Reactions of Dihydrogen(norbornadiene) Complexes

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Dihydrogen(olefin) complexes have been proposed as active species in catalytic hydrogenation reactions. We have studied the hydrogen-transfer reactions of dihydrogen(olefin) complexes, especially those containing the norbornadiene (NBD) ligand, in order to address the following questions: (i) how the alignment of a H_2 ligand relative to an olefin ligand may affect their reactivity; (ii) in general, what is the detailed pathway for intramolecular hydrogen transfer from an H_2 ligand to an olefin ligand; and (iii) how will the hydrogen transfer reactions proceed in the presence of both an H_2 and a hydride ligand.

Introduction

Over the last two decades, extensive studies have been carried out on dihydrogen transition metal complexes, especially on their syntheses and structural characterizations.[1,2] There has also been an interest in their reactivities and roles in catalysis.[3] Dihydrogen complexes of the types $[M(R)(H_2)L_n]$ and $[M(olefin)(H_2)L_n]$ have been proposed as intermediates in catalytic hydrogenation reactions.[4−7] As model complexes for reactions involving intramolecular hydrogen transfer from a coordinated dihydrogen ligand to the α-carbon atom of a σ-bonded carbon ligand, several dihydrogen complexes containing σ-bonded carbon ligands (e.g. alkynyl,[8] alkenyl,[9] and aryl[10]) have been synthesized in recent years. Intramolecular hydrogen transfer from a coordinated dihydrogen ligand to the α-carbon atom of the R

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Chak Po Lau (center) was born in Hong Kong and he received his undergraduate and graduate training in the United States. He earned his PhD under the guidance of the late Professor Carl H. Brubaker, Jr. at the Michigan State University in 1977. After his postdoctoral stay with the late Professor William E. Hatfield and Professor Maurice Brookhart at the UNC at Chapel Hill, he joined the Beijing Institute of Chemistry in China as an associated scientist. He returned to Hong Kong and became a lecturer at the then Hong Kong Polytechnic in 1983, and he is now Professor at the Department of Applied Biology & Chemical Technology of the Hong Kong Polytechnic University. His research interest includes homogeneous catalysis, transition-metal hydride chemistry, and hydrogen bond (dihydrogen bond) mediated chemical reactions.

MICROREVIEWS: This feature introduces the readers to the authors' research through a concise overview of the selected topic. Reference to important work from others in the field is included.

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group in [M(R)(H_2)L_n] has been demonstrated with well-defined dihydrogen complexes.[8–9]

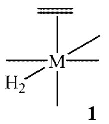
The current review is related to intramolecular hydrogen transfer reactions involving complexes of the type [M(olefin)(H_2)L_n]. The reactions are interesting because they are relevant to catalytic hydrogenation reactions. In addition, a detailed study on intramolecular hydrogen transfer from H_2 to olefin ligands may help to develop a field of chemistry based on the coupling of σ-bonds and unsaturated substrates.

In the past few years, we have tried to generate reactive dihydrogen(olefin) complexes in order to study the intramolecular hydrogen transfer from an H_2 ligand to olefin ligands. In particular, we wish to address the following questions.

(i) Structures **1** and **2** show two possible ways of arranging an H_2 ligand and an olefin ligand around a metal center if rotation of the olefin about the metal−olefin bond can effectively be restricted. With the restriction, the M−H_2 bond could be perpendicular to the olefin double bond (**1**) or parallel to the olefin double bond (**2**). The different arrangements of the H_2 ligand relative to the olefin ligand may affect the reactivity. This has been suggested by M. Poliakoff et al. when explaining the formation of norbornene (NBE) and nortricyclene in the photocatalytic hydrogenation of norbornadiene (NBD) using [M(CO)$_6$].[11] We wish to see if similar reactions can also occur with other systems.

(ii) There are several possible pathways to transfer a dihydrogen ligand to an olefin ligand. For example, the dihydrogen ligand may undergo oxidative addition to give a dihydride intermediate before the hydrogen transfer; the hydrogen transfer reactions could proceed through a concerted mechanism (simultaneous transfer of the two hydrogen atoms to a double bond); or through a stepwise mechanism in which one of the hydrogen atoms from the coordinated H_2 is transferred to the olefin to give an alkyl(hydrido) complex, followed by reductive elimination. It is of interest to see which of the possible pathways is operative.

(iii) The presence of a hydride ligand in dihydrogen(olefin) complexes may affect the reactivity of the dihydrogen(olefin) complexes. It would be interesting to see how the hydrogen transfer reactions will proceed in the presence of both an H_2 and a hydrido ligand.



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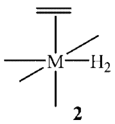

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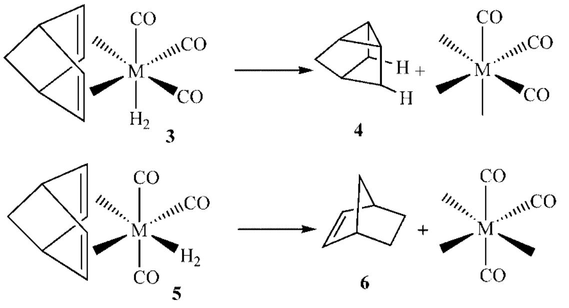
In this review, we will summarize the catalytic hydrogenation reactions involving dihydrogen(olefin) complexes and our recent work, aiming at addressing the above-mentioned questions.

Discussion

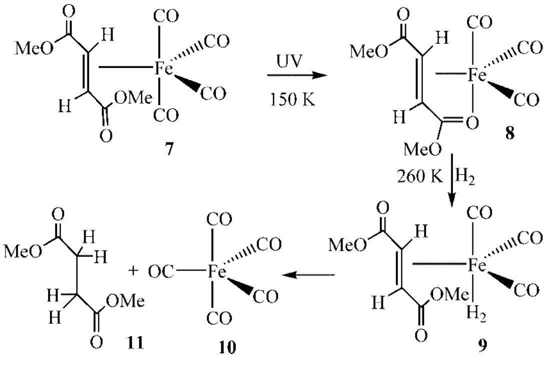
Dihydrogen(olefin) Complexes in Catalytic Hydrogenation

Catalytic hydrogenation reactions involving dihydrogen(olefin) complexes have been suggested for several systems. In some cases, the dihydrogen(olefin) intermediates have been detected. Complexes [M(CO)$_6$] (M = Cr, Mo, and W)[11] are photocatalytically active for the hydrogenation of olefins. When norbornadiene is used as the substrate, the hydrogenation reactions give a mixture of norbornene and nortricyclene. After a detailed investigation by UV laser photolysis of [M(CO)$_6$] and [M(η^4-NBD)(CO)$_4$] in the presence of H_2 and D_2, it was suggested that nortricyclene (**4**) is produced through the intermediates *fac*-[M(H_2)(η^4-NBD)(CO)$_3$] (**3**), while norbornene (**6**) is generated through the intermediates *mer*-[M(H_2)(η^4-NBD)(CO)$_3$] (**5**) (Scheme 1). Intramolecular hydrogen transfer within [Cr(H_2)(η^4-NBD)(CO)$_3$] is supported by the fact that the decay of the IR signals does not depend on the hydrogen pressure. Involvement of the dihydrogen intermediates in the hydrogenation reactions is also supported by an in situ NMR spectroscopic investigation of hydrogenation with parahydrogen.[12] A number of dihydrogen(olefin) complexes related to the catalytic system have been characterized by IR spectroscopy, e.g. *cis*-[M(H_2)(η^2-C_2H_4)(CO)$_4$] (M = Cr, Mo, W), *mer*-[M(H_2)(η^2-C_2H_4)$_2$(CO)$_3$] (M = Mo, W), *fac*-[M(H_2)(η^4-NBD)(CO)$_3$] (M = Cr, Mo, W), *mer*-[M(H_2)(η^4-NBD)(CO)$_3$] (M = Cr, Mo, W), and [M(H_2)(η^2-NBD)(CO)$_4$] (M = Mo, W).



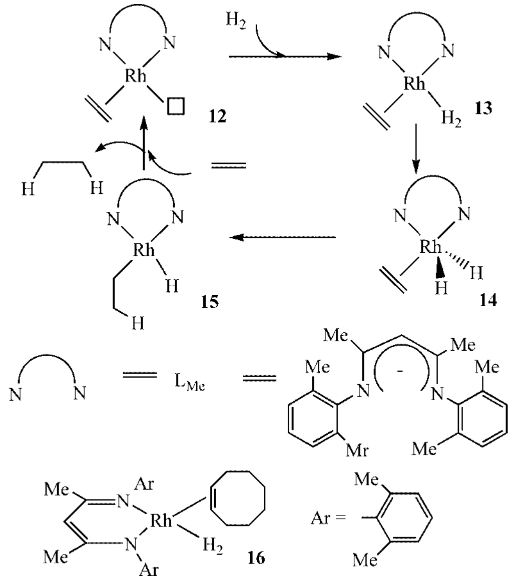
Scheme 1

In a related study,[13] Poliakoff et al. studied the hydrogenation of dimethyl fumarate (DF) using [Fe(CO)$_4$(η^2-DF)] (**7**). When irradiated, **7** (in a polyethylene matrix) reacts with H_2 to give dimethyl succinate (**11**) and [Fe(CO)$_5$] (**10**). The reaction sequence is shown in Scheme 2. The intermediates [Fe(CO)$_3$(η^4-DF)] (**8**) and [Fe(CO)$_3$(H_2)(η^2-DF)] (**9**) have been detected by FT-IR spectroscopy.



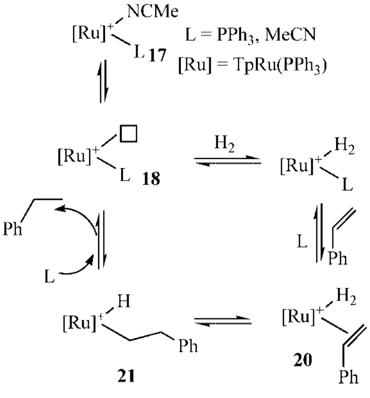
Scheme 2

Budzelaar et al. recently reported catalytic hydrogenation reactions using rhodium complexes, such as [$L_{Me}Rh(CH_2{=}CH_2)_2$], [L_{Me}Rh(COE)], and [L_{Me}Rh(COE)(CH_3CN)] [L_{Me} = (2,6-$C_6H_3Me_2$)NCMeCHCMeN(2,6-$C_6H_3Me_2$)].[14] The dihydrogen(olefin) complexes [Rh{(2,6-$C_6H_3Me_2$)-NCMeCHCMeN(2,6-$C_6H_3Me_2$)}(H_2)(olefin)] (**13**), which undergo oxidative addition reactions to give the dihydrido species **14**, were suggested as intermediates in the catalytic cycle, as shown in Scheme 3. The dihydrogen complex [Rh{(2,6-$C_6H_3Me_2$)NCMeCHCMeN(2,6-$C_6H_3Me_2$)}(H_2)-(COE)] (**16**) has been detected at low temperatures by NMR spectroscopy.



Scheme 3

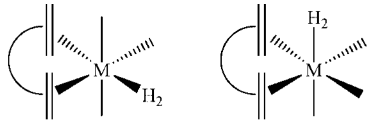
We have reported the catalytic hydrogenation of olefins using [Ru(Tp)(PPh_3)(L)(CH_3CN)]$^+$ (**17**) [Tp = hydrotris(1-pyrazolyl)borate; L = PPh_3, CH_3CN].[7] It was proposed that [Ru(Tp)(L)(H_2)(olefin)]$^+$ (**20**) is involved in the hydrogenation (Scheme 4), although the intermediate was not detected. It was suggested that the first hydrogen transfer might proceed through reactions analogous to the oxidative coupling of olefins.



Scheme 4

Modeling Reactions of Dihydrogen(olefin) Complexes

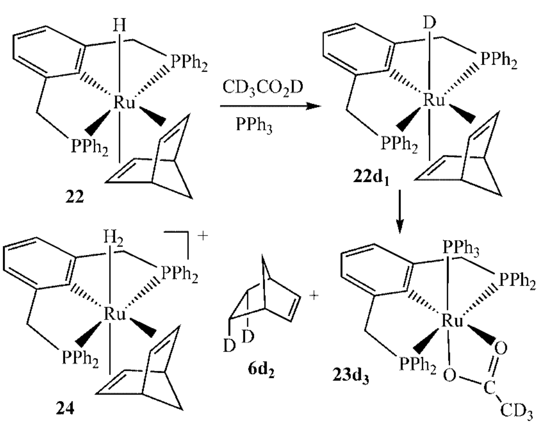
One of the main purposes of our work is to address how the relative arrangements of the H_2 and olefin ligands affect the hydrogen-transfer reactions. Structures **1** and **2** mentioned in the Introduction represent two ideal situations in which the olefin ligand has a specific orientational preference. However, monoolefin ligands do not necessarily show this kind of structural preference because the barriers of rotation about the metal-olefin bond are not prohibitively high.[15] Therefore, in our studies we have used diolefin ligands, such as NBD and COD, to restrict the rotation. Structures **A** and **B** show two possible structural isomers in which a diolefin ligand and an H_2 ligand are arranged in a *mer* and *fac* manner, respectively. Structure **A** models the structure of **1**, while structure **B** is closely related to structure **2**.



A **B**

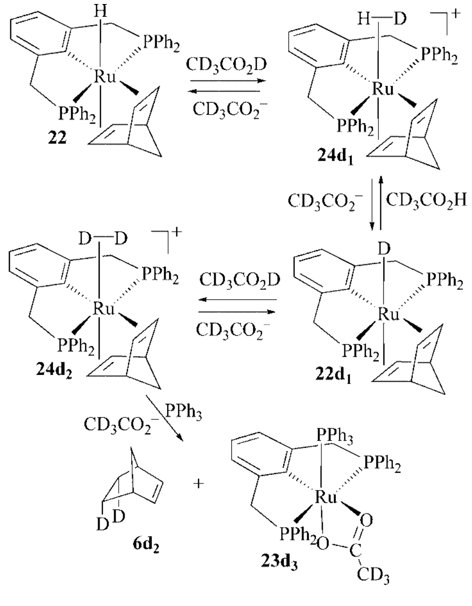
Complexes with a mer Arrangement of the H_2 and Diolefin Ligands

The protonation reactions of [RuH(NBD)(PCP)] (**22**) [PCP = 2,6-(PPh_2CH_2)$_2C_6H_3$] provide examples of studying the reactions of dihydrogen(olefin) complexes with a structural feature related to structure **1** (or **A**).[16] It was shown that protonation of complex **22** with excess CD_3CO_2D in the presence of PPh_3 gives [Ru(O_2CCD_3)(PPh_3)(PCP)] (**23d$_3$**) and partially deuterated (ca. 75% D in the *endo* positions) norbornene (see Scheme 5). The deuterium is only incorporated at the *endo* position of norbornene. In-situ NMR spectroscopic experiments revealed that Ru−H in **22** readily undergoes H/D exchange with CD_3CO_2D to give [RuD(NBD)(PCP)] (**22d$_1$**), and that the H/D exchange reaction is faster than the hydrogenation reaction.



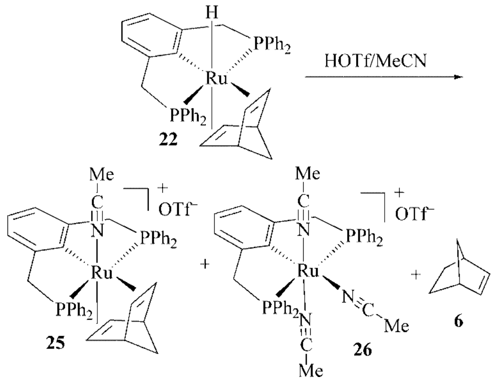
Scheme 5

Considering the fact that [RuH(H_2)(dppe)$_2$]$^+$ contains a dihydrogen ligand[17] and that norbornadiene (NBD) is less electron-donating than dppe, it was proposed that protonation of [RuH(NBD)(PCP)] (**22**) initially produces the dihydrogen complex [Ru(H$_2$)(NBD)(PCP)]$^+$ (**24**), which mediates the formation of norbornene and the H/D exchange reaction. A computational study[16] confirms that complex [Ru(H$_2$)(NBD){2,6-(PH$_2$CH$_2$)$_2$C$_6$H$_3$}]$^+$ (**30**), a model complex of **24**, is indeed a typical octahedral dihydrogen complex, with a short H−H bond (0.868 Å). Scheme 6 shows the proposed mechanism for the H/D exchange reaction of **22** with CD$_3$CO$_2$D, and the formation of NBE in the protonation reactions with acetic acid. Reaction of **22** with CD$_3$CO$_2$D could produce the η^2-H−D complex [Ru(HD)(NBD)(PCP)]$^+$ (**24d$_1$**), which can then be deprotonated by CD$_3$CO$_2^-$ to give **22d$_1$**. The mechanism is similar to those proposed for the H/D exchange of [W(D$_2$)(CO)$_3$(P*i*Pr$_3$)$_2$] with H$_2$O,[18] and for the H/D exchange of [Ru(Tp)(H$_2$)(PPh$_3$)$_2$]$^+$ with D$_2$O.[7] Hydrogen transfer within [Ru(H$_2$)(NBD)(PCP)]$^+$ or its isotopomers would give NBE. For example, [D$_2$]NBE could be formed from [Ru(D$_2$)(NBD)(PCP)]$^+$ (**24d$_2$**) (Scheme 6). Such a proposition is consistent with the fact that protonation of **22** with CD$_3$CO$_2$D gave deuterated NBE in which the deuterium is at the *endo* positions of NBE.



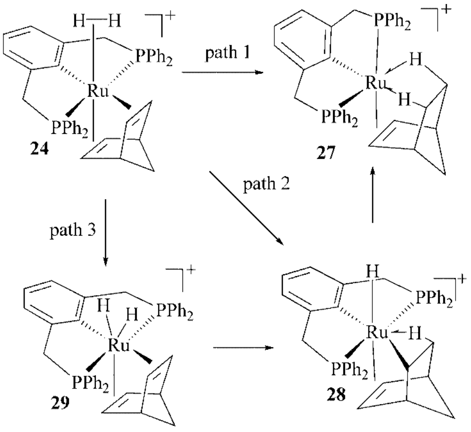
Scheme 6

Protonation of **22** with HOTf in the presence of acetonitrile produces [Ru(MeCN)(NBD)(PCP)]OTf (**25**) and [Ru(MeCN)$_3$(PCP)]OTf (**26**), along with NBE (Scheme 7). Formation of [Ru(MeCN)(NBD)(PCP)]OTf (**25**) supports the proposition that protonation of **22** initially produces the dihydrogen complex **24**, as [Ru(MeCN)(NBD)(PCP)]OTf could be easily formed by displacement of the H$_2$ ligand in [Ru(H$_2$)(NBD)(PCP)]OTf using MeCN. Apparently, [Ru(H$_2$)(NBD)(PCP)]OTf also undergoes a hydrogen-transfer reaction in the presence of MeCN to give norbornene and [Ru(MeCN)$_3$(PCP)]OTf.



Scheme 7

There are several possible reaction pathways for the hydrogenation of the NBD ligand in [Ru(H$_2$)(NBD)(PCP)]$^+$. As shown in Scheme 8, the hydrogen transfer reactions could proceed by a concerted mechanism (simultaneous transfer of the two hydrogen atoms of the H$_2$ ligand to the double bond) (path 1); or through a stepwise mechanism in which one of the hydrogen atoms of coordinated H$_2$ is transferred to NBD to give the alkyl(hydrido) complex [RuH(C$_7$H$_9$)(PCP)]$^+$ (**28**), followed by reductive elimination (path 2); or via a dihydrido intermediate **29**, prior to hydrogen transfer (path 3).



Scheme 8

Density functional calculations at the B3LYP level of theory were performed to examine the favorable reaction pathway for the conversion of the model complex [Ru(H$_2$)(NBD){2,6-(H$_2$PCH$_2$)$_2$C$_6$H$_3$}]$^+$ (**30**) to the assumed product [Ru(NBE){2,6-(H$_2$PCH$_2$)$_2$C$_6$H$_3$}]$^+$ (**31**).[16] Here, **30** and **31** are the model complexes of **24** and **27** proposed in Scheme 8, respectively.

The results from the calculation[16] eliminate the oxidative addition product, the dihydrido complex **29**, as an intermediate. The dihydrido species was found to correspond to a transition state (see below). The results are understandable, since it is unlikely that a complex can have both a stable dihydrogen and a stable dihydrido form, without changing the geometry significantly (i.e. both forms correspond to a minimum on the potential energy surface). The calculations also eliminate the concerted pathway.

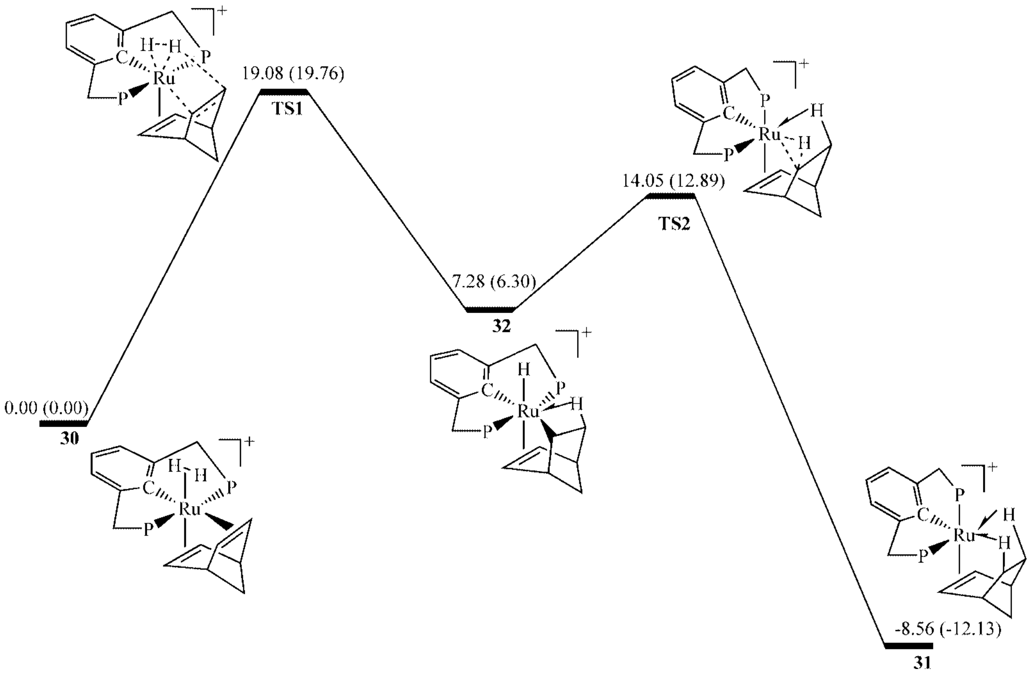
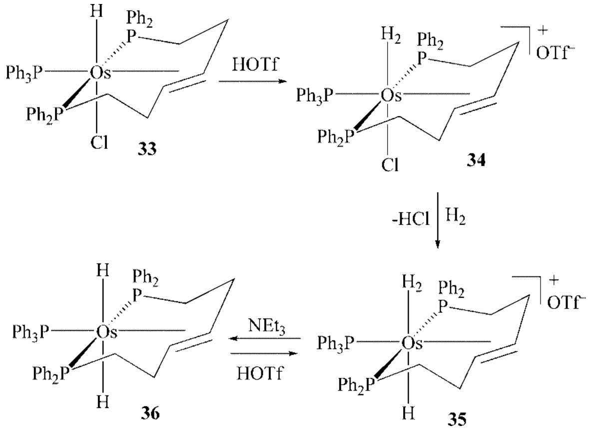


Figure 1. Schematic illustration of the reaction pathways of $[Ru(H_2)(NBD)(2,6\text{-}(PH_2CH_2)_2C_6H_3)]^+$, with calculated relative free energies [kcal/mol] and reaction energies [kcal/mol] (in parentheses), modified from ref.[16]

On the other hand, it was found that conversion of **24** to **27** through a stepwise process is feasible. Figure 1 shows the reaction steps for the conversion of **30** to **31** via **32** (the model complex of **28** proposed in Scheme 8), together with the relative free energies and reaction energies (in parentheses) calculated for all the species. The favorable stepwise mechanism involves two steps: one hydrogen atom of the coordinated H_2 ligand is transferred to NBD to form the pentagonal-bipyramidal intermediate **32** via the transition state **TS1**, with an energy barrier of 19.08 kcal/mol; the second hydrogen transfer then completes the hydrogenation of one of the two double bonds of NBD to form the NBE complex **31**, with a lower energy barrier of only 6.77 kcal/mol. As mentioned above, the first transition state (**TS1**) corresponds to a dihydrido species.

In another study on the reactivity of dihydrogen(olefin) complexes with a structural feature of **1** (or **A**), the protonation reaction of $[OsClH(PPh_3)\{Ph_2P(CH_2)_2CH{=}CH(CH_2)_2PPh_2\}]$ (**33**) has been investigated.[19] Protonation of **33** with HOTf produces the dihydrogen(olefin) complex $[OsCl(H_2)(PPh_3)\{Ph_2P(CH_2)_2CH{=}CH(CH_2)_2PPh_2\}]OTf$ (**34**), which has been characterized by NMR spectroscopy (Scheme 9).

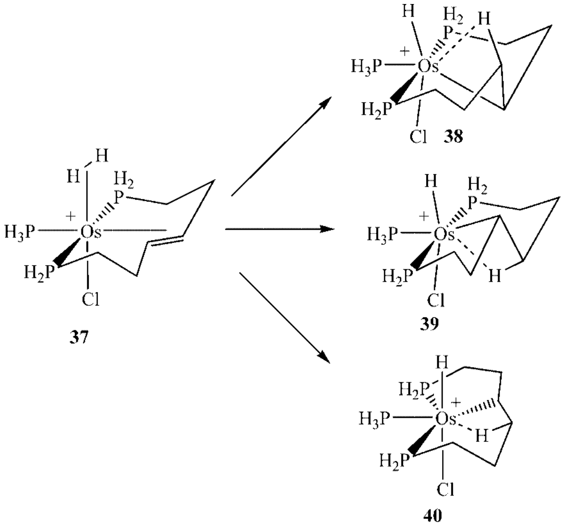
Interestingly, the coordinated olefin double bond in **34** could not be hydrogenated, even when a solution of **34** in CD_2Cl_2 was stored under a H_2 (1 atm) for 1 d. Instead, the fluxional hydrido(dihydrogen) complex $[OsH(H_2)(PPh_3)\{Ph_2P(CH_2)_2CH{=}CH(CH_2)_2PPh_2\}]OTf$ (**35**) is slowly produced when **34** is exposed to H_2. Protonation of $[OsH_2(PPh_3)\{Ph_2P(CH_2)_2CH{=}CH(CH_2)_2PPh_2\}]$ (**36**) with HOTf also produces **35**. The coordinated olefin double bond in **35** could not be hydrogenated either.



Scheme 9

These unexpected results were also examined by a computational study.[19] The calculated free energy change ($\Delta G°$) for the process, **37** + H_2 → $[OsCl(H_2)(PH_3)\{H_2P(CH_2)_6PH_2\}]^+$ (a model complex for the hydrogenated product of complex **34**), is ca. −1.0 kcal/mol, suggesting that the hydrogenation is thermodynamically feasible.

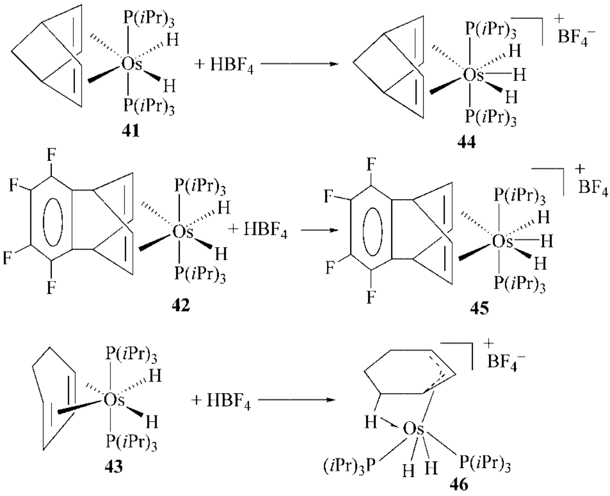
The computational study[19] found that the reaction was kinetically unfavorable, due to the constraint imposed by the $Ph_2P(CH_2)CH{=}CH(CH_2)_2PPh_2$ ligand. The reasons for the kinetically unfavorable reaction have been explained as follows. The optimized model complex $[OsCl(H_2)(PH_3)\{H_2P(CH_2)_2CH{=}CH(CH_2)_2PH_2\}]^+$ (**37**) contains an H_2 ligand with an H−H distance of 1.011 Å. The coordinated −HC=CH− unit is orientated in such a way that one olefinic carbon atom is closer to the η^2-H_2 ligand, while the other is further away. The possible intermediates (Scheme 10), which can lead to the hydrogenation product by a reductive elimination step, are all inaccessible due to the conformational constraint imposed by the $Ph_2P(CH_2)_3CH(CH_2)_2PPh_2$ ligand. **38** does not correspond to a minimum on the potential energy surface. In addition, the separation of the hydrido and the bonded alkyl ligands prevents the reductive elimination, which leads to a hydrogenated product. The activation energy leading to **39** is calculated to be as high as 50 kcal/mol since the hydrogen-receiving carbon atom is further away from the η^2-H_2 ligand in the starting dihydrogen complex (**37**). Once again, **40** is not a local minimum as the five ligands in the pseudo-pentagonal-bipyramidal structure are all sterically bulky. The situation is different from the PCP system. The PCP ligand is more flexible in terms of its coordination arrangement, and can stabilize an intermediate (see Figure 1) in which both the agostic H−C and the bonded alkyl group are *cis* to the hydrido ligand, allowing further reductive elimination.



Scheme 10

The results discussed above suggest that whether an dihydrogen(olefin) complex in which an H_2 ligand is *cis* to both carbon atoms of an olefinic group (structure **1** or **A**) would undergo hydrogen transfer or not, depends on the structures of the intermediates formed after the first hydrogen transfer. If a relatively stable intermediate, in which the hydrido and the bonded alkyl ligands are *cis* to each other, is formed, reductive elimination, which forms a bond between the hydrido and bonded alkyl ligands, becomes feasible. However, when the ligand environment does not allow such an intermediate to form, reductive elimination is not possible, therefore no hydrogenation reactions will proceed.

In a related study, Esteruelas et al. reported the protonation reactions of $[OsH_2(diolefin)(PiPr_3)_2]$ (diolefin = NBD: **41**; tetrafluorobenzobarrelene: **42**; and 1,3-hexadiene: **43**).[20] Protonation of **41** and **42** with HBF_4 does not lead to hydrogen-transfer products, but gives the trihydrido complexes **44** and **45**, respectively. Protonation of **43** with HBF_4 gives the cyclohexenyl complex **46** (Scheme 11).

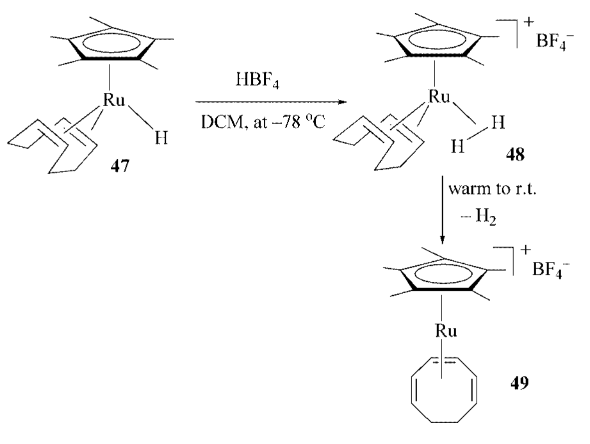


Scheme 11

Complexes with a fac Arrangement of the H_2 and Diolefin Ligands

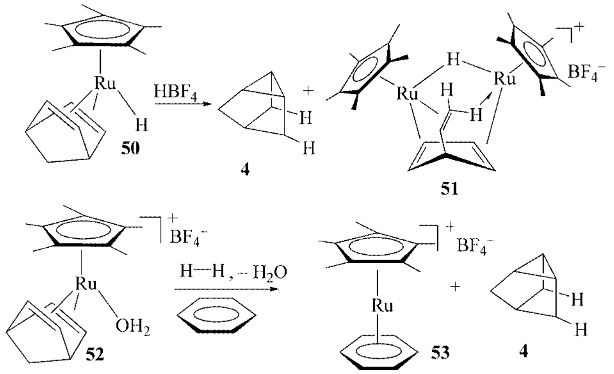
The reactions of dihydrogen(olefin) complexes with a structural feature related to structure **2** (or **B**) have previously been suggested for *fac*-$[M(H_2)(\eta^4\text{-NBD})(CO)_3]$ (M = Cr, Mo, W).[11]

The protonation reactions of [Cp*RuH(diolefin)] have been studied in order to further model reactions of dihydrogen(olefin) complexes with a structural feature related to structure **2** (or **B**).[21] Protonation of [Cp*RuH(COD)] (**47**) at −76 °C with HBF_4 produces the thermally unstable dihydrogen(olefin) complex $[Cp^*Ru(H_2)(COD)]BF_4$ (**48**), which was characterized by NMR spectroscopy at low temperature.[21] On warming up to room temperature, complex **48** undergoes a dehydrogenation reaction to give $[Cp^*Ru(\eta^6\text{-cyclooctatriene})]BF_4$ (**49**), rather than a hydrogenation reaction (Scheme 12). The successful characterization of **48** suggests that a dihydrogen complex can be obtained through protonation of [Cp*RuH(diolefin)].

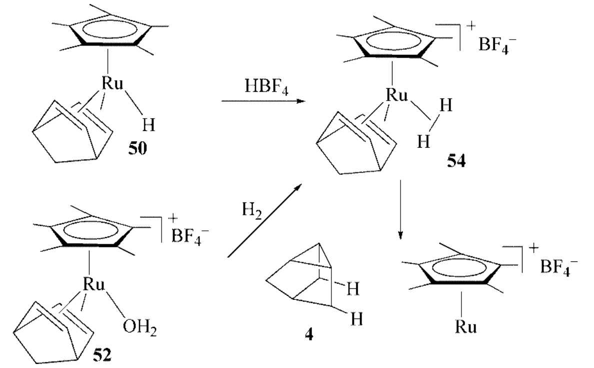


Scheme 12

Protonation of [Cp*RuH(NBD)] (**50**) in dichloromethane produces nortricyclene (**4**) and the dimetallic complex **51**.[21] Nortricyclene is also formed, along with the η^6-benzene complex **53**, when a benzene solution of [Cp*Ru(H_2O)(NBD)]BF_4 (**52**) is exposed to H_2 (Scheme 13).[22] Since the complex [Cp*Ru(H_2)(COD)]$^+$ contains a dihydrogen ligand, it was proposed that the reaction of [Cp*Ru(H_2O)(NBD)]BF_4 with H_2, or protonation of [Cp* RuH(NBD)], initially gives the dihydrogen complex [Cp* Ru(H_2)(NBD)]BF_4 (**54**), which undergoes a hydrogen-transfer reaction to give nortricyclene (**4**) and a [Cp*Ru]$^+$ fragment (Scheme 14). In dichloromethane, the [Cp*Ru]$^+$ fragment reacts with **50** to give the dimetallic complex **51**. In benzene solution, the [Cp*Ru]$^+$ fragment is trapped with benzene producing complex **53**.



Scheme 13



Scheme 14

The detailed reaction steps were examined by a computational study.[22] Complex [CpRu(H_2)(NBD)]$^+$ (**55**), a model complex of **54**, was calculated to be a typical dihydrogen complex with an H−H distance of 0.854 Å. Once again, a stepwise mechanism was found to be responsible for the hydrogen-transfer reaction of the model complex **55**, to give **57**. The computed energy profiles for the reactions are illustrated in Figure 2. In the hydrogen transfer reaction, the first hydrogen atom is transferred from the η^2-H_2 ligand to one of the olefinic carbon atoms, leading to the formation of the hydrido intermediate **56**, which contains an agostic interaction. The hydrogen transfer reaction occurs with an energy barrier of 5.5 kcal/mol. The first transition state **TS3** corresponds to a dihydrido species. The energy barrier for the first hydrogen-transfer step is much less than that of the PCP system described above. It is understandable that reductive elimination to give NBE could not proceed from intermediate **56** as the hydrido ligand and the alkyl carbon atom are separated by a C−H agostic ligand. On the other hand, the hydrido ligand can transfer to the other olefinic functionality with a very small energy barrier. The reactions of H_2 with NBD, to give nortricyclene, are both kinetically and energetically very favorable.

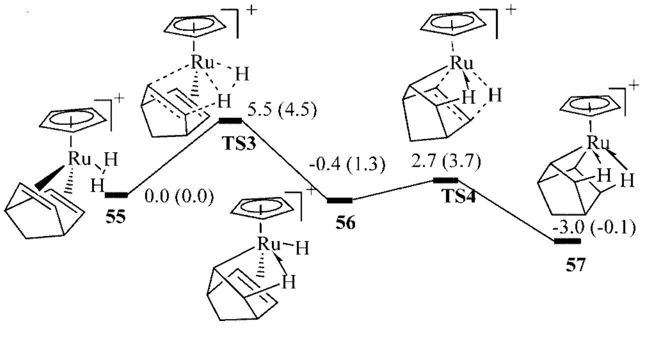
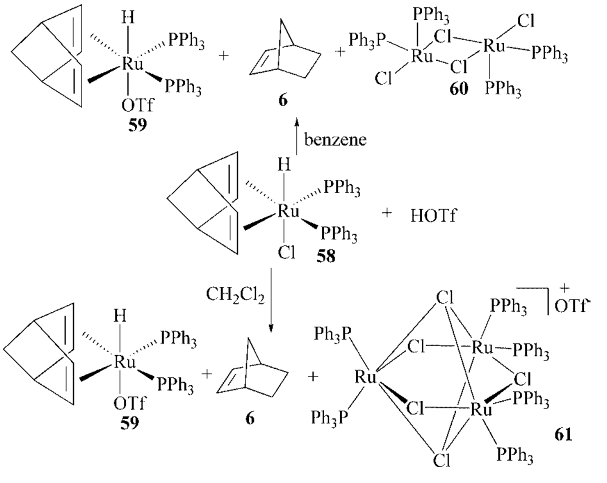


Figure 2. Schematic illustration of the reaction pathways of [CpRu(H_2)(NBD)]$^+$, with calculated relative free energies [kcal/mol] and reaction energies [kcal/mol] (in parentheses), modified from ref.[22]

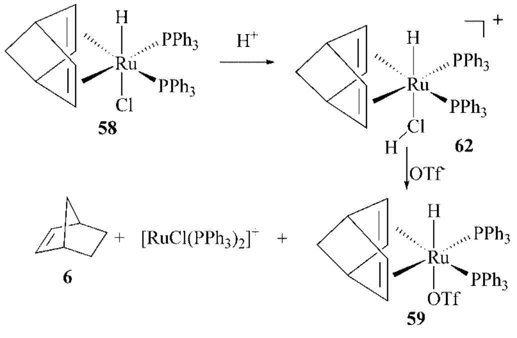
Reactions of dihydrogen(olefin) complexes with a structural feature related to **2** (or **B**) have also been studied through the protonation reactions of [RuH(Cl)(NBD)(PPh_3)$_2$].[23] Protonation of ruthenium complexes [RuH(X)L_4] {L_4 = (dppe)$_2$, X = Cl, Br;[24a,24b] L_4 = (dppp)$_2$, X = Cl;[24c] L_4 = (dcpe)$_2$, X = Cl;[24d] L_4 = (PPh_3)[2,6-(Ph_2PCH_2)$_2C_5H_3N$], X = Cl[25]} are known to give dihydrogen complexes of the type [M(X)(H_2)L_4]$^+$. Thus, it was expected that protonation of [MH(Cl)(NBD)(PPh_3)$_2$] could also produce the dihydrogen complex [MCl(H_2)(NBD)(PPh_3)$_2$]$^+$, which may undergo hydrogenation to produce nortricyclene, as in the case of *fac*-[M(H_2)(η^4-NBD)(CO)$_3$] (M = Cr, Mo, W)[11] and [Cp* Ru(H_2)(NBD)]$^+$.[21,22]

Interestingly, the expected hydrogenation product nortricyclene is not produced when [RuH(Cl)(NBD)(PPh_3)$_2$] (**58**) is protonated. Instead, protonation of **58** in C_6D_6 with a limiting amount of HOTf gives [RuH(OTf)(NBD)(PPh_3)$_2$] (**59**), norbornene (**6**) and [RuCl_2(PPh_3)$_2$]$_2$ (**60**) (Scheme 15). Protonation of **58** in dichloromethane with a limiting amount of HOTf gives [RuH(OTf)(NBD)(PPh_3)$_2$] (**59**), norbornene (**6**) and the unusual trimetallic complex [Ru_3Cl_5(PPh_3)$_6$]OTf (**61**). In these protonation reactions, the hydrido complex [RuH(OTf)(NBD)(PPh_3)$_2$] is presumably formed by protonation of the Cl ligand. The dimetallic complex [RuCl_2(PPh_3)$_2$]$_2$ (**60**) and the trimetallic complex [Ru_3Cl_5(PPh_3)$_6$]OTf (**61**) are presumably formed from the reaction of [RuCl(PPh_3)$_2$]$^+$ (generated whilst forming norbornene) with HCl {generated by protolysis of the chloride ligand of **58** to give [RuH(OTf)(NBD)(PPh_3)$_2$]}.



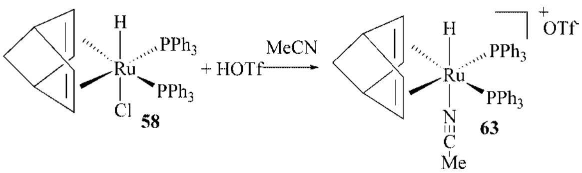
Scheme 15

In view of the fact that *fac*-[M(H_2)(η^4-NBD)(CO)$_3$] (M = Cr, Mo, W)[11] and [Cp*Ru(H_2)(NBD)]$^+$ [21,22] undergo hydrogen-transfer reactions to give nortricyclene, it was proposed that NBE may not be produced via the intermediate [RuCl(H_2)(NBD)(PPh$_3$)$_2$]$^+$. Instead, the formation of norbornene in the protonation reaction was thought to be related to the protonation of the chloro ligand (Scheme 16). Protonation of the chloro ligand could give the hydrogen chloride complex [RuH(HCl)(NBD)(PPh$_3$)$_2$]$^+$ (**62**), which can then undergo a hydrogen-transfer reaction to give NBE. A substitution reaction involving **62** would give [RuH(OTf)(NBD)(PPh$_3$)$_2$] (**59**). Protonation of halogeno ligands[26] has been observed during the protonation reactions of chloro(hydrido) complexes such as [PtHCl[P(tBu)$_2$Me]$_2$],[26] [OsH$_2$Cl$_2$(PiPr$_3$)$_2$],[27a] and [OsH$_2$Cl(NO)(PiPr$_3$)$_2$].[27b] Although well-characterized hydrogen halide complexes are still rare,[28] many alkyl halide complexes [M(XR)L$_n$][29] and halogeno complexes with an intra- or intermolecular MX···H interaction[30] have been reported.



Scheme 16

Protonation of the chloro ligand is supported by the following observations. [RuH(OTf)(NBD)(PPh$_3$)$_2$] was produced as one of the protonation products. In the presence of CH_3CN in C_6D_6 or CD_2Cl_2, [RuH(Cl)(NBD)(PPh$_3$)$_2$] (**58**) reacts rapidly with HOTf to give [RuH(CH_3CN)(NBD)(PPh$_3$)$_2$]OTf (**63**) as the only product [Equation (1)].



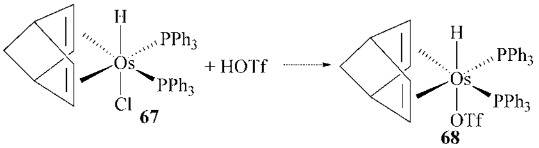
(1)

Involvement of the hydrogen chloride complex **62** in the formation of norbornene is consistent with the deuterium-labeling experiment, where protonation of [RuH(Cl)(NBD)(PPh$_3$)$_2$] with DOTf produced deuterated norbornene, in which the deuterium atom is at the *endo* position. This suggests that the deuterium atom is transferred to the olefin from the same side of the ruthenium center.

The feasibility of hydrogenation through the intermediate [RuH(HCl)(NBD)(PPh$_3$)$_2$]$^+$ was further supported by a computational study.[23] Calculations reveal that the model complex [RuH(HCl)(NBD)(PH$_3$)$_2$]$^+$ (**64**) is a reasonable species with a long Ru−Cl distance (2.838 Å) and that hydrogenation from the intermediate is both thermodynamically and kinetically favorable.

Figure 3 presents the energy profiles for the detailed reaction pathways starting from the hydrogen chloride complex **64** and the dihydrogen complex **64′**. The two starting complexes have comparable stability. The results from the calculation indicate that the reaction pathway starting from the hydrogen chloride complex **64** is both kinetically and thermodynamically more favorable than the pathway starting from the dihydrogen complex **64′**. The reaction pathway starting from the dihydrogen complex **64′** has to overcome two consecutive energy barriers, and gives the less stable precursor complex **66′** which leads to the formation of nortricyclene. One can conclude that the chloro ligand is indeed assisting the hydrogenation process by placing a hydrogen atom at a position proximal to the olefin ligand, through the HCl ligand. Clearly, the presence of the chloro ligand suppresses the formation of nortricyclene by the reaction starting from the dihydrogen complex.

In contrast to [RuH(Cl)(NBD)(PPh$_3$)$_2$], protonation of [OsH(Cl)(NBD)(PPh$_3$)$_2$] (**67**) with a limiting amount of HOTf in benzene or dichloromethane only produces [OsH(OTf)(NBD)(PPh$_3$)$_2$] (**68**) [Equation (2)]. Neither norbornene, nor nortricyclene, were observed in the protonation reactions. The different reactivities of the Os and Ru complexes has been attributed to the stronger metal−olefin interaction in the osmium complex and therefore, the Os−NBD bonds remain intact in the reactions.



(2)

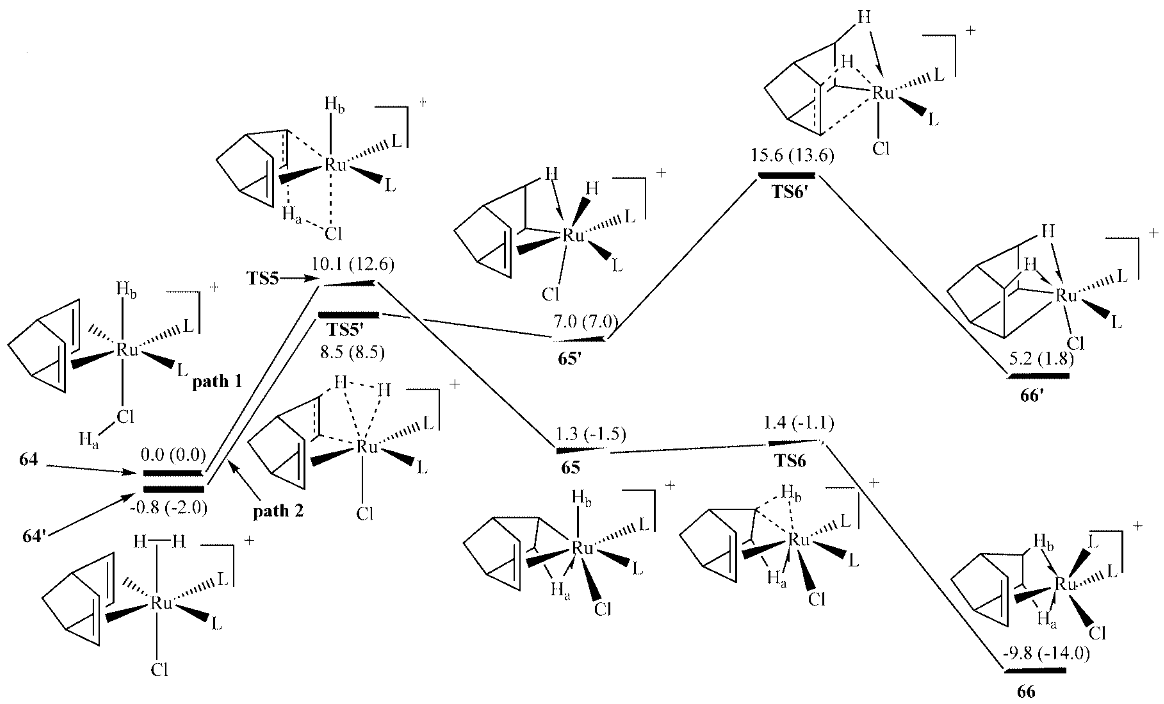
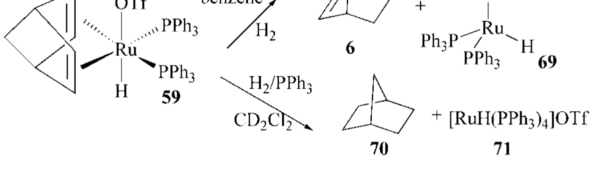


Figure 3. Schematic illustration of the reaction pathways of $[RuCl(H_2)(NBD)(PH_3)_2]^+$ and $[RuH(HCl)(NBD)(PH_3)_2]^+$, with calculated relative free energies [kcal/mol] and reaction energies [kcal/mol] (in parentheses), modified from ref.[23]

Dihydrogen(olefin) Complexes with an Additional Hydrido Functionality

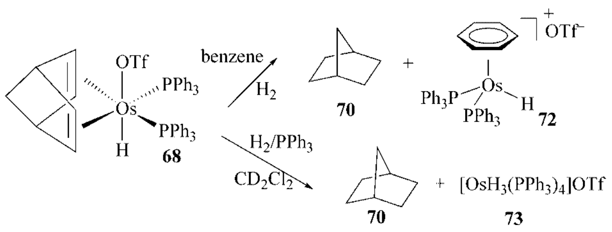
One might ask how the hydrogen transfer reaction will proceed in the presence of both H_2 and a hydrido ligand. Thus, the reactions of H_2 with $[MH(OTf)(NBD)(PPh_3)_2]$ (M = Ru, Os) have been carried out in order to answer the question.[31]

In benzene, complex $[RuH(OTf)(NBD)(PPh_3)_2]$ (**59**) reacts with H_2 to give norbornene (**6**) and the hydrido complex $[(\eta^6\text{-}C_6H_6)RuH(PPh_3)_2]OTf$ (**69**). In the presence of added PPh_3, complex **59** reacts with H_2 to give norbornane (**70**) and $[RuH(PPh_3)_4]OTf$ (**71**) (Scheme 17).



Scheme 17

The complex $[OsH(OTf)(NBD)(PPh_3)_2]$ (**68**) also reacts with H_2 in benzene to give norbornane (**70**) and the hydrido complex $[(\eta^6\text{-}C_6H_6)OsH(PPh_3)_2]OTf$ (**72**) (Scheme 18). In CD_2Cl_2 at room temperature, complex **68** reacts with H_2 in the presence of added PPh_3 to give norbornane and $[OsH_3(PPh_3)_4]^+$ (**73**).



Scheme 18

Since triflate is a weakly coordinating ligand that can readily be displaced under mild conditions,[32] and since a number of dihydrogen complexes of the type $[MH(H_2)(L_4)]^+$ (M = Ru, Os; L = phosphorus ligands) have previously been well characterized,[33] it was suggested that the first step of the reactions of $[MH(OTf)(NBD)(PPh_3)_2]$ with H_2 is to displace the triflate anion in $[MH(OTf)(NBD)(PPh_3)_2]$ with an H_2 molecule. This gives the dihydrogen complexes $[MH(H_2)(NBD)(PPh_3)_2]^+$ (M = Ru, Os), which lead to the hydrogenation of the NBD ligand. The norbornane is presumably formed by further hydrogenation of norbornene.

Density functional theory calculations[31] on the model complexes $[MH(H_2)(NBD)(PH_3)_2]^+$ (M = Ru, Os) confirm that complexes $[RuH(H_2)(NBD)(PH_3)_2]^+$ (**74**) and $[OsH(H_2)(NBD)(PH_3)_2]^+$ (**75**) are all typical dihydrogen complexes in which the nonclassical $\eta^2\text{-}H_2$ ligand is *trans* to the hydrido ligand and have short H−H distances of 0.793 and 0.831 Å, respectively. The related complex

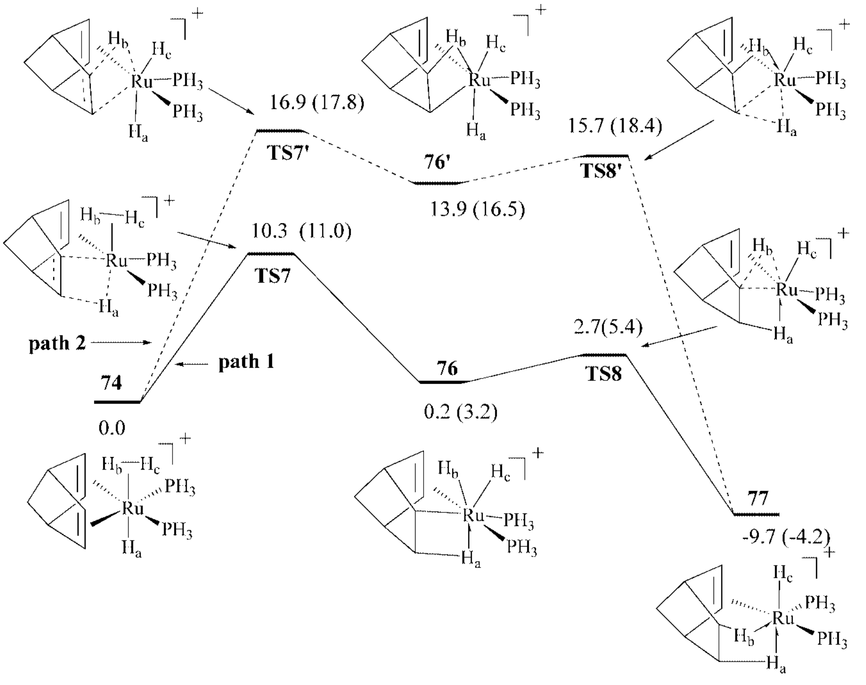


Figure 4. Schematic illustration of the reaction pathways of $[RuH(H_2)(NBD)(PH_3)_2]^+$, with calculated relative free energies [kcal/mol] and reaction energies [kcal/mol] (in parentheses), modified from ref.[31]

$[OsH_3(NBD)(PiPr_3)_2]^+$, where the two phosphane groups are *trans* to each other, is known to adopt a trihydrido structure.[20]

There are two possible routes for the hydrogenation of the NBD ligands in the dihydrogen complexes $[MH(H_2)(NBD)(PPh_3)_2]^+$ (M = Ru, Os): the NBD ligand can be hydrogenated by transfer of the first hydrogen atom either from the hydrido or the dihydrogen ligand to the olefin ligand, followed by transfer of the second hydrogen atom to give norbornene.

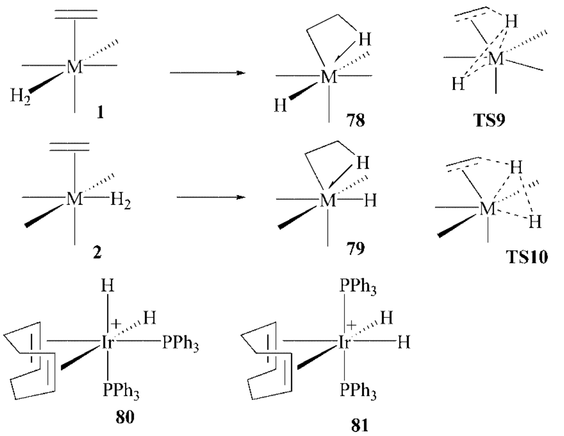
The computational study[31] shows that the hydrogen transfer reactions of $[MH(H_2)(NBD)(PPh_3)_2]^+$, i.e. the conversion of the model complex $[RuH(H_2)(NBD)(PH_3)_2]^+$ (**74**) to $[RuH(NBE)(PH_3)_2]^+$ (NBE = norbornene) (**77**), favors a pathway (Path 1 in Figure 4) starting with the hydrogen transfer from the hydrido ligand (H_a), followed by the cleavage of the dihydrogen ligand to form a *cis*-dihydrido intermediate **76**. The second hydrogen atom is then transferred from one (H_b) of the two hydrido ligands to complete the hydrogenation, giving the coordinated NBE complex **77**.

The overall lower activation energies of Path 1 compared with those of Path 2 have been related to the structures of the transition states **TS7** and **TS7′**.[31] The first transition state **TS7** of Path 1 is a nonclassical complex with a slightly longer H_b-H_c distance (0.841 Å). However, the first transition state **TS7′** of Path 2 has a much longer H_b-H_c distance (1.387 Å), and typical Ru−hydrido distances, notably Ru−H_a and Ru−H_c. The short Ru−H distances suggest that **TS7′** could be considered as a trihydrido species, with two hydrido ligands (H_a and H_c) *trans* (or nearly *trans*) to each other. This trihydrido structure, compared with that of **TS7**, has a relatively high energy because of the strong *trans* influence between H_a and H_c. The *trans* influence of a hydrido ligand weakens the metal−ligand interaction at the position *trans* to it, and thus destabilizes the system.[34]

Conclusion

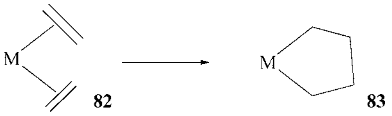
Dihydrogen(olefin) complexes have been proposed as active species in catalytic hydrogenation reactions. Hydrogen-transfer reactions of dihydrogen(olefin) complexes have been modeled with reactive dihydrogen(NBD) complexes, with different orientations of the olefin ligands relative to the H_2 ligand. They have also been studied by computational methods.

In the modeling reactions, the hydrogen transfer does not proceed through simultaneous transfer of the H_2 ligand to the olefin ligands, but through a stepwise pathway. Dihydrogen complexes in which the M−(H_2) bond is perpendicular to the olefin double bond (**1**) can transfer the first hydrogen atom of an H_2 ligand to an olefin ligand, to give an alkyl(hydrido) intermediate (**78**) in which the hydrido ligand is *cis* to an alkyl bond (Scheme 19). The intermediate can then transfer the second hydrogen atom to the substrate by reductive elimination, to form a bond between the hydrido and the bonded alkyl ligands, thus giving the normal hydrogenated products. Dihydrogen complexes in which the M−(H_2) bond is parallel to the olefin double bond (**2**) can transfer the first hydrogen atom of an H_2 ligand to an olefin ligand to give a alkyl(hydrido) intermediate (**79**) in which the hydrido ligand is separated from the alkyl bond by an agostic C−H bond. Reductive elimination from this intermediate is difficult as the hydrido ligand and the alkyl carbon atom are separated by the C−H agostic ligand. Instead, the hydrido ligand can transfer to other olefin ligands, if present, and lead to other products. The reaction energy barrier for the first hydrogen transfer for complexes with a structural feature related to **2** is found to be smaller than that for complexes with a feature of structure **1**. The situation is similar to the insertion reactions of **80** and **81**, where **80** undergoes insertion reactions 40 times faster.[35]



Scheme 19

In the first proton-transfer step, the dihydrido species in most cases of our studies were found to be transition states (rather than intermediates) in which one of the hydrido ligands has a weak interaction with the receiving carbon atom. In the transition state, the olefinic double bond is also lengthened relative to that in the starting complex. These transition states are denoted **TS9** and **TS10**. The first step of the hydrogen transfer reaction is similar to the oxidative coupling of olefins or acetylenes, as illustrated by Equation (3), for the conversion of **82** to **83**.[36] An interesting question can be asked as to whether other σ-ligands (e.g. C−H, Si−H, B−H) can undergo similar reactions with unsaturated substrates, such as olefins, acetylenes and ketones.



(3)

The presence of other ligands may affect the hydrogen-transfer reactions. For example, in the hydrogen-transfer reactions of $[MH(H_2)(NBD)(PPh_3)_2]^+$ (M = Ru, Os), the first hydrogen transfer from the hydrido ligand is preferred over that from the dihydrogen ligand; in the protonation of $[RuHCl(NBD)(PPh_3)_2]$, the dihydrogen complex $[MCl(H_2)(NBD)(PPh_3)_2]^+$ is not involved in the hydrogenation.

This article discussed the hydrogen-transfer reactions of dihydrogen(olefin) complexes in which the olefin ligands have a specific orientational preference. The study showed that intramolecular hydrogen transfer from dihydrogen to olefin ligands is feasible for dihydrogen(olefin) complexes in which the $M-H_2$ bond is perpendicular to the olefin double bond or parallel to the olefin double bond. It is expected that hydrogen-transfer reactions should also occur for complexes in which the olefin can rotate "freely", although further work is needed to confirm this.

Acknowledgments

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