous and heterogeneous catalysts. What is interesting is that these dihydrogen complexes are catalysts at all. Efficient hydrogenation catalysts have two or three very labile and sterically accessible coordination sites for hydrogen and unsaturate coordination. In addition they are usually electron-rich so that the splitting of dihydrogen into hydrides and migration of hydride to the unsaturate are processes of low activation energy. These characteristics are quite different from those of stable dihydrogen complexes: coordinative saturation and a relatively electron deficient, substitution inert, d^6 octahedral metal. Nevertheless, there are interesting aspects of catalysis involving dihydrogen complexes.

(ii) Dihydrogen complexes as catalysts or catalyst precursors

Many of the dihydrogen complexes are catalysts because they contain a labile dihydrogen ligand and a reactive hydride(s). This is illustrated by the simple H/D exchange reaction of the equation

$$H_2 + D_2 \overset{M(H_2)HL_n}{\rightleftharpoons} 2HD \qquad (127)$$

All of the complexes listed in Tables 13–15 in Sect. C which have efficient intramolecular H atom exchange and a labile dihydrogen ligand should catalyze eqn. (127). Specific examples of catalysts for eqn. (127) are listed in Table 27. All are based on platinum metals. The exception is Kubas' complex $W(H_2)(CO)_3(P^iPr_3)_2$, which slowly catalyzes this reaction in solution and in the solid state, possibly by an associative mechanism as discussed in Sect. C. The complex $[Fe(H_2)H(pp_3)]^+$ does not catalyze eqn. (127) because the dihydrogen ligand is not labile, even in boiling thf [64]. The reaction of deuterium with alcohols catalyzed by Crabtree's complex $[Ir(H_2)H(bq)(PPh_3)_2]^+$ is discussed in Sect. D. The mechanism of such reactions may be related to the action of the enzymes hydrogenase [215,233,291,292] and dehydrogenase [293] (see also Sect. D).

The dihydrogen complexes which hydrogenate alkenes and/or alkynes usually have a labile dihydrogen ligand and a hydride adjacent to the H_2, as in the case of the H/D catalysts above. Exceptions are complexes $[Fe(H_2)H(pp_3)]^+$,

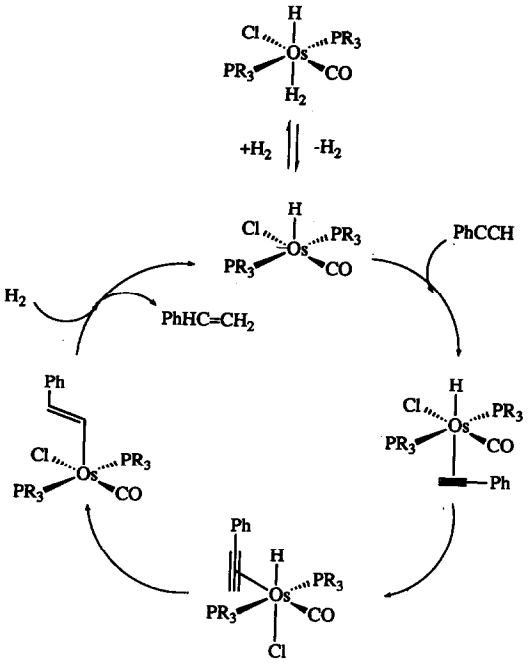
TABLE 27

Dihydrogen complexes as catalysts or catalyst precursors

Catalyst precursor	Reaction	Ref.
$W(H_2)(CO)_3(P^iPr_3)_2$	$H_2 + D_2 \rightleftharpoons 2HD$	204
$[Fe(H_2)H(P(OEt)_3)_4]^+$	$RC{\equiv}CH + H_2 \rightarrow RHC{=}CH_2$ R = *p*-tol, CMe_3, $SiMe_3$	259
$[Fe(H_2)H(pp_3)]^+$	$RC{\equiv}CH + H_2 \rightarrow RHC{=}CH_2$ R = Ph, $SiMe_3$, *n*-Pr, *n*-Pn, CH=CH(OMe)	184,250,263
	$2RC{\equiv}CH + H_2 \rightarrow RHC{=}CHCH{=}CHR$ R = $SiMe_3$	250
$[Ru(H_2)H(dppe)_2]^+$	$H_2 + D_2 \rightleftharpoons 2HD$	60
$[Ru(H_2)H(PR_3)_4]^+$ PR_3 = $PPh(OEt)_2$, $P(OEt)_3$	$RC{\equiv}CH + H_2 \rightarrow RHC{=}CH_2$ R = Ph, CMe_3, $SiMe_3$	75
$[Ru(H_2)H(pp_3)]^+$	$2HC{\equiv}CR \rightarrow Z{-}RC{\equiv}CCH{=}CHR$ R = $SiMe_3$, Ph	258
	$PhCH{=}CHCOMe + {}^iPrOH \rightarrow$ $RCH{=}CHCH(OH)Me + Me_2CO$	262
$Ru(H\cdots H)H_2(PPh_3)_3$	9-Me-anthracene + $H_2 \rightarrow$ 9-Me-an-H_8	196
	ketone + $H_2 \rightarrow$ alcohol	196
	ketone + $^iPrOH \rightarrow$ alcohol + Me_2CO	296
	$EtOH \rightarrow H_2 + CH_3CHO$	297,329
	$H_2 + D_2 \rightleftharpoons 2HD$	196
$(H_2)(dppb)Ru(\mu\text{-}Cl)_3$-Ru(Cl)(dppb)	$PhCH{=}CH_2 + H_2 \rightarrow PhCH_2CH_3$	37
	$H_2 + D_2 \rightleftharpoons 2HD$	37
	$MePhCO + {}^iPrOH \rightarrow MePhHCOH + Me_2CO$	37
(H_2)(p-n)$Ru(\mu\text{-}Cl)_2(\mu\text{-}H)$-Ru(H)$(PPh_3)_2$[a]	1-hexene + $H_2 \rightarrow$ hexane	15
$Ru_2(H_2)H(\mu\text{-}Cl)_2(\mu\text{-}H)(PR_3)_4$	1-alkene + $H_2 \rightarrow$ alkane	208,209
$[OsH_5(PMe_2Ph)_3]^+$	alkene + $H_2 \rightarrow$ alkane alkene = C_2H_4, cyclohexene	87
$Os(H_2)H(Cl)CO(P^iPr_3)_2$	$PhCCH + H_2 \rightarrow PhCHCH_2$	294
	$PhCHCH_2 + H_2 \rightarrow PhCH_2CH_3$	294
$[Rh(H\cdots H)(pp_3)]^+$	$RHC{=}CHR + H_2 \rightarrow RH_2CCH_2R$ R = CO_2Me	89
$[Ir(H_2)H_2(PMe_2Ph)_3]^+$	$H_2C{=}CH_2 + H_2 \rightarrow H_3CCH_3$	90,330
$[Ir(H_2)H(bq)(PPh_3)_2]^+$	$H_2 + D_2 \rightleftharpoons 2HD$	91
	$D_2 + ROH \rightleftharpoons HD + ROD$	190

[a] p-n = $FeCp(C_5H_3(CHMeNMe_2)P^iPr_2)$.

$(H_2)(dppb)RuCl_3RuCl(dppb)$, and $[Rh(H\cdots H)(pp_3)]^+$; all are catalysts as described below but the first has a non-labile H_2 ligand and the last two have no adjacent hydride. The mechanism proposed for the hydrogenation of phenylethyne to styrene by $Os(H_2)H(Cl)CO(PR_3)_2$ ($PR_3 = P^iPr_3$, PMe^tBu_2) in isopropanol at 60°C is probably typical of the cycles for many of these catalysts (Scheme 3) [294]. The dihydrogen complex serves as a source of the five-coordinate species $OsH(Cl)CO(PR_3)_2$ which



Scheme 3.

is thought to be within the catalytic cycle. The unsaturated substrate coordinates and the hydride migrates to the unsaturate to give a vinyl ligand in this case, or an alkyl in the case of alkene hydrogenation. Hydrogenolysis of the vinyl or alkyl completes the cycle. The hydrogenolysis reaction could involve a dihydrogen intermediate (see Sect. D). In the case of these Os complexes, as long as PhCCH is present, styrene product is not hydrogenated. However, as soon as the alkyne is consumed, styrene hydrogenation proceeds at a rate ten times that of alkyne hydrogenation. The explanation for this is that the alkyne rapidly reacts with Os complexes in solution to give the vinyl complex $Os(CH{=}CHPh)(Cl)CO(PR_3)_2$, which is a thermodynamic sink. Hydrogenolysis of this complex is the turnover limiting step. Styrene is unable to coordinate until this vinyl complex is consumed.

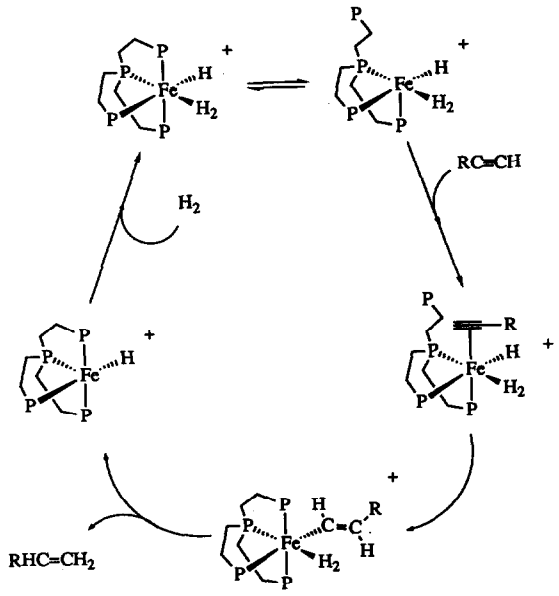
The complexes $[Ru(H_2)H(PR_3)_4]^+$ (PR_3 = $PPh(OEt)_2$, $P(OEt)_3$ and $P(OMe)_3$) in CH_2Cl_2 are all active for the hydrogenation of 1-alkynes to 1-alkenes at 25°C, 1 atm H_2. The catalyst dies after about 30 turnovers with the formation of complexes containing the but-1-en-3-yn-2-yl ligand η^3-RHC=CC≡CR. A complex containing this ligand, $[Ru(PhC{\equiv}CC{=}CHPh)(PPh(OEt)_2)_4]BPh_4$, was characterized by a single crystal X-ray diffraction study [75]. The coupling of alkynes to give such ligands is a typical reaction of such group 8 cationic complexes (see below).

The complex $[Ir(H_2)H_2(PMe_2Ph)_3]^+$ in CH_2Cl_2 hydrogenates 2-butyne to *cis*-2-butene, 1-butene and butane at 22°C [295]. Again, it appears that the lability

of the dihydrogen ligand serves to provide a coordinatively unsaturated and reactive complex, in this case $[IrH_2(PMe_2Ph)_3]^+$. In this case, a proposed intermediate is the crystallographically characterized complex, $[Ir(MeC{\equiv}CMe)(PMe_2Ph)_3]^+$.

There are distinctive aspects to the selective hydrogenation of 1-alkynes to alkenes catalyzed by dihydrogen complexes of iron. First, examples of iron-based homogeneous catalysts are rare and yet two dihydrogen complexes, $[Fe(H_2)H(pp_3)]^+$ in thf and $[Fe(H_2)H(P(OEt)_3)_4]^+$ in CH_2Cl_2 are active at 25°C for this reaction. Second, there is evidence that the pp_3 complex coordinates alkyne, not via loss of H_2, but instead by dissociation of one of the $-CH_2CH_2PPh_2$ "arms" of the pp_3 ligand (Scheme 4) [263]. This is a rare example of a dihydrogen complex thought to be within the catalytic cycle. In Scheme 4, hydrogenation proceeds via coordination of the alkyne and migration of the hydride to give a vinyl intermediate which is then hydrogenolyzed by the cis dihydrogen ligand. This last reaction can be viewed as an intramolecular heterolytic cleavage of dihydrogen (see Sect. D). The dissociation of the pp_3 "arm" is thought to be the turnover limiting step [184]. The study of the catalysis by $[Fe(H_2)H(P(OEt)_3)_4]^+$ is in progress [259].

The coupling of alkynes is an alternative reaction to their hydrogenation in certain cases. Of the 1-alkynes examined for hydrogenation (see Table 27), only one, trimethylsilylethyne, undergoes concurrent hydrogenation and coupling at 66°C catalyzed by species derived from $[Fe(H_2)H(pp_3)]^+$ in thf [263]. Under these conditions, a mixture of trimethylsilylethene and 1,4-bis(trimethylsilyl)butadiene was obtained in a ratio 2.2:9.8. In contrast, the complex $[Ru(H_2)H(pp_3)]^+$ is a catalyst



Scheme 4.

precursor for the dimerization of 1-alkynes almost exclusively to Z-1,4-disubstituted enynes [258]. An intermediate was characterized by X-ray diffraction and shown to be $[Ru(\eta^3\text{-}Me_3SiCCCCHSiMe_3)(pp_3)]^+$. The dihydrogen ligand appears to function as a good leaving group in these reactions.

Several of the platinum metal complexes of Table 27 are alkene hydrogenation catalysts. The hydrogenation of styrene to ethylbenzene proceeds at 1 atm H_2, 60°C in isopropanol in the presence of $Os(H_2)H(Cl)CO(P^iPr_3)_2$ [294]. The dimeric Ru complexes of the table hydrogenate 1-alkenes in *N,N*-dimethylacetamide at 1 atm H_2 [15,37]. The chloride bridges in these complexes provide additional sites of coordinative unsaturation at the metal so that 1-hexene coordination might proceed without dihydrogen dissociation in these cases. Methylene chloride solutions of $[OsH_5(PMe_2Ph)_3]^+$ at 25°C catalyze the hydrogenation of ethylene with 1 atm H_2 and cyclohexene with 70 atm H_2 [87]. The cation $[Ir(H_2)H_2(PMe_2Ph)_3]^+$ in CH_2Cl_2 is also active at 25°C and 1 atm H_2 for ethylene hydrogenation [90]. In all of these reports of Os and Ir dihydrogen complexes, facile H_2 loss from the complex is stressed as an important factor in the activation of the catalyst. In contrast, the complex $[Rh(H\cdots H)(pp_3)]^+$ was proposed to hydrogenate the C=C bond of dimethylmaleate in a two-step process: (1) proton transfer, and then, (2) hydride transfer [89]. No further details have emerged, but such a mechanism has recently been proposed for stoichiometric reduction of acetone by $[Os(H_2)(NH_3)_5]^{3+}$ (see below).

The complex $Ru(H\cdots H)H_2(PPh_3)_3$ is an active catalyst for a variety of processes. In the presence of 1 atm H_2, a toluene solution of this compound at 55°C hydrogenates 9-methylanthracene to 1,2,3,4,5,6,7,8-octahydro-9-methyl-anthracene [196]. This catalyst also reduces unactivated ketones to alcohols. The hydrogenation of cyclohexanone to cyclohexanol proceeds at 21°C and 1 atm in toluene solvent; the following mechanism has been proposed [196].

$$RuH_4(PPh_3)_3 \rightleftharpoons RuH_2(PPh_3)_3 + H_2 \tag{128}$$

$$RuH_2(PPh_3)_3 + c\text{-}C_6H_{10}O \rightleftharpoons RuH_2(PPh_3)_3(c\text{-}C_6H_{10}O) \tag{129}$$

$$RuH_2(PPh_3)_3(c\text{-}C_6H_{10}O) + H_2 \rightarrow RuH_2(PPh_3)_3(c\text{-}C_6H_{11}OH) \tag{130}$$

$$RuH_2(PPh_3)_3(c\text{-}C_6H_{11}OH) + H_2 \xrightarrow{\text{fast}} RuH_4(PPh_3)_3 + c\text{-}C_6H_{11}OH \tag{131}$$

Here again, the themes of dihydrogen dissociation and hydride migration appear. Isopropanol can also be used as the source of hydrogen for the reduction of substituted cyclohexanones to mixtures of cis and trans alkylcyclohexanols at 25°C catalyzed by species derived from $Ru(H\cdots H)H_2(PPh_3)_3$ [142,296]. The high activity of this complex was attributed to the dihydrogen ligand being a good leaving group. No dihydrogen complexes were thought to be within the catalytic cycle. Similarly, the complex $[Ru(H_2)H(pp_3)]^+$ in thf at 40°C catalyzes the selective reduction of the ketone in α,β-unsaturated ketones with isopropanol or cyclopentanol as the source

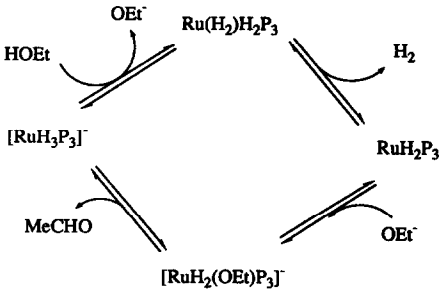
of hydrogen [262]. The dimeric Ru(dppb) complex of Table 27 catalyzes the solvent transfer hydrogenation of acetophenone to 1-phenylethanol at 25°C in isopropanol/KOH [37].

The lability of the H_2 ligand in $Ru(H\cdots H)H_2(PPh_3)_3$ is thought to be the important characteristic of the catalyst for the dehydrogenation of ethanol to acetaldehyde [297] in ethanol/NaOH solution at 150°C. The catalyst precursor is actually $Ru(N_2)H_2(PPh_3)_3$, which is rapidly converted to the dihydrogen complex under these conditions. The steps in this process are proposed to be related to the hydrogenation reaction represented by eqns. (128)–(131). However, anionic complexes are also implicated (Scheme 5). The reactive dihydrogen complex allows the ethoxide ion to coordinate in this cycle. Beta elimination gives acetaldehyde and the trihydride anionic complex. This hydride is basic enough to be protonated by ethanol to regenerate the dihydrogen complex.

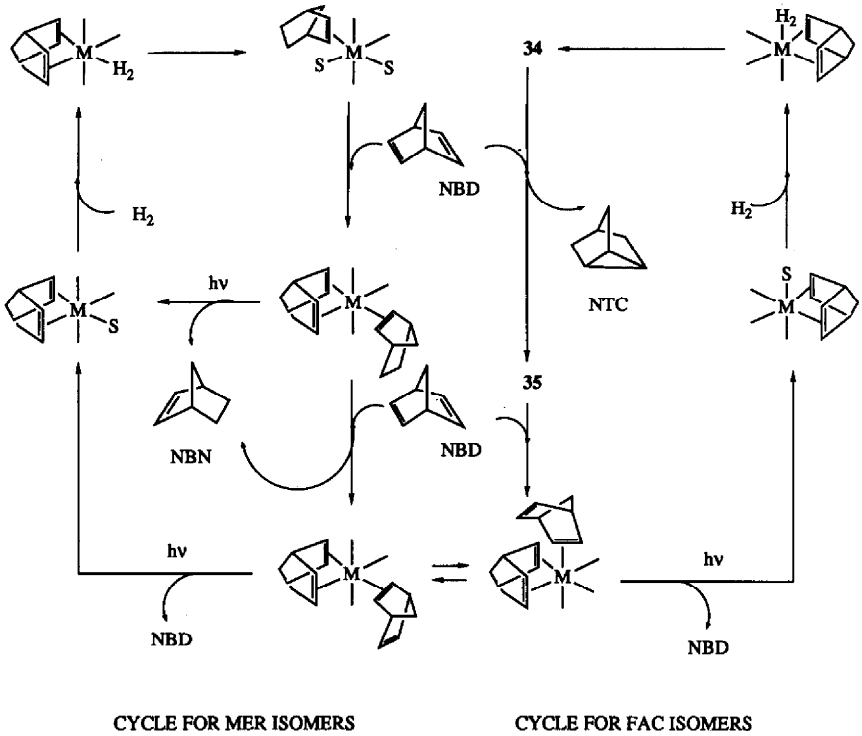
There are only a few cases where dihydrogen complexes are thought to be directly within the catalytic cycle. These include the $H_2/D_2/HD$ and D_2/ROH exchange reactions, the hydrogenation of alkynes by $[Fe(H_2)H(pp_3)]^+$, and the dehydrogenation of alcohols by $Ru(H\cdots H)H_2(PPh_3)_3$ as mentioned above. There are a few additional examples. The complex $Os(H_2)(SiEt_3)Cl(CO)(P^iPr_3)_2$ and its dihydride tautomer appear in the proposed cycle of the catalytic hydrosilylation of phenylethyne [298]. A nickel dihydrogen complex might be involved in the action of hydrogenase and nitrogenase [215]. The complex $Co(H_2)(C(O)R)(CO)_3$ has been proposed as an intermediate in the hydroformylation of olefins catalyzed by Co_2CO_8 [164,239] (see also Sect. D.(iv)).

The complexes mer- and fac-$M(H_2)(NBD)(CO)_3$ (M = Cr, Mo, NBD = norbornadiene) are proposed to be intermediates in the photocatalytic conversion of NBD to NBN (norbornene) and nortricyclene (NTC) in *n*-heptane at 20°C. The mer isomer is proposed to lead to formation of NBN while the fac isomer leads to the formation of nortricyclene (NTC) as in Scheme 6 [299].

The carbonyl ligands are not shown in Scheme 6 and "S" represents weakly coordinated solvent, *n*-heptane. We have introduced intermediates **34** and **35** of unknown structure to complete the catalytic cycle for NTC formation. The significant



Scheme 5.



Scheme 6.

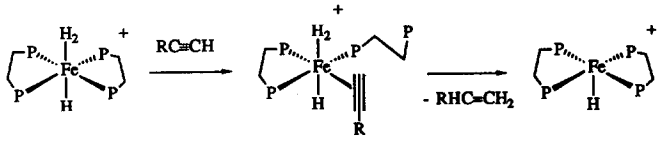
aspect to Scheme 6 is that the stereochemistry of the dihydrogen complex determines the structure of the hydrogenated product. The identity of several of the intermediates in this scheme was revealed by spectroscopic work utilizing supercritical liquid Xe as the solvent [51,299].

(iii) Reactions related to the catalytic cycles

There are some interesting stoichiometric reactions which either provide further information on the catalytic systems mentioned above or suggest the possibility of new catalysts. Two examples considered here are reactions of alkynes with dihydrogen complexes and the reduction of ketones by H^+/H^- transfer from a dihydrogen complex.

The hydrogenation of alkynes catalyzed by $[Fe(H_2)H(pp_3)]^+$ is thought to involve a dihydrogen–alkyne intermediate (Scheme 4). Such an intermediate has also been proposed in the stoichiometric reduction of 1-alkynes (eqn. (132)) during the formation of complexes $Fe(CCR)_2(dmpe)_2$ from $[Fe(H_2)H(dmpe)_2]^+$ and 4 equivalents of alkyne (eqn. (133)) [255].

Three catalytic systems were discussed in Sect. H.(ii) in which alkyne dimeriza-



(132)

$$[Fe(H_2)H(dmpe)_2]^+ + 4\,HCCR \rightarrow Fe(CCR)_2(dmpe)_2 + H^+ + 2\,RHC{=}CH_2 \quad (133)$$

tion was a side reaction (for complexes $[Fe(H_2)H(pp_3)]^+$ and $[Ru(H_2)H(PR_3)_4]^+$) or the main product of catalysis (for $[Ru(H_2)H(pp_3)]^+$). A common theme was the formation of complexes containing the but-1-en-3-yn-2-yl ligand η^3-RC≡CC=CHR$^-$. This reaction has also been observed in some stoichiometric reactions of dihydrogen complexes. Jia and Meek [66] report that $Ru(H_2)H_2$(cyttp) (cyttp = C_6H_5P-$(CH_2CH_2CH_2PCy_2)_2$) reacts with phenylethyne according to the equation

$$RuH_4(cyttp) + 3HC{\equiv}CPh \rightarrow Ru(CCPh)(\eta^3\text{-}PhC{\equiv}CC{=}CHPh)(cyttp) + 3H_2 \quad (134)$$

Similarly, the dihydrogen complex $[Fe(H_2)H(dmpe)_2]^+$ reacts with 1-alkynes to give complexes $[Fe(\eta^3\text{-}RC{\equiv}CC{=}CHR)(dmpe)_2]^+$ [255,256].

Harman and Taube [93(a)] reported a rapid reduction of acetone by the electrochemically generated complex $[Os(H_2)(NH_3)_5]^{3+}$. Since the Os(II) complex $[Os(H_2)(NH_3)_5]^{2+}$ is inactive in such a reaction and the Os(III) complex is acidic, the authors proposed an ionic hydrogenation mechanism where addition of H^+ occurs before transfer of H^-

$$[Os(H_2)(NH_3)_5]^{3+} + Me_2CO \rightarrow [OsH(NH_3)_5]^{2+} + [Me_2C(OH)]^+$$

$$\rightarrow [Os(NH_3)_5(HO)CHMe_2]^{3+} \quad (135)$$

Bullock reported that a mixture of $MoH(Cp)(CO)_3$ and HO_3SCF_3 reduces ^{t}BuHC=CH_2 to $Me_2HCCHMe_2$ via protonation, carbonium ion rearrangement, and hydride reduction [300]. An acidic dihydrogen complex, $[Mo(H_2)Cp(CO)_3]^+$, might be involved in this reaction. A similar ionic reduction of ketones by a mixture of $MoH_2(Cp)_2$ and strong acids was discovered by Ito et al. [301]. However, Norton et al. recently found that H^+ adds more rapidly to substrate than to metal hydride in the reduction of ketones/aldehydes by a variety of metal hydride/acid mixtures; therefore the formation of dihydrogen complexes as intermediates in the reaction is not necessary [302]. It will be interesting to see if catalytic cycles based on such an ionic hydrogenation mechanism can be devised. A promising stoichiometric reaction is the reduction of 1-benzyl-*N*,*N*-diethylnicotinamide hexafluorophosphate (an NAD^+ analogue) by H_2/Ru(oep)$(thf)_2$/py in thf [88]. The heterolytic cleavage of coordinated dihydrogen is postulated to be a key step in this reaction.

I. CONCLUSIONS

Dihydrogen complexes exist on a small island of stability that is surrounded by a sea of instability defined by the d configuration, d electron energy and orbital overlap associated with the metal and the size and other stereochemical properties of the ligands. Small changes in any of these factors push the complex off the island. The complexes can be unstable with respect to intra- or inter-molecular homolytic cleavage, intra- or inter-molecular heterolytic cleavage, evolution of H_2 gas, or hydrogenation of a ligand or non-coordinated substrate. Several of these reactions have parallels to the reactions of dihydride or polyhydride complexes. Some distinctive reactions of dihydrogen as opposed to dihydride complexes have emerged as noted below.

Intramolecular homolytic cleavage ($M(H_2)L_n$ to $M(H)_2L_n$) is more thermodynamically favorable for 5d versus 3d metals, for metals in low oxidation states with high-energy d electrons, for small, electron-donating ligands and for ligands that destabilize octahedral coordination or favor higher coordination numbers. Comparisons with the properties of the related dinitrogen complex, $M(N_2)L_n$, are useful in deciding if the H–H bond will split. Cleavage is likely to occur if $\nu(N_2)$ is less than 2050 cm^{-1} or if $E_{1/2}\{M(N_2)L_n^+/M(N_2)L_n\}$ is less than 0 V vs. Fc^+/Fc. However, an estimate of stability of the product dihydride must also be obtained before the outcome of the reaction can be reliably predicted; this is usually difficult to do using empirical methods. Isotopic substitution appears to favor $M(HD)L_n$ over $M(H)(D)L_n$. Even though there is a loss in rotational motion of the H_2 ligand when the dihydride is formed, the change in entropy for this reaction is not always negative; the nature of the ancillary ligands is also important. Usually, the ΔS value is close to zero (± 10 e.u.). Complexes with elongated dihydrogen units, $M(H\cdots H)L_n$ have thermodynamic properties which are similar to those of dihydrogen complexes $M(H_2)L_n$.

The activation enthalpy barrier for the intramolecular splitting of dihydrogen ranges from less than 10 to up to 20 kcal mol^{-1}; the activation entropy is negative. The $\Delta H^{\ddagger}$ probably arises because the metal has to change its coordination number and geometry and the ancillary ligands have to move in the process. The loss of the H–H bond could be balanced by M–H bond making so that this may not be an important enthalpic contribution to the barrier. Steric contributions to the barrier are important because of the changes in stereochemistry. A loss of rotational freedom of the H_2 might explain why $\Delta S^{\ddagger}$ is negative. A conclusive study of the change in the activation barrier as a function of changing electronics at the metal remains to be done; steric interactions would have to remain constant throughout the reaction to observe a systematic trend. Kinetic studies of this reaction are challenging because of the instability of the complexes in certain cases. When the kinetics are monitored by NMR, the rapid relaxation of the dihydrogen nuclei and the presence of other dynamic exchange processes sometimes complicate the analysis.

If a dihydrogen/dihydride equilibrium has a ΔG near to zero and a $\Delta G^{\ddagger}$ which

is greater than 10 kcal mol^{-1}, then both $M(H_2)L_n$ and $M(H)_2L_n$ tautomers can be observed by NMR. Several examples have been reported for 4d and 5d metals. There are no examples yet for 3d metals. This can be explained by the difficulty in forming seven-coordinate complexes on a small 3d metal and the weakness of the M–H bonds in the dihydride form under the electron-deficient conditions necessary for the stabilization of the dihydrogen form. In many cases, $\Delta H^{\ddagger}$ may be much less than 10 kcal mol^{-1} so that there is rapid equilibration of the tautomers. Further efforts are needed to distinguish between a rapidly interconverting mixture of tautomers and a single species with an elongated dihydrogen. Changes with temperature in NMR observable properties such as J(HD) could signal a perturbation of a rapid equilibrium. More crystallographic work is needed to resolve structural ambiguities in this area.

Further examples of the intermolecular homolytic splitting of dihydrogen should be sought out. Such reactions are difficult to study because the reactant dihydrogen complex is usually diamagnetic and the product monohydride is paramagnetic. These reactions are potentially of importance in a variety of catalytic homogeneous hydrogenation mechanisms.

The exchange of H atoms between dihydrogen and hydride ligands is a very common property of dihydrogen complexes. The $\Delta G^{\ddagger}$ values for a large number of exchange processes have been estimated from literature reports of instances of incomplete T_1 averaging or line-shape coalescence. In general, exchange is fastest when dihydrogen and hydride are located cis to each other. The presence of a cis interaction between H_2 and H ligands and the ease of an associative H–H–H mechanism may account for the low barrier to exchange. NMR studies of the complex $[Re(H_2)H_2(CO)(PMe_2Ph)_3]^+$ provide the best evidence for such an associative reaction. However, certain complexes with dihydrogen and hydride trans to each other also exhibit rapid exchange. For these complexes, a mechanism involving dissociation of the H–H bond to give a trihydride intermediate is favored. Factors that favor exchange in complexes *trans*-$[M(H_2)H(L_2)_2]^+$ (M = Fe, Ru, Os) are: high flexibility of the backbone of the chelating diphosphine L_2; large size of substituents to destabilize the octahedral geometry; electron-donating substituents on L_2; and metals of higher π basicity (Os > Fe > Ru). This last-mentioned ordering of metals is different from that for H atom exchange in six-coordinate hydride complexes $M(H)_2L_4$, (L = PR_3 or L_2 = dppe) [303].

Hydrogen atom exchange processes involving the dihydrogen ligand allow interesting stoichiometric and catalytic isotope exchange reactions to take place. More research is needed to learn how the reaction of D_2 gas with coordinatively saturated dihydrogen complexes can result in H/D exchange and the formation of HD complexes.

There are some distinctive features of the acidity of dihydrogen complexes with respect to that of related dihydride complexes. In general, dihydrogen complexes transfer protons to bases faster than dihydride complexes (kinetic acidity). However,

the thermodynamic acidity of a dihydrogen complex is not necessarily greater than that of its dihydride tautomer; the minor tautomer is the more acidic. In a hydride(dihydrogen) complex, $M(H_2)_xH_yL_z$, the thermodynamic acidities of the hydride and the dihydrogen ligands are identical unless rearrangement in the product is restricted.

Electron-deficient dihydrogen complexes are both labile and acidic. Very acidic dihydrogen complexes with pK_a values below 0 have been reported. An equation linking the pK_a of d^6 $M(H_2)L_5$ complexes to the H–H bond dissociation enthalpy and the d^6/d^5 reduction potential for the MHL_5 hydride allows the calculation of a range of possible pK_a values from published electrochemical ligand additivity parameters. The reactions of very acidic dihydrogen complexes appears to be a very promising area for future research.

Several mechanisms for intramolecular heterolytic cleavage of dihydrogen ligands have been identified and classified as either the protonation of a ligand lone pair or a metal–ligand bond. These may be catalyzed by an external base. It may be difficult to distinguish these mechanisms by kinetic methods with the exception of the external base catalysis mechanism for which the rate should depend on the concentration of the base. Very little data on the thermodynamics of such reactions have been reported, probably because the protonated ligand is often eliminated from the product complex. Studies of those systems in which the protonated product is not eliminated would be useful in order to determine the factors which influence the acidity of coordinated acids.

The intra- or intermolecular heterolytic cleavage of a dihydrogen ligand may be involved in a number of important catalytic reactions, including H/D exchange, hydroformylation, olefin hydrogenation, and possibly the reactions of hydrogenase and nitrogenase.

Dihydrogen elimination is a common reaction for $M(H_2)$ and $M(H\cdots H)$ complexes because of the weak $M-H_2$ binding compared with that of most other ligands. However, some complexes are surprisingly stable with respect to loss of H_2 gas. Complexes $M(H_2)L_n$ are not necessarily less thermodynamically or kinetically stable than related dihydride complexes, $M(H)_2L_n$. Comparisons with the properties of the related dinitrogen complex, $M(N_2)L_n$, are useful in deciding if H_2 will be lost easily. This is likely to occur if $\nu(N_2)$ is greater than 2150 cm^{-1} or if $E_{1/2}(M(N_2)L_n^+/M(N_2)L_n)$ is greater than 2 V vs. Fc^+/Fc. However, an estimate of the stability of the product five-coordinate complex must also be obtained before the outcome of the reaction can be reliably predicted. There are a few examples of dihydrogen complexes which readily lose H_2 when $\nu(N_2)$ is less than 2150 cm^{-1}. Thus, the use of spectroscopic data as rough indicators of the strength of dihydrogen binding has limitations. These should be supplemented or replaced wherever possible by quantitative thermodynamic and kinetic data, which are at present in short supply. The high enthalpy of N_2 loss compared with that of H_2 loss makes N_2 a stronger ligand at low temperatures. However, at higher temperatures, entropy factors make H_2 a stronger ligand than N_2. This may also be true for D_2 versus H_2.

In the absence of potentially substituting reagents, the coordinatively unsaturated complex produced by H_2 loss may or may not be more stable than the original dihydrogen complex. The stability of the dihydrogen complex with respect to H_2 loss is increased if the complex contains a 5d metal and if the ligands are electron donating (especially for the later transition metals) and are not potentially chelating. The trend in qualitative stabilities of isostructural dihydrogen complexes of group 6 and 8 metals is 5d > 3d > 4d or, less commonly, 5d > 4d > 3d. Quantitative data for $M(H_2)(CO)_3(PCy_3)_2$ show that the 5d(W) complex is both kinetically and thermodynamically more stable than the 3d (Cr) complex. The reasons for the trends are not clear.

In general, dihydrogen complexes ($M(H_2)$ or $M(H \cdots H)$) lose H_2 more quickly than classical hydrides, but there are already some exceptions. As more data become available, more exceptions should come to light. The rate of elimination of H_2 can no longer be used as a criterion for distinguishing $M(H_2)$ from $M(H)_2$ complexes.

Several types of reaction involve the loss of the H_2 ligand. These include replacement of the H_2 by a wide range of ligands; substitution followed by an intramolecular reaction, usually involving a hydride migration; exchange of H_2 and another ligand between complexes; and elimination followed by dimerization of the resulting coordinatively unsaturated complex.

There are only a few electrochemical studies of dihydrogen complexes. Two complexes, $Re(H \cdots H)Cl(PMePh_2)_4$ and $[Os(H \cdots H)(NH_3)_5]^{2+}$, display a reversible, one-electron oxidation, whereas several undergo irreversible oxidations. So far, two common decomposition routes of oxidized dihydrogen complexes have been identified. The first is H_2 evolution after oxidation and the second is loss of a proton. The oxidation of $[Os(H_2)(NH_3)_5]^{2+}$ is irreversible in acetone because the product $Os(III)(H_2)$ complex reduces acetone to isopropanol. This paradoxical reaction, where an oxidation turns the complex into a more potent reducing agent, is a futher pathway to decomposition of oxidized dihydrogen complexes. Additive electrochemical parameters for ligands in six-coordinate complexes can be used to estimate potentials for the one-electron oxidation of dihydrogen complexes. In general the agreement is good.

Reactions where the dihydrogen ligand is retained are rare. Examples of the following reactions of dihydrogen complexes are known or proposed: substitution of ancillary ligands in the complex; protonation of the complex; cis–trans isomerization of the complex; counterion exchange; and insertion reactions of ancillary ligands in the complex.

Do dihydrogen complexes have unusual properties as catalysts? There are no catalysts of unusually high activity or selectivity among the complexes which have been tested so far. However, homogeneous hydrogenation catalysts based on iron are rare and so it is of interest that two iron dihydrogen complexes, $[Fe(H_2)H(pp_3)]^+$ and $[Fe(H_2)H(P(OEt)_2Ph)_4]^+$, catalyze the reduction of 1-alkynes to alkenes. Certain dihydrogen complexes are also catalysts for $H_2/D_2/HD$ exchange, the hydrogenation

of alkenes, dienes, anthracenes and ketones, the dehydrogenation of alcohols and the dimerization of alkynes. Dihydrogen complexes have been implicated as intermediates in olefin hydroformylation and hydrosilylation processes. Several complexes of the type $M(H_2)HL_n$ are $H_2/D_2/HD$ exchange catalysts or hydrogenation catalysts because they readily dissociate H_2 to allow the coordination of the substrate (D_2, alkene, alkyne) to the metal and the reaction of the substrate with the cis hydride ligand. A few catalysts appear to be exceptions to this rule, including $[Fe(H_2)H(pp_3)]^+$ for the hydrogenation of alkynes and $M(H_2)(CO)_3(nbd)$ for the hydrogenation of norbornadiene. The postulated dihydrogen complex $[Os(H_2)(NH_3)_5]^{3+}$ is thought to reduce acetone to isopropanol via a unique sequence of H^+ and H^- transfer.

Dihydrogen and hydride are the simplest ligands in coordination chemistry. And yet they provide a gamut of reactions, some complicated by the particle/wave duality of hydrogen nuclei. The simplicity of these ligands makes a combined effort of theoretical treatment and quantitative experimental work a rewarding exercise in understanding the chemistry and physics of reactions of these and other ligands.

ACKNOWLEDGEMENTS

This work was supported by grants to R.H.M. from the Natural Sciences and Engineering Research Council of Canada and from the donors of the Petroleum Research Fund administered by the American Chemical Society. Drs. G. Albertin, C. Bianchini, D. Cole-Hamilton, R. Crabtree, J. Eckert, O. Eisenstein, D. Gusev, S. Jackson, G. Kubas, F. Maseras, M. Saburi, S. Simpson, H. Taube, L. Venanzi and H. Werner are thanked for articles supplied. We are grateful to Prof. A. Poë for comments on part of the paper and T. Burrow, P. Maltby, M. Schlaf, C. Schweitzer, S. Brinkman, L. Jessop and C. Morris for their help.

NOTE ADDED IN PROOF

Two significant papers have appeared after the writing of this review. Lin and Hall [331] have calculated ab initio the relative stabilities of classical and non-classical polyhydrides. They report several factors which should be added to those of Table 3. The stability of trans hydride ligands is significantly destabilizing and influences the stability and structure of isomers; thus the proposed intermediate complex of eqn. (33) might be of unreasonably high energy. A diagonal line through Ru and Ir divides classical (left-hand side) and non-classical (right-hand side) polyhydrides for neutral complexes without strong π-accepting ligands [331].

Bianchini et al. report that $[Co(H)_2(pp_3)]BPh_4 \cdot 2THF$ is a white, classical, octahedral dihydride complex which dissolves in THF to give the red, trigonal-bipyramidal dihydrogen complex $[Co(H_2)(pp_3)]^+$. The red dihydrogen isomer crystallized as the PF_6^- salt but the X-ray diffraction study failed to locate the hydrogen

atoms [332]. This is a further example of a low-energy dihydrogen/dihydride interconversion process (refer to eqn. (12)). Dinitrogen can displace dihydrogen from both the dihydrogen and dihydride isomers in the solid state.

REFERENCES

1 G.J. Kubas, R.R. Ryan, B.I. Swanson, P.J. Vergamini and H.J. Wasserman, J. Am. Chem. Soc., 106 (1984) 451.
2 G.J. Kubas, Acc. Chem. Res., 21 (1988) 120.
3 G.J. Kubas, Comments Inorg. Chem., 7 (1988) 17.
4 R.H. Crabtree and D.G. Hamilton, Adv. Organomet. Chem., 28 (1988) 299.
5 R.A. Henderson, Transition Met. Chem. (London), 13 (1988) 474.
6 (a) G.J. Kubas, C.J. Unkefer, B.I. Swanson and E. Fukushima, J. Am. Chem. Soc., 108 (1986) 7000.
(b) P.J. Vergamini, H.J. Wasserman, T.F. Koetzle, R.R. Ryan and G.J. Kubas, unpublished results.
7 J.S. Ricci, T.F. Koetzle, M.T. Bautista, T.M. Hofstede, R.H. Morris and J.F. Sawyer, J. Am. Chem. Soc., 111 (1989) 8823.
8 L.S. Van Der Sluys, J. Eckert, O. Eisenstein, J.H. Hall, J.C. Huffman, S.A. Jackson, T.F. Koetzle, G.J. Kubas, P.J. Vergamini and K.G. Caulton, J. Am. Chem. Soc., 112 (1990) 4831.
9 G.J. Kubas, C.J. Burns, J. Eckert, S.W. Johnson, A.C. Larsen, P.J. Vergamini, C.J. Unkefer, G.R.K. Khalsa, S.A. Jackson and D. Eisenstein, J. Am. Chem. Soc., in press.
10 L. Brammer, J.A.K. Howard, O. Johnson, T.F. Koetzle, J.L. Spencer and A.M. Stringer, J. Chem. Soc. Chem. Commun., (1991) 241.
11 B. Chaudret, G. Chung, O. Eisenstein, S.A. Jackson, F.J. Lahoz and J.A. Lopez, J. Am. Chem. Soc., 113 (1991) 2314.
12 F.A. Cotton and R.L. Luck, Inorg. Chem., 30 (1991) 767.
13 S.J. Litster, A.D. Redhouse and S.J. Simpson, Proceedings of the Conference Chemistry of the Platinum Group Metals, University of Cambridge, 1990, Paper C-48.
14 R.H. Morris, J.F. Sawyer, M. Shiralian and J. Zubkowski, J. Am. Chem. Soc., 107 (1985) 5581.
15 C. Hampton, W.R. Cullen and B.R. James, J. Am. Chem. Soc., 110 (1988) 6918.
16 Y. Kim, H. Deng, D.W. Meek and A. Wojcicki, J. Am. Chem. Soc., 112 (1990) 2798.
17 G.J. Kubas, J. Chem. Soc. Chem. Commun., (1980) 61.
18 R.H. Hauge, Z.H. Kafafi and J.L. Magrave, NATO ASI Ser. Ser. B, 158 (1987) 787.
19 C. Jarque, O. Novaro, M.E. Ruiz and J. Garcia-Prieto, J. Am. Chem. Soc., 108 (1986) 3507.
20 H. Nakatsuji and M. Hada, J. Am. Chem. Soc., 107 (1985) 8264.
21 C.A. Nicolaides and P. Valtazanos, Chem. Phys. Lett., 174 (1990) 489.
22 G.A. Ozin and J. Garcia-Prieto, J. Am. Chem. Soc., 108 (1986) 3099.
23 M. Rivera, J.F. Harrison and A. Alvarado-Swaisgood, J. Phys. Chem., 94 (1990) 6969.
24 M. Sanchez, F. Ruette and A.J. Hernandez, J. Phys. Chem., 96 (1992) 823.
25 J.K. Burdett, O. Eisenstein and S.A. Jackson, in A. Dedieu (Ed.), Transition Metal Hydrides: Recent Advances in Theory and Experiment, VCH, New York, 1991, p. 149.
26 C.A. Tsipis, Coord. Chem. Rev., 108 (1991) 163.
27 (a) J. Bertran, F. Maseras, M. Duran and A. Lledos, in S.J. Formosinho, I.G. Csizmadia and L.G. Arnaut (Eds.), Theoretical and Computational Models for Organic Chemistry,

NATO ASI Series, 1992, in press.
(b) A.G. Ginzburg and A.A. Bagatur'yants, Metaloorg. Khim., 2 (1989) 249.
28 P.J. Desrosiers, L.H. Cai, Z.R. Lin, R. Richards and J. Halpern, J. Am. Chem. Soc., 113 (1991) 4173.
29 K.A. Earl, G. Jia, P.A. Maltby and R.H. Morris, J. Am. Chem. Soc., 113 (1991) 3027.
30 X.-L. Luo, J.A.K. Howard and R.H. Crabtree, Magn. Reson. Chem., 29 (1991) S89.
31 G.J. Kubas, J. Less Common Met., 173 (1991) 475.
32 (a) J. Eckert, Spectrochimica Acta, Part A, 48 (1992) 363.
(b) K.W. Zilm, R.A. Merrill, M.W. Kummer and G.J. Kubas, J. Am. Chem. Soc., 108 (1986) 7837.
33 A.A. Gonzalez, S.L. Mukerjee, S.-J. Chou, Z. Kai and C.D. Hoff, J. Am. Chem. Soc., 110 (1988) 4419.
34 G.J. Kubas, R.R. Ryan and C.J. Unkefer, J. Am. Chem. Soc., 109 (1987) 8113
35 D.M. Gusev, A.B. Vymenits and V.I. Bakhmutov, Inorg. Chem., 31 (1992) 1.
36 M.A. Esteruelas, E. Sola, L.A. Oro, O. Meyer and H. Werner, Angew. Chem. Int. Ed. Engl., 27 (1988) 1563.
37 A.M. Joshi and B.R. James, J. Chem. Soc. Chem. Commun., (1989) 1785.
38 A. Mezzetti, A. Delzotto, P. Rigo and E. Farnetti, J. Chem. Soc. Dalton Trans., (1991) 1525.
39 C. Bianchini, C. Mealli, M. Peruzzini and F. Zanobini, J. Am. Chem. Soc., 109 (1987) 5548.
40 D.G. Gusev, V.I. Bakhmutov, V.V. Grushin and M.E. Volpin, Inorg. Chim. Acta, 175 (1990) 19.
41 D.G. Gusev, V.I. Bakhmutov, V.V. Grushin and M.E. Volpin, Inorg. Chim. Acta, 177 (1990) 115.
42 (a) M. Mediati, G.N. Tachibana and C.M. Jensen, Inorg. Chem., 29 (1990) 3.
(b) M. Mediati, G.N. Tachibana and C.M. Jensen, Inorg. Chem., 31 (1992) 1827.
43 S.P. Nolan and T.J. Marks, J. Am. Chem. Soc., 111 (1989) 8538.
44 M.T. Haward, M.W. George, P. Hamley and M. Poliakoff, J. Chem. Soc. Chem. Commun., (1991) 1101.
45 S.P. Church, F.-W. Grevels, H. Hermann and K. Schaffner, J. Chem. Soc. Chem. Commun., (1985) 30.
46 R.K. Upmacis, M. Poliakoff and J.J. Turner, J. Am. Chem. Soc., 108 (1986) 3645.
47 R.L. Sweany, J. Am. Chem. Soc., 107 (1985) 2374.
48 R.R. Andrea, M.A. Vuurman, D.J. Stufkens and A.D. Oskam, Recl. Trav. Chim. Pays Bas, 105 (1986) 372.
49 Y. Ishikawa, R.A. Weersink, P.A. Hackett and D.M. Rayner, Chem. Phys. Lett., 142 (1987) 271.
50 S.A. Jackson, R.K. Upmacis, M. Poliakoff, J.J. Turner, J.K. Burdett and F.-W. Greves, J. Chem. Soc. Chem. Commun., (1987) 678.
51 S.A. Jackson, P.M. Hodges, M. Poliakoff, J.J. Turner and F.W. Grevels, J. Am. Chem. Soc., 112 (1990) 1221.
52 R.L. Sweany, J. Am. Chem. Soc., 108 (1986) 6986.
53 S.M. Howdle and M. Poliakoff, J. Chem. Soc. Chem. Commun., (1989) 1099.
54 G.E. Gadd, R.K. Upmacis, M. Poliakoff and J.J. Turner, J. Am. Chem. Soc., 108 (1986) 2547.
55 R.L. Sweany and F.N. Russell, Organometallics, 7 (1988) 719.
56 R.L. Sweany, M.A. Polito and A. Moroz, Organometallics, 8 (1989) 2305.
57 A.A. Gonzalez and C.D. Hoff, Inorg. Chem., 28 (1989) 4295.

58 R.L. Sweany and A. Moroz, J. Am. Chem. Soc., 111 (1989) 3577.
59 M.S. Chinn, D.M. Heinekey, N.G. Payne and C.D. Sofield, Organometallics, 8 (1989) 1824.
60 M.T. Bautista, E.P. Cappellani, S.D. Drouin, R.H. Morris, C.T. Schweitzer, A. Sella and J. Zubkowski, J. Am. Chem. Soc., 113 (1991) 4876.
61 E.P. Cappellani, P.A. Maltby, R.H. Morris, C.T. Schweitzer and M.R. Steele, Inorg. Chem., 28 (1989) 4437.
62 G.G. Hlatky and R.H. Crabtree, Coord. Chem. Rev., 65 (1985) 1.
63 D.G. Hamilton and R.H. Crabtree, J. Am. Chem. Soc., 110 (1988) 4126.
64 C. Bianchini, M. Peruzzini and F. Zanobini, J. Organomet. Chem., 354 (1988) C19.
65 R.H. Crabtree and D.G. Hamilton, J. Am. Chem. Soc., 108 (1986) 3124.
66 G.C. Jia and D.W. Meek, Organometallics, 10 (1991) 1444.
67 U.E. Bucher, T. Lengweiler, D. Nanz, W. Von Philipsborn and L.M. Venanzi, Angew. Chem. Int. Ed. Engl., 29 (1990) 548.
68 X.-L. Luo and R.H. Crabtree, J. Am. Chem. Soc., 112 (1990) 6912.
69 X.-L. Luo, D. Michos and R.H. Crabtree, Organometallics, 11 (1992) 237.
70 X.L.R. Fontaine, E.H. Fowles and B.L. Shaw, J. Chem. Soc. Chem. Commun., (1988) 482.
71 M.V. Baker, L.D. Field and D.J. Young, J. Chem. Soc. Chem. Commun., (1988) 546.
72 M.T. Bautista, K.A. Earl, P.A. Maltby and R.H. Morris, J. Am. Chem. Soc., 110 (1988) 4056.
73 N. Bampos and L.D. Field, Inorg. Chem., 29 (1990) 587.
74 G. Albertin, S. Antoniutti and E. Bordignon, J. Am. Chem. Soc., 111 (1989) 2072.
75 G. Albertin, P. Amendola, S. Antoniutti, S. Ianelli, G. Pelizzi and E. Bordignon, Organometallics, 10 (1991) 2876.
76 P. Amendola, S. Antoniutti, G. Albertin and E. Bordignon, Inorg. Chem., 29 (1990) 318.
77 T.V. Ashworth and E. Singleton, J. Chem. Soc. Chem. Commun., (1976) 705.
78 K. Aoyagi, M. Ogasawara, H. Takeuchi, T. Takahashi and M. Saburi, in Proceedings of the 37th Symposium on Organometallic Chemistry, Osaka, Japan, 1990.
79 T. Tsukahara, H. Kawano, Y. Ishii, T. Takahashi, M. Saburi, T. Uchida and S. Adutagawa, Chem. Lett., (1988) 2055.
80 M. Saburi, K. Aoyagi, T. Takahashi and Y. Uchida, Chem. Lett., (1990) 601.
81 C. Bianchini, P.J. Perez, M. Peruzzini, F. Zanobini and A. Vacca, Inorg. Chem., 30 (1991) 279.
82 F.M. Conroy-Lewis and S.J. Simpson, J. Chem. Soc. Chem. Commun., (1986) 506.
83 F.M. Conroy-Lewis and S.J. Simpson, J. Chem. Soc. Chem. Commun., (1987) 1675.
84 M.S. Chinn and D.M. Heinekey, J. Am. Chem. Soc., 112 (1990) 5166.
85 G. Jia and R.H. Morris, J. Am. Chem. Soc., 113 (1991) 875.
86 A.R. Siedle, R.A. Newmark, G.A. Korba, L.H. Pignolet and P.D. Boyle, Inorg. Chem., 27 (1988) 1593.
87 T.J. Johnson, J.C. Huffman, K.G. Caulton, S.A. Jackson and O. Eisenstein, Organometallics, 8 (1989) 2073.
88 (a) J.P. Collman, P.S. Wagenknecht, R.T. Hembre and N.S. Lewis, J. Am. Chem. Soc., 112 (1990) 1294.
(b) J.P. Collman, P.S. Wagenknect, J.E. Hutchinson, N.S. Lewis, M.A. Lopez, R. Guilard, M. L'Her, A.A. Bother-By and P.K. Mishra, J. Am. Chem. Soc., 114 (1992) 5654.
89 C. Bianchini, C. Mealli, A. Meli, M. Peruzzini and F. Zanobini, J. Am. Chem. Soc., 110 (1988) 8725.
90 E.G. Lundquist, K. Folting, W.E. Streib, J.C. Huffman, O. Eisenstein and K.G. Caulton, J. Am. Chem. Soc., 112 (1990) 855.

91 R.H. Crabtree, M. Lavin and L. Bonneviot, J. Am. Chem. Soc., 108 (1986) 4032.
92 F.A. Cotton and R.L. Luck, J. Chem. Soc. Chem. Commun., (1988) 1277.
93 (a) W.D. Harman and H. Taube, J. Am. Chem. Soc., 112 (1990) 2261.
(b) Z.W. Li and H. Taube, Science, 256 (1992) 210.
94 T. Arliguie, B. Chaudret, R.H. Morris and A. Sella, Inorg. Chem., 27 (1988) 598.
95 P. Zanello, Comments Inorg. Chem., 10 (1991) 339.
96 R.H. Crabtree and J.M. Quirk, J. Organomet. Chem., 199 (1980) 99.
97 R.M. Bullock, C.E.L. Headford, K.M. Hennessy, S.E. Kegley and J.R. Norton, J. Am. Chem. Soc., 111 (1989) 3897.
98 H. Rabaa and J.Y. Saillard, J. Organomet. Chem., 330 (1987) 397.
99 E. Matarassotchiroukhine, J. Chem. Soc. Chem. Commun., (1990) 681.
100 D.L. Lichtenberger and A. Raichaudhuri, Organometallics, 9 (1990) 1686.
101 U. Schubert, K. Bahr and J. Mueller, J. Organomet. Chem., 327 (1987) 357.
102 X.-L. Luo and R.H. Crabtree, J. Am. Chem. Soc., 111 (1989) 2527.
103 S.M. Howdle, M.A. Healy and M. Poliakoff, J. Am. Chem. Soc., 112 (1990) 4804.
104 U. Schubert, E. Kunz, B. Harkers, J. Willnecker and J. Meyer, J. Am. Chem. Soc., 111 (1989) 2572.
105 H. Piana, U. Kirchgassner and U. Schubert, Chem. Ber., 124 (1991) 743.
106 P. Mura, A. Segre and S. Sostero, Inorg. Chem., 28 (1989) 2853.
107 P. Bergamini, S. Sostero, O. Traverso, P. Mura and A. Segre, J. Chem. Soc. Dalton Trans., (1989) 2367.
108 J.M. Millar, R.V. Kastrup, M.T. Melchior, I.T. Horvath, C.D. Hoff and R.H. Crabtree, J. Am. Chem. Soc., 112 (1990) 9643.
109 K.W. Zilm and J.M. Millar, Adv. Magn. Opt. Reson., 15 (1990) 163.
110 K.W. Zilm, D.M. Heinekey, J.M. Millar, N.G. Payne and P. Demuo, J. Am. Chem. Soc., 111 (1988) 3088.
111 D.M. Heinekey, J.M. Millar, T.F. Koetzle, N.G. Payne and K.W. Zilm, J. Am. Chem. Soc., 112 (1990) 909.
112 K.W. Zilm, D.M. Heinekey, J.M. Millar, N.G. Payne, S.P. Neshyba, J.C. Duchamp and J. Szczyrba, J. Am. Chem. Soc., 112 (1990) 920.
113 D.M. Heinekey, N.G. Payne and C.D. Sofield, Organometallics, 9 (1990) 2643.
114 D.M. Heinekey, J. Am. Chem. Soc., 113 (1991) 6074.
115 J.A.K. Howard, O. Johnson, T.F. Koetzle and J.L. Spencer, Inorg. Chem., 26 (1987) 2930.
116 D.G. Gusev, A.B. Vymenits and V.I. Bakhmutov, Inorg. Chem., 30 (1991) 3116.
117 M. Brookhart, D.M. Lincoln, M.A. Bennett and S. Pelling, J. Am. Chem. Soc., 112 (1990) 2691.
118 S.A. Jackson and O. Eisenstein, J. Am. Chem. Soc., 112 (1990) 7203.
119 R.A. Henderson, J. Chem. Soc. Chem. Commun., (1987) 1670.
120 C. Bianchini, M. Peruzzini and F. Zanobini, J. Organomet. Chem., 390 (1990) C16.
121 J. Halpern, L.S. Cai, P.J. Desrosiers and Z.R. Lin, J. Chem. Soc. Dalton Trans., (1991) 717.
122 J.E. Bercaw, Pure Appl. Chem., 62 (1990) 1151.
123 R.G. Bergman, J. Organomet. Chem., 400 (1990) 273.
124 R.H. Crabtree, in C.L. Hill (Ed.), Activation and Functionalization of Alkanes, Wiley, New York, 1989, p. 79.
125 W.D. Jones, in C.L. Hill (Ed.), Activation and Functionalization of Alkanes, Wiley, New York, 1989, p. 111.
126 R.N. Perutz, Pure Appl. Chem., 62 (1990) 1103.
127 A.E. Shilov, in C.L. Hill (Ed.), Activation and Functionalization of Alkanes, Wiley, New York, 1989, p. 1.

128 M. Tanaka and T. Sakakura, Pure Appl. Chem., 62 (1990) 1147.
129 P.J. Hay, J. Am. Chem. Soc., 109 (1987) 705.
130 Y. Jean, O. Eisenstein, F. Volatron, B. Maouche and F. Sefia, J. Am. Chem. Soc., 108 (1986) 6587.
131 Y. Jean, A. Lledos, B. Maouche and R. Aiad, J. Chim. Phys. Phys. Chim. Biol., 84 (1987) 805.
132 R.H. Morris, K.A. Earl, R.L. Luck, N.J. Lazorowych and A. Sella, Inorg. Chem., 26 (1987) 2674.
133 R.H. Morris, Inorg. Chem., 31 (1992) 1471.
134 A.B.P. Lever, Inorg. Chem., 29 (1990) 1271.
135 A.B.P. Lever, Inorg. Chem., 30 (1991) 1980.
136 T. Ziegler, V. Tschinke, L. Fan and A.D. Becke, J. Am. Chem. Soc., 111 (1989) 9177.
137 M. Saburi, K. Aoyagi, T. Kodama, T. Takahashi, Y. Uchida, K. Kozawa and T. Uchida, Chem. Lett., (1990) 1909.
138 G.L. Geoffroy and M.S. Wrighton, Organometallic Photochemistry, Academic Press, New York, 1979.
139 A. Veillard, Chem. Phys. Lett., 170 (1990) 441.
140 P.E. Bloyce, A.J. Rest, I. Whitwell, W.A.G. Graham and R. Holmes-Smith, J. Chem. Soc. Chem. Commun., (1988) 846.
141 M.V. Baker and L.D. Field, J. Am. Chem. Soc., 109 (1987) 2825.
142 M.B. Sponsler, B.H. Weiller, P.O. Stoutland and R.G. Bergman, J. Am. Chem. Soc., 111 (1989) 6841.
143 F. Maseras, M. Duran, A. Lledos and J. Bertran, J. Am. Chem. Soc., 113 (1991) 2879.
144 T.E. Sloan, in G.L. Geoffroy (Ed.), Inorganic and Organometallic Stereochemistry, Vol. 12, Wiley, New York, p. 2.
145 G.J. Kubas, R.R. Ryan and D.A. Wrobleski, J. Am. Chem. Soc., 108 (1986) 1339.
146 G.R.K. Khalsa, G.J. Kubas, C.J. Unkefer, L.S. Vandersluys and K.A. Kubat-Martin, J. Am. Chem. Soc., 112 (1990) 3855.
147 K. Zhang, A.A. Gonzalez and C.D. Hoff, J. Am. Chem. Soc., 111 (1989) 3627.
148 G. Jia, A.J. Lough and R.H. Morris, Organometallics, 11 (1992) 161.
149 O.B. Ryan and M. Tilset, J. Am. Chem. Soc., 113 (1991) 9554.
150 X. Luo and R.H. Crabtree, Inorg. Chem., 28 (1989) 3775.
151 C. Bianchini, F. Laschi, M. Peruzzini, F.M. Ottaviani, A. Vacca and P. Zanello, Inorg. Chem., 29 (1990) 3394.
152 F. Maseras, M. Duran, A. Lledós and J. Bertrán, Inorg. Chem., 28 (1989) 2984.
153 D.G. Gusev, A.B. Vymenits and V.I. Bakhmutov, Inorg. Chim. Acta, 179 (1991) 195.
154 H.C. Clark and M.J. Hampden Smith, J. Am. Chem. Soc., 108 (1986) 3829.
155 A.L. Sargent, M.B. Hall and M.F. Guest, J. Am. Chem. Soc., 114 (1992) 517.
156 P. Zhou, A.A. Vitale, J. San Filippo, Jr. and W.H. Saunders, Jr., J. Am. Chem. Soc., 107 (1985) 8049.
157 M.J. Burk, M.P. McGrath, R. Wheeler and R.H. Crabtree, J. Am. Chem. Soc., 110 (1988) 5034.
158 D.G. Gusev, A.B. Vymenits and V.I. Bakhmutov, Mendeleev Chem. J., (1991) 24.
159 D.G. Gusev, personal communication, 1992.
160 R.L. Sweany, Organometallics, 5 (1986) 387.
161 G. Parkin and J.E. Bercaw, J. Chem. Soc. Chem. Commun., (1989) 255.
162 G. Parkin and J.E. Bercaw, Polyhedron, 7 (1988) 2053.
163 B.R. James, Homogeneous Hydrogenation, Wiley, New York, 1973.
164 M. Orchin and W. Rupilius, Catal. Rev., 6 (1972) 85.

165 B.B. Wayland, S. Ba and A.E. Sherry, Inorg. Chem., 31 (1992) 148.
166 J.P. Collman, J.E. Hutchinson, P.S. Wagenknecht, N.S. Lewis, M.A. Lopez and R. Guilard, J. Am. Chem. Soc., 112 (1990) 8206.
167 T.H. Chao and J.H. Espenson, J. Am. Chem. Soc., 100 (1978) 129.
168 R.H. Crabtree and M. Lavin, J. Chem. Soc. Chem. Commun., (1985) 794.
169 P. Meakin, L.J. Guggenberger, W.G. Peet, E.L. Muetterties and J.P. Jesson, J. Am. Chem. Soc., 95 (1973) 1467.
170 F. Maseras, M. Duran, A. Lledós and J. Bertrán, J. Am. Chem. Soc., 114 (1992) 2922.
171 H. Rabaa, J.Y. Saillard and R. Hoffmann, J. Am. Chem. Soc., 108 (1986) 4327.
172 M.E. Thompson, S.M. Baxter, A.R. Bulls, B.J. Burger, M.C. Nolan, B.D. Santarsiero, W.P. Schaefer and J.E. Bercaw, J. Am. Chem. Soc., 109 (1987) 203.
173 D.M. Heinekey, N.G. Payne and G.K. Schulte, J. Am. Chem. Soc., 110 (1988) 2303.
174 A. Antinolo, B. Chaudret, G. Commenges, M. Fajardo, F. Jalon, R.H. Morris, A. Otero and C.T. Schweitzer, J. Chem. Soc. Chem. Commun., (1988) 1210.
175 B. Chaudret, G. Commenges, F. Jalon and A. Otero, J. Chem. Soc. Chem. Commun., (1989) 210.
176 D.H. Jones, J.A. Labinger and D.P. Weitekamp, J. Am. Chem. Soc., 111 (1989) 3087.
177 C.R. Bowers, D.H. Jones, N.D. Kurur, J.D. Labinger, M.G. Pravica and D.P. Weitekamp, Adv. Magn. Reson., 14 (1990) 269.
178 J.C. Barthelat, B. Chaudret, J.P. Daudey, P. Deloth and R. Poilblanc, J. Am. Chem. Soc., 113 (1991) 9896.
179 T. Arliguie, B. Chaudret, J. Devillers and R. Poilblanc, C. R. Acad. Sci. Paris Ser. II, 305 (1987) 1523.
180 H. Werner, S. Stahl and W. Kohlmann, J. Organomet. Chem., 409 (1991) 285.
181 W. Kohlmann, Doctoral Dissertation, University of Würzburg, 1991.
182 D.M. Heinekey and T.G.P. Harper, Organometallics, 10 (1991) 2891.
183 M.T. Bautista, K.A. Earl, P.A. Maltby, R.H. Morris, C.T. Schweitzer and A. Sella, J. Am. Chem. Soc., 110 (1988) 7031.
184 C. Bianchini, A. Meli, M. Peruzzini, P. Frediani, C. Bohanna, M.A. Esteruelas and L.A. Oro, in M. Graziani and C.N.R. Rao (Eds.), Advances in Catalyst Design. Proceedings of Workshop, Trieste, Italy, World Scientific, Singapore, 1991, p. 267.
185 J.B. Lambert and J.W. Keepers, J. Magn. Reson., 38 (1980) 233.
186 H. Strehlow and J. Frahm, Ber. Bungsenges. Phys. Chem., 79 (1975) 57.
187 H. Shanan-Atidi and K.H. Bar-Eli, J. Phys. Chem., 74 (1970) 961.
188 M.T. Bautista, K.A. Earl and R.H. Morris, Inorg. Chem., 27 (1988) 1124.
189 M. Saunders, M.H. Jaffe and P. Vogel, J. Am. Chem. Soc., 93 (1971) 2558.
190 A.C. Albeniz, D.M. Heinekey and R.H. Crabtree, Inorg. Chem., 30 (1991) 3632.
191 T.E. Burrow, A. Hills, D.L. Hughes, J.D. Lane, N.J. Lazarowych, M. Maguire, R.H. Morris and R.L. Richards, J. Chem. Soc. Chem. Commun, (1990) 1757.
192 K.I. Gell, B. Posin, J. Schwartz and G.M. Williams, J. Am. Chem. Soc., 104 (1982) 1846.
193 J.K. Burdett and M.R. Pourian, Organometallics, 6 (1987) 1684.
194 J.K. Burdett, J.R. Phillips, M.R. Pourian, M. Poliakoff and J.J. Turner, Inorg. Chem., 26 (1987) 3054.
195 G. Jia and D.W. Meek, J. Am. Chem. Soc., 111 (1989) 757.
196 D.E. Linn and J. Halpern, J. Am. Chem. Soc., 109 (1987) 2969.
197 G. Strathdee and R. Given, Can. J. Chem., 53 (1975) 106.
198 D. Nanz, W. von Philipsborn, U.E. Bucher and L.M. Venanzi, Magn. Reson. Chem., 29 (1991) S38.
199 L.F. Rhodes and K.G. Caulton, J. Am. Chem. Soc., 107 (1985) 259.

200 H.H. Brintzinger, J. Organomet. Chem., 171 (1979) 337.
201 E.M. Kober and P.J. Hay, The Challenge of d and f Electrons, Theory and Computation. ACS Symp. Ser., 394 (1989) 92.
202 G. Pacchioni, J. Am. Chem. Soc., 112 (1990) 80.
203 K. Zhang, A.A. Gonzalez, S.L. Mukerjee, S.J. Chou, C.D. Hoff, K.A. Kubatmartin, D. Barnhart and G.J. Kubas, J. Am. Chem. Soc., 113 (1991) 9170.
204 G.K. Kubas, C.J. Burns, G.R.K. Khalsa, L.S. Van Der Sluys, G. Kiss and C.D. Hoff, submitted for publication.
205 M.S. Chinn and D.M. Heinekey, J. Am. Chem. Soc., 109 (1987) 5865.
206 S.A. Jackson and O. Eisenstein, Inorg. Chem., 29 (1990) 3910.
207 M. Cazanoue, Z.L. He, D. Neibecker and R. Mathieu, J. Chem. Soc. Chem. Commun., (1991) 307.
208 C. Hampton, T.W. Dekleva, B.R. James and W.R. Cullen, Inorg. Chim. Acta., 145 (1988) 165.
209 T.W. Dekleva, I.S. Thorburn and B.R. James, Inorg. Chim. Acta, 100 (1985) 49.
210 M.J. Camenzind, B.R. James, D. Dolphin, J.W. Sparapany and J.A. Ibers, Inorg. Chem., 27 (1988) 3054.
211 L.D. Field, A.V. George, T.W. Hambley, E.Y. Malouf and D.J. Young, J. Chem. Soc. Chem. Commun., (1990) 931.
212 P.L. Gaus, S.C. Kao, M.Y. Darensbourg and L.W. Arndt, J. Am. Chem. Soc., 106 (1984) 4752.
213 S.E. Boyd, L.D. Field, T.W. Hambley and D.J. Young, Inorg. Chem., 29 (1990) 1496.
214 R.K. Upmacis, G.E. Gadd, M. Poliakoff, M.B. Simpson, J.J. Turner, R. Whyman and A.F. Simpson, J. Chem. Soc. Chem. Commun., (1985) 27.
215 R.H. Crabtree, Inorg. Chim. Acta, 125 (1987) L7.
216 J. Chatt, A.J. Pearman and R.L. Richards, Nature, 253 (1975) 39.
217 G. Jia, R.H Morris and C.T. Schweitzer, Inorg. Chem., 30 (1991) 593.
218 F. Conroy-Lewis, S.J. Simpson, L. Brammer and A.G. Orpen, J. Organomet. Chem., 406 (1991) 197.
219 R.T. Weberg and J.R. Norton, J. Am. Chem. Soc., 112 (1990) 1105.
220 S.S. Kristjansdottir and J.R. Norton, in A. Dedieu (Ed.), Transition Metal Hydrides: Recent Advances in Theory and Experiment, VCH, New York, 1991, Chap. 10.
221 S.D. Drouin, G. Jia and R.H. Morris, unpublished results.
222 P.S. Pregosin and R.W. Kunz, ^{31}P and ^{13}C NMR of Transition Metal Phosphorus Complexes, Springer-Verlag, New York, 1979, p. 16.
223 S. Jans-Burli and P.S. Pregosin, Magn. Reson. Chem., 23 (1985) 198.
224 E. Buncel and B. Menon, J. Am. Chem. Soc., 99 (1977) 4457.
225 S.S. Kristjansdottir, A.E. Moody, R.T. Weberg and J.R. Norton, Organometallics, 7 (1988) 1983.
226 M. Tilset and V.D. Parker, J. Am. Chem. Soc., 111 (1989) 6711.
227 M. Tilset and V.D. Parker, J. Am. Chem. Soc., 112 (1990) 2843.
228 G. Herzberg, J. Mol. Spectrosc., 33 (1970) 147.
229 J.A. Simões and J.L. Beauchamp, Chem. Rev., 90 (1990) 629.
230 P.G. Jessop, G. Rastar and B.R. James, Inorg. Chem., in preparation.
231 E.P. Cappellani, S.M. Drouin, G. Jia, P.A. Maltby, R.H. Morris and C.T. Schweitzer, work in progress, 1992.
232 P. Hamon, L. Toupet, J.-R. Hamon and C. Lapinte, Organometallics, 11 (1992) 1429.
233 M. Zimmer, G. Schulte, X.L. Luo and R.H. Crabtree, Angew. Chem. Int. Ed. Engl., 30 (1991) 193.

234 P.J. Brothers, Prog. Inorg. Chem., 28 (1981) 1.
235 O.B. Ryan, M. Tilset and V.D. Parker, Organometallics, 10 (1991) 298.
236 F. Wochner and H.H. Brintzinger, J. Organomet. Chem., 309 (1986) 65.
237 Z. Lin and T.J. Marks, J. Am. Chem. Soc., 109 (1987) 7979.
238 R.F. Heck and D.S. Breslow, J. Am. Chem. Soc., 83 (1961) 4023.
239 L. Versluis and T. Ziegler, Organometallics, 9 (1990) 2985.
240 P.B. Chock and J. Halpern, J. Am. Chem. Soc., 88 (1966) 3511.
241 A.A. Vitale and J. San Filippo, Jr., J. Am. Chem. Soc., 104 (1982) 7341.
242 E. Folga, T. Ziegler and L. Fan, New J. Chem., 15 (1991) 741.
243 R.F Jordan, C.S. Bajgur, W.E. Dasher and A.L. Rheingold, Organometallics, 6 (1987) 1041.
244 A.C. Albeniz, G. Schulte and R.H. Crabtree, Organometallics, 11 (1992) 242.
245 M.L. Steigerwald and W.A. Goddard, J. Am. Chem. Soc., 106 (1984) 308.
246 D. Sellmann, I. Barth and M. Moll, Inorg. Chem., 29 (1990) 176.
247 M.D. Fryzuk, C.D. Montgomery and S.J. Rettig, Organometallics, 10 (1991) 467.
248 R. Koelliker and D. Milstein, J. Am. Chem. Soc., 113 (1991) 8524.
249 G.J. Kubas and R.R. Ryan, Polyhedron, 5 (1986) 473.
250 C. Bianchini, A. Meli, M. Peruzzini, F. Vizza and F. Zanobini, Organometallics, 8 (1989) 2080.
251 M.J. Burk and R.H. Crabtree, J. Am. Chem. Soc., 109 (1987) 8025.
252 T. Arliguie and B. Chaudret, J. Chem. Soc. Chem. Commun., (1989) 155.
253 R.H. Crabtree and M. Lavin, J. Chem. Soc. Chem. Commun., (1985) 1661.
254 K. Osakada, K. Ohshiro and A. Yamamoto, Organometallics, 10 (1991) 404.
255 L.D. Field, A.V. George, E.Y. Malouf, I.H.M. Slip and T.W. Hambley, Organometallics, 10 (1991) 3842.
256 A. Hills, D.L. Hughes, M. Jimenez-Tenorio, G.J. Leigh, C.A. McGeary, A.T. Rowley, M. Bravo, C.E. McKenna and M.C. McKenna, J. Chem. Soc. Chem. Commun., (1991) 522.
257 A. Hills, D.L. Hughes, M. Jimenez-Tenorio and G.J. Leigh, J. Organomet. Chem., 391 (1990) C41.
258 C. Bianchini, M. Peruzzini, F. Zanobini, P. Frediani and A. Albinati, J. Am. Chem. Soc., 113 (1991) 5453.
259 G. Albertin, S. Antoniutti and E. Bordignon, Proc. 21 Congr. Naz. di Chim. Inorg., Bressanone, 1991.
260 G.C. Jia and D.W. Meek, Inorg. Chem., 30 (1991) 1953.
261 R. Ellis, R.A. Henderson, A. Hills and D.L. Hughes, J. Organomet. Chem., 333 (1987) C6.
262 C. Bianchini, E. Farnetti, P. Frediani, M. Graziani and A. Polo, J. Chem. Soc. Chem. Commun., (1991) 1336.
263 C. Bianchini, A. Meli, M. Peruzzini, P. Frediani, C. Bohanna, M.A. Esteruelas and L.A. Oro, Organometallics, 11 (1992) 138.
264 Y. Kim, J. Gallucci and A. Wojcicki, J. Am. Chem. Soc., 112 (1990) 8600.
265 G.J. Leigh and M. Jimenez-Tenorio, J. Am. Chem. Soc., 113 (1991) 5862.
266 M. Freni, D. Giusto and P. Romiti, Gazz. Chim. Ital., 105 (1975) 435.
267 F.A. Cotton and R.L. Luck, Inorg. Chem., 28 (1989) 2181.
268 J. Eckert, G.J. Kubas and R.P. White, Inorg. Chem., 31 (1992) 1550.
269 H.J. Wasserman, G.J. Kubas and R.R. Ryan, J. Am. Chem. Soc., 108 (1986) 2294.
270 S. Antoniutti, G. Albertin, P. Amendola and E. Bordignon, J. Chem. Soc. Chem. Commun., (1989) 229.
271 E. Miyazaki, J. Catal., 65 (1980) 84.

272 J. Eckert, A. Albinati, R.P. White, C. Bianchini and M. Peruzzini, Inorg. Chem., in press.
273 J. Eckert, G.J. Kubas, J.H. Hall, P.J. Hay and C.M. Boyle, J. Am. Chem. Soc., 112 (1990) 2324.
274 F.M. Bickelhaupt, E.J. Baerends and W. Ravenek, Inorg. Chem., 29 (1990) 350.
275 M. Bautista, K.A. Earl, R.H. Morris and A. Sella, J. Am. Chem. Soc., 109 (1987) 3780.
276 M. Saburi, personal communication, 1991.
277 I.E. Rachidi, O. Eisenstein and Y. Jean, New. J. Chem., 14 (1990) 671.
278 J.F. Riehl, Y. Jean, O. Eisenstein and M. Pelissier, Organometallics, 11 (1992) 729.
279 (a) M. Sato, T. Tatsumi, T. Kodama, M. Hidai and T. Uchida, J. Am. Chem. Soc., 100 (1978) 4447.
(b) Y. Ishikawa, P.A. Hackett and D.M. Rayner, J. Phys. Chem., 93 (1989) 652.
280 A. Mezzetti, A. Delzotto, P. Rigo and N.B. Pahor, J. Chem. Soc. Dalton Trans., (1989) 1045.
281 M. Bacci and C.A. Ghilardi, Inorg. Chem., 13 (1974) 2398.
282 A.A. Gonzalez, in T.J. Marks (Ed.), Bonding Energetics in Organometallic Compounds, American Chemical Society, New York, 1990, p. 133.
283 Handbook of Chemistry and Physics, Chemical Rubber Co., 62nd edn., 1981.
284 J.W. Bruno, J.C. Huffman and K.G. Caulton, J. Am. Chem. Soc., 106 (1984) 1663.
285 D.L. Packett and W.C. Trogler, J. Am. Chem. Soc., 108 (1986) 5036.
286 D.A. Wink and P.C. Ford, J. Am. Chem. Soc., 108 (1986) 4838.
287 M.T. Costello and R.A. Walton, Inorg. Chem., 27 (1988) 2563.
288 J.A.K. Howard, S.A. Mason, O. Johnson, I.C. Diamond, S. Crennell, P.A. Keller and J.L. Spencer, J. Chem. Soc. Chem. Commun., (1988) 1502.
289 M. Saburi, K. Aoyagi, H. Takeuchi, T. Takahashi and Y. Uchida, Chem. Lett., (1990) 991.
290 Z.-W. Li and H. Taube, J. Am. Chem. Soc., 113 (1991) 8946.
291 M.J. Maroney, G.J. Colpas, C. Bagyinka, N. Baidya and P.K. Mascharak, J. Am. Chem. Soc., 113 (1991) 3962.
292 C. Fan, M. Teixeira, J. Moura, I. Moura, B. Huynh, J. Le Gall, H.D. Peck and B.M. Hoffman, J. Am. Chem. Soc., 113 (1991) 20.
293 S.P.J. Albracht, Recl. Trav. Chim. Pays Bas, 106 (1987) 173.
294 A. Andriollo, M.A. Esteruelas, U. Meyer, L.A. Oro, D.R.A. Sanchez, E. Sola, C. Valero and H. Werner, J. Am. Chem. Soc., 111 (1989) 7431.
295 G. Marinelli, I.E.-I. Rachidi, W.E. Streib, O. Eisenstein and K.G. Caulton, J. Am. Chem. Soc., 111 (1989) 2346.
296 Y.R. Lin and Y.F. Zhou, J. Organomet. Chem., 381 (1990) 135.
297 D. Morton, D.J. Cole-Hamilton, I.D. Utuk, M. Paneque-Sosa and M. Lopez-Poveda, J. Chem. Soc. Dalton Trans., (1989) 489.
298 M.A. Esteruelas, L.A. Oro and C. Valero, Organometallics, 10 (1991) 462.
299 P.M. Hodges, S.A. Jackson, J. Jacke, M. Poliakoff, J.J. Turner and F.W. Grevels, J. Am. Chem. Soc., 112 (1990) 1234.
300 R.M. Bullock and B.J. Rappoli, J. Chem. Soc. Chem. Commun., (1989) 1447.
301 T. Ito, M. Koga, S. Kurishima, M. Natori, N. Sekizuka and K. Yoshioka, J. Chem. Soc. Chem. Commun., (1990) 988.
302 J.R. Norton, C.J.C. Lawrie and M.A. Rodkin, National Meeting of the American Chemical Society, San Francisco, 1992, Paper Inorg. 610.
303 P. Meakin, E.L. Muetterties and J.P. Jesson, J. Am. Chem. Soc., 95 (1973) 75.
304 J.P. Jesson, in E.L. Muetterties (Ed.), Transition Metal Hydrides, Dekker, New York, 1971, Chap. 4.
305 K.E. Earl, M.Sc. Thesis, University of Toronto, 1987.

306 S.D. Drouin, M.Sc Thesis, University of Toronto, 1991.
307 M.T. Bautista, M.Sc. Thesis, University of Toronto, 1988.
308 E.P. Sarjeant and B. Dempsey, Ionisation Constants of Organic Acids in Aqueous Solution, Pergamon Press, Oxford, 1979.
309 P. Ballinger and F.A. Long, J. Am. Chem. Soc., 82 (1960) 795.
310 R.W. Alder, P.S. Bowman, W.R.S. Steele and W.R.S. Winterman, J. Chem. Soc. Chem. Commun., (1968) 723.
311 T. Allman and R.G. Goel, Can. J. Chem., 60 (1982) 716.
312 C.A. Streuli, Anal. Chem., 32 (1960) 985.
313 G. Jia and R.H. Morris, Inorg. Chem., 29 (1990) 581.
314 M.N. Golovin, M.M. Rahman, J.E. Belmonte and W.P. Giering, Organometallics, 4 (1985) 1981.
315 E.P. Cappellani, M.Sc. Thesis, University of Toronto, 1990.
316 L.S. Van Der Sluys, M.M. Miller, G.J. Kubas and K.G. Caulton, J. Am. Chem. Soc., 113 (1991) 2513.
317 X.L. Luo and R.H. Crabtree, J. Chem. Soc. Chem. Commun., (1990) 189.
318 X.L. Luo and R.H. Crabtree, J. Chem. Soc. Dalton Trans., (1991) 587.
319 M. Sato, T. Tatsumi, T. Kodama, M. Hidai, T. Uchida and Y. Uchida, J. Am. Chem. Soc., 100 (1978) 4447.
320 M. Aresta, P. Giannoccaro, M. Rossi and A. Sacco, Inorg. Chim. Acta, 5 (1971) 115.
321 G.M. Bancroft, M.J. Mays, B.E. Prater and F.P. Stefanini, J. Chem. Soc. A, (1970) 2146.
322 C.A. Ghilardi, S. Midollini, L. Sacconi and P. Stoppioni, J. Organomet. Chem., 205 (1981) 193.
323 L.S. Van Der Sluys, G.J. Kubas and K.G. Caulton, Organometallics, 10 (1991) 1033.
324 R.O. Harris, N.K. Hota, L. Sadavoy and J.M.C. Yuen, J. Organomet. Chem., 54 (1973) 259.
325 P.A. Maltby and R.H. Morris, unpublished results, 1992.
326 M.V. Baker and L.D. Field, J. Organomet. Chem., 354 (1988) 351.
327 G. Jia, D.W. Meek and J.C. Gallucci, Inorg. Chem., 30 (1991) 403.
328 F. Conroy-Lewis, A.D. Redhouse and S.J. Simpson, J. Organomet. Chem., 366 (1989) 357.
329 D. Morton and D.J. Cole-Hamilton, J. Chem. Soc. Chem. Commun., (1988) 1154.
330 E.G. Lundquist, J.C. Huffman, K. Folting and K.G. Caulton, Angew. Chem. Int. Ed. Engl., 27 (1988) 1165.
331 Z.Y. Lin and M.B. Hall, J. Am. Chem. Soc., 114 (1992) 6102.
332 C. Bianchini, C. Mealli, M. Peruzzini and F. Zanobini, J. Am. Chem. Soc., 114 (1992) 5905.