Intermolecular H···H Bonding and Proton Transfer in Semisandwich Re and Ru Complexes

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The reactions of transition metal (TM) hydrides (Cp)Re(H)(NO)(CO), (Cp)Ru(H)(CO)(PH_3), and (Cp)Re(H)(NO)(PH_3) with poor, moderate, and strong proton donors HR (H_2O, $HOCF_3$, and H_3O^+) are studied using DFT B3PW91. The reaction pathway depends on the relative proton-attracting powers of the TM and hydride H atoms, as well as on the proton donor ability of HR. In the case where these two atoms have comparable basicity, (Cp)Re(H)(NO)(CO) forms an intermolecular H···H bonding intermediate upon reaction with both poor and strong proton donors H_2O and H_3O^+. This is followed by rearrangement to η^2-H_2 by proton transfer over a very small barrier. The reaction of (Cp)Ru(H)(CO)(PH_3) with its highly nucleophilic hydride yields H···H bonding complexes with moderate proton donor $HOCF_3$, whereas the strong donor H_3O^+ produces only the η^2-H_2 structure. Rapid rearrangement of η^2-H_2 to cis-dihydride is possible although the trans-dihydride is more stable. For both types of hydride, a reaction pathway through a H···H bonding complex is preferred over direct interaction of HR with the TM atom, forming the corresponding dihydride. The latter pathway is favored for (Cp)Re(H)(NO)(PH_3), where the TM atom is the more basic. In this case cis- and trans-dihydride complexes form upon reaction with H_3O^+ without any H···H and η_2-H_2 intermediates. Although the trans-structure is more stable than the cis-, a PH_3 ligand favors the cis-direction of H_3O^+ attack by recoordination of H_2O from the hydride atom to a hydrogen of the PH_3 group.

Introduction

Transition metal (TM) hydride complexes involving intermolecular MH···HR bonding (where M is a TM and HR is a proton donor) have been the focus of recent intensive experimental[1−4] and theoretical[5,6] investigation. Such an intermolecular H···H bond has been found by Crabtree et al.[1] in the $ReH_5(PPh_3)_3$·indole·C_6H_6 system in the solid state and by Epstein and Berke in such systems as $WH(CO)_2(NO)L_2$·acidic alcohols·hexane (L = PMe_3, PEt_3, $P(O^iPr)_3$, $P(Ph)_3$)[2] and $ReH_2(CO)(NO)L_2$·perfluoro-*tert*-butyl alcohol·hexane (L = PMe_3, PEt_3, $PiPr_3$)[3] in solution. In these compounds, H···H bonding is preferred over other possible types of H-bonds. The discovery of H···H bonding has opened a new field of investigation of TM complexes and warrants a reconsideration of certain reaction mechanisms, such as formation of dihydrogen η^2-H_2 complexes and base-promoted heterolytic splitting of dihydrogen in reactions of TM hydrides with proton donors.

In our recent work[6] intermolecular H···H bonding was studied by DFT methods for systems containing hexacoordinated monohydride Mo and W and proton donors HR (HF, H_2O, H_3O^+). According to our results, the stability of H···H bonded complexes depends upon the proton donor ability of HR and the nature of cis- and trans-ligands: H···H bonded complexes exist in the case of poor and moderate proton donor HR, strong trans π-acceptor, and strong σ-donor cis-ligands. The change of π-acceptor trans-ligand into a σ-ligand transforms H···H bonded complex to a dihydride structure. On the other hand, the interaction of $MoH(NO)(CO)_2(PH_3)_2$ with the strong π-acceptor NO in trans-position and strong acid hydronium leads to aqua-η^2-H_2 ion-molecular complex; the H···H bonded complex was not identified on that reaction pathway. These theoretical results highlight the possibility of three distinct types of complexes and the interconversion between them: H···H bonded, molecular η^2-H_2, and classical dihydride. We concluded in our earlier work[6] that the H···H bonded complex may be considered as a sort of intermediate on the pathway of formation of the molecular η^2-H_2 and classical dihydride complexes. This idea has been supported by recent NMR study of proton-transfer equilibrium between a hydride and coordinated dihydrogen in the $[(dppm)_2HRu(H)]$·phenol system by Ayllon et al.,[4] where the H···H bonded form was thought to be an intermediate. IR spectroscopic evidence of H···H → η^2-H_2 interconversion in semisandwich complexes of Re and Ru has been reported by Epstein.[7]

The present work focuses on the specific role of the H···H bonded complexes in reactions of TM hydrides with proton donors. Of particular interest here is the dependence of the behavior of the system, depending on the relative stability of the η^2-H_2 and dihydride forms and on the proton donor ability of HR. Specific TM systems examined by the DFT method include (Cp)Re(CO)(NO)H···HR (R = OH, H_2O^+), (Cp)Ru(PH_3)(CO)H···HR (R = OCF_3, H_2O^+), and (Cp)Re(PH_3)(NO)H···H_3O^+.

Method of Calculation

All calculations were carried out at the DFT[8] level, using nonlocal correction B3PW91[9,10] within the context of the GAUSSIAN 94 package.[11] The basis set was of pseudopotential type[12] with a standard LANL2DZ contraction.[11] As demonstrated in our earlier paper,[6] this scheme of calculation provides a good compromise between accuracy and computational efficiency for the pertinent TM complexes. We found previously[6] that DFT correctly reflects the trends for these types of compounds. Points of which to be more cautious are related to the tendency of DFT potential energy surfaces (PES) to be

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extraordinarily flat. In particular, DFT underestimates the values of barriers and energy differences between minima and overestimates the bonding energies. Owing to the inordinate flatness of the DFT surface, it was impossible sometimes to unambiguously identify a structure as a true minimum. In such cases, the optimization procedure was interrupted when the energy was stable to within 10^{-6} hartree.

Energies of all types of intermolecular interactions were calculated as the difference between the total energy of the complex and the sum of total energies of the interacting subunits. No attempts were made to correct basis set superposition error.

Results and Discussion

1. Conceptual Framework. The H···H bonding complexes are observed in certain cases only:[6] TM hydrides may afford η^2-H_2 or dihydride forms upon reactions with HR without any H···H intermediates. It is hence important to attempt to identify the conditions that lead to formation of H···H bonded intermediates. We begin by supposing that the result of the interaction between a proton donor and a TM hydride depends to some degree on the relative proton-attracting power of the TM atom itself and the hydride hydrogen. Three different possibilities were hence considered. Complexes that may ultimately form both η^2-H_2 and dihydride complexes are designated as the first type. Those that form only η^2-H_2 complex are referred to as the second type, and the third type consists of those complexes that yield only the dihydride form.

Our choice of systems to consider is guided by previous work by Hay[13] and by Jean,[14] who showed that mixtures of σ-donor and strong π-acceptor coligands are optimal for formation of the η^2-H_2 form, whereas a more basic transition metal strengthens the stability of the dihydride form. Indeed the MP2 and CCSD(T) study of ligand effects in transition metal dihydrogen complexes by Dapprich and Frenking,[15] and our own DFT results,[6] are in good agreement with this set of ideas. In general, the stability of the η^2-H_2 complex is favored by high nucleophilicity of the hydride hydrogen, while the dihydride structures are dependent upon the electron donor ability of the TM atom. In this sort of language, the nucleophilicity or "hydridicity" of H would be expected to be greatest in hydrides of the second type while the third type is favored by greater nucleophilicity of the TM atom. The first type might thus be expected in cases of competitive nucleophilicity of the hydride hydrogen and transition metal atom. The η^2-H_2 complex is likely formed by prior formation of a H···H bonded intermediate, followed by rearrangement, whereas the dihydride is not liketly to arise from a H···H bonded complex.

As has been shown by Chinn et al. by NMR,[16] the protonation ($HBF_4{\cdot}Et_2O$) of the neutral hydride (Cp)Re(CO)(NO)H yields a mixture of two species that are identified as $[(Cp)Re(CO)(NO)(\eta^2\text{-}H_2)]^+BF_4^-$ and $[(Cp)Re(CO)(NO)(H)_2]^+BF_4^-$. The latter dihydride complex adopts a pseudo-square-pyramidal geometry with the hydride ligands in transoid positions (although ^{1}H NMR data do not rule out the possibility of a highly fluxional cis-geometry). The interconversion rate between η^2-H_2 and trans-dihydride forms was estimated approximately by spin saturation transfer experiments, yielding a preference for η^2-H_2 by 1.0 kcal/mol, with an interconversion barrier of about 10 kcal/mol. Therefore, the (Cp)Re(CO)(NO)H hydride appears to be a complex of the first type. According to experimental work,[17] the protonation of $(Cp)Ru(PPh_3)(CO)H$ leads to the η^2-H_2 structure while the interaction between HR and $(Cp)Re(PPh_3)(NO)H$ affords only cationic dihydride complex.[18] Therefore, these hydrides were identified as likely candidates for the second and third types, respectively. To simplify our calculations, we replace the PPh_3 group by PH_3.

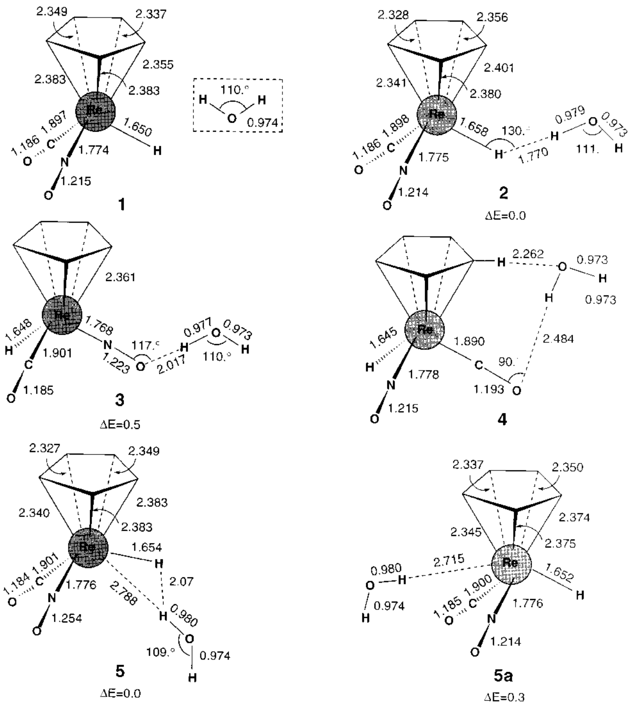


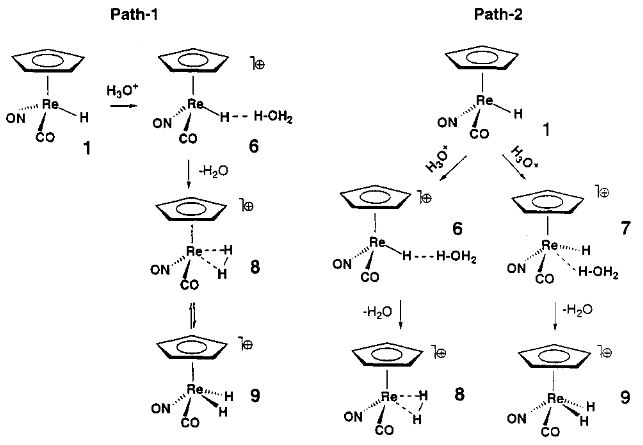
Figure 1.

2. Complexes of the First Type. Coexistence of H···H Bonding, η^2-H_2, and Dihydride Complexes in (Cp)Re(CO)(NO)H·HR Systems. As a first step, the basicity of the transition metal atom, the hydride hydrogen, and other possible proton–acceptor ligands are compared in the reaction of the poor proton donor H_2O with complexes expected to belong to the first category, (Cp)Re(CO)(NO)H, **1**. The H atom of H_2O was allowed to interact with likely nucleophilic centers of **1**, thereby forming interactions ReH···HO, NO···HO, CO···HO, and Re···HO (cis- and trans-) in the complexes represented by **2**, **3**, **4**, **5**, **5a**, respectively.

Some details of the B3PW91 geometries of **1**–**5a** are illustrated in Figure 1, along with their relative energetics. Most stable, with a binding energy of 10.9 kcal/mol (and equal in energy with one another), are complexes **2** and **5**, containing H···H and Re···H interactions. The trans-version of **5**, **5a**, is some 0.3 kcal/mol less stable. Complex **3** lies 0.2 kcal/mol higher still in energy, with its NO···HO interaction. We were unable to identify a complex with a pure CO···HO interaction: the closest minimum on the surface corresponds to **4** in Figure 1. Note that the distance between the pertinent O and H atoms is 2.48 Å, and the C–O···H angle is quite bent at 90°. A stronger contact is present between the water oxygen and one of the H atoms of the cyclopentadiene ring, with an O···H distance of 2.26 Å.[19] These DFT results agree with experimental work[3] that found evidence of the ReH···HR and ReNO···HR complexes, along with a slight preference for the H···H interaction; the CO ligand was not identified as a site of coordination.

The degree of elongation of the internal OH bond of the water molecule provides a good measure of the strength of any H-bond interaction. This stretching, relative to the isolated water molecule, is equal to 0.006 and 0.005 Å for complexes **5** and **2**, respectively, the two most strongly bound. Even though slightly less stable, a stretch of 0.006 appears in *trans*-**5a**. The O–H bond is stretched by only 0.003 Å in **3**, and not at all in

SCHEME 1



4 where there is some question as to whether this H atom participates in a H-bond at all. According to our DFT results for hexacoordinated TM hydrides,[6] H−R bond stretching appears to be characteristic of H···H bonding complexes in general. In summary, the calculated results support the equal ability of the hydride H and Re atoms in **1** to attract the proton of the weak acid, as well as the preference of the H···H and the Re···H interactions over other possibilities.

In order to study reactions with stronger proton donors, the interaction of H_3O^+ with the H and Re atoms of the hydride **1** was computed. One may suppose that two pathways predominate. The hydronium ion can attack the hydrogen, forming intermediate **6** with a H···H bond, which may then transform by proton transfer and loss of water into η^2-H_2 complex **8**, which in turn interconverts to dihydride form **9** (path 1 in Scheme 1). In a second reaction path, the hydronium attacks either hydride H or Re atoms with approximately equal likelihood, forming H···H and Re···H intermediate complexes **6** and **7**, respectively. These steps are followed by transformation to η^2-H_2 and dihydride complexes **8** and **9**, respectively (path 2 in Scheme 1). Both paths have some experimental support. For example, in the protonation of the chelating phosphine hydrides (Cp)-Ru($PPh_2(CH_2)_nPPh_2$)H ($n = 1-3$) Simpson and Controy-Lewis[20] proposed that the η^2-H_2 and dihydride complexes arise by two different protonation pathways, consistent with path 2. In contrast, kinetic and thermodynamic consideration of equilibrium between dihydride and η^2-H_2 forms of related complexes of Re[21] demonstrated that the H_2 complexes are the kinetic products of protonation of the neutral hydride precursors. The initially formed molecular H_2 complexes then undergo isomerization by an intramolecular rearrangement to yield equilibrium mixtures of the dihydride and η^2-H_2 complexes. According to these authors, the trans-structure of the dihydride is preferred, although the possibility of the cis- form was not excluded. These results are in general support of path 1.

An important issue concerns the relative stability of the trans- and cis-forms of the dihydride. The energies and geometries of model cation complexes η^2-H_2 **8**, cis-dihydride **9**, and trans-dihydride **9a**, formed by protonation of hydride **1**, were all computed and the results are illustrated in Figure 2. The η^2-H_2 cation **8** is 0.4 kcal/mol more stable than cis-dihydride **9**, but less stable than the trans-form **9a** by 1.8 kcal/mol. The geometries of η^2-H_2 and the cis-dihydride are quite different in some respects. The H--H distance in **8** is 0.920 Å, only 0.176 Å longer than the distance computed by the same method for the free H_2 molecule. The interhydrogen distance in **9** is significantly longer: 1.467 Å.

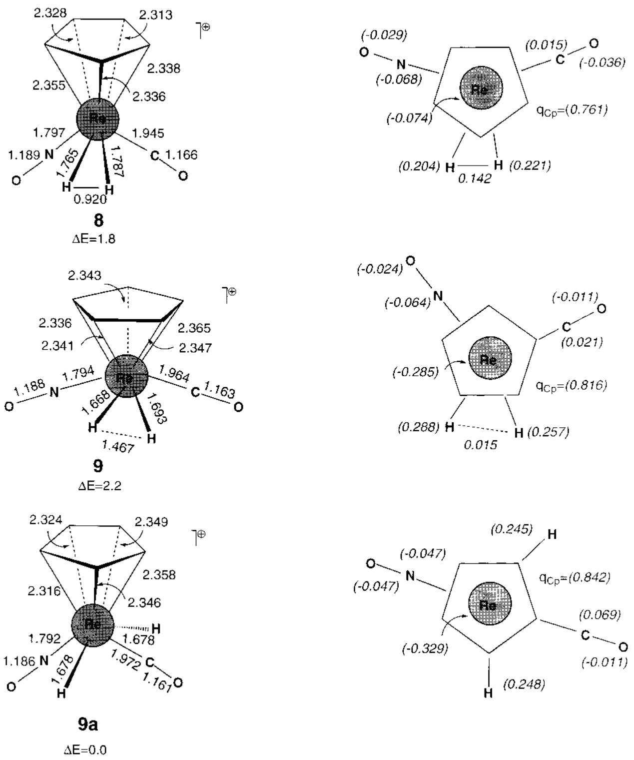


Figure 2.

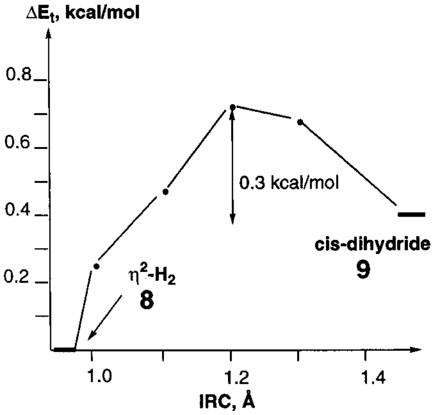


Figure 3.

Examination of Mulliken charges reveals that a large portion of the positive charge in the **8**, **9**, and **9a** cations is localized on the Cp ring (0.761, 0.816, and 0.842, respectively). The Cp ring charge is quite a bit smaller in **1** (0.28), so it is logical to infer that the interaction of hydride **1** with a proton donor is accompanied by electron density transfer from the Cp ring to the metal atom. Analogous electron transfer from Cp to a metal atom upon formation of M···H bonding has been reported by McKee[22] for protonated ferrocene and in our recent paper[23] for the system $(Cp)_2Os{\cdot}H_2O$.

As has been shown by extended Hückel (EH) calculations of η^2-H_2 complexes,[15] H--H bond cleavage leading to dihydride structure is allowed by symmetry, so the reaction barrier may not be very high. The barrier for this interconversion was estimated by moving along the reaction coordinate from **8** to **9**. The H--H distance was chosen as reaction coordinate and was increased in steps of 0.1 Å, optimizing all other geometrical parameters at each step. The B3PW91 potential energy profile is depicted in Figure 3. A relatively smooth profile was obtained for the H--H cleavage, with a low barrier of only 0.3 kcal/mol.

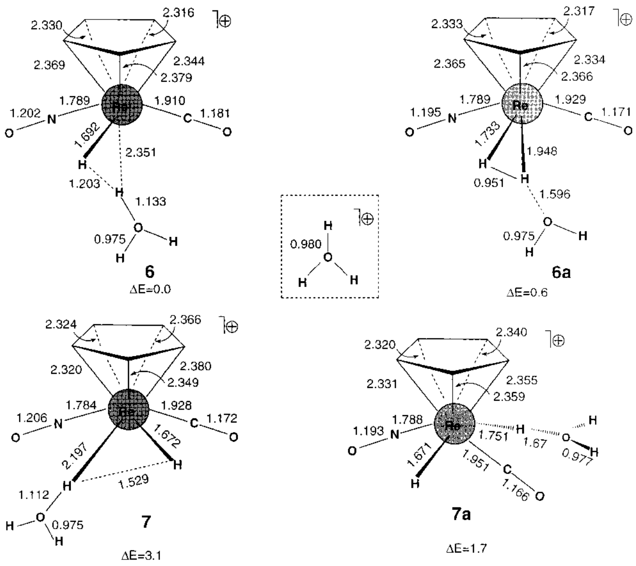


Figure 4.

Such a small value supports the possibility of rapid η^2-H_2 ↔ cis-dihydride rearrangement. Indeed, this theoretical result may help explain why it has proven so difficult to experimentally determine the H···H distance in η^2-H_2 complexes.[24] This difficulty may be due to the rapid rearrangements that occur between the flexible structures corresponding to shallow minima.

The next step involved examination of the direct interaction between H_3O^+ and hydride **1**. Four minima were located: ReH···H−OH_2 complex **6**, η^2-H_2 complex **6a**, and *cis*- and *trans*-Re···H−OH_2 complexes **7** and **7a**. As indicated in Figure 4, the hydronium attacks the metal center forming a sort of three-centered Re···H_{H_3O}···H bond with bond lengths of 2.197 and 1.529 Å, respectively, in **7**. Structures **7** and **7a** could easily be precursors to *cis*-**9** and *trans*-**9a** dihydrides, respectively; however, complexes **7** and **7a** are clearly less stable than **6**. Our computed result of 1.1 kcal/mol as the energetic preference of structure **6a** vs **7a** agrees nicely with an experimental estimate[16] of 1.0 kcal/mol. As judged by the stretching of the H−O bond in hydronium, the interaction is stronger in **6**, consistent with its greater stability. In summary, the energetic preference for **6** over **7** would tend to favor path 1.

The transfer of a proton in H···H complex **6** from the water molecule to the hydride atoms leads to η^2-H_2 form **6a**, which is 0.6 kcal/mol less stable than **6**. The equilibrium geometry of **6a** is shown in Figure 4. The H···OH_2 distance elongates by 0.463 Å and the H-H distance shortens by 0.252 Å upon proton transfer. In general, **6a** may be considered as an ion-molecular aqua-complex. The H--H distance in aqua-complex **6a** is only 0.031 Å longer than in "pure" η^2-H_2 complex **8**. The change in Re−H bond lengths is more significant: the Re−H_{H_2O} distance elongates by 0.161 Å, while the other Re−H length shortens by 0.028 Å upon complexation with the water.

The Re−H_{H_2O} distance was chosen as reaction coordinate for calculating an estimate of the potential energy profile of proton transfer **6** → **6a**, illustrated in Figure 5. The B3PW91 barrier to proton transfer is very small (about 0.1 kcal/mol), not surprising for cationic systems.[24,25] When comparing the geometries of **6** and **6a**, one may suppose that the barrier to proton transfer for the most part depends upon the energy needed to cleave the H−R bond. Indeed, our preliminary B3PW91 calculations of Ru and Re hydride complexes with the weak proton donor H_2O yielded a barrier converting the H···H species to η^2-H_2 of about 40 kcal/mol. Such a high barrier is consistent with experimental observations[8] in half-sandwich complexes of Re and Ru with alcohols that are poor acis. Previous B3PW91 calculations of $(dppm)_2HRuH\cdots H_2O$ indicate that the η^2-H_2 form is 10.7 kcal/mol more stable than the H···H congener. This value agrees with an experimental value for the complex with the more acid proton donor $(dppm)_2HRuH\cdots HOPh$ of 17 ± 3 kcal/mol.[4] In summary, in the case of weak and moderate proton donors, this barrier can reach high values as in experiment[8] and may disappear in case of very strong proton donors like H_3O^+. Of course, as the barrier drops, the presence of two distinct minima becomes similarly questionable.

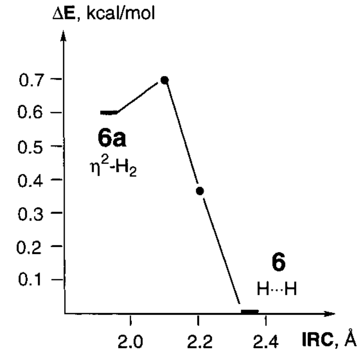


Figure 5.

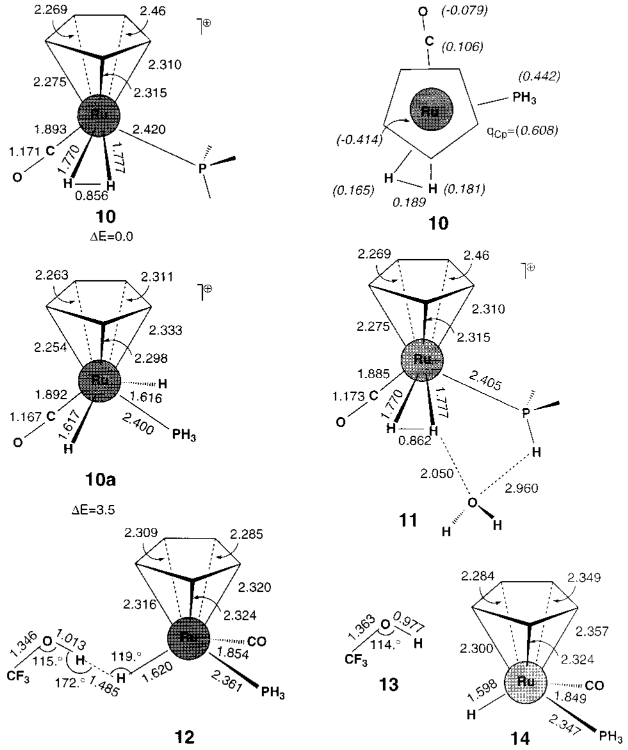


Figure 6.

3. Complexes of the Second Type. (Cp)Ru(PH_3)(CO)H·HR Systems. According to experiment, (Cp)Ru(PH_3)(CO)H yields only the η^2-H_2 cation upon reaction with HR. This might suggest that the proton-attracting power of the hydride hydrogen is higher than that of the Ru atom. Indeed, the calculated results presented in Figure 6 indicate that the cis-dihydride form does not exist. Attempts to locate such a minimum were unsuccessful as it transformed into η^2-H_2 structure **10** during optimization. Trans-isomer **10a** is 3.5 kcal/mol less stable than **10**. Kinetic studies[21] are consistent with the preponderance of the η^2-H_2 form

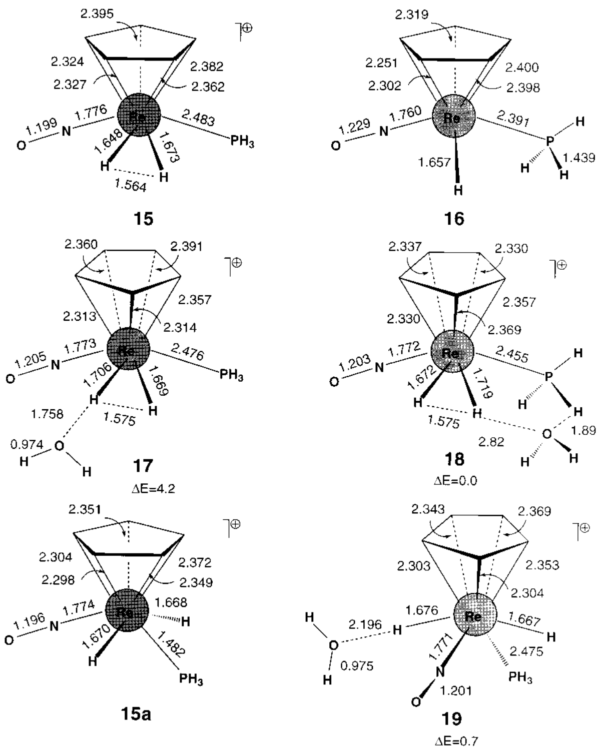


Figure 7.

as [CpRu(dmdppe)(η^2-H_2)][BF_4] is preferred over the corresponding trans-dihydride, with an intervening barrier of 20 kcal/mol.

When subjected to interaction by a hydronium ion, complex **11** is formed with no intermediates. This structure may be categorized as a loose ion-molecular aqua-η^2-H_2 complex, subsequent to proton transfer to the metal. A proton donor more moderate than the ionic hydronium, CF_3OH (**13**), does not transfer its proton. Instead, the interaction with hydride **14** yields the neutral H···H complex **12**. The binding energy of **12** is 9.8 kcal/mol, and the two interacting hydrogens are separated by 1.485 Å. In comparison, the still poorer proton donor H_2O results in H···H distances with TM hydrides of 1.7–1.8 Å (see Figure 1 and refs 2 and 7). On the basis of these results, one may conclude that in the case of the second type of hydride, the strength of the H···H complex (and, probably, the height of the barrier for proton transfer to form the η^2-H_2 structure) is largely determined by the proton donor ability of HR.

4. Complexes of the Third Type. (Cp)Re(PH_3)(NO)H·H_3O^+ Systems. The products of interaction of the strong proton donor H_3O^+ with a hydride of the third type (Cp)Re(PH_3)(NO)H are described in Figure 7. The substitution of the CO ligand of **1** by PH_3 makes the TM center a stronger proton acceptor. Consequently, interaction of HR with hydride **16** yields the dihydride structure only. Indeed, our DFT calculations indicate that the η^2-H_2 structure is not a minimum on the surface; it transforms during optimization into cis-dihydride structure **15**. Trans-dihydride **15a** is 4.3 kcal/mol more stable than cis-. Since Re is a stronger nucleophilic center than the hydride hydrogen of **16**, hydronium attacks the metal center forming three aqua-dihydrogen complexes **17**, **18**, and **19**. Structure **17** is characterized by the attack of the hydronium upon the Re atom from the side of the NO ligand. This attack leaves the water molecule coordinated with one of the hydride hydrogens; the interaction energy is 16 kcal/mol. Hydronium attacks Re from the side of the PH_3 coligand in **18**. While transferring a proton to the transition metal, OH_2 recoordinates to a H atom of the PH_3 group. Complex **18** is 3.8 kcal/mol more stable than 1.7. If **16** is attacked by H_3O^+ in the trans-position, complex **17a** is obtained, 0.7 kcal/mol higher in energy than **18**. This result emphasizes the multifaceted role that coligands may play in the entire process. Although trans-isomer **15a** is more stable than cis-**15**, attack in the cis-position (from the side of the PH_3 ligand) is preferred in terms of the subsequent rearrangement to **18**. Phosphine groups had earlier been considered as σ-donor ligands only. Our computed results indicate phosphine coligands can act as a carrier of R upon interaction of a transition metal hydride with HR. Structures containing H···H bonding were not observed on this pathway.

Conclusions

The pathway of reaction of the TM hydride and proton donor HR is apparently controlled to a large degree by the relative proton-attracting power of the hydride hydrogen vs the TM atom. If the hydride is the stronger base of the two, HR attacks that atom. However, the formation of the H···H bonding complex depends also upon the proton donor ability of HR. In the case of a poor or moderate proton donor, a complex of H···H bonding type forms and there is likely a proton-transfer barrier of significant height for the subsequent $MH\cdots HR \rightarrow M(\eta^2\text{-}H_2)^+R^-$ reaction. This barrier may in fact disappear in the case of a strong proton donor such as H_3O^+. When the TM atom is a stronger proton attractor, HR attacks this metal atom, forming dihydride (cis- or trans-) structures. Trans dihydride structures are more stable than cis- in all cases considered. Coligands like PH_3 may play an important role as "carrier" of R and favor HR attack in the cis-direction.

In the case that the hydride and TM atoms are of approximate equal basicity, the intermolecular H···H bonding complex forms in the first reaction step, followed by rearrangement via proton transfer to molecular $M(\eta^2\text{-}H_2)^+R^-$ complex and then, probably, to trans-dihydride $(H-M-H)^+R^-$. A rapid rearrangement $M(\eta^2-H_2)^+R^- \rightleftharpoons$ cis-dihydride is possible as well. A H···H bonding complex is observed even in cases of very strong proton donors such as H_3O^+.

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