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Site selectivity in reactions of metal hydride halide complexes with acids

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Abstract

Protonolysis, protonation and hydrogen bond-formation reactions with metal hydride halide (L_nMHX) complexes are reviewed. The site selectivity (hydride vs halide) for these reactions is found to be highly variable, with many examples of either case. In fact, several systems are in equilibrium between protonated (or hydrogen-bonded) hydride and halide ligands. The more reactive site depends primarily on the accessibility of the hydride ligands and the polarity of the metal hydride bonds. Protonation at hydride is a common synthetic method for metal halide dihydrogen complexes, $M(H_2)X$, which are rather well represented. In contrast, halide protonation gives metal hydride (hydrogen halide) complexes, MH(XH), for which only a few examples are established. However, H···X bonding in $M(H_2)X$ complexes, "invisible" to NMR techniques, has generally not been ruled out. The lighter halides form stronger hydrogen bonds, and are more prone to protonation than the heavier halides. Thus, fluoride is the best halide ligand for electrophilic removal, while iodide ligands are best suited to withstand acidic conditions. © 1997 Elsevier Science S.A.

Keywords: Protonation; Dihydrogen complex; Halide; Hydride

1. Introduction

An emerging question is the site selectivity of proton transfer to late transition metal complexes containing at least one hydride and one halide ligand. While proton transfer is probably the most ubiquitous and conceptually simple chemical reaction, the question of whether proton transfer occurs preferentially to metal-bound hydride or halide remains contentious, with no commonly-held intuition or "rule of thumb". Other than its impact on the study of η^2-dihydrogen complexes, this issue is relevant to many important metal-catalyzed processes, including H/D exchange, halocarbon reductions and hydrogenations. It is also of interest, by analogy of halide to alkoxide or amide, to OH and NH oxidative addition reactions.

This review addresses the most important controlling influences in determining the site of electrophilic attack on a metal complex containing both a hydride and a halide ligand, and also discusses the influences of this consideration on observed reactivity. Literature is surveyed from the last 11 years relevant to protonation reactions of metal complexes containing *both* a hydride and a halide ligand. Recently published related reviews include Henderson's discussion of protonation of metal alkene and alkyne complexes [1], and a treatment of unusual hydrogen bonding by Crabtree et al. [2].

In the past 16 years, the number of dihydrogen complexes, often synthesized by protonation of a metal hydride complex, has risen from one to well over 200 [3]. However, this tremendous explosion in the *number* of H_2 complexes is not balanced by the increase in the known *types* of H_2 complexes. For example, dihydrogen ligands are almost always found attached to octahedral metal centers. There are no known anionic or paramagnetic H_2 complexes. Furthermore, only moderate systematic changes have been allowed in the attendant ligands. Few H_2 complexes have been characterized with ligands other than PR_3, NR_3, CO, C_5H_5, Cl and H. One

reason for this restricted range of complexes that can contain dihydrogen ligands is the acidity of coordinated H_2 [3]d. Thus, basic attendant ligands are generally incompatible. More specifically, no dihydrogen complexes are known with silyloxide, fluoride, cyanide, amide, azide, alkyl, aryl, phosphide or oxide ligands. By far the most prevalent lone pair-bearing ligands in H_2 complexes are the halides. Thus, halide–dihydrogen complexes provide an interesting "test case" for comparing the basicity of hydride vs lone pair-bearing ligands.

The halide–dihydrogen class of complexes is fairly well represented. These compounds merit discussion since the position of the tautomeric equilibrium between $MX(H_2)$ and $MH(HX)$ (Eq. (1), X = halide ligand) is a thermodynamic indicator of the intramolecular competition of

$$L_nMX(H_2) \rightleftarrows L_nMH(HX) \quad (1)$$

hydride vs halide for a proton. The relatively few examples of preferential protonation (or protonolysis) at the halide ligand are also presented, and some reasons why this class of compounds may be under-represented are discussed. A few metal halide–dihydrogen complexes lose HX (not H_2!) when a new ligand is introduced, demonstrating a facile tautomeric interconversion in Eq. (1).

Many late transition metal hydride halides are formally protonated at the metal center. These products can be derived from complexes protonated at either H or X, after the generated H_2 or HX ligand has been oxidatively added [4]. However, it is not clear whether an intermediate HX or H_2 complex mediates these reactions, or the protonation occurs directly at the metal center. Formation of a hydrogen bond is the first step in proton transfer reactions taking place in non-aqueous solvents [5]a. Therefore, instances of hydrogen bonding to metal-hydride or metal-halide provide insight into the proton's preferred site of attack. Finally, the reactions of metal hydride halide complexes with electrophiles other than H^+ are addressed.

2. Influences of bond polarity and steric hindrance

2.1. Polarity

Simple, known chemical reactions can be extended by analogy to predict an electrophile's attack at either a halide ligand or a hydride ligand, depending on one's perspective. The argument is presented here by consideration of two extreme characterizations of the M–H bond, ionic or covalent. The selectivity of an added electrophile for H or X depends partly on which bonding description is more accurate in the transition metal hydride bond in question.

An excellent case can be made for protonation at the hydride ligand of a metal complex, by simply considering the difference in reactivity between KCl and KH upon dissolution into water. The former innocently dissociates into solvated ions, while the latter deprotonates the solvent with a release of H_2 gas. This difference is easily explained by comparing the electronegativities of the atoms involved;

electronegative Cl is quite content to bear an extra electron, while the much less electronegative H atom is not so accommodating. Accordingly, the pK_b for H^- is -21, while the pK_b for Cl^- is about $+21$. That is, hydride *anions* are about 10^{42} times more basic than chloride *anions*.

On the other hand, protonation at the halide ligand of a metal complex is a reasonable alternative. Examples from organic chemistry of a halogen "ligand" being protonated in preference to a hydrogen "ligand" have been established for over 20 years. Specifically, strong acids can protonolyze the halide of halocarbons, leaving the C–H bonds untouched. The inferred intermediate halonium ions are sometimes even observed (e.g. Eq. (2)) [6]. The proton's preference

$$CH_3I + H^+ \rightarrow CH_3IH^+ \quad (2)$$

for halide in these reactions is quite sensible; the one electron of the H atom participates in covalent bonding, while Cl has three lone pairs to react with an electrophile.

These two examples represent two extremes of chemical bonding; KH and KCl have quite ionic bonds, whereas C–H and C–Cl bonds are mainly covalent. An acid will react with H when it is supplied as hydride (KH), but not when it is covalently bound (R_3CH), in which case the acid preferentially attacks the lone pairs of halide. The M–H bonding description is not so clear in late transition metal complexes. An H atom attached to a late transition metal is still *formally* a hydride ligand, and often reacts accordingly. However, several metal "hydride" complexes are actually quite acidic [3]d. It is not surprising then, that some hydride ligands should be neither acidic nor basic, and the M–H bonding accurately described as covalent. Such a covalent M–H bond could likely behave similarly to a CH bond in reactions with electrophiles. That is, metal hydride halide complexes with covalent MH bonds might be *expected* to be protonated at the halide ligand. Thus, the polarity of the M–H bond is a key influence in directing a metal hydride halide complex's site of reactivity with electrophiles.

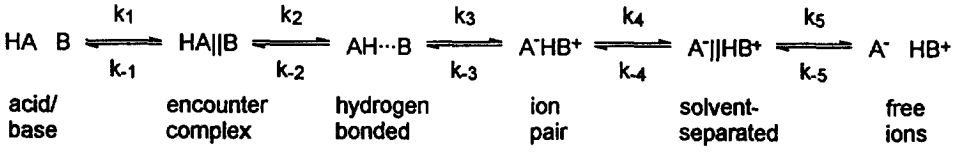
2.2. Steric hindrance

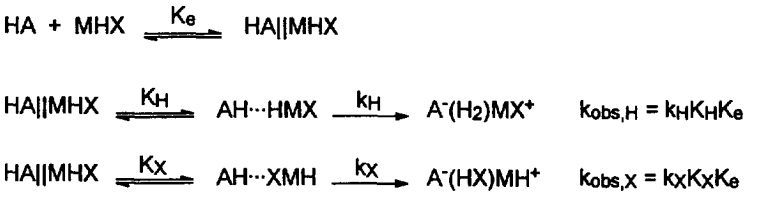
The relative accessibility of the hydride and halide ligands can affect the selectivity of a protonation reaction. Steric effects are generally not considered to affect the rates of protonation reactions of molecules with *only one* basic site, according to an analysis of Scheme 1. The "encounter complex" formed between acid and base is sufficiently long-lived to have several molecular collisions, and thus steric impediments to hydrogen-bond formation are kinetically almost irrelevant [5]b. However, in the special case of the reaction of an acid and a molecule containing *two* basic sites, the *relative* steric hindrances to the two sites become important. The same encounter complex is formed regardless of the eventual site of proton transfer, but now the two different possibilities for hydrogen-bond formation generate two separate important hydrogen-bonding equilibria. In fact, a simple equation for the relative rates of protonation at hydride vs protonation at halide can be deduced

(Eq. (3)) [7]. In this equation, k_H and k_X are

$$\frac{k_{obs,H}}{k_{obs,X}} = \frac{k_H K_H}{k_X K_X} \tag{3}$$

determined by which site is the most electron-rich, but K_H and K_X values primarily reflect the relative accessibility (steric factors) of the two sites.





Scheme 1.

3. Protonation at hydride

The expression "protonation at hydride" is somewhat misleading, since it is really the metal–hydride *bond* which is protonated. True protonation of a hydride ligand would yield an η^1-H_2 (end-bound) ligand, which is not an established binding mode for H_2. Protonation at the M–H bond yields η^2-H_2 complexes (edge-bound), which is the only mode established so far. Throughout this review, "protonation at hydride" and "protonation of the metal hydride bond" are used interchangeably, and understood to lead to edge-bound H_2 complexes.

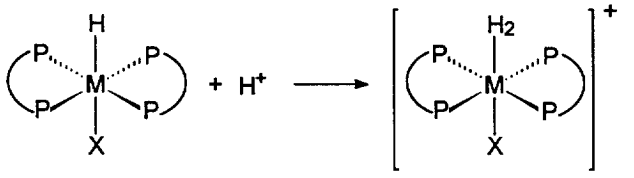
A hydride can be protonolyzed as a way of creating a site of reactivity at the metal via H_2 loss [8]. More recently, protonation of M–H bonds has become a popular method for generating dihydrogen complexes [3]. Yet there are relatively few cases of attempted protonation of a hydride ligand bound to a metal atom with an attendant halide ligand. Dihydrogen complexes containing halide ligands represent one half of the equilibrium of Eq. (1). Furthermore, the lone pairs of these attendant ligands can participate in intramolecular bonding (π donation) or intermolecular bonding (bridge formation), allowing the development of new classes of dihydrogen complexes. Halide ligands also provide a synthetic handle for later transformations such as metathesis, reduction or electrophilic abstraction.

Dihydrogen complexes are primarily characterized by NMR measurements of

spin–lattice relaxation time constants (T_1 values) and HD coupling constants (J_{HD}) of partially deuterated isotopomers. The T_1 of a ^1H nucleus is primarily determined by its proximity to other dipolar nuclei (such as other hydrogens). As a consequence of very short HH distances in dihydrogen ligands, the ^1H nuclei of these ligands relax very quickly (low T_1 values). Finding the minimum T_1 with respect to temperature (T_{1min}) simplifies the mathematical relationship between T_1 and HH distance, allowing this distance to be calculated [9]. While the use of this method in a quantitative fashion has been repeatedly revised and questioned [10], it is generally agreed that within a series of dihydrogen complexes, lower T_{1min} values indicate shorter HH distances. Use of J_{HD} coupling constants directly observable in $L_nM(HD)$ isotopomers is more straightforward; higher HD couplings indicate shorter HD distances, and therefore shorter HH distances in the perprotio isotopomers. An empirical, roughly linear relationship between J_{HD} and HH distance has been reported [11].

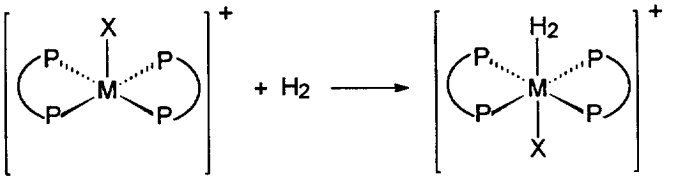
3.1. Cationic $[L_nMX(H_2)]^+$ complexes

Cationic halide–dihydrogen complexes have generally been synthesized either by protonation of a neutral metal hydride halide complex, or by addition of H_2 to a cationic metal halide complex. One relevant system of complexes is $[(P_2)_2MX(H_2)]^+$ (P_2 = chelating diphosphine; M = Ru, Os). For example, Mezzetti et al. have shown that protonation (HBF_4) of *trans*-$(dcpe)_2MClH$ (M = Ru, Os) gives dihydrogen complexes $[(dcpe)_2MCl(H_2)]^+$ (dcpe = 1,2-bis(dicyclohexylphosphino)ethane), with chloride *trans* to H_2 (Eq. (4)) [12]. The osmium complex



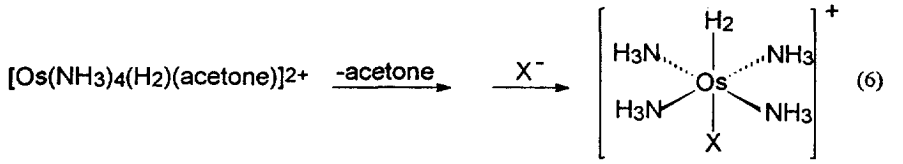
(4)

was later reformulated as having a "stretched" [13] dihydrogen ligand, $[(dcpe)_2OsCl(H\cdots H)]^+$ [14]. The ruthenium complexes *trans*-$[(PP)_2RuCl(H_2)]^+$ (PP = 1,2-bis(diethylphosphino)ethane, 1,2-bis(diphenylphosphino)–ethane) are also synthesized by protonation (HBF_4 or HPF_6) of their conjugate bases [15]. In all of these cases, the complexes can also be formed by H_2 addition to the five-coordinate metal chlorides (Eq. (5)). The synthesis by these different methods is a clear indication that these complexes have a thermodynamic preference for the dihydrogen side of Eq. (1).



(5)

The series of complexes $[Os(NH_3)_4(H_2)X]^+$ (X=Cl, Br, I) have been formed by addition of X^- to $[Os(NH_3)_4(H)_2](BPh_4)_2$ in d_6-acetone [16] (Eq. (6)). The 16e dihydride complex cation in



(6)

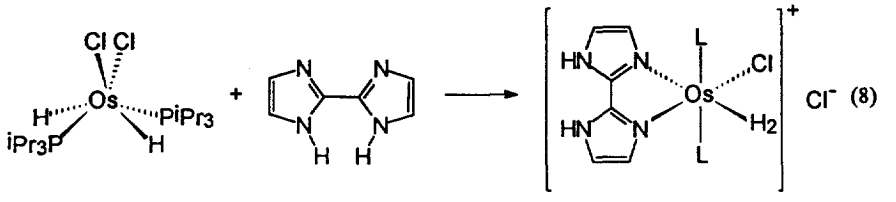
this reaction is generated via loss of acetone from $[Os(NH_3)_4(H_2)(d_6\text{-acetone})]^+$. This method of dihydrogen ligand generation (Eq. (7)) is relatively infrequently used, and involves formal *reduction*

$$L_nM(H)_2 + L' \rightarrow L_nML'(H_2) \quad (7)$$

($Os^{IV} \rightarrow Os^{II}$) of the metal center, upon addition of L'. The initial products are *trans* isomers. While characterization by T_{1min} is precluded in all cases by solvent freezing, HD coupling constants provide an estimate of the relative degree of H–H bonding in these complexes. The J_{HD} (Hz) values follow the trend Cl^- (10.2) < Br^- (11.8) < I^- (12.5) [17], showing that the chloride complex has the longest HH bond. Once again, these complexes are best characterized as having elongated (stretched) H_2 ligands [18]. Over a period of several hours, the complexes isomerize to the *cis* configuration.

Li and Taube have also thoroughly characterized the highly related series, $[Os(en)_2(H_2)X]^+$ (en = ethylenediamine), prepared in the same way as the tetraammine species [19]. The same trend in J_{HD} (Hz) is observed (X *trans* to H_2): Cl^- (7.2) < Br^- (8.0) < I^- (9.1). The iodide ligand in this series behaves remarkably differently from the lighter halides. At equilibrium, I^- is favored to be *cis* to H_2 ($K_{cis/trans} = 1.5$), whereas the *cis* isomers are unobserved for X = Cl^- or Br^-. The H_2 distance in *cis*-$[Os(en)_2(H_2)I]^+$ ($J_{HD} = 15.2$ Hz) is significantly shorter than it is in the *trans* isomer. Also present in this series of complexes are the pseudohalides, X = OD^- and EtS^-. The deuteroxide complex is the only known example of a dihydrogen complex with a unidentate oxygen-based co-ligand. Its existence seems to indicate that the dihydrogen ligand itself is not very acidic, since no proton is transferred to the basic hydroxide ligand.

Using a variation of this general method (Eq. (7)) for generating dihydrogen complexes, Esteruelas has synthesized halide–dihydrogen complexes by neutral ligand addition to an unsaturated (16-electron) dihydride complex [20]. Addition of 2,2′-biimidazole (H_2bim) to $(P^iPr_3)_2OsCl_2(H)_2$ yields d^6 octahedral $[(P^iPr_3)_2Os(H_2bim)Cl(H_2)]Cl$, with *trans* phosphines and chloride *cis* to H_2 (Eq. (8)). In this case (unlike the above examples), no solvent loss is required to



Cl^- (8)

generate the reactive 16e $L_2OsCl_2(H)_2$ complex, which is somewhat stabilized by intramolecular π donation from the chloride ligands [21].

In an attempt to form a rare unsaturated dihydrogen complex, $(P^iPr_3)_2OsI_2(H)_2$ was protonated [22]. Although $HP^iPr_3^+$ was the only detectable phosphorous-containing final product, an intermediate was detected at low temperature (Eq. (9)) when HOTf was used. The hydrides of

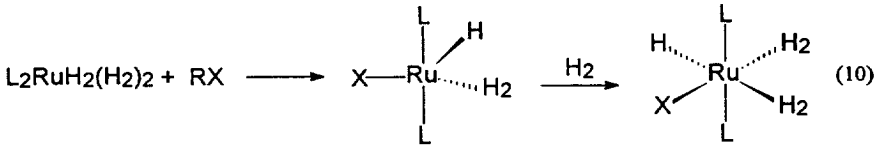
$$L_2OsI_2(H)_2 + HOTf \rightarrow [L_2OsI_2H(H_2)]^+ \ (-70\ ^\circ C) \tag{9}$$

the intermediate have a short T_{1min} value (32 ms/300 MHz), but no detectable HD coupling. The metastability of the complex precludes a definitive structural assignment, but $[(P^iPr_3)_2OsI_2H(H_2)]^+$ is the most likely based on comparisons to known hydride–dihydrogen complexes. This reaction contrasts sharply the reaction observed for protonation of $(P^iPr_3)_2OsX_2(H)_2$ with X = Cl or Br (see Section 4.3).

3.2. *Neutral $L_nMX(H_2)$ complexes*

A wide variety of neutral halide–dihydrogen complexes have been synthesized. Neutral dihydrogen complexes are generally less acidic than the cationic complexes in Section 3.1, and the anionic conjugate bases are unknown, precluding protonation as a viable synthetic pathway. Therefore, synthesis has generally been performed by H_2 addition to a 16-electron metal halide complex. Halides stabilize 16-electron complexes by ligand-to-metal π donation [21], making them ideal precursors to H_2 complexes.

The first reported unsaturated (16e) dihydrogen complexes contain halide or pseudohalide ligands [23–25]. Christ and coworkers have synthesized the series of five-coordinate complexes $L_2RuXH(H_2)$ (L = PCy_3, X = Cl, I, SCy, SPh, S^{t}Bu [23]; L = P^iPr_3, X = Cl, I [24]) by addition of CH_2Cl_2, CH_3I or RSH to $L_2RuH_2(H_2)_2$ (Eq. (10)). A trend in the HH distances can be seen according to the T_{1min} values (ms, 250 MHz). The fastest relaxation (lowest T_{1min}) is observed for H_2 ligands with the shortest HH distances. For the $(PCy_3)_2RuXH(H_2)$ system, the



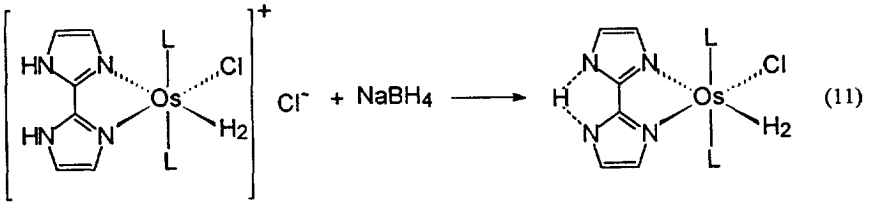
(10)

order Cl ≈ I (30) < SCy (36) < S^{t}Bu (38) is observed, corresponding to a change in HH distance of a few hundredths of an ångström. This trend is consistent with more Ru→H_2 backbonding in complexes with better π-donating ligands (SR > Cl,I). For $(P^iPr_3)_2RuIH(H_2)$, J_{HD} of 13.5 Hz was calculated from the averaged HD coupling of 4.5 Hz observed in the fast-exchange limiting spectrum. The unsaturated hydride complexes react with H_2 to form six-coordinate species assigned the formula $L_2RuXH(H_2)_2$ based on short T_{1min} values (250 MHz, X = Cl (10 ms), I (12 ms)). Unfortunately, for neither of these bis-dihydrogen species is an HD coupling observ-

able, which is generally the best indicator for the number of dihydrogen ligands in a polyhydride [26].

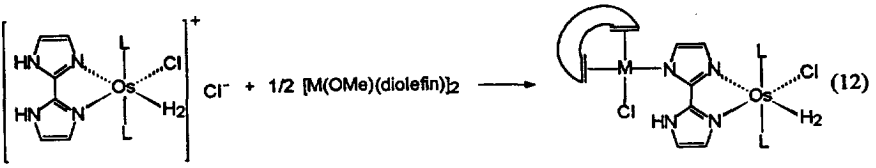
The potential for halide ligands to bridge between metal centers has allowed the first synthesis of bimetallic dihydrogen complexes [27,28]. These complexes have the general formula $L_2Ru(H)(\mu\text{-}X)_3Ru(H_2)L_2$ (Fig. 1). The diruthenium complexes $L_2RuH(\mu\text{-}H)(\mu\text{-}X)_2Ru(H_2)L_2$, ($L=P(p\text{-}CH_3C_6H_5)_3$, PPh_3, $AsPh_3$; X=Cl, Br) were originally formulated as having all classical hydride ligation, but later re-assigned as H_2-complexes based on short T_1 values. Measurement of minimum T_1 values is precluded for the H_2 ligands, whose signals begin to coalesce with those of the other hydride ligands at the relevant temperatures. Later, complexes with chelating diphosphines, $(H_2)(dppb)Ru(\mu\text{-}Cl)_3RuCl(dppb)$ [29], and $(PN)(H_2)Ru(\mu\text{-}H)(\mu\text{-}Cl)_2RuH(PPh_3)_2$ [30] (dppb=1,4-bis(diphenylphosphino)-butane, $PN=[\eta^5\text{-}C_5H_3\{CH(Me)(NMe_2)\}PPh_2]Fe(\eta^5\text{-}C_5H_5)$) were also reported to have bound dihydrogen ligands. It is unsurprising that there should be no H···X bonding in these complexes, since bridging halides have diminished basicity.

The previously described cationic dihydrogen complex $[(P^iPr_3)_2Os(H_2bim)Cl(H_2)]^+$ (Eq. (8)) is deprotonated by $NaBH_4$ at the coordinated nitrogen-containing ligand (*not* at H_2), yielding $(P^iPr_3)_2Os(Hbim)Cl(H_2)$ (Eq. (11)) [20]. This unusual site of deprotonation (for an H_2 complex)



(11)

indicates that the H_2 ligand in this cationic complex is less acidic than the coordinated H_2bim ligand. Deprotonation by the basic organometallic $[M(\mu\text{-}OMe)(diolefin)]_2$ dimers forms heterobimetallic H_2 complexes with a bridging biimidazole (Eq. (12)) [20]. In this way the



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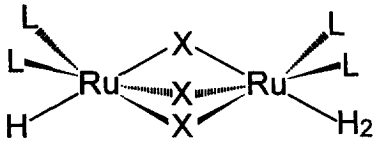
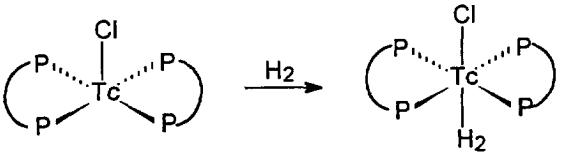


Fig. 1. The first discovered bimetallic dihydrogen complexes, with bridging halide ligands.

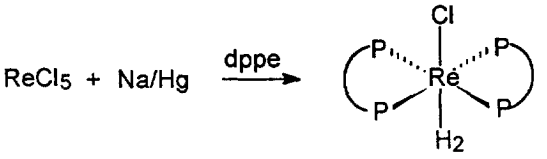
complexes $(P^iPr_3)_2OsCl(H_2)(\mu\text{-}\eta^2,\eta^1\text{-Hbim})MCl(diolefin)$ (M = Rh, Ir, diolefin = 1,5-cyclooctadiene; M = Ir, diolefin = tetrafluorobenzobarrelene) have been synthesized. Unlike the diruthenium complexes, one metal center is completely remote from the H_2 ligand in these heterobimetallic complexes.

The only known dihydrogen complex of technetium is *trans*-$[(dppe)_2TcCl(H_2)]$, synthesized by addition of H_2 to the five-coordinate 16-electron precursor (Eq. (13)) [31]. An



(13)

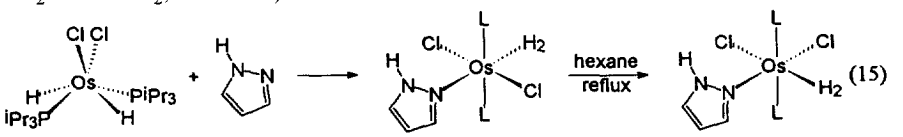
analogous rhenium complex, *trans*-$[(PMePh_2)_4ReCl(H_2)]$ is formed by sodium amalgam reduction of $ReCl_5$ under hydrogen in the presence of the phosphine (Eq. (14)) [32]. The rhenium complex has been proposed to possibly contain an asymmetrically-bound H_2 ligand [33].



(14)

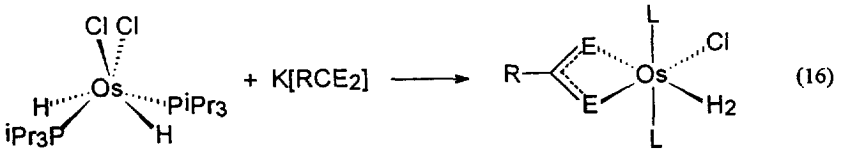
Esteruelas and coworkers have also been able to make neutral dihydrogen complexes by the method of Eq. (7) [20]. Addition of pyrazole (Hpz) to $(P^iPr_3)_2OsCl_2(H)_2$ forms $(P^iPr_3)_2Os(Hpz)Cl_2(H_2)$ with *trans* chlorides (Eq. (15)). Upon refluxing in hexane, this kinetic isomer is converted to the thermodynamically favored *cis* isomer, characterized by X-ray diffraction (see Section 7 for additional discussion).

The first dihydrogen complexes containing S-donating ligands were formed by metathesis reactions of $(P^iPr_3)_2OsCl_2(H)_2$. Reactions of $K[RCE_2]$ ($RCE_2 = EtOCS_2$, MeCOS) with this



(15)

complex give dihydrogen complexes $(P^iPr_3)_2Os(\eta^2\text{-}RCE_2)Cl(H_2)$ (Eq. (16)) [34]. In this reaction, chloride (a monodentate ligand) is replaced with a chelating ligand, yet the coordination number remains six because the two hydrides merge to form a dihydrogen ligand. In this sense, this synthetic method also resembles Eq. (7).

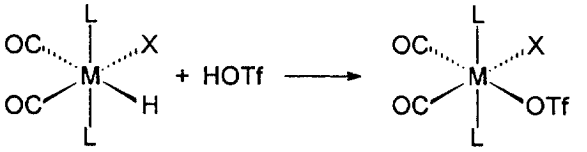


(16)

Complexes $(P^iPr_3)_2M(CO)ClH$ (M = Ru [35], Os [36]), $(P^iPr_3)_2OsX_2(H)_2$ (X = Cl [37], Br, I [38]), $(P^iPr_3)_2OsX(H)_3$ [39] (X = Cl, Br, I), $(P^iPr_3)_2IrX_2H$ (X = Cl [40], Br [41]), $L_2IrCl(H)_2$ (L = P^iPr_3 [42], PCy_3, P^tBu_3 [43], P^tBu_2Me [41]) and $(P^iPr_3)_2IrX(H)_2$ [43] (X = Br, I) add H_2 to form molecular hydrogen adducts. Only two of these products, $L_2OsX_2(H)_2(H_2)$ and $L_2OsX(H)_3(H_2)$, have non-octahedral metal centers. In the case of $(P^iPr_3)_2IrX_2H(H_2)$ (X = Cl, Br), two different isomers have been observed in solution. The kinetic isomers with *trans* halide ligands have very labile H_2 ligands with extremely short (<0.8 Å) H–H distances. The H_2 ligands in the thermodynamic *cis* isomers are less labile with longer H–H distances (>1.0 Å). All of the dihydrogen complexes in the above list contain H_2 *cis* to halide. In several cases, this arrangement is an unavoidable result of having more than one halide ligand. The electronic reasons for H_2 to bind *cis* to halide have been discussed [40]. One additional advantage of chloride *cis* to H_2 is the possibility of additional stabilization by hydrogen bonding between H_2 and X. This type of hydrogen bonding would go unnoticed by normal spectroscopic techniques, and would most likely require single crystal neutron diffraction studies to verify. In fact, such an interaction has been observed by neutron diffraction (see Section 7).

3.3. *Protonolysis of L_nMHX with loss of H_2*

Treatment of $(PPh_3)_2Os(CO)_2BrH$ or $(PPh_3)_2Ru(CO)_2ClH$ with HOTf results in elimination of H_2 and coordination of triflate (Eq. (17)) [44]. These complexes are highly reactive toward N_2H_4



(17)

and are precursors to the first examples of coordinated N_2H_2, potentially quite important to the understanding of N_2 reduction by H_2.

Protonation (HPF_6) of a rhenium complex with a chelating thiolate ligand, $(PPh_3)_2Re(NS)(H)_4$ (NS = 2-mercaptoquinoline), occurs at hydride, with elimination of H_2 [45]. The resulting inferred $(PPh_3)_2Re(NS)(H)_3^+$ fragment then dimerizes via sulfur bridges or reacts with alkynes to form terminal alkylidynes. The chelate effect of the sulfur-containing ligand leaves the possibility open of unobserved reversible protonation at sulfur on $(PPh_3)_2Re(NS)(H)_4$.

4. Proton transfer to halide

4.1. *HX as a ligand*

There are several examples of *protonolysis* of a metal-bound halide by a strong acid [46], which requires only that the acid has a lower pK_a value than the HX

produced. There are very few examples of *protonation* at halide (vide infra), needing an acid with a lower pK_a than the *coordinated* hydrohalic acid produced. The acidity of a coordinated HX ligand has not been measured, and may be either greater or less than that of uncoordinated HX. It seems reasonable to expect an HX ligand in a cationic complex to be much more acidic than uncoordinated HX, and an HX ligand in a neutral complex to be slightly less acidic than uncoordinated HX. This expectation is based on a comparison of the conjugate base strengths: $[L_nMX]^- \approx X^- \gg L_nMX$. Both anions are more electron-rich and therefore more basic than the neutral conjugate base. Filled–filled interactions with metal d-orbitals may raise the energy of the halide orbitals in $[L_nMX]^-$, enhancing its basicity. However, an extremely electron-poor metal center may actually remove electron density from halide lone pairs, decreasing their basicity. Thus, synthesis of *neutral* HX complexes should be more facile than synthesis of cationic ones.

Fischer and coworkers report the spectroscopic (IR, NMR, MS) characterization of the hydrohalide complexes, $(CO)_5W(XH)$ (X=Cl, Br, I) by addition of HX to $(CO)_5W{=}C(OMe)Ph$ [47]. The heavier halide analogs were found to be more stable than the lighter ones. The authors noticed a $20\,cm^{-1}$ *increase* in ν_{W-I} for $(CO)_5W(IH)$ compared to $[(CO)_5WI]^-$, which they attributed to partial double bond character in the W–I bond of the neutral, zwitterionic species. Weak $^2J_{WH}$ coupling of 8.5 Hz was observed for $(CO)_5W(IH)$, and ~6.5 Hz for $(CO)_5W(BrH)$. When excess HI is added to $[(CO)_5WI]^-$, a nearly 1:1 mixture of $[(CO)_5WI]^-$ and $(CO)_5W(IH)$ is observed by IR. Thus, iodide is apparently slightly *more* basic than $[(CO)_5WI]^-$. The reduced basicity of the coordinated iodide ligand could be an influence of the strong π acid *trans* to it.

It is important to realize that the easily-obtained NMR values J_{HD} and T_{1min} (described in Section 3) both provide information regarding H–H interactions, but give *no* indication of the extent (if any) of H–X bonding. In fact, it will be shown that the only established examples of coordinated HX involve either an NMR-active halide (F) or metal (W,Pt). Perhaps this difficulty in spectroscopically detecting H···X bonding is partly responsible for the lack of study of HX complexes relative to H_2 complexes.

4.2. Protonation at halide in preference to hydride

The complex *trans*-$(P^tBu_3)_2PtHCl$ can be protonated at low temperature by HOTf or $HBAr_4$ (Ar=3,5-$(CF_3)_2C_6H_3$) to give a product assigned the chemical formula $[(P^tBu_3)_2PtH(HCl)]^+$ (Eq. (18)) [48]. Alternatively, addition of HCl to $[(P^tBu_3)_2PtH]^+$ yields the same product (Eq. (19)). This proposed HCl adduct has a hydride chemical shift of −20.5 ppm.

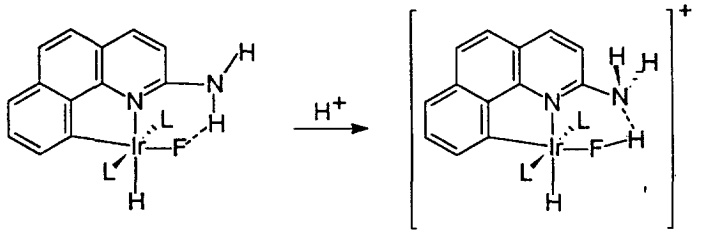
$$L_2PtHCl + H^+ \rightarrow [L_2PtH(HCl)]^+ \quad (18)$$

$$[L_2PtH]^+ + HCl \rightarrow [L_2PtH(HCl)]^+ \quad (19)$$

Irradiation of the hydride signal for the three-coordinate cation (at −36.1 ppm) in a mixture of it and the HCl adduct diminishes the central line (*not* the Pt-satellites)

of the adduct's hydride signal. This behavior is best explained by the Pt–H bond being retained as the HCl ligands travel between $[L_2PtH]^+$ moieties. Unfortunately, no discrete ^1H NMR signal is observed for the coordinated HCl ligand, due to fast exchange with other acidic protons. The HCl adduct decomposes above -50 °C.

Protonation of an octahedral iridium(III) hydride fluoride complex occurs at the fluoride ligand (Eq. (20)) [49]. The assignment of an Ir–F–H···N configuration rather than Ir–F···H–N is based

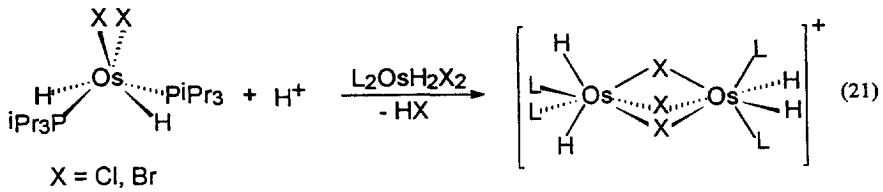


(20)

on the large H–F coupling constant of 440 Hz, and the downfield ^1H chemical shift. Observations of $^2J_{PF}$ and $^2J_{HF}$ (hydride) couplings indicate that the Ir–F bond is maintained after the protonation. The HF ligand is held in place by hydrogen bonding to the pendant amino group. Even with this additional stabilization, HF is lost upon warming above -63 °C. Addition of H^+ to a similar complex without the pendant amino group leads to rapid and irreversible protonolysis of the fluoride ligand.

4.3. *Protonolysis of halide in preference to hydride*

Adding acid (HBF_4 or HOTf) to $(P^iPr_3)_2OsX_2(H)_2$ (X = Cl [50], Br [22]) results in loss of 0.5 equivalents of HX, and formation of the trihalide-bridged dimers, $[\{(P^iPr_3)_2Os(H)_2\}_2(\mu\text{-}X)_3]^+$ (Eq. (21)). This protonolysis of a halide ligand sharply contrasts the behavior of the iodide analog and several other examples discussed in Section 3. Perhaps this remarkable behavior can be explained by considering the structure of the complex being protonated. These six-coordinate starting complexes have a non-octahedral geometry, in which one molecular hemisphere contains



(21)

only halide ligands while the other hemisphere holds two phosphines (P–Os–P angle is 112°) and two hydrides. The hydrides are therefore sterically protected by the bulky phosphines [51], which shield them from the approaching proton (lowering

K_H in Eq. (3)). One other factor is that k_H of Eq. (3) may also be decreased by the covalent nature of the Os–H bonds (i.e. non-hydridic hydrogens, see Section 6).

Protonation of $(P^iPr_3)_2OsCl(H)_3$ at $-70\,^\circ C$ very quickly gives the products $[(P^iPr_3)_2OsH_3(H_2)_2]^+$ and $[\{(P^iPr_3)_2Os(H)_2\}_2(\mu\text{-}Cl)_3]^+$ [22]. The reaction requires two equivalents of acid per three equivalents of Os (Eq. (22)). The extensive ligand rearrangements necessary

$$3L_2OsCl(H)_3 + 2H^+ \rightarrow [(L_2OsH_2)_2Cl_3]^+ + [L_2OsH_3(H_2)_2]^+ \quad (22)$$

require transfer of both HCl and H_2, but the *initial* site of protonation is unknown.

While silicon is not generally considered a metal, its ability to be hypervalent allows it some variation in coordination number (if not oxidation state), and so it has some metal-like chemical properties. The very powerful acid HOTf is capable of protonating even Si–C bonds (Eq. (23)). Thus, $(CH_3)_4Si + HOTf$ produces Me_3SiOTf and CH_4 [52]. However, when given the opportunity, the acid will attack a halide "ligand" (Eq. (24)) [53].

$$(CH_3)_4Si + HOTf \rightarrow (CH_3)_3SiOTf + CH_4 \quad (23)$$

$$^tBuMe_2SiCl + HOTf \rightarrow {}^tBuMe_2SiOTf + HCl \quad (24)$$

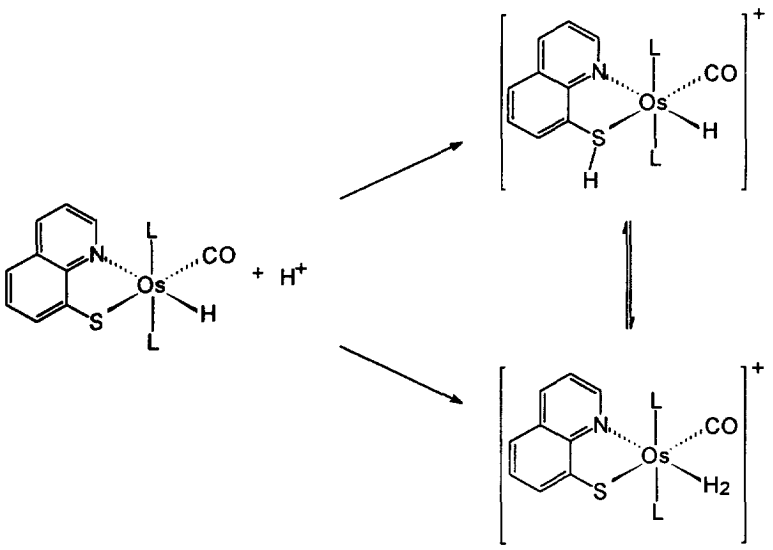
5. Reversible migration of a proton from hydride to pseudohalide

Alkoxide–dihydrogen complexes are unknown, but the less basic alkylthiolate ligands can coexist with H_2 ligands. In some cases, the equilibrium of Eq. (25) is nearly isoenergetic. In fact, Jessop and Morris have observed H/D interchange between hydride and coordinated thiol (Eq. (26)) [54]. They found the forward reaction of Eq. (26) to proceed unimolecularly in

$$L_nM(H_2)(SR) \rightleftarrows L_nM(H)(HSR) \quad (25)$$

$$L_nM(H)(DSR) \rightleftarrows L_nM(D)(HSR) \quad (26)$$

$[(PCy_3)_2Ir(H)_2(DS(CH_2)_3SD)]^+$, and therefore propose that an η^2-HD complex mediates the exchange. Using a ligand additivity model [55], Schlaf and Morris recently developed a system in which both isomers of Eq. (25) are observed simultaneously [56]. They find that protonation of $Os(H)(CO)(quS)(PPh_3)_2$ with HBF_4 occurs competitively at sulfur or hydride, yielding a mixture of $[Os(H)(CO)(quSH)(PPh_3)_2]^+$ and $[Os(H_2)(CO)(quS)(PPh_3)_2]^+$ (Scheme 2) [57]. The S-protonated product is favored kinetically (perhaps for steric reasons). The equilibrium shifts slightly toward the S-protonated product at higher temperatures, indicating that ΔS^0 in Eq. (25) is slightly positive.



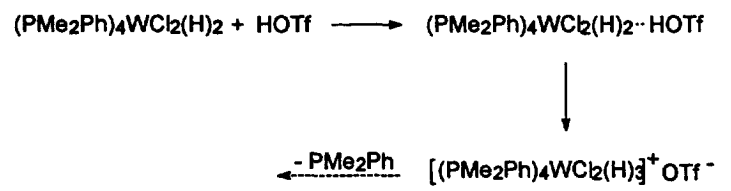
Scheme 2.

6. Protonation at the metal center

Protonation of a metal center differs from protonation at hydride or halide only by the formal oxidation state and coordination number of the metal center in the product. Metal protonation is formally a two-electron oxidation of the metal, whereas the metal oxidation state remains unchanged upon protonation of a ligand. Thus, a metal in its highest oxidation state *cannot* be protonated. It remains unclear in most cases whether the proton approaches the metal directly, or via a hydride or halide (or other) ligand [58].

Protonation of $(PMe_2Ph)_4WCl_2(H)_2$ with HOTf starts a series of reactions in motion (Scheme 3) [59]. The initial product is kinetically persistent only below -70 °C, so that complete characterization is impossible. However, the bright green color indicates that there are still d electrons (not W^{VI}). Two "hydride" signals at -2.5 and $+2.4$ ppm (unknown integration) are observed. Some reasonable structural alternatives are $[(PMe_2Ph)_4WCl_2(H)(H_2)]^+$ and $[(PMe_2Ph)_4WCl(H)_2(HCl)]^-$ (the proton must be in fast exchange between the two chlorides). Hydrogen-bonded triflic acid (either to hydrides or halides) was also suggested as a possibility. Above -70 °C, protonation at the metal center is completed, giving $[(PMe_2Ph)_4WCl_2(H)_3]^+$. Further warming leads to loss of phosphine, and eventually decomposition. The dibromide and chloride–bromide complexes were found to behave quite similarly, although no intermediate was observed prior to protonation of W. The analogous diiodide complex was not protonated cleanly, attributed to facile H_2 loss from the starting material.

The enthalpies of protonation of a wide array of metal complexes have been measured by Angelici, and this work has been reviewed [60]. The basicity of the metal in complexes $CpM(PR_3)_2X$ (M = Ru, Os; X = I, Br, Cl, H) was found to



Scheme 3.

increase in the order I < Br < Cl ≪ H for two different phosphines (Table 1). In this series, the hydride complexes are much more basic than halide ones. Furthermore, a metal center with an attached chloride is more basic than one with attached iodide. While this trend opposes expected values from electronegativities of the halides, it correlates very well with their gas-phase proton affinities. Angelici considers two additional explanations: (1) the increase in coordination number upon protonation is less favored by the bulkier halides, and (2) the overall ($\sigma+\pi$) donicity of chloride is higher than that of I [61]. Since these are *thermodynamic* measurements, no *mechanistic* insight (as to the initial site of protonation) is gained.

Angelici offers an interesting insight into the nature of the Os–H bond in $CpOs(PPh_3)_2H$, based on an analysis of thermodynamic data. Relative pK_a values for different acids can be approximated from differences in ΔH values (assuming $\Delta\Delta S^0$ is negligible). The pK_a's of $[CpOs(PPh_3)_2IH]^+$ and $[CpOs(PPh_3)_2(H)_2]^+$ differ by about 17. This tremendous difference in acidity (the iodide cation complex is 10^{17} times more acidic) is nearly as large as that observed upon one-electron oxidation of a number of transition metal hydride complexes [62]. Thus, it seems that if the iodide complex contains an Os^{II} center, then the hydride complex must have something nearing Os^{I}, implying a *covalent* Os–H bond. As mentioned earlier, a covalent M–H bond can skew site selectivity toward halide, since the situation approximates that of R_2CHX. For example, the Os–H bond in $(P^iPr_3)_2OsH_2Cl_2$ may also be quite covalent, directing protonolysis to the chloride ligand (Section 4).

7. Hydrogen bonding

Hydrogen bonding has been observed to both metal-bound hydride and halide ligands. Since proton transfer in non-aqueous solvents occurs through initial formation of a hydrogen bond, preferences in hydrogen bonding for hydride vs halide are

Table 1
Enthalpies of protonation of $CpM(PR_3)_2X$, for protonation at the metal center

X	$-\Delta H$ (Ru)		$-\Delta H$ (Os)	
	R = Me	R = Ph	R = Me	R = Ph
I	20.6	–	26.6	14.1
Br	20.9	–	29.4	16.3
Cl	21.2	–	–	19.7
H	–	29.7	–	37.3

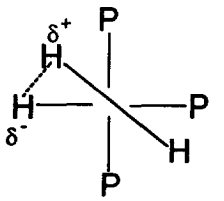
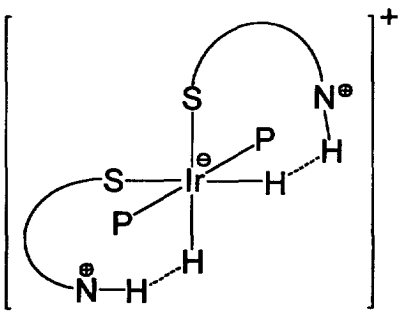
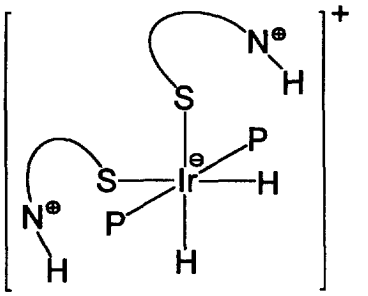


Fig. 2. The "*cis* effect" in $L_3Fe(H)_2(H_2)$, viewed down the H_2–Fe–H axis. The Fe atom and one hydride are not shown.



in CD_2Cl_2



in d_8-THF

Fig. 3. This iridium complex shows hydrogen bonding to hydrides in CD_2Cl_2, but not in d_8-THF.

of great relevance. Special attention is given to cases where a metal hydride competes directly with a metal halide for a hydrogen bond.

7.1. Hydrogen bonding to metal hydrides

Evidence for hydrogen bonding to a metal hydride was reported as early as 27 years ago, when ν_{RhH} in $[RhH(NH_3)_5](Z)_2$ was found to depend strongly on the choice of anion, Z [63]. The authors found $Z = Br^-$ to form stronger hydrogen

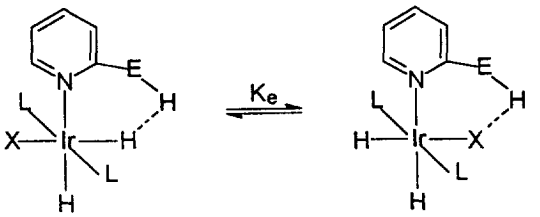
bonds than $Z=I^-$, with Rh–H stretching frequencies of 2015 and 2045 cm^{-1}, respectively. This unusual type of hydrogen bonding requires a partial positive charge on metal "hydride" ligands.

Hydrogen bonding from hydride to coordinated H_2 is quite clearly demonstrated in the structure of $(PEtPh_2)_3Fe(H)_2(H_2)$, determined by neutron diffraction [64]. The dihydrogen ligand in this complex is rotated from the P–Fe–P plane which would provide the greatest $M \rightarrow H_2$ backbonding, in order to approach an Fe–(H) bond (Fig. 2). The stabilization provided by this distortion has been called the "*cis* effect". Mulliken analysis in an ab initio study [65] shows that the two hydrogen atoms of the coordinated H_2 ligand are not equally charged. The one closer to Fe–(H) has a positive charge (0.79), while the other has a slight negative charge (1.01). Thus, the "*cis* effect" is simply an attraction between the electron-rich classical hydride and one electron-deficient H atom of the dihydrogen ligand. In short, the interaction strongly resembles a hydrogen bond.

There have been several IrH···HO and IrH···HN hydrogen bonds characterized (in complexes without halide ligands) by neutron diffraction [66], HH coupling constants [67], T_1 measurements and NOE difference spectroscopy [68]. These hydrogen bond distances range from 1.8–2.4 Å, have (roughly) estimated bond strengths of 4–5 kcal mol^{-1}, and J_{HH} of 0–6 Hz. The presence of an IrH···HO hydrogen bond was found to activate the metal hydride toward σ-bond metathesis reactions [69]. Interested readers are referred to the recent review by Crabtree et al. [2].

Hydrogen bonds to hydrides of an iridium complex reported by Lough and coworkers form reversibly [70]. The structure of the complex in Fig. 3 is different in CD_2Cl_2 than it is in d_8-THF. In CD_2Cl_2, there are two intramolecular IrH···HN hydrogen bonds (no H- bonds to solvent Cl), whereas in THF, the NH hydrogen bonds to oxygen atoms of the THF solvent molecules. Furthermore, the addition of two equivalents of Ph_3PO to a CD_2Cl_2 solution of the complex disrupts the intramolecular hydrogen bonds in preference for intermolecular bonding to oxygen of Ph_3PO. One final observation is that there is seemingly no tendency for hydrogen bonding to the S atom of the chelating ligand, even though S is as accessible as H (both being bound directly to Ir). Thus, there is qualitative evidence for the NH hydrogen bond strength following the order R_2O, $R_3PO > L_nIrH > L_nIrS$, R_3CCl.

The most thorough quantitative study of hydrogen bonding to metal hydrides and halides is that reported by Peris and coworkers [71]. They were able to design a system in which intramolecular hydrogen bonding occurs competitively to either a halide or a hydride ligand (Eq. (27)). By measuring the relative populations of the two isomers shown in Eq. (27), the authors found



(27)

L = PPh_3; E = O, NH; X = F,Cl,Br,I

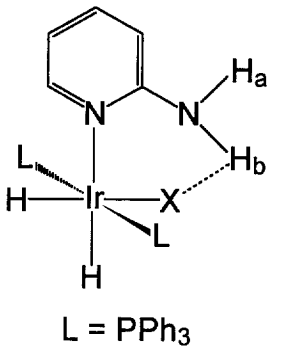


Fig. 4. This class of iridium complexes were used to estimate hydrogen bond strengths (Ir–X···HN) by measuring the barrier to rotation about the C–N bond. The barrier was measured by NMR lineshape analysis of the coalescence of H_a and H_b.

the strength of the EH···XIr bond to follow the order X = F (1) > H > Cl (0.49) > Br (0.12) > I (0). The numbers in parentheses are the equilibrium ratios of $L_nMX\cdots H$ to $L_nMH\cdots H$ species. In this case, hydrogen bonding is stronger to hydride than to halides (except F^-). In other words, $K_H > K_X$ (Scheme 1) in this system. However, the preference is slight, and both configurations are observed in solution (except when $X = I^-$). The hydrogen bond strengths (kcal mol^{-1}) were estimated by measuring the barrier to rotation about the C–N bond in Fig. 4 (exchange of H_a and H_b by NMR), and subtracting the rotation barrier in the free ligand. These values follow the above trend, and are given in Table 2.

Furthermore, the authors found a remarkable influence of the ligand *trans* to hydride on its hydrogen bond strength (Fig. 4). The XIrH···HN bond strength (in kcal mol^{-1}), measured by barrier to rotation about the C–N bond in Fig. 4, is found to be dramatically lower when X is electronegative (Table 2): X = F < Cl < Br < H. This is an extremely important point, because it demonstrates how easily the affinity of a hydride ligand for an incoming proton can be affected by fairly minor changes in the metal's coordination sphere.

7.2. *Hydrogen bonding to metal halides*

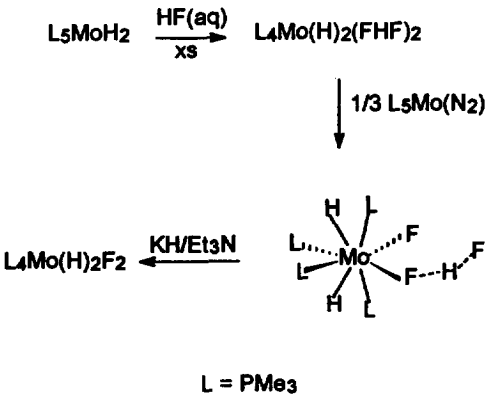
Both intra- and intermolecular Cl···H hydrogen bonding are observed in the structure of the complex $(P^iPr_3)_2IrCl_2H(H_2)$, determined by neutron diffraction [40].

Table 2
Estimated hydrogen bond strengths (kcal mol^{-1}) for the iridium complexes illustrated in Fig. 4

X	HMX···HN	XMH···HN
F	5.2	<2.9
H	5.0	5.0
Cl	2.1	2.9
Br	1.8	3.0
I	<1.3	3.3

The intramolecular hydrogen bond has a Cl···H separation of 2.65 Å between H and a *cis* chloride. An intermolecular hydrogen bond with a Cl···H separation of 2.64 Å causes the complex to crystallize as an infinite chain of molecules linked by hydrogen bonds. In both interactions in this complex, the "protons" (η^2-H_2 ligands) prefer metal-bound chloride to metal-bound hydride (there are no significant H···H contacts other than that in the H_2 ligand). Once again, the H–H bonding (η^2-H_2) ligand in this complex was detected by NMR measurements, whereas the H···Cl hydrogen bonding went completely unnoticed before the neutron diffraction study.

The solid-state structure of a molybdenum bifluoride (FHF^-) complex was recently determined by X-ray diffraction. The complex is best synthesized by addition of excess HF to form a postulated bis(bifluoride) complex, followed by abstraction of one equivalent of HF (Scheme 4) [72]. The Mo–F bond to the bifluoride is about 0.05 Å longer than the more pedestrian Mo–F bond in this structure. The F···F separation in the bound bifluoride is greater than in bifluoride salts, indicating weakened F···H···F hydrogen bonding. In fact, the hydrogen bond is essentially lost in solution, where an NMR spectroscopic signature similar to that of HF is observed. This bifluoride complex is similar to the HF complex reported by Patel and Crabtree [49], in that the MFH linkage is held intact by an additional interaction.



Scheme 4.

The characterization of the complex $(P^iPr_3)_2Os(Hpz)Cl_2(H_2)$ [20] (*trans* phosphines, *cis* chlorides) by X-ray diffraction was mentioned earlier (Section 3.2). The authors note that Cl1 *trans* to H_2 has a *longer* Os–Cl1 distance (2.496(2) Å) than Cl2 *trans* to nitrogen of Hpz (2.426(2) Å), attributed to H_2 having a greater *trans* influence than the nitrogen ligand (Fig. 5). An alternate plausible explanation for this difference is hydrogen bonding. The Hpz ligand has a β-NH group, whose nitrogen is calculated [73] to be 2.9 Å from Cl1. Assuming an N–N–H angle of 120°, and N–H distance of 1.0 Å, this results in a Cl···H distance of about 2.1 Å, much shorter than those assigned as hydrogen bonds in the iridium complex characterized by neutron diffraction. It is therefore possible that the Os–Cl1 distance is lengthened as a consequence of hydrogen bonding. Accordingly, this complex has

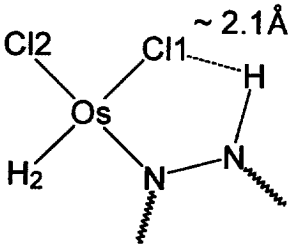
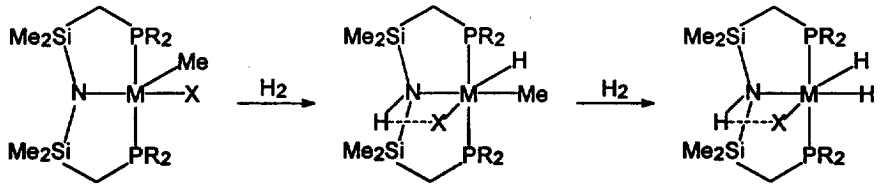


Fig. 5. A hydrogen bond from Cl1 to H could explain the lengthened Os–Cl1 distance in comparison to Os–Cl2.

an acute Cl1–Os–N angle of 85.0(2)° to maximize the apparent Os–Cl···HN hydrogen bond. Thus, perhaps no conclusions should be drawn about the relative *trans* influences of H_2 and the N-based ligand in this complex, when one considers the influences of hydrogen bonding.

The research group of Fryzuk has exploited an MX···HN (M = Rh, Ir; X = Br, I) hydrogen bond in order to control the stereochemistry of H_2 addition across an Ir–N bond (Scheme 5) [74]. Interestingly, the product has NH hydrogen-bonded to a halide, even though a metal hydride is also accessible. The preference must be significant, since this product is not what one would predict for concerted H_2 addition across an M–N bond; the observed structure is most likely *thermodynamically* preferred. The H···X bond is maintained even after further reaction with H_2. In this example, a hydrogen bond is "used" to control the stereochemistry of the reaction. Yet there is no clear reason to have anticipated the H···X hydrogen bond to be stronger than the alternate H···H hydrogen bond, which would have led to the opposite stereochemistry in the products. Based on the work of Peris et al., the opposite stereochemistry may in fact be obtainable by using a complex with an iodide rather than chloride ligand.



Scheme 5.

Hampton and coworkers have observed evidence for ^{n}BuOH coordinated and hydrogen-bonded to a Ru complex containing two chlorides and a hydride [75]. They propose that OH is hydrogen-bonded to the chloride ligand (Fig. 6), without consideration of the alternate OH···HRu configuration. While the absolute configuration of this proposed species is not of consequence to the conclusions of the work, this is an example of a structure assigned according to an intuitive preference for

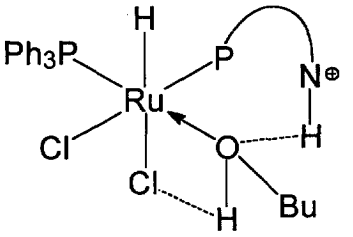


Fig. 6. A hydrogen bond to chloride was proposed in this ^{n}BuOH adduct although hydrogen bonding to a hydride ligand is equally possible.

drawing a hydrogen bond to a chloride ligand rather than hydride. While this assignment accords with the observations of Fryzuk, it contrasts the studies of Peris (Section 7.1), where hydrogen bonding was observed preferentially to hydride.

8. Elimination of HCl from $M(H_2)Cl$ complexes

One simple method for conversion of a metal halide to a hydride is subjection of the complex to an H_2 atmosphere in the presence of a base. Presumably, H_2 coordinates or oxidatively adds to the metal center, and the resulting complex is dehydrohalogenated. In some cases, no base is added, but the reaction is driven by phase-transfer conditions. The reductive elimination of HCl from transition metal complexes has been reviewed [76]. However, the remarkable observations by two research groups of HCl elimination from well-characterized dihydrogen complexes *without any added base* (Eq. (28)) have appeared since that review, and deserve further consideration.

$$L_nMCl(H_2)+CO\rightarrow L_nM(CO)H+HCl \tag{28}$$

Esteruelas and coworkers report the synthesis of $L_2Os(CO)Cl_2(H_2)$ ($L=P^iPr_3$) by reaction of $L_2Os(CO)ClH$ with HCl [77]. By NMR experiments and observations, the product dihydrogen complex is shown to have *trans*-phosphines and *cis*-chlorides. A minimum T_1 value of 15 ms (300 MHz) and J_{HD} of 20.1 Hz clearly establish the hydrogen ligation as η^2-H_2. However, addition of CO to the complex in C_6D_6 leads to loss of HCl rather than H_2, and formation of $L_2Os(CO)_2HCl$. The authors propose a mechanism involving initial dissociation of Cl^-, followed by CO coordination and then deprotonation by Cl^- (Scheme 6). While this mechanism is reasonable, there is an alternative (Scheme 7): reversible reductive elimination of HCl from the dihydrogen complex (which could already have a H–H···Cl hydrogen bond) to form the 16-electron species $L_2Os(CO)Cl(H)$. Even if this equilibrium loss favors the 18-electron complex side, CO could scavenge the 16-electron complex.

Similarly, Chin and coworkers have observed the replacement of HCl (not H_2) when CO is bubbled through a CH_2Cl_2 solution of *trans*-$[(dppe)_2Ru(H_2)Cl]^+$ [15]. Once again, the dihydrogen ligand is well-characterized by a T_{1min} of 25 ms (400 MHz) and J_{HD} of 25.9 Hz. In this case, proton transfer to the chloride ligand

$$L_2OsCl_2(CO)(H_2) \rightleftharpoons [L_2OsCl(CO)(H_2)]^+ + Cl^-$$

$$[L_2OsCl(CO)(H_2)]^+ + CO \longrightarrow [L_2OsCl(CO)_2(H_2)]^+$$

$$[L_2OsCl(CO)_2(H_2)]^+ + Cl^- \longrightarrow L_2OsCl(CO)_2H + HCl$$

Scheme 6.

$$L_2OsCl_2(CO)(H_2) \rightleftharpoons L_2OsCl(CO)H + HCl$$

$$L_2OsCl(CO)H + CO \longrightarrow L_2OsCl(CO)_2H$$

Scheme 7.

is frustrated by the *trans* disposition of the chloride and dihydrogen ligands. However, the authors suggest that one arm of a diphosphine ligand can swing off to transport the proton from the H_2 ligand to the chloride ligand. The resulting HCl ligand is then very quickly displaced by incoming CO. In order for $[(dppe)_2Ru(H)(HCl)]^+$ to be available in a kinetically significant concentration, chloride must compete against hydride fairly successfully for the proton.

9. Other electrophiles

Ziegler–Natta type polymerization catalysts are usually a combination of a Lewis acid and Cp'_2MXY (Cp' = any imaginable derivative of cyclopentadienyl; M = Zr, Ti; X, Y = Cl, H, alkyl). The number of combinations is staggering and this field has been extensively reviewed [78]. The electrophile generally attacks chloride in preference to hydride or methyl. In these systems, one would expect to have "hydridic" H-ligands on these early transition metals, favoring electrophilic attack at hydride. However, steric factors must be quite dominant when the incoming electrophile is so large (relative to H^+).

The complex $Ir(PEt_3)_3Cl$ was reported to react very quickly with Me_3SiOTf to form $(PEt_3)_2Ir(\eta^2\text{-}Et_2PCH_2CH_2)H(OTf)$ [79]. A similar hydride complex, $Ir(PMe_3)_3H$, reacts very slowly with Me_3SiOTf, yielding $[(PMe_3)_4IrH(SiMe_3)]OTf$. The former reaction (silylation at Cl) is analogous to protonation at chloride, while the latter reaction (silylation at Ir) corresponds to protonation at the metal. Unfortunately, the difference in phosphines precludes reliable relevant speculation about the different reaction rates.

The unsaturated complex $(P^iPr_3)_2RuHCl(CO)$ reacts with AgOTf (ca. 1.5 equivalents) to give an active catalyst for the dimerization of methyl acrylate (MA) [80]. Observation of a white precipitate (presumably AgCl) and *no* free P^iPr_3 (by ^{31}P NMR) led the authors to propose $[(P^iPr_3)_2RuH(CO)(MA)]^+$ as the active catalytic species. In this case, the lattice energy of AgCl is an important driving force. It is worth noting that silver ions also have a demonstrated affinity for hydride ligands,

forming M–H–Ag bonds [81]. Thus, formation of AgCl was not a foregone conclusion.

Halide exchange has been effected by addition of Me_3SiX (X=Br, I) to $(P^iPr_3)_2OsCl_2(H)_2$ [80] or $(PMe_2Ph)_4WCl_2(H)_2$ [53]. In the former case (Eq. (29)), both halides are exchanged, whereas in the latter case (Eq. (30)), only one is exchanged (even when excess Me_3SiX is added). In both systems, the hydride ligands remain intact.

$$(PiPr_3)_2OsCl_2(H)_2 + 2Me_3SiX \underset{X=Br,\ I}{\rightarrow} (PiPr_3)_2OsX_2(H)_2 \quad (29)$$

$$(PMe_2Ph)_4WCl_2(H)_2 + Me_3SiX \underset{X=Br,\ I}{\rightarrow} (PMe_2Ph)_4WClX(H)_2 \quad (30)$$

Unlike H^+, larger electrophiles seem to categorically attack at halide in preference to hydride. Steric factors may once again be the most important influence in these reactions with bulky electrophiles. The electron density of a hydride ligand resides primarily in the *metal—hydride bond*, which is generally less accessible than *lone pairs* on a halide ligand. Bulkier electrophiles may find access to the M–H bonds much more difficult than access to halide lone pairs.

10. Summary

There is a marked tendency for the lighter halides to react with H^+ more readily than the heavier halides. This phenomenon is clearly shown by hydrogen bonding equilibrium studies, and protonolysis reactions. Therefore, iodide is the best candidate for maintaining an M–X bond under acidic conditions, while fluoride is the most effective as a leaving group in electrophilic transformations. Because secondary bonding is often important in reaction mechanisms, one should recognize that simply changing a halide ligand can alter the strength of a hydrogen bond, and thereby change the reaction mechanism or rate.

Fluoride has categorically prevailed over hydride in competition for protons including intermolecular and intramolecular hydrogen-bond formation, protonation and protonolysis reactions. There are no examples of a metal hydride fluoride complex receiving a proton at the hydride ligand. In contrast, fluoride has been shown to be protonated or, more often, protonolyzed instead of hydride. In addition to the examples cited in this review, there are many cases of HF elimination from metal hydride complexes in reactions involving fluorocarbons [82].

While there are far more $MX(H_2)$ complexes known than $MH(XH)$, it is not fair to generalize that protonation occurs preferentially at hydride rather than halide ligands. For one reason, the $MX(H_2)$ complexes studied are very similar. The only non-octahedral examples are $(PR_3)_2RuXH(H_2)$, $(PR_3)_2OsX_2(H)_2(H_2)$ [83] and $(PR_3)_2OsX(H)_3(H_2)$. None of these are synthesized by protonation, and for neither of the osmium examples is H···X bonding disproved. Even in octahedral complexes, facile HCl loss and studies of hydrogen bonding have shown that the dihydrogen–

halide vs hydride–hydrochloric acid tautomeric equilibrium can be nearly thermoneutral.

The few non-octahedral complexes reported have generally shown a tendency to be protonated at halide in preference to hydride. Both d^8 square planar $(PR_3)_2PtClH$ and d^4 trigonal antiprismatic $(PR_3)_2OsCl_2(H)_2$ [84] show evidence for proton transfer to halide. Furthermore, the d^2 eight-coordinate $(PR_3)_4WCl_2(H)_2$ may very well initially interact with the incoming proton via its halide ligands. In addition to being non-octahedral, these complexes have the common characteristic of having unsaturated (16e), 5d metal centers. Furthermore, the phosphines in these complexes fairly effectively shield the hydrides. More experimentation is needed to determine which of these characteristics direct protonation away from the hydride ligands.

Hydrohalic acids remain highly unusual and elusive ligands. On the other hand, there are several alkyl halide complexes known [85], which are less prone to oxidative addition. Correspondingly, dialkylhalonium ions are much more common than acid halonium ions [6]. The most conspicuous reason why HX is such a poor ligand is that it is highly prone to dissociation. Even the known examples of HX ligands suffer from this problem. However, the HX ligand also very readily undergoes oxidative addition. Because the product of HX oxidative addition is indistinguishable from that of protonation at the metal center (Section 6), many of those complexes formally protonated at the metal may initially receive the proton via a halide ligand. While protonation at halide is rare, hydrogen bonds (the first step in proton transfer) form nearly isoenergetically to hydride or halide ligands. Thus, halide ligands may often play the role of mediating proton transfer, without being the final bearer of the added proton.

Steric factors should be considered when there is direct competition of different sites within a molecule for an electrophile. The possibilities of hydrogen bonding to coordinated halide ligands should be recognized in $MX(H_2)$ complexes, even though such interactions are not as easily detected as are short H–H separations. Hydrogen bonding to metal-bound hydride or halide can be an important structural influence, which should be identified and considered when analyzing solid-state structures.

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References

[1] R.A. Henderson, Angew. Chem. Int. Ed. Engl. 35 (1996) 946.
[2] R.H. Crabtree, P.E.M. Siegbahn, O. Eisenstein, A.L. Rheingold, T.F. Koetzle, Acc. Chem. Res. 29 (1996) 348.

[3] (a) D.M. Heinekey, W.J. Oldham, Jr., Chem. Rev. 93 (1993) 913; (b) P.G. Jessop, R.H. Morris, Coord. Chem. Rev. 121 (1992) 155; (c) R.H. Crabtree, Acc. Chem. Res. 23 (1990) 95; (d) S.S. Kristjánsdóttir, J.R. Norton, in: A. Dedieu (Ed.), Transition Metal Hydrides: Recent Advances in Theory and Experiment, VCH Publishers, New York, 1991.
[4] The terms oxidative addition and reductive elimination refer to overall reactions, with no mechanistic implications (i.e. concerted vs stepwise).
[5] E. Caldin, V. Gold, Proton-Transfer Reactions, Chapman and Hall, London, 1975: (a) B.H. Robinson, chap. 5, p. 121; (b) J.E. Crooks, chap. 6, p. 153.
[6] G.A. Olah, Halonium Ions, Wiley–Interscience, New York, 1975.
[7] These equations assume that proton transfer is essentially irreversible (i.e. k_{-3} is negligible). This assumption is reasonable when very strong acids such as HBF_4, HPF_6 and HOTf are used.
[8] Some examples: (a) M.L. Christ, S. Sabo-Etienne, G. Chung, B. Chaudret, Inorg. Chem. 33 (1994) 5316; (b) K. Osakada, K. Ohshiro, A. Yamamoto, Organometallics 10 (1991) 404; (c) A. Yamamoto, J. Organomet. Chem. 500 (1995) 337.
[9] R.H. Crabtree, Acc. Chem. Res. 23 (1990) 95.
[10] (a) M.T. Bautista, K.A. Earl, P.A. Maltby, R.H. Morris, C.T. Schweitzer, A. Sella, J. Am. Chem. Soc. 110 (1988) 7031; (b) P.J. Desrosiers, L. Cai, Z. Lin, R. Richards, J. Halpern, J. Am. Chem. Soc. 113 (1991) 4173; (c) D.G. Gusev, R. L. Kuhlman, K.B. Renkema, O. Eisenstein, K.G. Caulton, Inorg. Chem. 35 (1996) 6775.
[11] D.M. Heinekey, T.A. Luther, Inorg. Chem. 35 (1996) 4396.
[12] A. Mezzetti, A. Del Zotto, P. Rigo, E. Farnetti, J. Chem. Soc. Dalton Trans. (1991) 1525.
[13] "Stretched" (intermediate length) dihydrogen ligands are arbitrarily defined to have H–H distances of 1.0–1.5 Å.
[14] A. Mezzetti, E. Zangrando, A. Del Zotto, P. Rigo, J. Chem. Soc. Chem. Commun. (1994) 1597.
[15] B. Chin, A.J. Lough, R.H. Morris, C.T. Schweitzer, C. D'Agostino, Inorg. Chem. 33 (1994) 6278.
[16] Z.-W. Li, H. Taube, J. Am. Chem. Soc. 113 (1991) 8946.
[17] T. Hasegawa, Z. Li, S. Parkin, H. Hope, R.K. McMullan, T.F. Koetzle, H. Taube, J. Am. Chem. Soc. 116 (1994) 4352.
[18] See theoretical calculations by J.S. Craw, G.B. Backsay, N.S. Hush, J. Am. Chem. Soc. 116 (1994) 5937.
[19] Z.-W. Li, H. Taube, J. Am. Chem. Soc. 116 (1994) 9506.
[20] M.A. Esteruelas, F.J. Lahoz, L.A. Oro, E. Oñate, N. Ruiz, Inorg. Chem. 33 (1994) 787.
[21] K.G. Caulton, New J. Chem. 18 (1994) 25 and references therein.
[22] R. Kuhlman, W.E. Streib, J.C. Huffman, K.G. Caulton, J. Am. Chem. Soc. 118 (1996) 6934.
[23] M.L. Christ, S. Sabo-Etienne, B. Chaudret, Organometallics 13 (1994) 3800.
[24] T. Burrow, S. Sabo-Etienne, B. Chaudret, Inorg. Chem. 34 (1995) 2470.
[25] The only other example is a d^8-square planar complex of Pt. D.G. Gusev, J.U. Notheis, J.R. Rambo, B.E. Hauger, O. Eisenstein, K.G. Caulton, J. Am. Chem. Soc. 116 (1994) 7409.
[26] (a) K.T. Smith, M. Tilset, R. Kuhlman, K.G. Caulton, J. Am. Chem. Soc. 117 (1995) 9473; (b) B. Moreno, S. Sabo-Etienne, B. Chaudret, A. Rodriguez, F. Jalon, S. Trofimenko, J. Am. Chem. Soc. 116 (1994) 2635.
[27] C. Hampton, T.W. Dekleva, B.R. James, W.R. Cullen, Inorg. Chim. Acta 145 (1988) 165.
[28] The bimetallic $(PCy_3)_2(H)Ru(\mu\text{-}H)_3Ru(H_2)(PCy_3)_2$ was reported at about the same time as the chloride-bridged complexes. T. Arliguie, B. Chaudret, R.H. Morris, A. Sella, Inorg. Chem. 27 (1988) 598.
[29] A.M. Joshi, B.R. James, J. Chem. Soc. Chem. Commun. (1989) 1785.
[30] C. Hampton, W.R. Cullen, B.R. James, J. Am. Chem. Soc. 110 (1988) 6918.
[31] A.K. Burrell, J.C. Bryan, G.J. Kubas, J. Am. Chem. Soc. 116 (1994) 1575.
[32] F.A. Cotton, R.L. Luck, Inorg. Chem. 28 (1989) 2181.
[33] F.A. Cotton, R.L. Luck, Inorg. Chem. 30 (1991) 767.
[34] M.A. Esteruelas, L.A. Oro, N. Ruiz, Inorg. Chem. 32 (1993) 3793.
[35] D.G. Gusev, A.B. Vymenits, V.I. Bakhmutov, Inorg. Chem. 31 (1992) 2.
[36] (a) M.A. Esteruelas, E. Sola, L.A. Oro, U. Meyer, H. Werner, Angew. Chem. Int. Ed. Engl. 27

(1988) 1563;(b) A. Andriollo, M.A. Esteruelas, U. Meyer, L.A. Oro, R.A. Sanchez-Delgado, E. Sola, C. Valero, H. Werner, J. Am. Chem. Soc. 111 (1989) 7431.
[37] D.G. Gusev, V.F. Kuznetsov, I.L. Eremenko, H. Berke, J. Am. Chem. Soc. 115 (1993) 5831.
[38] R. Kuhlman, D.G. Gusev, I.L. Eremenko, H. Berke, J.C. Huffman, K.G. Caulton, J. Organomet. Chem., accepted.
[39] D.G. Gusev, R. Kuhlman, G. Sini, O. Eisenstein, K.G. Caulton, J. Am. Chem. Soc. 116 (1994) 2685.
[40] A. Albinati, V.I. Bakhmutov, K.G. Caulton, E. Clot, J. Eckert, O. Eisenstein, D.G. Gusev, V.V. Grushin, B.E. Hauger, W.T. Klooster, T.F. Koetzle, R.K. McMullan, T.J. O'Loughlin, M. Pélissier, J.S. Ricci, M.P. Sigalas, A.B. Vymenits, J. Am. Chem. Soc. 115 (1993) 7300.
[41] V.I. Bakhmutov, A.B. Vymenits, V.V. Grushin, Inorg. Chem. 33 (1994) 4413.
[42] M. Mediati, G.N. Tachibana, C.M. Jensen, Inorg. Chem. 31 (1992) 1827.
[43] T. Le-Husebo, C.M. Jensen, Inorg. Chem. 32 (1993) 3797.
[44] T.-Y. Cheng, A. Ponce, A.L. Rheingold, G.L. Hillhouse, Angew. Chem. Int. Ed. Engl. 33 (1994) 657.
[45] M. Leeaphon, A.L. Ondracek, R.J. Thomas, P.E. Fanwick, R.A. Walton, J. Am. Chem. Soc. 117 (1995) 9715.
[46] (a) G.A. Lawrance, Chem. Rev. 86 (1986) 17 and references therein;(b) T. Daniel, N. Mahr, H. Werner, Chem. Ber. 126 (1993) 1403;(c) C. Diver, G.A. Lawrance, J. Chem. Soc. Dalton Trans. (1988) 931.
[47] E.O. Fischer, S. Walz, G. Kreis, F.R. Kreißl, Chem. Ber. 110 (1977) 1651.
[48] D.G. Gusev, B.E. Hauger, U. Notheis, J.R. Rambo, M. Pellisier, O. Eisenstein, K.G. Caulton, J. Am. Chem. Soc., submitted.
[49] B.P. Patel, R.H. Crabtree, J. Am. Chem. Soc. 118 (1996) 13105.
[50] R. Kuhlman, W.E. Streib, K.G. Caulton, Inorg. Chem. 34 (1995) 1788.
[51] The X-ray structure has been reported for the dichloride complex. M. Aracama, M.A. Esteruelas, F.J. Lahoz, J.A. Lopez, U. Meyer, L.A. Oro, H. Werner, Inorg. Chem. 30 (1991) 288.
[52] M. Demuth, G. Mikhail, Synthesis (1982) 827.
[53] E.J. Corey, H. Cho, C. Rucker, D.H. Hua, Tetrahedron Lett. 22 (1981) 3455.
[54] P.G. Jessop, R.H. Morris, Inorg. Chem. 32 (1993) 2236.
[55] R.H. Morris, Inorg. Chem. 31 (1992) 1471.
[56] M. Schlaf, R.H. Morris, J. Chem. Soc. Chem. Commun. (1995) 625.
[57] Actually, two stereoisomers of each product are formed, since the quinoline ligand can be oriented with sulfur either *cis* or *trans* to the CO ligand.
[58] For example of protonation at a metal center via a dihydrogen complex, see: R.A. Henderson, K.E. Oglieve, J. Chem. Soc. Dalton Trans. (1993) 3431.
[59] H. Rothfuss, D.G. Gusev, K.G. Caulton, Inorg. Chem. 34 (1995) 2894.
[60] R.J. Angelici, Acc. Chem. Res. 28 (1995) 51.
[61] J.T. Poulton, K. Folting, W.E. Streib, K.G. Caulton, Inorg. Chem. 31 (1992) 3190.
[62] M. Tilset, J. Am. Chem. Soc. 114 (1992) 2740 and references therein.
[63] K. Thomas, J.A. Osborn, A.R. Powell, G. Wilkinson, J. Chem. Soc. A (1968) 1801.
[64] 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, K.G. Caulton, J. Am. Chem. Soc. 112 (1990) 4831.
[65] J.-F. Riehl, M. Pélissier, O. Eisenstein, Inorg. Chem. 31 (1992) 3344.
[66] (a) R.C. Stevens, R. Bau, D. Milstein, O. Blum, T.F. Koetzle, J. Chem. Soc. Dalton Trans. (1990) 1429; (b) J. Wessel, J.C. Lee, Jr., E. Peris, G.P.A. Yap, J.B. Fortin, J.S. Ricci, G. Sini, A. Albinati, T.F. Koetzle, O. Eisenstein, A. Rheingold, R.H. Crabtree, Angew. Chem. Int. Ed. Engl. 34 (1995) 2507.
[67] J.C. Lee, Jr., A.L. Rheingold, B. Muller, P.S. Pregosin, R.H. Crabtree, J. Chem. Soc. Chem. Commun. (1994) 1021.
[68] S.Park, R. Ramachandran, A.J. Lough, R.H. Morris, J. Chem. Soc. Chem. Commun. (1994) 2201.
[69] J.C. Lee Jr., E. Peris, A.L. Rheingold, R.H. Crabtree, J. Am. Chem. Soc. 116 (1994) 11014.
[70] A.L. Lough, S. Park, R. Ramachandran, R.H. Morris, J. Am. Chem. Soc. 116 (1994) 8356.
[71] E. Peris, J.C. Lee Jr., J.R. Rambo, O. Eisenstein, R.H. Crabtree, J. Am. Chem. Soc. 117 (1995) 3485.
[72] V.J. Murphy, T. Hascall, J.Y. Chen, G. Parkin, J. Am. Chem. Soc. 118 (1996) 7428.

[73] The calculation uses published bond distances and assumes a planar arrangement of Cl1, Os and the two N atoms, with the Os–N–N angle of 120°.
[74] M.D. Fryzuk, P.A. MacNeil, S.J. Rettig, J. Am. Chem. Soc. 109 (1987) 2803.
[75] C.R.S.M. Hampton, I.R. Butler, W.R. Cullen, B.R. James, J.-P. Charland, J. Simpson, Inorg. Chem. 31 (1992) 5509.
[76] V.V. Grushin, Acc. Chem. Res. 26 (1993) 279.
[77] M.A. Esteruelas, F.J. Lahoz, E. Oñate, L.A. Oro, C. Valero, B. Zeier, J. Am. Chem. Soc. 117 (1995) 7935.
[78] H.H. Brintzinger, D. Fischer, R. Müllhaupt, B. Rieger, R.M. Waymouth, Angew. Chem. Int. Ed. Engl. 34 (1995) 1143 and references therein.
[79] M. Aizenberg, D. Milstein, J. Chem. Soc. Chem. Commun. (1994) 411.
[80] R. Sustmann, H.J. Hornung, T. Schupp, B. Putzke, J. Mol. Catal. 85 (1993) 149.
[81] A. Albinati, S. Chaloupka, F. Demartin, T.F. Koetzle, H. Rüegger, L.M. Venanzi, M.K. Wolfer, J. Am. Chem. Soc. 115 (1993) 169 and references therein.
[82] J.L. Kiplinger, T.G. Richmond, C.E. Osterberg, Chem. Rev. 94 (1994) 373.
[83] Assuming only one H_2 ligand in these complexes. These complexes lose HX under phase-transfer (toluene/water) conditions and H_2 atmosphere.
[84] D.G. Gusev, R. Kuhlman, J.R. Rambo, H. Berke, O. Eisenstein, K.G. Caulton, J. Am. Chem. Soc. 117 (1995) 281.
[85] (a) R.J. Kulawiec, R.H. Crabtree, Coord. Chem. Rev. 99 (1990) 89; (b) C.H. Winter, W.R. Veal, C.M. Garner, A.M. Arif, J.A. Gladysz, J. Am. Chem. Soc. 111 (1989) 4766.