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Structural, acidity and chemical properties of some dihydrogen/hydride complexes of Group 8 metals with cyclopentadienyls and related ligands

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Contents

Abstract 84
1. Introduction 84
2. Structural aspects of hydride complexes of the formula $[LMH_2(L')(L'')]^{n+}$ (L = Cp, Cp*, Tp, $n = 1$; L = ^{R}Cn, PMP, $n = 2$): ligand and metal effects on the relative stability of dihydride and dihydride tautomers 85
   2.1 $[(C_5R_5)MH_2(L)(L')]^+$ complexes 86
   2.2 Dihydrogen complexes with TpM fragments 89
   2.3 Hydride complexes with ^{R}Cn and PMP ligands 90
3. Acidity properties of dihydrogen complexes 92
   3.1 Pseudo aqueous pK_a measurements of dihydrogen complexes 92
   3.2 Comments on the acidity properties of dihydrogen complexes 95
4. Reactions mediated by dihydrogen complexes 97
   4.1 Reactions involving heterolytic cleavage of the dihydrogen ligand 97
   4.2 Proton transfer reactions between coordinated dihydrogen and olefin ligands 101
Summary 103
Acknowledgements 105
References 105

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Abstract

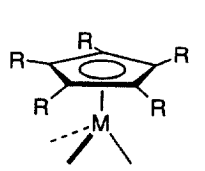
The structures of Group 8 metal complexes $[LMH_2(L')(L'')]^+$ (L = cyclopentadienyls, hydrotris(pyrazolyl)borate (Tp)) and $[LMH_2(L')(L'')]^{2+}$ (L = 1,4,7-triazacyclononane derivatives (^RCn), 1,3-$(Ph_2PCH_2)_2C_5H_3N$ (PMP)) are compared. While complexes $[(C_5R_5)MH_2(L')(L'')]^+$ (M = Fe, Ru, Os) at room temperature can exist in either the dihydride form, or the dihydrogen form, or a mixture of both, the analogous Tp, ^RCn, and PMP complexes are all in the dihydrogen form. Equilibrium studies have shown that the relative acidities of these hydride complexes are strongly affected by the auxiliary ligands, metals, and possibly also the H–H interaction. $[TpM(H_2)(PR_3)_2]^+$ (M = Ru, Os) were found to be slightly more acidic than the analogous $[CpMH_2(PR_3)_2]^+$ complexes, and the dicationic ^RCn dihydrogen complexes $[^RCnM(H_2)(L')(L'')]^{2+}$ are much more acidic than the corresponding Cp and Tp analogs. Significant acidity enhancement upon substitution of PPh_3 for CO is observed for related dihydrogen complexes such as $[RuCl(H_2)(L)(PMP)]^+$, $[TpRu(H_2)(L)(PPh_3)]^+$, and $[^HCnRu(H_2)(L)(PPh_3)]^{2+}$ (L = CO, PPh_3). At the end of the article, several reactions which may involve heterolytic cleavage of the dihydrogen ligand and proton transfer from coordinated dihydrogen to olefin ligands are described.

Keywords: Dihydrogen; Hydride; Ruthenium; Osmium; Iron; Acidity

1. Introduction

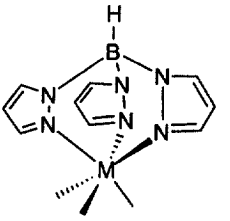
Since the first report of dihydrogen complexes by Kubas et al. in 1984 [1], this unique class of complexes have been intensively studied, especially with respect to their preparation, characterization, structural and catalytic properties [2,3]. These studies have indicated that dihydrogen complexes are widely spread and the stability of the dihydrogen tautomers relative to the corresponding dihydride forms is critically dependent on the metals and auxiliary ligands. It has also been demonstrated that dihydrogen complexes are more than intermediates for oxidative addition reactions of the H_2 molecule. They can have their own reactivities, and participate in interesting stoichiometric and catalytic reactions, although this aspect has previously been less explored.

Cyclopentadienyls [4], hydrotris(pyrazolyl)borate (Tp) [5], 1,4,7-triazacyclononane derivatives (^RCn) [6,7] and $(Ph_2PCH_2)_2C_5H_3N$ (PMP) [8,9] are very useful ligands in organometallic chemistry and homogeneous catalysis. These ligands are similar in that they are formally six electron donors on the ionic model and occupy three coordination sites in metal complexes as illustrated by structures **1–4**.

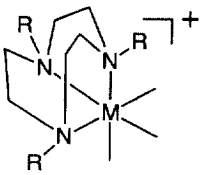


1a, R = H, CpM

1b, R = Me, Cp*M

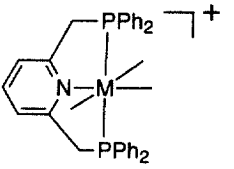


2, TpM



3a, R = H, ^{H}CnM^{+}

3b, R =Me, ^{Me}CnM^{+}



4, M(PMP)$^{+}$

We are interested in employing such ligands to study the chemical properties of dihydrogen complexes and to explore reactions mediated by dihydrogen complexes. To this end, we have prepared and characterized a number of Group 8 metal hydride/dihydrogen complexes with these ligands. The acidity properties of many of the hydride/dihydrogen complexes have been investigated by equilibrium studies. We also explored the uses of dihydrogen complexes in stoichiometric and catalytic reactions. In this presentation, we will summarize these results in terms of the effects of metals and ligands on the relative stability of dihydrogen and dihydride tautomers and on the relative acidities of hydride complexes; and the roles of dihydrogen complexes in stoichiometric and catalytic reactions. It is not the intention of the authors to include here all the results on the related topics in the literature. Thus many excellent relevant works from other groups could not, unfortunately, be included.

2. Structural aspects of hydride complexes of the formula $[LMH_2(L')(L'')]^{n+}$ (L = Cp, Cp*, Tp, $n = 1$; L = ^{R}Cn, PMP, $n = 2$): ligand and metal effects on the relative stability of dihydride and dihydride tautomers

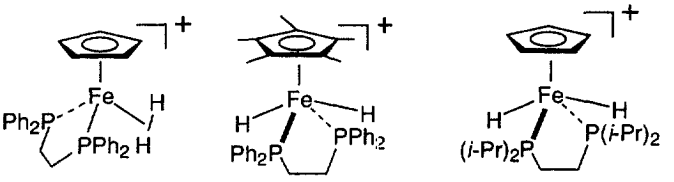
As a first step towards the goals of studying chemical properties of dihydrogen complexes supported by Cp, Cp*, Tp, ^{R}Cn, and PMP and exploring reactions mediated by these complexes, we have prepared and characterized a series of Group 8 metal hydride complexes with these ligands, in order to learn the ability of these ligands to stabilize the dihydrogen ligand. In this section, the structural aspect of Group 8 metal complexes of the formula $[LMH_2(L')(L'')]^{n+}$ (L = Cp, Cp*, Tp, $n = 1$; L = ^{R}Cn, PMP, $n = 2$) will be discussed. Other Group 8 metal hydride complexes such as MH_4L_3 (L = phosphines, CO) [10], $[MH_3L_4]^{+}$ (L = monophos-

phines, monophosphites) [11,12], $[MH_3(PP)_2]^+$ (PP = chelating phosphines) [13–18], $[MCl(H_2)(PP)_2]^+$ (PP = chelating phosphines) [15,18e,19–21] and $[MH(H_2)(PP_3)]^+$ ($PP_3 = P(CH_2CH_2PR_2)_3$) [22–24] have been well studied for the same purpose by other workers.

2.1. $[(C_5R_5)MH_2(L)(L')]^+$ complexes

Complexes of the formula $[(C_5R_5)MH_2(L)(L')]^+$ (M = Fe [25–28], Ru [29–40], Os [41–43]) show interesting structural variations. At room temperature, these complexes can exist in the dihydrogen form $[(C_5R_5)M(H_2)(L)(L')]^+$ or the dihydride form $[(C_5R_5)MH_2(L)(L')]^+$, or a mixture of both, depending on the metals, C_5R_5, L, L′ and even the sizes of the chelating rings if (L)(L′) are chelating diphosphines.

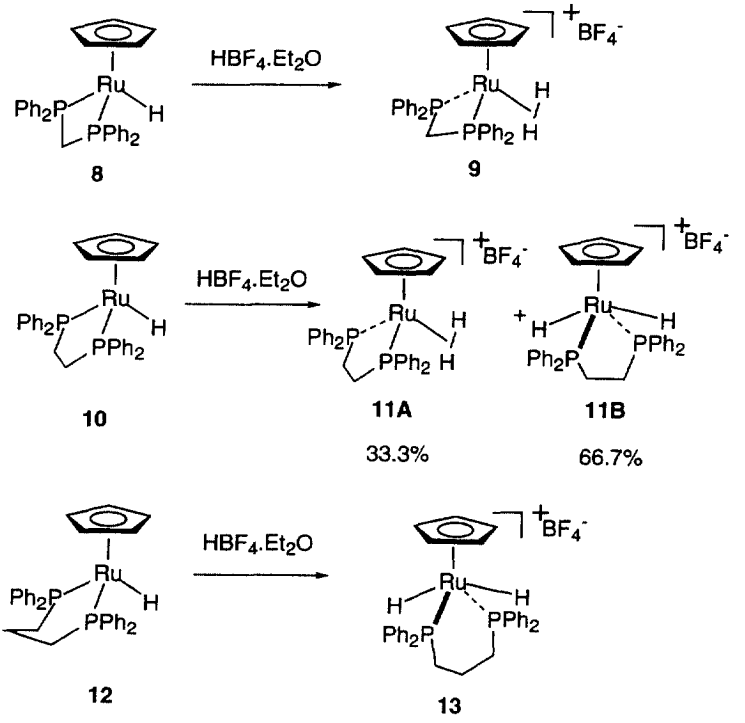
For iron complexes of the formula $[(C_5R_5)FeH_2(L)(L')]^+$, the dihydrogen form is adopted for the CO-containing complexes $[CpFe(H_2)(CO)(PR_3)]BAr'_4$ ($PR_3 = PEt_3$, PPh_3, $Ar' = 3,5\text{-}(CF_3)_2C_6H_3$) [25] and the bis(phosphine)-supported complexes $[CpFe(H_2)(PP)]^+$ (PP = dppe (**5**), dppp) [26]. The dihydride form is adopted for the more electron rich complexes *trans*-$[Cp^*FeH_2(dppe)]^+$ (**6**) [27] and *trans*-$[(C_5R_5)FeH_2(dippe)]^+$ (dippe = $(i\text{-Pr})_2PCH_2CH_2P(i\text{-Pr})_2$; R = H (**7**), Me) [28]. As illustrated by complexes **5**, **6** and **7**, drastic structural change occur when the ligands are modified 'slightly'.



5 **6** **7**

For ruthenium complexes of the formula $[(C_5R_5)RuH_2(L)(L')]^+$, the dihydride form is usually observed for the monophosphine complexes *trans*-$[(C_5R_5)RuH_2(PR_3)_2]^+$ [29–33]. The dihydrogen form is observed for the CO-containing complexes $[(C_5R_5)Ru(H_2)(CO)(PR_3)]^+$ [33,34] and $[(C_5Me_5)Ru(H_2)(CO)_2]^+$ [35] and the isocyanide complex $[CpRu(H_2)(CN\text{-}t\text{-}Bu)(PPh_3)]^+$ [36]. Interestingly, complexes $[CpRu(H_2)(CO)(PCy_3)]^+$ [33] and $[CpRu(H_2)(CO)(P(i\text{-}Pr)_3)]^+$ [34] have been reported to be in equilibrium with a small amount of *trans*-$[CpRuH_2(CO)(PCy_3)]^+$ and *trans*-$[CpRuH_2(CO)(P(i\text{-}Pr)_3)]^+$, respectively.

Analogous ruthenium complexes with chelating diphosphines have been reported to adopt either the dihydride form *trans*-$[(C_5R_5)RuH_2(PP)]^+$ or the dihydrogen form $[(C_5R_5)Ru(H_2)(PP)]^+$ or a mixture of both, depending on the chelating phosphines and C_5R_5 [29,30,33,37–40]. Chelating ligands with smaller bite angles favor the dihydrogen form. For example, Simpson et al. reported that protonation of CpRuH(dppm), CpRuH(dppe) and CpRuH(dppp) produced $[CpRu(H_2)(dppm)]^+$, $[CpRu(H_2)(dppe)]^+$/*trans*-$[CpRuH_2(dppe)]^+$ (in a ratio of 1:2) and *trans*-$[CpRuH_2(dppp)]^+$, respectively (Eqs. 1–3) [37].



(1, 2, 3)

A mixture of dihydrogen and dihydride complexes were also obtained by protonation of CpRuH(PP) (PP = dmpe ($Me_2PCH_2CH_2PMe_2$) [33], prophos ($Ph_2PCH_2CHMePPh_2$) [33], dmdppe ($Me_2PCH_2CH_2PPh_2$) [33], dape ((p-$CH_3OC_6H_4)_2PCH_2CH_2P(p$-$C_6H_4OCH_3)_2$) [29], dtfpe (($p$-$CF_3C_6H_4)_2PCH_2CH_2P(p$-$C_6H_4CF_3)_2$) [29]) and Cp*RuH(dppm) [29,30]). It is interesting to note that although Cp*RuH(dppm) and CpRuH(dmpe) are more electron rich than $CpRuH(PPh_3)_2$, the protonated products of these monohydride complexes are $[Cp^*Ru(H_2)(dppm)]^+$/*trans*-$[Cp^*RuH_2(dppm)]^+$ (2:1 ratio), $[CpRu(H_2)(dmpe)]^+$/*trans*-$[CpRuH_2(dmpe)]^+$ (6:1 ratio), and *trans*-$[CpRuH_2(PPh_3)_2]^+$, respectively.

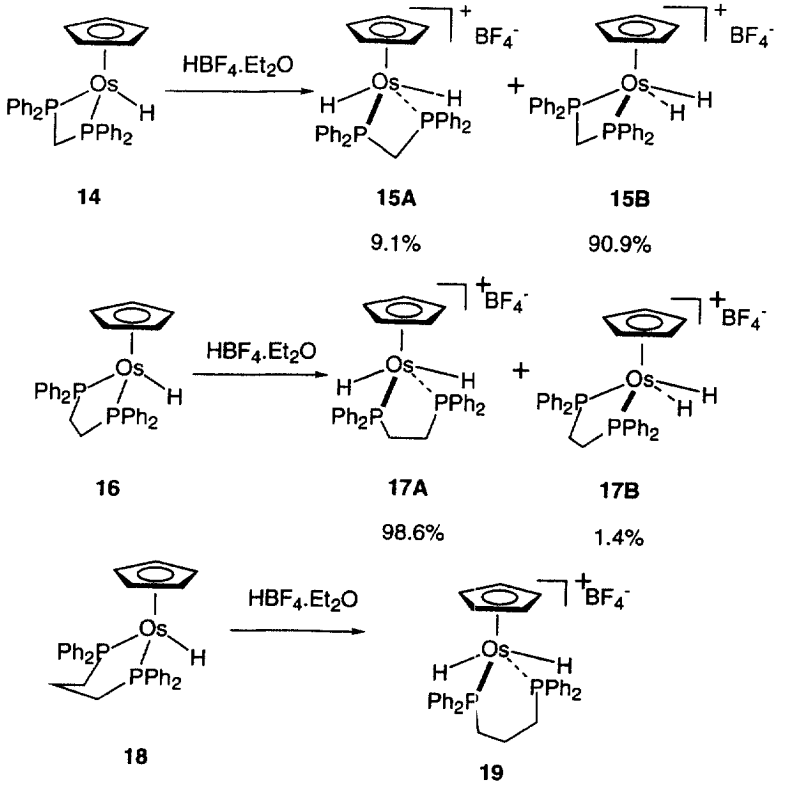
Replacement of Cp with Cp* could decrease the relative stability of the dihydrogen form. Thus, while the dihydrogen form is observed for $[CpRu(H_2)(dppm)]BF_4$ [37], the corresponding Cp* complex exists as a mixture of $[Cp^*Ru(H_2)(dppm)]BF_4$ and *trans*-$[Cp^*RuH_2(dppm)]BF_4$ in a ratio of 2:1 [29,30]. $[Cp^*RuH_2(dppe)]BF_4$ only exists in the dihydride form [40], but the corresponding Cp complex exists as a mixture of $[CpRu(H_2)(dppe)]BF_4$ and $[CpRuH_2(dppe)]BF_4$ in a ratio of 1:2 [37]. $[CpFe(H_2)(dppe)]^+$ is stable at room temperature [26], but $[Cp^*Fe(H_2)(dppe)]BF_4$ is only stable at low temperature and isomerizes to *trans*-$[Cp^*FeH_2(dppe)]BF_4$ on warming to room temperature [27]. The decreased stability of the dihydrogen form for the Cp* complexes can be attributed to the higher electron donating ability of

the Cp* ligand, which leads to extensive backdonation from the metal to the σ* orbital of H_2 to break the H–H bond.

The metal effect on the relative stability of dihydrogen and dihydride forms can be seen by comparing the thermodynamically stable structures of complexes $[CpMH_2(PP)]^+$ (M = Fe, Ru; PP = dppe, dppp). For analogous complexes, the relative stability of the dihydrogen form decreases when iron is replaced by ruthenium. For example, protonation of CpMH(dppp) (M = Fe, Ru) at room temperature produced the dihydrogen complex $[CpFe(H_2)(dppp)]^+$ [26], and the dihydride complex *trans*-$[CpRuH_2(dppp)]^+$ [37], respectively. Such a trend in the relative stability of dihydrogen and dihydride forms is consistent with the fact that the relative energy of d electrons involved in backdonation to the σ* orbital of the dihydrogen ligand increases down a group.

It is expected that the osmium analogs should have the least tendency to form dihydrogen complexes. Indeed, all the reported complexes $[CpOsH_2(PR_3)_2]^+$ [41] $[CpOsH_2(PP)]^+$ (PP = dppm, dppe, dppp) [26] and even the CO-containing complex $[CpOsH_2(CO)(P(i\text{-}Pr)_3)]^+$ [42] are classic dihydride complexes. Protonation of $Cp^*OsH(CO)_2$ produced a mixture of the dihydride complex $[Cp^*OsH_2(CO)_2]^+$ and the dihydrogen complex $[Cp^*Os(H_2)(CO)_2]^+$ [43].

Dihydride complexes of the type $[(C_5R_5)MH_2(PR_3)_2]^+$ (M = Ru, Os) usually adopt *trans* geometry. However, we have recently shown that protonation of CpOsH(PP) (PP = dppm, dppe) at room temperature produced a mixture of *cis* and *trans* isomers of $[CpOsH_2(PP)]BF_4$ (Eqs. 4 and 5) [26].



(4, 5, 6)

At room temperature in dichloromethane solution, $[CpOsH_2(dppm)]BF_4$ and $[CpOsH_2(dppe)]BF_4$ exist as a mixture of *cis* and *trans* isomers in ratios of 10:1 and 1:70, respectively. The dppp complex $[CpOsH_2(dppp)]BF_4$, prepared by protonation of CpOsH(dppp) (Eq. 6), behaves similarly to $[CpOsH_2(PPh_3)_2]^+$ and adopts only the *trans* geometry. The relatively large size of osmium and small bite angles of dppm and dppe are the most likely factors contributing to the stability of *cis*-$[CpOsH_2(PP)]^+$.

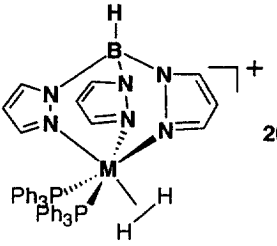
2.2. Dihydrogen complexes with TpM fragments

Hydrotris(pyrazolyl)borate has often been regarded as an analogous ligand to cyclopentadienyls, because they are all formally six-electron donors on the ionic model and occupy three facial coordination sites in metal complexes. Obviously, there are subtle differences in their electronic, steric properties and coordination geometries. Such differences could result in different ability of these ligands to stabilize the dihydrogen ligand.

While complexes of the type $[(C_5R_5)MH_2(L)(L')]^+$ (M = Fe, Ru, Os) can have stable dihydride or the dihydrogen structures, the reported analogous Tp complexes are all dihydrogen complexes. Thus ruthenium dihydrogen complexes including $[TpRu(H_2)(PPh_3)(L)]BF_4$ (L = PPh_3, CH_3CN, CO) [44–46], $[TpRu(H_2)(PP)]^+$ (PP = dppe [45], dippe ($(i\text{-}Pr)_2CH_2CH_2P(i\text{-}Pr)_2$) [46]), $[TpRu(H_2)(CO)(P(i\text{-}Pr)_3)]^+$ [47] and $[TpRu(H_2)(H_2O)(PCy_3)]^+$ [48] were produced from the protonation reactions of the corresponding monohydride complexes. Osmium dihydrogen complexes $[TpOs(H_2)(PPh_3)_2]BF_4$ [49] and $[TpOs(H_2)(CO)((P(i\text{-}Pr)_3)]^+$ [47] have been obtained similarly.

It should be mentioned that Chaudret et al. have previously reported several other types of ruthenium dihydrogen complexes with hydrotris(pyrazolyl)borate and related ligands including $TpRuH(H_2)_2$ and $TpRuH(H_2)(L)$ (L = PCy_3, Et_2NH, py, THT) [48,50]. During the course of investigating decarbonylation reactions of alcohols with $TpRuH(CH_3CN)(PPh_3)$, we have recently prepared and characterized the TpRu dihydrogen complex $TpRuH(H_2)(PPh_3)$ [51].

Dihydrogen complexes $[TpM(H_2)(PPh_3)_2]^+$ (**20**, M = Ru, Os) can be regarded as the analogs of the classic dihydride complexes $[CpMH_2(PPh_3)_2]^+$ (**21**). The dihydrogen complex $[TpOs(H_2)(CO)(P(i\text{-}Pr)_3)]^+$ can be regarded as the analog of the classic dihydride complex $[CpOs(H_2)(CO)(P(i\text{-}Pr)_3)]^+$. $TpRuH(H_2)(PPh_3)$ (**22**) can be regarded as the analog of the classic trihydride complexes $Cp^*RuH_3(PPh_3)$ [52] and $CpRuH_3(PPh_3)$ (**23**) [53]. Thus, although both Tp and Cp are isoelectronic and facially coordinate to ruthenium and osmium, they have different ability to stabilize the dihydrogen ligand. That Tp ligand has a higher ability than Cp or Cp* to stabilize the dihydrogen ligand has also been noted for Ir [54] and Rh [55] complexes, as exemplified by the structures of $[Cp^*IrH_3(PMe_3)]^+$ and $[TpIrH(H_2)(PMe_3)]^+$ [54].



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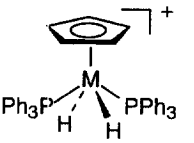

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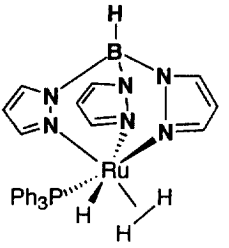
M = Ru, Os



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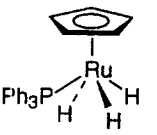

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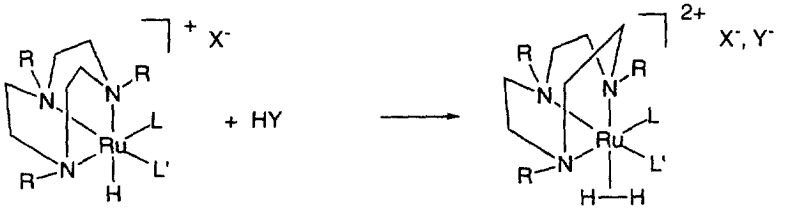
The relative electron-richness of CpM and TpM fragments could not explain the higher ability of TpM fragments to stabilize the dihydrogen ligand. Electrochemical study on $LMH(PPh_3)_2$ (L = Tp, Cp, M = Ru, Os) has shown that analogous Tp and Cp complexes undergo electrochemical oxidation at very similar potentials for a given metal [49]. In addition, $[TpOs(PPh_3)_2]^+$ fragment must be more electron rich than $[CpOs(CO)(P(i\text{-}Pr)_3)]^+$. Yet, $[TpOs(H_2)(PPh_3)_2]^+$ is a dihydrogen complex, but $[CpOsH_2(CO)(P(i\text{-}Pr)_3)]^+$ is a dihydride complex. The higher ability of Tp than Cp to stabilize the dihydrogen ligand is likely related to the higher tendency of TpM fragments to form six-coordinated complexes [56]. It has been suggested that TpM fragments have strongly directional frontier orbitals to bind three additional ligands to form octahedral complexes while cyclopentadienyl ligands are rather ineffective in promoting strongly directional frontier orbitals due to their symmetry and diffuse electron clouds. The sterically more demanding nature of the Tp ligand compared to Cp is another driving force for the higher preference of TpM to form six-coordinated complexes. Thus CpM can form seven-coordinated complexes easily, but TpM have low tendency to do so in order to achieve strong σ-bonding interaction with the other three ligands. The argument can at least partially account for complexes such as $[CpMH_2(PPh_3)_2]^+$ and $CpMH_3(PR_3)$ being classical hydride complexes (formally seven-coordinate complexes), but the analogous Tp complexes being dihydrogen complexes (formally six-coordinate complexes).

2.3. Hydride complexes with ^{R}Cn and PMP ligands

The difference in the ability of Tp and Cp in stabilizing the dihydrogen ligand promoted us to synthesize and characterize Group 8 hydride complexes with the

related ligands ^{R}Cn and PMP. ^{R}Cn and PMP are related to Cp, Cp* and Tp in that are formally six electron donor on the ionic model. However, ^{R}Cn and PMP are neutral ligands while Cp, Cp* and Tp are mono-negative ligands. In addition, ^{R}Cn, Cp, Cp* and Tp occupy formally three facial positions, but PMP usually coordinates to metals meridionally.



24, R = H, (L)(L') = $(PPh_3)_2$; $X^- = Y^- = BF_4^-$

25, R = H, (L)(L') = (CO) (PPh_3) ; $X^- = Y^- = BF_4^-$

26, R = Me, (L)(L') = dppe, $X^- = Y^- = CF_3SO_3^-$

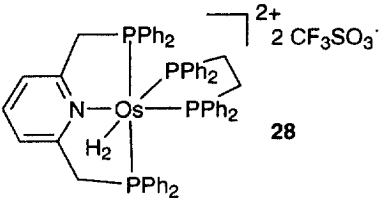
27, R = Me, (L)(L') = (CO) (PPh_3), $X^- = PF_6^-$, $Y^- = CF_3SO_3^-$ (7)

Protonation of $[^{R}CnRuH(L)(L')]^+$ (R = H, (L)(L') = dppe, $(CO)(PPh_3)$; R = Me, (L)(L') = $(PPh_3)_2$, $(CO)(PPh_3)$) with $HBF_4 \cdot Et_2O$ or CF_3SO_3H produced the corresponding dihydrogen complexes $[^{R}CnRu(H_2)(L)(L')]^{2+}$ (Eq. 7) [45]. Thus ^{R}Cn is similar to Tp in that dihydrogen complexes $[TpRu(H_2)(L')(L'')]^+$ and $[^{R}CnRu(H_2)(L)(L')]^{2+}$ are stable with respect to homolytic cleavage of the H_2 ligand.

Subtle differences in the Tp and ^{R}Cn dihydrogen complexes are noted. The H–H interaction in ^{R}Cn complexes is weaker than that in the corresponding Tp complexes as indicated by the fact the ^1J(HD) coupling constants of the isotopomers of the ^{R}Cn complexes are consistently smaller than those of the Tp counterparts, although $[^{R}CnRu(L)(L')]^{2+}$ fragments are more electron deficient than the corresponding $[TpRu(L)(L')]^+$ fragments as indicated by the oxidation potentials of TpRuH(L)(L') and $^{[R}CnRuH(L)(L')]^+$. The stronger H–H interaction in the Tp complexes may be related to the fact that Tp is a better π accepting ligand than ^{R}Cn.

The existence of the dihydrogen complexes $[^{R}CnRu(H_2)(L)(L')]^{2+}$ is probably not surprising, as several related dicationic dihydrogen complexes have been reported for iron, ruthenium and osmium, for example, *trans*-$[Fe(H_2)(L)(dppe)_2]^{2+}$ (L = CO, CNH) [57], $[Ru(H_2)(CO)(dppp)_2]^{2+}$ [15], $[Os(H_2)(NH_3)_5]^{2+}$ [58], *trans*-$[Os(H_2)(dppe)_2(CH_3CN)]^{2+}$ [59], $[M(H_2)(CO)(bpy)(PPh_3)_2]^{2+}$ (M = Ru, Os; bpy = 2,2'-bipyridyl) [60], $[Os(H_2)(CO)(bpy)_2]^{2+}$ [60], $[Os(H_2)(NCCH_3)_3(P(i\text{-}Pr)_3)_2]^{2+}$ [61], $[Os(H_2)(HSPh)(dppe)_2]^{2+}$ [62], and $[Os(H_2)(CO)(dppp)_2]^{2+}$ [15].

We have also characterized several dihydrogen complexes with the PMP ligand, including $[Os(H_2)(PMP)(dppe)]^{2+}$ (**28**) [63], $[Ru(H_2)Cl(CO)(PMP)]^+$ (**29**) and $[M(H_2)Cl(PPh_3)(PMP)]^+$ (**30**, M = Ru, Os) [64]. These later complexes can be regarded as the analogs of the well studied dihydrogen complexes $[M(H_2)Cl(dppe)_2]^+$ (**31**) [19,20].



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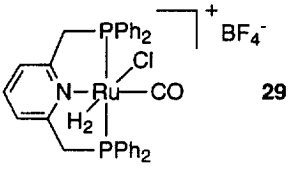

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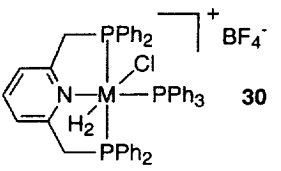

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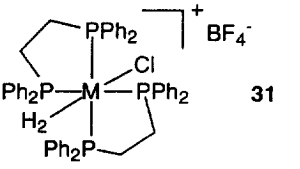
M = Ru, Os



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M = Ru, Os

3. Acidity properties of dihydrogen complexes

3.1. Pseudo aqueous pK_a measurements of dihydrogen complexes

One of the most important properties of dihydrogen complexes is that the coordinated dihydrogen ligand can be heterolytically cleaved by a base. Knowledge about the acidity properties of dihydrogen complexes may help to understand the mechanisms of stoichiometric and/or catalytic reactions involving dihydrogen complexes and to develop new catalytic processes. In this regards, it is of interest to estimate pK_a values of dihydrogen complexes, in order to gain information on the factors affecting the relative acidities of dihydrogen complexes.

In principle, the pK_a value of a dihydrogen complex can be obtained by studying the equilibrium shown in Eq. (8), using the relationship $pK_a(M(H_2)^+) = pK_a(BH^+) + pK_{eq}$, where K_{eq} is the equilibrium constant.

$$M(H_2)^+ + B \Leftrightarrow MH + BH^+ \quad (8)$$

As transition metal hydride complexes are normally insoluble in water, the equilibrium studies are usually performed in organic solvents such as alcohols, acetonitrile, acetone, THF and dichloromethane. In acetonitrile, alcohols and acetone, the true pK_a values of metal hydride complexes can be obtained as pK_a values of many acids BH^+ are known in these solvents. For example, Heinekey et al. have measured the pK_a value (17.6) of $[CpRu(H_2)(dmpe)]^+$ in CD_3CN in reference to that of $HNEt_3^+$ [33], Berke et al. were able to determine the pK_a value (11.5) of $[OsH(H_2)(PMe_3)_4]^+$ in CH_3OH in reference to that of CH_3OH [11]. Unfortunately, pK_a values of many dihydrogen complexes could not be obtained in acetonitrile or alcohols because of the low solubility of hydride complexes in these solvents and/or strong coordination ability of the solvents. As a result, many equilibrium studies have been performed in solvents such as THF and CH_2Cl_2. A major drawback of

Table 1
Acidity measurements of selected dihydrogen/hydride complexes

Entry	$M(H_2)^+/MH_2^+$	B	$pK_a(M(H_2)^+/MH_2^+)$[a] (solvent)	J(HD)[b]	Ref.
1	*trans*-$[CpRuH_2(PPh_3)_2]^+$	PCy_3	8.3 (CD_2Cl_2)		[29]
2	*trans*-$[CpRuH_2(PMe_3)_2]^+$	Proton sponge	21.4 (CH_3CN)[c]		[32b]
3	$[CpRu(H_2)(dppm)]^+$	$CpRuH(PPh_3)_2$	7.1 (CD_2Cl_2)	21.9	[29]
4	$[CpRu(H_2)(dtfpe)]^+$	P(*p*-tolyl)$_3$	4.3 (CD_2Cl_2)	25.3	[29]
5	*trans*-$[CpRuH_2(dtfpe)]^+$	P(*p*-tolyl)$_3$	4.4 (CD_2Cl_2)		[29]
6	$[CpRu(H_2)(dppe)]^+$	$CpRuH(PPh_3)_2$	7.0 (CD_2Cl_2)	24.9	[29]
7	*trans*-$[CpRuH_2(dppe)]^+$	$CpRuH(PPh_3)_2$	7.3 (CD_2Cl_2)		[29]
8	*trans*-$[CpRuH_2(dppp)]^+$	$CpRuH(PPh_3)_2$	8.4 (CD_2Cl_2)		[29]
9	$[CpRu(H_2)(dape)]^+$	$CpRuH(PPh_3)_2$	8.1 (CD_2Cl_2)	24.3	[29]
10	*trans*-$[CpRuH_2(dape)]^+$	$CpRuH(PPh_3)_2$	8.5 (CD_2Cl_2)		[29]
11	$[CpRu(H_2)(dmpe)]^+$	NEt_3	17.6 (CD_3CN)[c]	22.1	[33]
12	*trans*-$[Cp^*RuH_2(PPh_3)_2]^+$	P(*t*-Bu)$_3$	11.1 (THF)		[30]
13	*trans*-$[Cp^*RuH_2(PMePh_2)_2]^+$	P(*t*-Bu)$_3$	12.1 (THF)		[29]
14	*trans*-$[Cp^*RuH_2(PMe_2Ph)_2]^+$	$Cp^*RuH(PMePh_2)_2$	14.3 (THF)		[30]
15	*trans*-$[Cp^*RuH_2(PMe_3)_2]^+$	$Cp^*RuH(PMe_2Ph)_2$	16.3 (THF)		[30]
16	$[Cp^*Ru(H_2)(dppm)]^+$	$CpRuH(PPh_3)_2$	9.2 (THF)	20.9	[29]
17	*trans*-$[Cp^*RuH_2(dppm)]^+$	$CpRuH(PPh_3)_2$	8.8 (THF)		[29]
18	*trans*-$[Cp^*RuH_2(dppp)]^+$	$Cp^*RuH(dppm)$	10.4 (THF)		[30]
19	*trans*-$[CpOsH_2(dppm)]^+$	$CpRuH(PPh_3)_2$	10.0 (CD_2Cl_2)		[49]
20	*cis*-$[CpOsH_2(dppm)]^+$	$CpRuH(PPh_3)_2$	10.9 (CD_2Cl_2)		[49]
21	*trans*-$[CpOsH_2(dppe)]^+$	$CpRuH(PPh_3)_2$	11.8 (CD_2Cl_2)		[49]
22	*cis*-$[CpOsH_2(dppe)]^+$	$CpRuH(PPh_3)_2$	9.9 (CD_2Cl_2)		[49]
23	*trans*-$[CpOsH_2(dppp)]^+$	CpOsH(dppe)	13.4 (CD_2Cl_2)		[49]
24	*trans*-$[CpOsH_2(PPh_3)_2]^+$	CpOsH(dppp)	13.4 (CD_2Cl_2)		[49]
25	$[TpRu(H_2)(CO)(PPh_3)]^+$	$[^HCnRu(CO)(PPh_3)]^+$	0.6 (CD_2Cl_2)[d]	33.3	[45]
26	$[TpRu(H_2)(PPh_3)_2]^+$	CpRuH(dppm)	7.6 (CD_2Cl_2)	32.0	[45]
28	$[TpRu(H_2)(CH_3CN)(PPh_3)]^+$	$CpRuH(PPh_3)_2$	8.9 (CD_2Cl_2)[e]	33.0	[45]
29	$[TpRu(H_2)(dppe)]^+$	CpRuH(dppm)	7.9 (CD_2Cl_2)	32.5	[45]
30	$[TpOs(H_2)(CO)(P(i\text{-}Pr)_3)]^-$	PPh_3	9.3 (CD_2Cl_2)[f]	25.8	[47]
31	$[TpOs(H_2)(PPh_3)_2]^+$	$CpRuH(PPh_3)_2$	8.8 (CD_2Cl_2)	24.8	[45]
32	$[^HCnRu(H_2)(CO)PPh_3)]^{2+}$	Et_2O	−1.3 (CD_2Cl_2)[d]	31.8	[45]
33	$[^HCnRu(H_2)(PPh_3)_2]^{2+}$	$RuHCl(dppe)_2$	4.5 (CD_2Cl_2)	29.4	[45]
34	$[^{Me}CnRu(H_2)(CO)PPh_3)]^{2+}$	Et_2O	−2.6 (CD_2Cl_2)[d]	31.0	[45]
35	$[^{Me}CnRu(H_2)(dppe)]^{2+}$	$RuHCl(dppe)_2$	3.8 (CD_2Cl_2)	29.4	[45]
36	$[FeH(H_2)(PMe_3)_4]^+$	$OsH_2(PMe_3)_4$	10.6 (THF)		[11]
37	$[FeH(H_2)(dtfpe)_2]^+$	$OsH_2(dtfpe)_2$	7.8 (THF)[g]	32	[13]
38	$[FeH(H_2)(dppe)_2]^-$	Proton sponge	12.1 (THF)[g]	30	[13]
39	$[RuH(H_2)(PMe_3)_4]^+$	$OsH_2(PMe_3)_4$	11.2 (THF)	30.6–32.7	[11]
40	$[RuH(H_2)(dppe)_2]^+$	$Cp^*RuH(PMe_2Ph)_2$	14 (THF)[g]	32	[13]
41	$[RuH(H_2)(dppe)_2]^+$	$Cp^*RuH(PMe_2Ph)_2$	15.0(THF)[h]	32	[13]
42	$[RuH(H_2)(dtfpe)_2]^+$	$OsH_2(dtfpe)_2$	9.0 (THF)[g]	33	[13]
43	$[RuH(H_2)(dtfpe)_2]^+$	$OsH_2(dtfpe)_2$	10.0 (THF)[h]	33	[13]
44	$[RuH(H_2)(dppp)_2]^+$	NEt_3	10.2 (CD_2Cl_2)	32	[15]
45	$[RuH_3(dppf)_2]^+$	PPh_2Et	4.4 (CD_2Cl_2)		[20]
46	$[OsH(H_2)(PMe_3)_4]^+$	CH_3OH	11.5 (CH_3OH)		[11]
47	$[OsH(H_2)(dtfpe)_2]^+$	$CpRuH(PPh_3)_2$	8.4 (THF)[g]	28	[13]
48	$[OsH(H_2)(dtfpe)_2]^+$	$CpRuH(PPh_3)_2$	9.2 (THF)[h]	28	[13]

Table 1 (Continued)

Entry	$M(H_2)^+/MH_2^+$	B	$pK_a(M(H_2)^+/MH_2^+)$[a] (solvent)	J(HD)[b]	Ref.
49	$[OsH(H_2)(dppe)_2]^+$	$Cp^*RuH(PMePh_2)_2$	12.7 (THF)[g]	25.5	[13]
50	$[OsH(H_2)(dppe)_2]^+$	$Cp^*RuH(PMePh_2)_2$	13.6 (THF)[h]	25.5	[13]
51	$[OsH_3(dppp)_2]^+$	NEt_3	10.3 (CD_2Cl_2)		[15]
52	$[RuCl(H_2)(CO)(PMP)]^+$	Et_2O	−2.8 (CD_2Cl_2)[i]	30.1	[64]
53	$[RuCl(H_2)(PPh_3)(PMP)]^+$	P(*p*-tolyl)$_3$	5.1 CD_2Cl_2)[j]	28.0	[64]
54	$[RuCl(H_2)(dppe)_2]^+$	PPh_2Et	6.0 CD_2Cl_2)	25.9	[20]
55	$[RuCl(H_2)(dppp)_2]^+$	PPh_3	4.4 (CD_2Cl_2)	24.4	[15]
56	$[OsCl(H_2)(PPh_3)(PMP)]^+$	$CpRuH(PPh_3)_2$	7.5 (CD_2Cl_2)	17.7	[64]
57	$[OsCl(H_2)(dppe)_2]^+$	PMe_2Ph	7.4 (CH_2Cl_2)	13.9	[19]
58	$[OsCl(H_2)(dppp)_2]^+$	NEt_3	12.5 (CD_2Cl_2)	11	[15]
59	$[OsBr(H_2)(dppe)_2]^+$	P(*p*-$MeOC_6H_4$)$_3$	5.4 (CD_2Cl_2)	13.7	[19]
60	$[Ru(H_2)(CO)(dppp)_2]^{2+}$	$CF_3SO_3^-$	ca. −6 (CD_2Cl_2)	34	[15]
61	$[Os(H_2)(CO)(dppp)_2]^{2+}$	$CF_3SO_3^-$	−5.7 CD_2Cl_2)	32	[15]
62	$[Os(H_2)(CH_3CN)(dppe)_2]^{2+}$	Et_2O/H_2O	ca. −2 (CD_2Cl_2)	21.4	[59]

[a] Unless otherwise stated, the pK_a value was obtained by studying the equilibrium (room temperature) shown in Eq. (8), using the relationship $pK_a(MH_2^+) = pK_a(BH^+, \text{aqueous}) + pK_{eq}$, where K_{eq} is the equilibrium constant. See text for abbreviations of ligands.

[b] ^1J(HD) for the correspond HD isotopomers.

[c] True pK_a value in CD_3CN.

[d] Determined at 193 K.

[e] Determined at 243 K.

[f] Determined at 213 K.

[g] Conjugated base is *cis*-$MH_2(PP)_2$.

[h] Conjugated base is *trans*-$MH_2(PP)_2$.

[i] Determined at 203 K.

[j] Determined at 253 K.

using THF or CH_2Cl_2 as the solvent is that not many pK_a data of reference acids BH^+ are available in these solvents. Thus true pK_a values could not be obtained. In practice, pseudo aqueous pK_a values of $M(H_2)^+$ are estimated in these solvents using the relationship $pK_a(M(H_2)^+, \text{pseudo aqueous}) = pK_a(BH^+, \text{water}) + pK_{eq}$. It should be stressed that the pseudo aqueous pK_a values of hydride complexes thus obtained should be different from the true pK_a values in CH_2Cl_2 or THF or water, as the true pK_a values of reference acids BH^+ in dichloromethane or THF are usually unknown and must be different from those in water. In addition, as the differences in the pK_a values of the reference acids BH^+ in organic solvents may be difference from those in water, the differences in the pK_a values of the dihydrogen complexes may not be accurate, especially when the pseudo aqueous pK_a values are obtained relative to different types of reference acids BH^+ or in different solvents. However, the pseudo aqueous pK_a values, with proper precautions, can still provide valuable information on the relative acidities of dihydrogen complexes.

In the past few years, we have estimated pseudo aqueous pK_a values of a number of complexes such as $[TpM(H_2)(L)(L')]^+$ [45,49], $[^RCnRu(H_2)(L')(L')]^{2+}$ [45], $[CpOsH_2(PR_3)_2]^+$ [49], and $[MCl(H_2)(L)(PMP)]^+$ (M = Ru, Os; L = PPh_3, CO) [64]

in dichloromethane. The pseudo aqueous pK_a values of complexes such as $[(C_5R_5)RuH_2(PR_3)_2]^+$ [29,30,33], $[MH(H_2)(PR_3)_4]^+$ (M = Fe, Ru, Os) [11,13,15], $[MCl(H_2)(PP)_2]^+$ (M = Fe, Ru, Os; PP = diphosphines) [15,19,20], and $[M(L)(H_2)(PP)_2]^{2+}$ (M = Ru, Os; PP = diphosphines, L = CO, CH_3CN) [15,59] have also been similarly determined by other groups. For reference and comparison, the measurements of pseudo aqueous pK_a values of selected dihydrogen and hydride complexes by us as well as others are listed in Table 1.

3.2. Comments on the acidity properties of dihydrogen complexes

As shown in Table 1, the acidities of dihydrogen complexes are strongly affected by the auxiliary ligands and metals. Like classic hydride complexes [65], the acidities of isostructural dihydrogen complexes usually decrease as the ligands become more electron donating, and as the metal is replaced successively by a heavier metal in the same group. The H–H interaction may also affect the acidities of dihydrogen complexes. In order to see the effect of H–H bonding on acidities, J(HD) coupling constants for some of the HD isotopomers are also listed in Table 1.

Auxiliary ligands appear to play a dominant role in determining the acidity properties of dihydrogen complexes. The pseudo-aqueous pK_a values indicate that $[TpM(H_2)(PR_3)_2]^+$ (M = Ru, Os) are slightly more acidic than the analogous $[CpMH_2(PR_3)_2]^+$ complexes [45]. The Group 6 hydride complexes $TpMH(CO)_3$ (M = Cr, Mo, W) are also found to be more acidic than $CpMH(CO)_3$ (M = Cr, Mo, W) [66,67]. On the other hand, the dicationic dihydrogen complexes $[^RCnM(H_2)(L)(L')]^{2+}$ are much more acidic than the corresponding Cp and Tp analogs. Complexes $[M(H_2)(dppe)(PMP)]^{2+}$ (M = Ru, Os) are so acidic that $[MH(dppe)(PMP)]^+$ could not be pronotated by HBF_4 in the presence of water in dichloromethane [63]. Several related highly acidic dicationic dihydrogen complexes have been reported, for example, *trans*-$[Os(H_2)(dppe)_2(CH_3CN)]^{2+}$ has a pseudo aqueous pK_a value close to −2 [59], $[M(H_2)(CO)(dppp)_2]^{2+}$ (M = Ru; Os) have pseudo aqueous pK_a values close to −6 [15], $[Os(H_2)(CO)(bpy)(PPh_3)_2]^{2+}$ can be deprotonated by diethylether [60]. It should be mentioned that dicationic dihydrogen complexes are not necessarily stronger acids than monocationic ones, for example, $[Os(H_2)(NH_3)_5]^{2+}$ was reported to be a weak acid and is stable to the moderately strong base NaOMe [58a].

Substitution of PPh_3 for CO is known to change by 5–8 pK_a units in the acidities of related classic hydride complexes. For example, $MnH(CO)_5$ [68] and $MnH(CO)_4(PPh_3)$ [69] have pK_a(CH_3CN) of 15.1 and 20.4, respectively, $CpCrH(CO)_3$ [70] and $CpCrH(CO)_2(PPh_3)$ [71] have pK_a(CH_3CN) of 13.3 and 21.8, respectively, $HCo(CO)_4$ [68] and $HCo(CO)_3(PPh_3)$ [68] have pK_a(CH_3CN) of 8.3 and 15.4, respectively. Significant acidity enhancement is also observed for closely related dihydrogen complexes such as $[RuCl(H_2)(L)(PMP)]^+$ [64], $[TpRu(H_2)(L)(PPh_3)]^+$, and $[^HCnRu(H_2)(L)(PPh_3)]^{2+}$ [45] (L = CO, PPh_3). The effect of H, Cl, and Br on the relative acidities of $[OsX(H_2)(dppe)_2]^+$ has been studied by Morris et al. The acidities of these complexes increase in the order of H < Cl < Br [19].

Replacement of the Ph group in $[MH(H_2)(Ph_2PCH_2CH_2PPh_2)_2]^+$ (M = Ru, Os) with a more electron-donating group will decrease the acidities of the dihydrogen complexes [13]. Similarly, it was observed that acidities of $[CpRuH_2(PR_3)_2]^+$ [29,30,32] and $[^{H}CnRu(H_2)(PR_3)_2]^{2+}$ [45] are more acidic than the corresponding $[Cp^*RuH_2(PPh_3)_2]^+$ and $[^{Me}CnRu(H_2)(PR_3)_2]^{2+}$. It is interesting to note that the effect of substituents on the nitrogen atoms of ^{R}Cn on the acidity is less pronounced than that of C_5R_5.

Even the chelating ring size could affect the acidity properties of hydride complexes. The acidities of *trans*-$[CpOsH_2(PP)]BF_4$ (PP = dppm, dppe, dppp) [49], *trans*-$[CpRuH_2(PP)]BF_4$ (PP = dppm, dppe, dppp) [29], *trans*-$[Cp^*RuH_2(PP)]BF_4$ (PP = dppm, dppp) [29,30], and $[CpOsHBr(PP)]BF_4$ (PP = dppm, dppp) [41a] were shown to decrease as the size of the chelating ring increases. The trend in the acidity is in line with the relative electron donating ability of the chelating ligands [72]. In contrast, increment in the acidity with increasing chelating ring size has been observed for *cis*-$[CpOsH_2(PP)]^+$ [49], $[CpRu(H_2)(PP)]^+$ (PP = dppm, dppe) [29], $[RuCl(H_2)(PP)_2]^+$ (PP = dppe, dppp) [15,20], $[FeH(CO)_2(PP)]^+$ [73] and $[MH(CO)_2(PP)_2]^+$ (M = Mo, W) [74]. The trend in the acidities of these metal complexes is just reverse to that expected from the basicities of the chelating ligands. For $[FeH(CO)_3(PP)]^+$ and $[MH(CO)_2(PP)_2]^+$ (M = Mo, W), steric effects have been proposed as the cause for the increased acidities of metal complexes with larger chelating rings [73,74].

Ruthenium dihydrogen complexes such as $[RuCl(H_2)(PPh_3)(PMP)]BF_4$ [64], $[TpRu(H_2)(PPh_3)_2]^+$ [45,49], $[RuCl(H_2)(dppe)_2]^+$ [19,20], $[RuX(H_2)(dppp)_2]^+$ (X = H, Cl) [15], and $[RuH(H_2)(PMe_3)_4]^+$ [11] are all more acidic than the corresponding analogous osmium complexes. The trend is similar to that observed for classic hydride complexes such as $[CpMH_2(PPh_3)_2]^+$ (M = Ru, Os) [13,49] and $H_2M(CO)_4$ ($pK_a(CH_3CN)$ = 18.7 (M = Ru), 20.8 (M = Os)) [68]. Such a trend is probably expected as Os–H bonds are usually stronger than Ru–H bonds.

H–H interaction in dihydrogen complexes may also influence the acidities. Presence of strong H–H interaction may make dihydrogen complexes less acidic than that suggested by the general trend in the acidities of classic hydride complexes. A good example of the effect of H–H interaction on acidities is provided by the observation that the more electron rich trihydride complex $[RuH_3(dppf)_2]^+$ (dppf = $(Ph_2PC_5H_4)_2Fe$) is more acidic than the less electron rich dihydrogen complex $[RuH(H_2)(dppe)_2]^+$ [20]. We have observed that $[^{Me}CnRu(H_2)(CO)(PPh_3)]^{2+}$ is more acidic than $[^{H}CnRu(H_2)(CO)(PPh_3)]^{2+}$ [45]. The unusual order may be related to the stronger H–H bonding in the latter complex as indicated by the *J*(HD) coupling constants for the HD isotopomers.

As stated previously, classic osmium complexes are usually less acidic than the isostructural ruthenium hydride complexes. However, it has been observed that $[OsH(H_2)(dppe)_2]^+$ [13] and $[Os(H_2)(CO)(quS)(PPh_3)_2]^+$ (quS = quinoline-8-thiolate) [75] are more acidic than the analogous ruthenium complexes $[RuH(H_2)(dppe)_2]^+$ and $[Ru(H_2)(CO)(quS)(PPh_3)_2]^+$, respectively. Stronger H–H bonding in the ruthenium complexes has been suggested as one of the reasons for the weaker acidities of the ruthenium complexes. We also noted that the difference

in the pseudo aqueous pK_a values of $[TpM(H_2)(PPh_3)_2]BF_4$ (M = Ru, Os, ΔpK_a = 1.3) is smaller than that of the Cp analogs *trans*-$[CpMH_2(PPh_3)_2]BF_4$ (M = Ru, Os, $\Delta pK_a = 5.1$) [49]. The difference in the metal effect could also be related to the stronger H–H bonding in the TpRu complex. The influence of H–H bonding on acidities is supported by the estimated M–H bond energies.

4. Reactions mediated by dihydrogen complexes

Dihydrogen complexes have been proposed to be involved in a number of interesting stoichiometric and catalytic reactions, for example, reductions of unsaturated organic compounds, H/D exchange reactions, dehydrogenation reactions, and hydrogenase and nitrogenase catalyzed reactions [3]. The roles of dihydrogen complexes in these reactions are dependent on the chemical properties of dihydrogen complexes. In this section, we will describe several reactions which may involve heterolytic cleavage of the dihydrogen ligand and proton transfer from coordinated dihydrogen to olefin ligands.

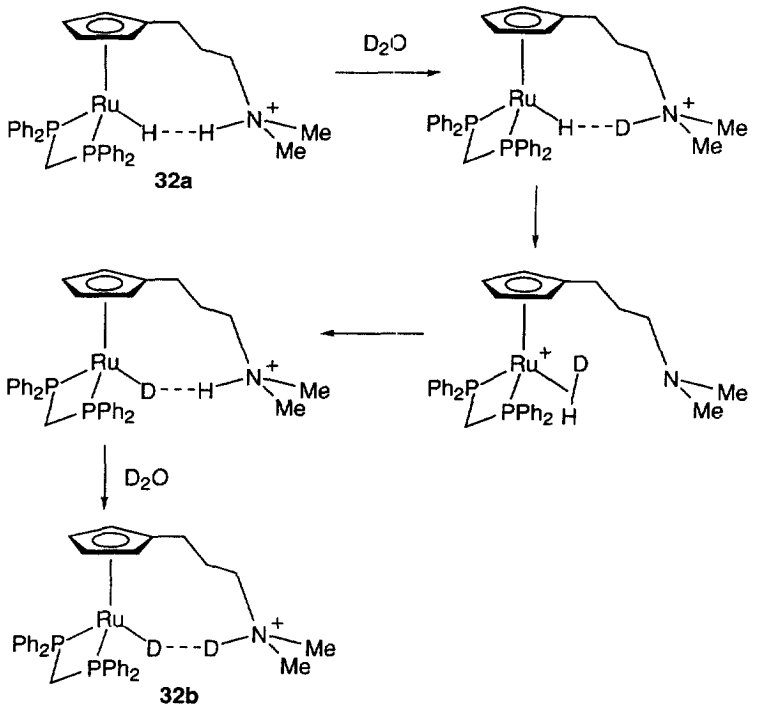
4.1. Reactions involving heterolytic cleavage of the dihydrogen ligand

Heterolytic cleavage of the dihydrogen ligand is such an important property of dihydrogen complexes that a number of interesting reactions involving this reactivity have been reported in the past few years.

Heterolytic cleavage of the dihydrogen ligand has been proposed to be involved in H/D exchange reactions [76–81], for example, in the reactions of $[IrH_2(HSCH_2CH_2CH_2SH)(PCy_3)_2]^+$ and $[IrH_2(SC_5H_4NH)_2(PCy_3)_2]^+$ with D_2 to give $[IrD_2(DSCH_2CH_2CH_2SD)(PCy_3)_2]^+$ and $[IrD_2(SC_5H_4ND)_2(PCy_3)_2]^+$, respectively [76], and in the reactions of $IrH_3(2\text{-}C_6H_4NH_2)(PPh_3)_2$ with CD_3OD to give $IrD_3((2\text{-}C_6H_4ND_2)(PPh_3)_2)$ [77a]. Complexes containing M–H···H–O, M–H···H–N, and M–H···H–S hydride–proton interactions reported recently can be regarded as the intermediates for the isotope exchange reactions [18a,76–78,82].

Lau et al. recently reported that complex **32a**, which contains an N–H···H–Ru interaction, also undergo H/D exchange with D_2O (Scheme 1) [83]. The H/D exchange reaction was believed to occur by first H/D exchange between the N–H and D_2O to give a N–D functional group, followed by H/D exchange between the N–D and the metal hydride via a dihydrogen intermediate. As reported by Bianchini et. al, even the deuterium in acetone-d_6 can be exchanged with the protons of the dihydrogen ligand in $[OsH(H_2)(P(CH_2CH_2PPh_2)_3)]^+$ [22b]. A proposed mechanism for the interesting reaction is shown Scheme 2 [22b].

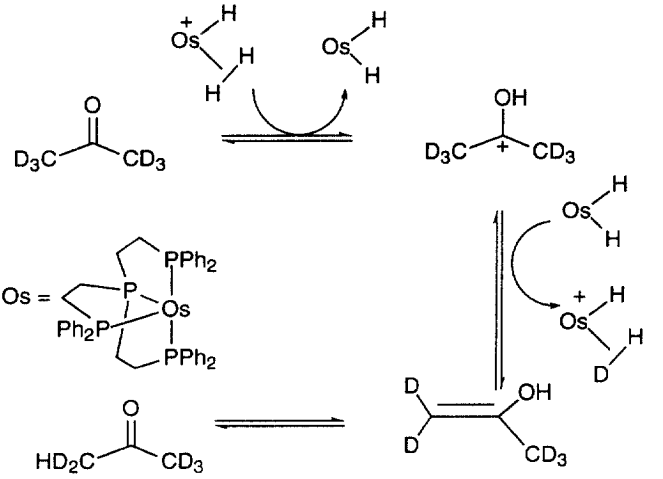
Reversible deprotonation and dissociation of dihydrogen ligands can be invoked to explain catalytic H/D exchange reactions between D_2/protic solvents or H_2/deuterated solvents. For example, $[Ni(o\text{-}C_6H_4(OH)CH{=}N{-}NHCSNH_2)_2]^{2+}$ can catalyze H/D exchange between D_2 and EtOH [78], $[RhH(L)(^{bu}S_4)]$ (L = CO, PCy_3, $^{Bu}S_4$ = 1,2-bis(2-mercapto-3,5-di-*t*-butylphenylthio)ethane^{2-}) can catalyze H/D exchange between D_2 and EtOH in the presence of acid [80]. We have recently shown



Scheme 1.

that $[TpRu(H_2)(PPh_3)_2]^+$ can also catalyze H/D exchange between D_2O and H_2 [44]. A proposed mechanism for the H/D exchange reaction is shown in Scheme 3.

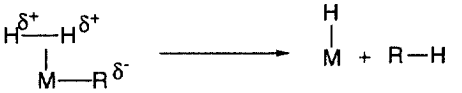
H/D exchange reactions mediated by dihydrogen complexes may also occur in $[TpRu(PPh_3)_x(CH_3CN)_{3-x}]^+$ ($x = 1, 2$) catalyzed olefin hydrogenation reactions in hydrous THF. Complexes $[TpRu(PPh_3)_x(CH_3CN)_{3-x}]^+$ ($x = 1, 2$) in anhydrous THF show moderate catalytic activity for the hydrogenation of olefins [44]. Enhancement on the catalytic activity was observed in the presence of water or NEt_3. Interestingly, when D_2O, instead of H_2O, was added to the system, incorporation of deuterium into the hydrogenation products was observed. For example, $PhCH{=}CH_2$ can be hydrogenated to give $Ph{-}CH_2CH_3$, $Ph{-}CHD{-}CH_3$, $Ph{-}CH_2{-}CH_2D$ and $Ph{-}CHD{-}CH_2D$. To account for the enhanced catalytic activity of these complexes and for the formation of deuterated products, a mechanism (using styrene as an example) of the hydrogenation reactions catalyzed by these complexes in the presence of D_2O is proposed in Scheme 4. In this mechanism, the first step is the generation of the dihydrogen complexes $[TpRu(H_2)(PPh_3)_x(CH_3CN)_{2-x}]^+$ ($x = 0, 1$) which have been established by NMR experiments. The catalytic cycle is completed by insertion of styrene into the Ru–H bond, followed by protolysis of the Ru–alkyl with HD_2O^+. Thus in this proposed mechanism, olefins are reduced through a stepwise H^-/H^+ transfer process. As shown in Scheme 4, $PhCHDCH_2D$



Scheme 2.

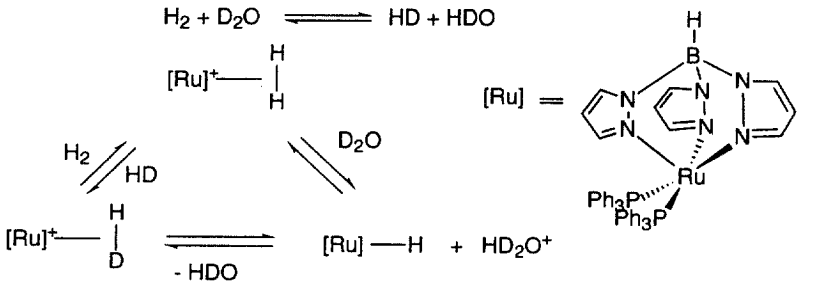
can be produced via the ruthenium deuteride complexes as a result of H/D exchange between H_2 and D_2O. Similar mechanisms are probably involved in the hydrogenation of olefins catalyzed by $[(C_6H_6)Ru(CH_3CN)_3](BF_4)_2$ and *cis*-$[Ru(6,6'\text{-}Cl_2bpy)_2(OH_2)_2](CF_3SO_3)_2$ in biphasic aqueous/organic solvent systems [84].

Alkyl dihydrogen complexes $L_nM(H_2)R$ could undergo intramolecular proton transfer reactions to form L_nMH and RH (Eq. 9).

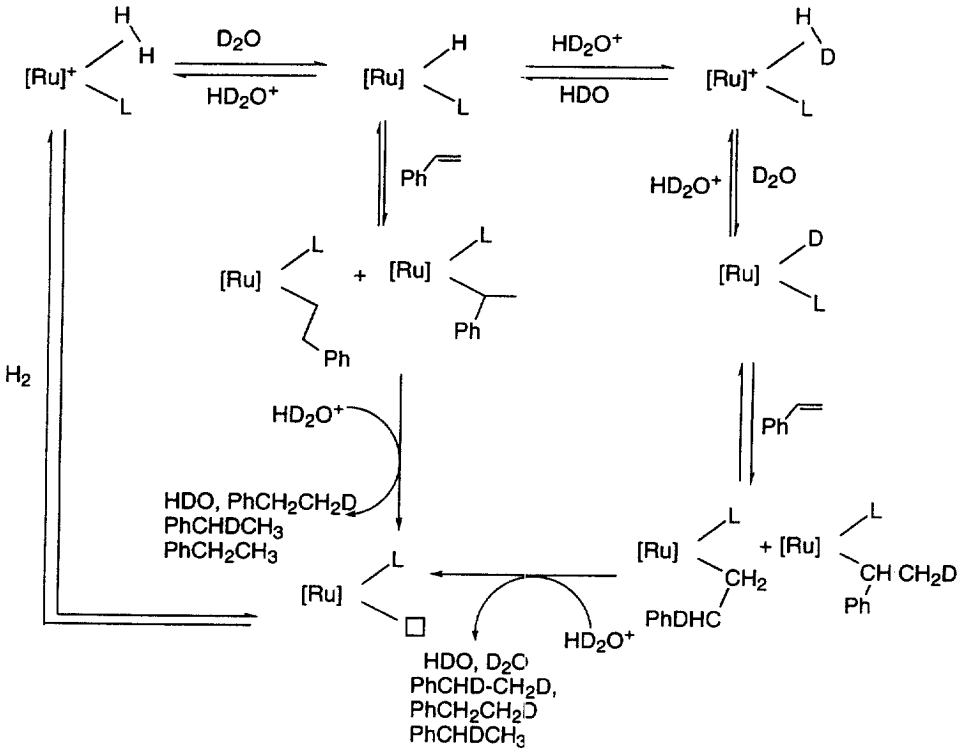


(9)

The reaction can be regarded as an intramolecular acid/base reaction. Reversible protonation of the C≡CPh ligand by the H_2 ligand in $[Ru(H_2)(C{\equiv}CPh)(dippe)_2]^+$ [85] has been observed in solution by NMR experiments. Reversible protonation of aryl ligands by an η^2-H_2 ligand could explain the fluxionality of complexes



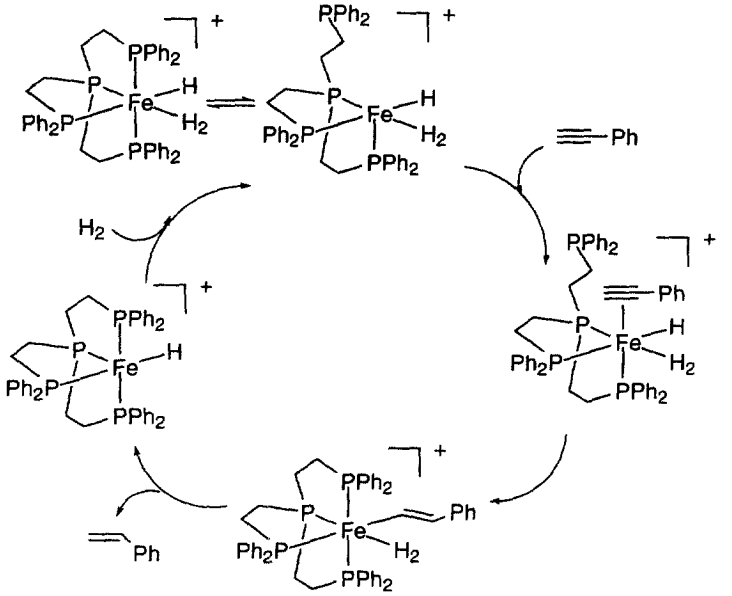
Scheme 3.



Scheme 4. [Ru] = [TpRu(PPh$_3$)]; L = PPh$_3$, CH$_3$CN; and HD_2O^+ represents the deuterated species $H_xD_{3-x}O^+$.

[IrH(diphpyH)(PR$_3$)$_2$]$^+$ (diphpyH$_2$ = diarylpyridines) [86]. Intramolecular protonation of alkyls by a coordinated H_2 ligand has been invoked to account for the reactions of some d^0 alkyl complexes with H_2 to give hydride complexes and alkanes [87], and for the catalytic activities of complexes such as [FeH(H_2)(PP$_3$)]$^+$ (PP$_3$ = P(CH$_2$CH$_2$PPh$_2$)$_3$) [88] and RuHCl(PPh$_3$)$_3$ [89] for hydrogenation of acetylenes and olefins. The key role of the dihydrogen complexes in the hydrogenation reactions is illustrated in Scheme 5 using [FeH(H_2)(PP$_3$)]$^+$ as the catalyst. Thus the unsaturated substrates are also hydrogenated without going through oxidative addition/reductive elimination steps, but through a stepwise H^-/H^+ transfer process. Probably, similar proton transfer steps are involved in the hydrogenation of olefins and acetylenes using [RuH(H_2)(PP$_3$)]$^+$ (PP$_3$ = P(CH$_2$CH$_2$PPh$_2$)$_3$) [90] and OsHCl(CO)(P(*i*-Pr)$_3$)$_2$ [91] as catalysts.

It is well known that β-carbons of vinyl, acetylide and vinylidene ligands can be attacked by electrophiles. Thus there is a possibility that a coordinated dihydrogen ligand may also attack the β-carbons of these ligands. An interesting example of such reactivity has recently been reported by Esteruelas et al., in which proton transfer from H_2 to β-carbons of vinylidene ligands has been proposed for the



Scheme 5.

reactions of $OsH_2Cl_2(P\text{-}i\text{-}Pr)_3)_2$ with HC≡CR to give carbyne complexes $OsHCl_2(\equiv CCH_2R)(P\text{-}i\text{-}Pr)_3)_2$ [92].

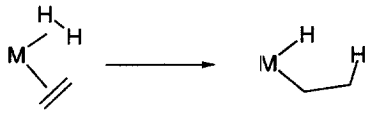
Since dihydrogen complexes have a wide range of acidities, some of them may be acidic enough to protonate uncoordinated olefins or acetylenes. Such a reactivity is potentially useful for catalytic ionic hydrogenation [93] and oligomerization/polymerization of olefins. To test the possibility of using molecular dihydrogen complexes to initiate olefin oligomerization and ionic hydrogention, we have treated styrene with 1 atm of H_2 in the presence of $[Os(PMP)(dppe)](CF_3SO_3)_2$ or $[Os(H_2O)(PMP)(dppe)](CF_3SO_3)_2$. Preliminary experiments showed that styrene was predominantly dimerized to give $PhCH(CH_3)CH{=}CHPh$. It was believed that $PhCH(CH_3)CH{=}CHPh$ was produced from the carbon cation $PhCHCH_3^+$ formed by protonation of $PhCH{=}CH_2$ with $[Os(H_2)(PMP)(dppe)](CF_3SO_3)_2$ [63].

There are many other reported reactions related to heterolytic cleavage of the dihydrogen ligand, for example, in the protonation of coordinated dinitrogen ligand in $W(N_2)_2(dppe)_2$ by $[RuH(H_2)(dppp)_2]^+$ and $[CpRu(H_2)(dtfpe)]^+$ [94], in the reaction of $Cp^*_2Ti(py)=S$ with H_2 to give $Cp^*_2TiH(SH)$ [95], in the catalytic reduction of CO_2 by Rh(hfacac)(dppp) [96], and in the catalytic hydrogenation of *N*-methylacridinium by $[Cp^*Ru(N_2)(dppm)]^+$ [97].

4.2. Proton transfer reactions between coordinated dihydrogen and olefin ligands

In principle, a coordinated dihydrogen ligand may transfer one of the protons to coordinated unsaturated substrates such as olefins and acetylenes as illustrated in

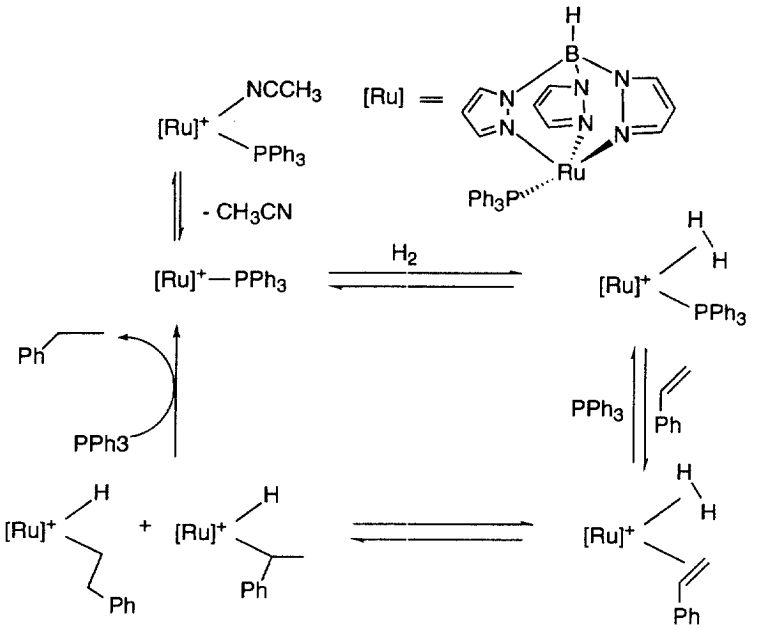
Eq. 10. The reaction is analogous to the well known oxidative coupling reactions of coordinated olefins and acetylenes as illustrated in Eq. 11 [98]. Although interesting, examples of reactions shown in Eq. 10 or even olefin dihydrogen complexes are still very rare. As an example, complexes $M(H_2)(\eta^4\text{-NBD})(CO)_3$ (M = Cr, Mo and W) and $M(H_2)(\eta^2\text{-NBD})(CO)_4$ (M = Mo and W), which have been detected by IR spectroscopy, have been proposed as the intermediates for photocatalytic hydrogenation of norbornadiene using $M(CO)_6$ [99].



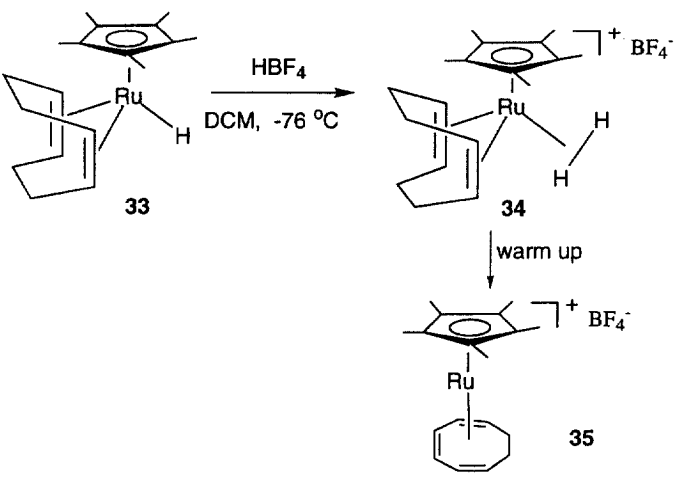
(10)

(11)

As mentioned previously, $[TpRu(PPh_3)_2(CH_3CN)]^+$ shows moderate activity for catalytic hydrogenation of olefins in anhydrous THF. A mechanism (using styrene as an example) for the reaction is suggested in Scheme 6, which involves the formation of the dihydrogen intermediate $[TpRu(H_2)(PPh_3)(olefin)]^+$, followed by proton transfer from the H_2 ligand to the olefin ligand and then reductively elimination. The alternative mechanism which involves the dihydride intermediate



Scheme 6.



Scheme 7.

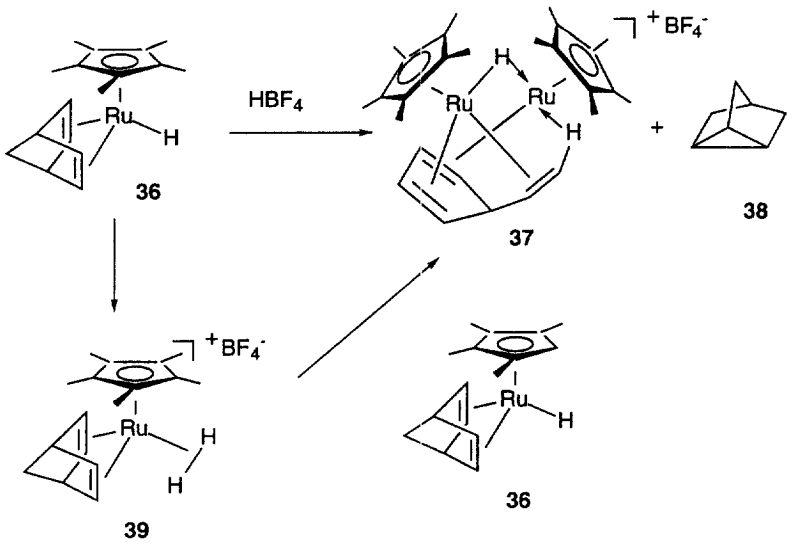
$[TpRuH_2(PPh_3)(olefin)]^+$ is unlikely, because oxidative addition of H_2 to the less electron rich fragment $[TpRu(PPh_3)(olefin)]^+$ is not expected since the more electron rich fragment $[TpRu(PPh_3)_2]^+$ forms the stable dihydrogen complex $[TpRu(H_2)(PPh_3)_2]^+$ (note PPh_3 is a better electron donor than olefins like $PhCH{=}CH_2$).

The protonation reactions of Cp*RuH(diene) (diene = COD, NBD) have been investigated, in order to further model reactions shown in Eq. 10. Reaction of Cp*RuH(COD) (**33**) [100] in CD_2Cl_2 with $HBF_4 \cdot OEt_2$ at $-76°C$ produced $[Cp^*Ru(H_2)(COD)]BF_4$ (**34**) (Scheme 7) [101]. The dihydrogen complex **34** represents a very rare example of dihydrogen complexes with only hydrocarbon ligands. Previously reported dihydrogen complexes usually contained auxiliary ligands such as phosphines, CO, CNR, hydride and halides. Unfortunately, the dihydrogen complex is unstable and decomposed to give the dehydrogenated product $[Cp^*Ru(\eta^6\text{-}1,3,5\text{-}COT)]BF_4$ (**35**).

Protonation of Cp*RuH(NBD) (**36**) in dichloromethane with $HBF_4 \cdot OEt_2$ produced a 1:1 mixture of nortricyclene and the novel bimetallic complex **37**, in which the two ruthenium centers are bridged by the vinylcyclopentadiene formed by skeletal rearrangement of NBD involving C–C/C–H bond cleavage reactions (Scheme 8). The nortricyclene and the bimetallic complex **37** are likely formed via the dihydrogen complex $[Cp^*Ru(H_2)(NBD)]^+$ (**39**), although the later complex was not detected in the NMR experiments [101].

5. Summary

Hydride complexes of Cp, Cp*, Tp, ^{R}Cn and PMP can have different structural properties. For example, $TpRuH(H_2)(PPh_3)$ and $[LRu(H_2)(PPh_3)_2]^{n+}$ ($n = 1$, L =



Scheme 8.

Tp; $n = 2$, L = ^{R}Cn and PMP) are dihydrogen complexes; Cp*$RuH_3(PPh_3)$ and $[CpRuH_2(PPh_3)_2]^+$ are classic hydride complexes. Complexes of the formula $[(\eta^5\text{-}C_5R_5)MH_2(L)(L')]^+$ (M = Fe, Ru, Os; PP = chelating diphiosphine) can adopt pure dihydrogen form, or a mixture of dihydrogen and *trans*-dihydride form, or pure *trans*-dihydride form, or a mixture of *cis*- and *trans*-dihydride forms, depending on the metals, C_5R_5, L, L′ and the chelating ring size if (L)(L′) are chelating phosphines. Smaller chelating ring sizes increase the stability of dihydrogen or *cis*-dihydride forms.

The pseudo aqueous pK_a values of complexes such as $[TpM(H_2)(L)(L')]^+$ (M = Ru, Os), $[^{R}CnRu(H_2)(L)(L')]^{2+}$, $[CpOsH_2(PR_3)_2]^+$, and $[MCl(H_2)(L)(PMP)]^+$ (M = Ru, Os; L = PPh_3, CO), $[CpRuH_2(PR_3)_2]^+$, $[MH(H_2)(PP)_2]^+$ (M = Fe, Ru, Os; PP = diphosphines), $[MCl(H_2)(PP)]^+$ (M = Fe, Ru, Os), and $[M(L)(H_2)(PP)_2]^{2+}$ (M = Fe, Ru, Os; L = CO, CH_3CN) have been estimated from equilibrium studies in organic solvents by us as well as others. Like classic hydride complexes, the acidities of most of the isostructural dihydrogen complexes decreases as ligands become more electron donating, and as the metal is replaced successively by a heavier metal in the same group. A few exceptions to the general trend have been noted, which could be related to the strong H–H interaction.

Dihydrogen complexes have interesting chemical properties, which enable them to play active roles in stoichiometric and catalytic reactions. A dihydrogen ligand can transfer protons to bases, alkyls, vinylidenes, coordinated and free olefins. Many interesting reactions involving dihydrogen complexes can be rationalized with these chemical reactivities. It is expected that more reactions mediated by dihydrogen complexes will be discovered in the future.

Acknowledgements

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