FULL PAPERS

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Hydrogen/Deuterium Exchange Reactions of Olefins with Deuterium Oxide Mediated by the Carbonylchlorohydridotris(triphenylphosphine)ruthenium(II) Complex

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Abstract: The catalytic properties of several ruthenium, osmium and rhodium hydride complexes for hydrogen/deuterium (H/D) exchange between olefins and deuterium oxide (D₂O) were investigated. The most effective catalytic precursor was found to be the carbonylchlorohydridotris(triphenylphosphine)-ruthenium(II) complex. Through H/D exchange between metal hydride and D₂O, and reversible olefin insertion into an Ru–H(D) bond, protons attached

to olefinic carbons and alkyl chains of olefins can all undergo H/D exchange with D_2O . The catalytic reactions can be used to deuterate both terminal and internal olefins, for example, styrene, stilbene and cyclooctene.

Keywords: alkenes; hydrides; isotopes; osmium; ruthenium

Introduction

Deuterium labeled compounds are useful for a wide range of applications. For example, they can be used as deuterated solvents, regents for mechanistic studies, labeled drugs, and starting materials for deuterated polymers. As a result, there has been much interest in developing effective methodology to synthesize such compounds.^[1] Transition metal-catalyzed direct H/D exchange between organic compounds and appropriate deuterium sources, being a very attractive approach to deuterated compounds, has been actively explored by various researchers. In the past, many transition metal-catalyzed H/D exchange reactions of organic substrates with $D_2^{[2]}$ and deuterated organic solvents such as benzene, acetone and alcohols^[3] have been reported. Although D_2O is the cheapest source of deuterium, it has been less used previously in metal-catalyzed H/D exchange reactions. The situation, however, is changing, as several systems have been found in recent years to catalyze the H/D exchange between D₂O and organic substrates^[4-12] including aromatics, saturated hydrocarbons and alcohols.

This work concerns H/D exchange between olefins and D_2O . Deuteration of olefins is interesting, because many readily available compounds contain a C=C double bond and because olefins are useful starting materials for making other compounds. While several H/D exchange reactions involving olefins and deuterated organic solvents have been reported,^[13] it is surprising to note that much less work has been carried out on direct catalytic H/D exchange between olefins and D₂O, even compared with reactions involving saturated hydrocarbons and D₂O. The high temperature-dilute acid method has been explored in the 1980s for the H/D exchange between D₂O and olefins.^[14] However, the method suffers from side reactions of skeletal rearrangements, or polymerization and oligomerization of olefins.

There are only scattered reports of transition metal-mediated H/D exchange reactions between olefins and D_2O . In the area of heterogeneous catalysis, it has been reported that perdeuterated cyclic olefins such as cyclohexene and cyclooctene could be obtained by Pd/C-catalyzed H/D exchange with D_2O at elevated temperature $(>140 \,^{\circ}\text{C})$,^[15] or under hydro-thermal conditions $(250 \,^{\circ}\text{C/5 MPa})$.^[16] In the area of homogeneous catalysis, Fels et al. showed that α,β -unsaturated carboxylic acid derivatives can undergo H/ D exchange reactions at the β -position with D₂O in the presence of Ir(COD)(acac) (2 mmol%, 90 °C), presumably through cyclometallated intermediates.^[17] Matsubara et al. demonstrated that cyclic olefins such as cyclohexene and cyclodecene can undergo H/D exchange with D₂O under irradiation of microwaves in the presence of $RuCl_2(PPh_3)_3$ (5 mol%, 140°C, 0.34 MPa).^[18] Morrill et al. observed that partial deut-



eration of octene, cyclohexene, and styrene occurred when the substrates were treated with D₂O in the presence of RhCl₃/BH₃.^[19] Milstein et al. reported that the H/D exchange between D_2O and terminal olefins such as styrene and tert-butylethylene can be achieved with the cyclometallated rhodium complex $\{[(t-Bu)_2PCH_2C_6H_4]RhH(solv)_3\}^+$ (60 °C, 24 h, TON = 60 for styrene).^[20] Very recently, Grotjahn et al. described H/D exchange of D₂O and a series of olefins catalyzed by a [CpRu] complex.^[21] Despite the impressive progress, searching for catalytic systems that can efficiently catalyze the H/D exchange reactions of olefins with D₂O under mild conditions for a wide range of olefin substrates is still desirable. In this work, we wish to report that H/D exchange reactions between D₂O and olefins can be mediated by the airstable, readily available ruthenium hydride complex $RuHCl(CO)(PPh_3)_3$.

Results and Discussion

Selection of Catalysts

Previous studies on the chemistry of hydride and dihydrogen complexes have demonstrated that certain hydride complexes can undergo H/D exchange with $D_2O^{[22]}$ or deuterated alcohols^[23] to give deuteride complexes. In many cases, the H/D exchange reactions could proceed through dihydrogen complexes^[24] or dihydrogen-bonded species.^[25] Insertion of olefin into a metal-hydride bond and the reverse reaction (β-H elimination) are well known organometallic reactions.^[26] We thus envisioned that H/D exchange between olefins and D₂O could proceed through H/D exchange between a metal hydride and D₂O and reversible olefin insertion into an M-H(D) bond, as illustrated in Scheme 1.

As the first step to explore the possibility of using well defined hydride complexes as catalysts to mediate H/D exchange between olefins and D_2O , we have first studied the H/D exchange reactions of D₂O with

Scheme 1.

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metal hydride complexes such as RuHCl(CO)(PPh₃)₃ (1), $OsHCl(CO)(PPh_3)_3$ (2), $RuHCl(PPh_3)_3$ (3) and $RhH(CO)(PPh_3)_3$ (4). Previous studies have demonstrated that $RuHCl(CO)(PPh_3)_3$ (1) can undergo in-sertion reactions with alkynes,^[27,28] allenes^[29] and functionalized olefins such as 2-vinylipyridine, and allylic amines.^[30] Insertion reactions of $RuHCl(PPh_3)_3$ (3),^[31,32] OsHCl(CO)(PPh_3)_3 (2)^[33,34] and RhH(CO)- $(PPh_3)_3$ (4)^[35,36] with alkynes and allenes have also been reported. In view of the reported reactivity toward unsaturated substrates, one might expect that these hydride complexes may undergo reversible insertion reactions with olefins and are potential candidates for catalyzing H/D exchange between olefins and D₂O, if they can undergo H/D exchange reactions with D_2O .

It was found experimentally that ca. 63% of the hydride of $RuHCl(CO)(PPh_3)_3$ (1) was replaced with deuterium, after a mixture of 1 and D_2O in a molar ratio of 1:55 was heated at 100°C in THF for one hour [Eq. (1)]. Under similar conditions, ca. 41% of the hydride of $OsHCl(CO)(PPh_3)_3$ (2) was replaced with deuterium [Eq. (2)]. RuHCl(PPh₃)₃ (3) also undergoes an H/D exchange reaction with D_2O . In this case, incorporation of deuterium into both hydride and the phenyl group of PPh₃ occurred as determined by ²D NMR. Thus, the content of deuteration at the hydride site cannot be accurately determined. We have also carried out H/D exchange reactions between the hydride complex RhH(CO)(PPh₃)₃ (4) and D_2O . Unfortunately, the extent of H/D exchange could not be accurately determined because the complex partially decomposed to triphenylphosphine oxide and some unidentified species during the experiment.

The H/D exchange reactions of the six-coordinate 18e complexes MHCl(CO)(PPh₃)₃ (M = Ru, Os) probably involve dihydrogen (B) or dihydrogen bonded species (A or A') illustrated in [Eq. (3), as was proposed previously for other related systems.^[37] The hydride in RuHCl(PPh₃)₃ could be similarly deuterated.

The catalytic properties of the hydride complexes for H/D exchange between D₂O and olefins were then investigated using styrene as the model substrate. The results are summarized in Table 1. When a 0.5 M solution of styrene was heated at 100°C with D₂O (13.5 molar equiv.) in 2 mL dioxane for 1 h in the presence of RuHCl(CO)(PPh₃)₃ (3 mol%), the ¹H and ²D NMR data indicate that *ca*. 85% of the olefinic protons were replaced with deuterium while no deuteration occurred for the phenyl ring. The percentage of deuterium incorporated into the styrene is essentially equal to the statistical percentage of deuterium on O of the heavy water and the vinyl carbons of styrene, indicating that complete scrambling of deuterium and hydrogen on O and vinyl C sites has been attained (entry 1, Table 1). Styrene with over 95% deu-







Table 1. Selection of catalysts for H/D exchange reactions of olefins with $D_2 O^{[a]}$

	H H H + D ₂ O -	catalyst	\rightarrow	
Entry	Catalyst	$%D_{\text{theo.}}$	Time [h]	%D _{exp.}
1	RuHCl(CO)(PPh ₃) ₃ (1)	90.0	1	85% D 84%
2	RuHCl(dppe) ₂	89.9	4 .5	14% D 11% D 10%
3	RuHCl(PPh ₃) ₃ (3)	90.1	4.5	9% D 4% D D 9%
4	OsHCl(CO)(PPh ₃) ₃ (2)	89.9	1	12% D 12% D 11%
5	OsHCl(CO)(PPh ₃) ₃ (2)	90.6	4.5	87% D 87% D 0 D 86%
6	RhH(CO)(PPh ₃) ₃ (4)	90.3	4.5	11% D 12% D 13%

^[a] The H/D exchange reaction between styrene (1 mmol) and D_2O (99.9%) (13.56 mmol) was carried out in dioxane (2 mL) under N_2 at 100 °C in a Schlenk tube with 3 mol% of catalyst. % $D_{\text{theo.}}$ is the statistical percentage of D when we consider the hydrogen atoms associated with water and the vinyl group of styrene and the hydride of the catalyst. % $D_{\text{exp.}}$ is percentage of D determined experimentally. terium incorporation can be obtained if the exchange reaction was repeated twice.

The hydride complex $OsHCl(CO)(PPh_3)_3$ (2) was also found to be active for the reaction, but the catalytic reaction proceeds much more slowly (entries 4 and 5). RuHCl(dppe)₂ (entry 2), RuHCl(PPh₃)₃ (3) (entry 3) and $RhH(CO)(PPh_3)_3$ (4) (entry 6) are rather inactive. The poorer activity of RuHCl(PPh₃)₃ (3) and $RhH(CO)(PPh_3)_3$ (4) could be related to their side reactions during H/D exchange reactions with D_2O . In the case of 3, the aryl groups of the phosphine ligands also undergo the H/D exchange. For 4, decomposition of the complex was observed. Further study showed that $RuHCl(CO)(PPh_3)_3$ (1) is very efficient for the catalytic reaction and the reaction can be accomplished even with 0.1 mol% of the catalyst. The H/D reaction can be carried out in other solvents such as dichloromethane, chloroform and THF.

Substrate Scope of the Catalytic Reactions

As shown in Table 2, RuHCl(CO)(PPh₃)₃ can also effectively mediate the H/D exchange between D_2O and other terminal olefins that do not have a strong coordinating group. With 3 mol% of the catalyst, almost complete scrambling of deuterium and hydrogen on O and vinyl C sites is accomplished in 3.5 h. However, the reaction involving 4-vinylpyridene gives an unsatisfactory result, likely due to the competing coordination of pyridine (entry 6).

The ruthenium complex **1** can also mediate the H/ D exchange between internal alkenes and D₂O. Thus, after a mixture of *trans*-stilbene and D₂O in 1:9 molar ratio was heated in the presence of 3 mol% of catalyst **1** at 100 °C for 4.5 h, *ca.* 82.5% of the vinyl protons were replaced with deuterium (theoretically, 90% of

Table 2. H/D	exchange	reactions	of	terminal	alkenes	with
D ₂ O. ^[a]						

Entry	Sub/D ₂ O/cat	%D _{theo.}	Time [h]	%D _{exp.}
1	1:13.52:0.03	90.00	3.5	$\begin{array}{c} & & & & & & & & \\ & & & & & & & \\ & & & & & & & \\ & & & & & & & \\ & & & & & & & \\ & & & & & & & \\ & & & & & & & \\ & & & & & & & \\ & & & & & & & \\ & & & & & & & \\ & & & & & & & \\ & & & & & & & \\ & & & & & & & \\ & & & & & & & \\ & & & & & & & \\ & & & & & & & \\ & & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & & \\$
2	1:18.0:0.03	90.00	3.5	$\begin{array}{c} & 85\% \\ & & \\ & & \\ DO \end{array} \begin{array}{c} & & & \\ & &$
3	1:13.52:0.03	90.01	3.5	88% D _c D _a 89%
4	1:13.50:0.03	90.00	3	89.6% D 89.6% EtO_Si D 89.6% EtO_OEt
5	1:13.59:0.03	90.05	19	$\begin{array}{c} 90\% \\ D_{a} \\ 85\% \\ D_{c} \\ D_{c} \\ D_{b} \\ 85\% \end{array} O CH_{3} \\ O CH_{2} \\ D_{b} \\ 85\% \\ \end{array}$
6	1:13.56:0.029	90.03	69	$N \xrightarrow{25\% D_b} D_c 34\%$

^[a] The reaction was carried out with 3 mol% of RuHCl(CO)(PPh₃)₃ in dioxane (2 mL) under N₂ at 100 °C in a Schlenk tube. $D_{\text{theo.}}$ is the statistical percentage of D when we consider the hydrogen atoms associated with water and the vinyl group of styrene and the hydride of the catalyst. $D_{\text{exp.}}$ is percentage of D determined experimentally. For entries 4 and 5, the reactions were carried out in THF-*d* in an NMR tube.

the vinyl protons could be replaced with deuterium). When *cis*-stilbene was subjected to the same reaction conditions, deuterated *trans*-stilbene in which 82% of the vinyl protons were replaced with deuterium was obtained, a result derived from isomerization as well as H/D exchange (Scheme 2).

We have also studied H/D exchange reactions of olefins having alkyl substituents. Heating a mixture of the internal olefin (*Z*)-PhCH=CHCH₃ and D_2O in a molar ratio of 1:22 in the presence of **1** resulted in incorporation of deuterium into both the vinyl and methyl positions. The vinyl protons undergo H/D ex-





change at a faster rate than the methyl protons. Thus, in 1.5 h, H/D exchange mainly occurred for the vinyl protons and *ca.* 88%, 87%, and 31.6% D were found at the carbons of Ph*C*, *C*Me and *Me*, respectively. After the mixture had been heated for 10 h, *ca.* 88%, 87% and 77.3% D (theoretically, 89.9% of the vinyl and methyl protons could be replaced with deuterium) were found at the carbons of Ph*C*, *C*Me and *Me*, respectively [Eq. (4)].

We have tested the catalytic reaction using ethylbenzene as the substrate. Under similar reaction conditions, ethylbenzene does not undergo the H/D exchange, indicating that the olefinic moiety is necessary.

Incorporation of deuterium in the vinyl positions is expected to proceed through the general mechanism shown in Scheme 1. The incorporation of deuterium in the methyl group of PhCH=CHMe could occur by two possible pathways. The first possibility involves isomerization of PhCH=CHMe to PhCH₂CH=CH₂, then H/D exchange with D_2O for the olefinic protons, and finally isomerization again as illustrated in Scheme 3. The interconversion of PhCH=CHMe and PhCH₂CH=CH₂ under the catalytic conditions is consistent with the fact that PhCD=CDCD₃ was also obtained in the deuteration experiment starting from PhCH₂CH=CH₂. A control experiment shows that PhCH₂CH=CH₂ is completely converted to PhCH= CHMe when it was heated for 2.25 h in the presence of ca. 3 mol% of 1. Since PhCH=CHMe is more stable than PhCH₂CH=CH₂, it is not surprising that the vinyl protons undergo H/D exchange at a faster rate than those of the methyl group.

Another possibility is that the deuterium is incorporated into the methyl group of PhCH=CHMe by a 1,2-deuterium shift as illustrated in Scheme 4 for the conversion of PhCH=CDCH₃ to PhCH=CHCH₂D.



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Scheme 3.



Scheme 4.

The conversion occurs through a series of olefin insertion and β -hydrogen elimination.

To demonstrate that the 1,2-deuterium shift mechanism is indeed possible, we have prepared partially deuterated β -methylstyrene by heating a mixture of β -methylstyrene and D₂O in the presence of **1** for a short period of time (50 min). The sample of the partially deuterated β -methylstyrene contains *ca*. 86% and 19.7% deuterium at the vinyl and methyl positions, respectively. After the sample of the partially deuterated β -methyl styrene had been heated at 100 °C in dioxane in the presence of catalyst 1 for 2 h, redistribution of deuterium among the vinyl and methyl group was observed, giving β -methylstyrene with the percentages of deuteration at vinyl and methyl group of 45%, 46% and 44.3%, respectively [Eq. (5)].^[38] The results suggest that the 1,2-deuterium shift mechanism shown in Scheme 4 can cause the deuteration of the methyl group in β -methylstyrene.



In a further experiment to demonstrate that protons of the alkyl carbon chain linked to a double bond can undergo H/D exchange with D₂O, we have studied H/D exchange reactions of PhCH= CHCH₂CH₃.^[39] It was found that complete deuteration of the double bond as well as the side-chain can also be achieved after a mixture of PhCH= CHCH₂CH₃ and D₂O was heated in the presence of 3 mol% of **1** for 10 h (Scheme 5).

As expected, the ruthenium hydride complex also catalyzed the H/D exchange between cyclooctene and D_2O to give per-deuterated cyclooctene. *In-situ* monitoring by NMR suggests that the H/D exchange rates of the protons of vinyl group and the alkyl chain are similar. When 1-hexene was used as the substrate, the H/D exchange also occurred. Unfortunately, a complicated mixture was produced due to the shift of the double bond.

We have also investigated ruthenium-catalyzed H/ D exchange reactions of the trisubstituted olefin *trans*- α -methylstilbene (PhCMe=CHPh). After a mixture of *trans*- α -methylstilbene and D₂O in the presence of 3 mol% of **1** had been heated for 18 h, no H/ D exchange was observed. The lack of H/D exchange between D₂O and PhCMe=CHPh could be a result related to the fact that the substrate does not undergo insertion readily.

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Scheme 5.

Conclusions

In summary, we have found that the readily available hydride complex RuHCl(CO)(PPh₃)₃ can effectively catalyze H/D exchange reactions of D₂O with both terminal and internal alkenes. Through H/D exchange between metal hydride and D₂O, and reversible olefin insertion into a Ru–D(H) bond, protons attached to olefinic carbons and the alkyl chains of olefins can undergo H/D exchange with D₂O. The catalytic reactions can be used to deuterate both terminal and internal olefins, for example, styrene, stilbene and cyclooctene.

Experimental Section

All manipulations were carried out at room temperature under a nitrogen atmosphere using standard Schlenck techniques unless otherwise stated. Solvents were distilled under nitrogen from sodium benzophenone (hexane, ether, THF), sodium (benzene), or calcium hydride (CH₂Cl₂). RhH(CO)- $(PPh_3)_{3,}^{[40]}$ RuHCl(CO) $(PPh_3)_{3,}^{[41]}$ RuHCl $(PPh_3)_{3,}^{[42]}$ and OsHCl(CO)(PPh₃)₃^[43] were synthesized according to reported procedures. 1,4-Dioxane was purged with nitrogen for 10 min before use. Deuterium oxide, 99.9 atom% D, was purchased from Aldrich Chemical Co. and used as received. All other reagents were used as purchased from Aldrich Chemical Co., Acros Organics, International Laboratory USA, or Kodak. ¹H and ¹³C{¹H} NMR spectra were collected on a Bruker ARX 300 MHz spectrometer or a Bruker AV 400 MHz spectrometer. ²D NMR spectra were collected on a Bruker AV 400 MHz spectrometer.

Synthesis of (E)/(Z)-1-Phenylbut-1-ene^[44]

To a THF solution (5 mL) of propyltriphenylphosphonium bromide (2.17 g, 5.63 mmol) cooled at 0 °C by an ice-bath was slowly added a hexane solution of *tert*-butyllithium (1.6M, 3.6 mL, 5.76 mmol). The orange mixture was stirred at room temperature for 1 h. Then benzaldehyde (0.80 mL, 7.84 mmol) was added to the mixture to give a pale-yellow solution with some white precipitate. The reaction mixture

was heated at 78 °C overnight. Water (15 mL) and diethyl ether (15 mL) were added. The organic layer was separated and the aqueous layer was further extracted with diethyl ether (2×15 mL). The combined organic extract was washed with a sodium metabisulfite solution and brine solution and dried over MgSO₄. The crude product was purified by column chromatography using *n*-pentane as the eluent; Yield: 0.514 g (69.1%). The NMR data suggest that the product is a mixture of (*Z*)-PhCH=CHEt and (*E*)-PhCH=CHEt in a ratio of 1:1.14 (based on integration of CH₂ proton signals in the ¹H NMR spectrum).

Isomerization of (E)/(Z)-1-Phenylbut-1-ene to (E)-1-Phenylbut-1-ene



mixture of (E)/(Z)-1-phenylbut-1-ene (0.435 g, 3.29 mmol) prepared above and the ruthenium catalyst RuHCl(CO)(PPh₃)₃ (97 mg, 0.102 mmol, 3.09 mol%) in THF (1 mL) was heated at 100°C for 45 min. The solvent was removed under vacuum and the crude product was purified by column chromatography on silica gel using n-pentane as the eluent; yield: 0.381 g (87.6%). The ¹H NMR of the product indicates that it is mainly (E)-1-phenylbut-1-ene [(E)-PhCH=CHEt, I (87.7%)] together with (Z)-1-phenylbut-1-ene [(Z)-PhCH=CHEt, I' (4.4%)], (E)-PhCH₂CH= CHMe, II (6.1%) and (Z)-PhCH₂CH=CHMe, II' (1.8%). ¹H NMR (400 MHz, CDCl₃, 25 °C): $\delta = 7.36-7.17$ (m, 5.5 H, Ph of **I**, **I**', **II**, **II**'), 6.38 (d, *J*=15.6 Hz, 1 H, Ph-C*H*=CH of **I**), 6.31–6.23 (dt, J = 15.6, 6.4 Hz, 1 H, CH=CH) 5.59–5.54 (m, 0.24 H, CH=CH of I', II, II'), 3.41 (d, J=5.2 Hz, 0.04 H, PhCH₂ of II'), 3.32 (d, J=6.4 Hz, 0.14 H, PhCH₂ of II), 2.39-2.31 (m, 0.1 H, =CH-CH₂-CH₃ of I'), 2.27-2.20 (m, 2 H, $=CHCH_2CH_3$ of I), 1.72 (d, J=4.8 Hz, 0.06 H, $=CHCH_3$ of **II'**), 1.68 (d, J = 6 Hz, 0.21 H, =CHCH₃ of **II**), 1.11–1.07 (t, J = 7.6 Hz, 3H, CH₂CH₃ of I). The signal of the CH₃ group of **I'** is merged with that of the CH_3 of **I**.

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Isomerization of Allylbenzene

A mixture of allylbenzene (45 µL, 0.366 mmol) and RuHCl(CO)(PPh₃)₃ (105 mg, 0.011 mmol, 3.01 mol%), water (150 µL) in degassed dioxane (3 mL) was heated at 100 °C for 2.25 h. The product was extracted by diethyl ether and dried over MgSO₄. The crude product was then purified by column chromatography using *n*-pentane as the eluent; yield: 19 mg (43%). The ¹H NMR of the product is identical to that of (*E*)-PhCH=CHMe. ¹H NMR (300 MHz, CDCl₃, 25 °C): δ =7.36–7.19 (m, 5H, Ph), 6.43 (dd, *J*=16, 1.2 Hz, 1H, PhCH=), 6.29–6.24 (dq, *J*=15.6, 6.4 Hz, 1H, =CH-Me), 1.92–1.90 (dd, *J*=6.4, 1.6 Hz, 3H, =CHMe).

General Procedure of H/D Exchange Reactions between Metal Hydride Complexes and D₂O

A THF solution (2 mL) containing a metal complex (0.10 mmol) and D₂O (100 µL, 5.6 mmol) in a stoppered Schlenck tube was stirred and heated by an oil bath at 100 °C for 1 h. The solvents were removed under vacuum, the residue was washed with hexane (3 mL) and diethylether (2 mL×2), then dried under vacuum to give the product.

RuDCl(CO)(PPh₃)₃: RuHCl(CO)(PPh₃)₃ (95 mg, 0.10 mmol), D₂O (0.10 mL, 5.6 mmol); yield: 79 mg (83%); white solid. ¹H NMR (400 MHz, CD₂Cl₂, 298 K): $\delta = -7.24$ (br d, J = 82.8 Hz, 0.37 H, RuH), 7.06–7.32 (m, 45 H, Ph); ³¹P{¹H} NMR (161.9 MHz, CD₂Cl₂, 298 K): $\delta = 12.16$ (br s), 39.22 (br s); ²D NMR (61.42 MHz, CD₂Cl₂, 298 K): $\delta = -7.37$ (br).

OsDCI(**CO**)(**PPh**₃)₃: OsHCl(CO)(PPh₃)₃ (104 mg, 0.10 mmol), D₂O (0.10 mL, 5.6 mmol); yield: 96 mg (92%); white solid. ¹H NMR (300 MHz, CD₂Cl₂, 298 K): $\delta = -6.93$ (dt, J = 86.8, 24.4 Hz, 0.59 H, OsH), 7.02–7.31 (m, 45 H, Ph); ³¹P{¹H} NMR (161.9 MHz, CD₂Cl₂, 298 K): $\delta = 7.12$ (d, J = 11.9 Hz), -9.92 (t, J = 11.9 Hz); ²D NMR (61.42 MHz, CD₂Cl₂, 298 K): $\delta = -7.05$ (br).

RuDCl(PPh₃)₃: RuHCl(PPh₃)₃ (95 mg, 0.10 mmol), D₂O (0.10 mL, 5.6 mmol); yield: 72 mg (78%); purple solid. ¹H NMR (300 MHz, CD₂Cl₂, 298 K): $\delta = -18.23$ (q, J = 26.4 Hz, 0.8 H, RuH), 6.99–7.22 (m, 45 H, Ph); ³¹P[¹H] NMR (161.9 MHz, CD₂Cl₂, 298 K): $\delta = 57.33$ (br); ²D NMR (61.42 MHz, CD₂Cl₂, 298 K): $\delta = -18.11$ (br, 1D), 7.24 (br, 23 D), 7.69 (br, 7 D).

General Procedure for Screen Test of Metal Complexes for Catalytic H/D Exchange Peactions between Styrene and D₂O

A mixture of a catalyst (0.03 mmol), styrene (115 μ L, 1.00 mmol) and D₂O (242.5 μ L, 13.56 mmol) in dioxane (2 mL) in a stoppered Schlenck tube was stirred and heated by an oil bath at 100 °C for a given period of time. The reaction mixture was extracted with diethyl ether. The combined organic extract was washed with water and a brine solution and dried over MgSO₄. The crude product was purified by column chromatography on silica gel using *n*-pentane as the eluent. The product was characterized by ¹H and ²D NMR.

General Procedure of RuHCl(CO)(PPh₃)₃-Catalyzed H/D Exchange Reactions between Terminal Olefins and D_2O

A mixture of RuHCl(CO)(PPh₃)₃, olefin and D₂O in dioxane (2 mL) in a stoppered Schlenck tube was stirred and heated by an oil bath at 100 °C for a given period of time. The reaction mixture was cooled to room temperature and then extracted with diethyl ether. The combined organic extract was washed with water and a brine solution and dried over MgSO₄. The crude product was purified by column chromatography on silica gel using *n*-pentane as the eleunt.

Deuteration of Styrene



Styrene (115 μL, 1.00 mmol), RuHCl(CO)(PPh₃)₃ (280 mg, 29.4 μmol, 2.94 mol%), D₂O (242 μL, 13.5 mmol); reaction time: 1 h; yield: 81.3 mg (75.9%). Theoretical percentage of deuteration at the vinyl position=90.0%. ¹H NMR (400 MHz, CDCl₃, 25°C): δ =7.42–7.26 (m, 5H, Ph), 6.71 (m, 0.15H, Ph-CH_a=), 5.74 (m, 0.16H, =CH_b), 5.23 (m, 0.16H, =CH_c); ²D NMR (61.4 MHz, dichloromethane + CDCl₃, 25°C): δ =6.63 (s, D_a), 5.66 (s, D_b), 5.15 (s, D_c).

Deuteration of *p***-Methoxystyrene**



p-Methoxystyrene (97%, 66.5 μL, 0.485 mmol), RuHCl(CO)(PPh₃)₃ (14.5 mg, 15.2 μmol, 3.13 mol%); D₂O (121 μL, 6.77 mmol), dioxane (1 mL); reaction time: 3.5 h; yield: 50 mg (73%). Theoretical percentage of deuteration at the vinyl position = 90.3%. ¹H NMR (400 MHz, acetone d_6 , 25°C): δ = 7.53 (d, J = 8.8 Hz, 2H), 7.04 (d, J = 8.8 Hz, 2H), 6.81 (br, 0.16H, CH_a =), 5.76 (br, 0.16H, = CH_b), 5.21 (br, 0.16H, = CH_c), 3.93 (s, 3H, OCH₃); ²D NMR (61.4 MHz, acetone+acetone- d_6 , 25°C): δ = 6.83 (s, D_a), 5.78 (s, D_b), 5.23 (s, D_c).

Deuteration of 4-Vinylpyridine



4-Vinylpyridine (108 µL, 1.00 mmol), RuHCl(CO)(PPh₃)₃ (28.0 mg; 29.4 µmol, 2.91 mol%), D₂O (242.5 µL, 13.57 mmol); reaction time: 69 h; yield: 64 mg (59%). Theoretical percentage of deuteration at the vinyl position = 90.1%. ¹H NMR (400 MHz, CDCl₃, 25 °C): δ = 8.55 (d, *J* = 4.4 Hz, 2 H, Py), 7.27 (d, *J* = 5.6 Hz, 2 H, Py), 6.65 (m, 0.70 H, CH_a=), 5.95 (m, 0.75 H, =CH_b), 5.46 (m, 0.66 H,

= CH_c); ²D NMR (61.2 MHz, dichloromethane + CDCl₃, 25°C): $\delta = 6.61$ (s, D^a), 5.93 (s, D_b), 5.44 (s, D_c).

Deuteration of 2-Vinylnaphthalene



2-Vinylnaphthalene (98%, 78.8 mg, 0.500 mmol), RuHCl(CO)(PPh₃)₃ (14.4 mg, 15.1 µmol, 3.02 mol%); D₂O (121 µL, 6.77 mmol); reaction time: 3.5 h; yield: 61 mg (77.6%). Theoretical percentage of deuteration at the vinyl position = 90.0%. ¹H NMR (400 MHz, acetone- d_6 , 25 °C): δ =8.01 (m, 4H, naph), 7.87 (m, 1H, naph), 7.62 (m, 2H, naph), 7.09 (br s, 0.11 H, CH_a =), 6.09 (m, 0.12 H, CH_c), 5.46 (m, 0.12 H, =CH_b); ²D NMR (61.4 MHz, acetone + acetoned, 25 °C): δ =7.09 (s, D_a), 6.10 (s, D_c), 5.48 (s, D_b).

Deuteration of Triethoxyvinylsilane

The reaction was performed in an NMR tube. Triethoxyvinylsilane (97%, 55.5 µL 0.254 mmol), RuHCl(CO)(PPh₃)₃ (7.3 mg, 7.66 µmol, 3.02 mol%), D₂O (61.5 µL, 3.44 mmol); THF-*d* (0.3 mL); reaction time: 3 h. Theoretical percentage of deuteration at the vinyl position = 90.0%. ¹H NMR (300 MHz, THF-*d*, 25°C): δ = 6.01 (br, 0.31 H, *CH*=*CH*₂), 3.67–3.61 (q, *J*=7.02 Hz, 6H, OCH₂CH₃), 1.24–1.19 (t, *J*=7.02 Hz, 9H, OCH₂CH₃); ²D NMR (61.4 MHz, THF-*d*, 25°C): δ = 5.89 (br).

Deuteration of Ethyl Acrylate

The reaction was performed in an NMR tube. Ethyl acrylate (99%, 25 µL, 0.228 mmol), RuHCl(CO)(PPh₃)₃ (6.6 mg, 6.93 µmol, 3.04 mol%), D₂O (55.5 µL, 3.11 mmol), THF-*d* (0.3 mL); reaction time: 16.5 h. Theoretical percentage of deuteration at the vinyl position=90.1%. ¹H NMR (400 MHz, THF-*d*, 25 °C): δ =6.39 (br, 0.15 H, =CH_b), 6.17 (br, 0.1H, CH_a=), 5.91 (br, 0.15 H, =CH_c), 4.23 (q, J= 7.2 Hz, 2H, OCH₂CH₃), 1.32 (t, J=7.2 Hz, 3H, CH₂CH₃); ²D NMR (61.4 MHz, THF-*d*, 25 °C): δ =6.24 (s, D_b), 6.03 (s, D_a), 5.77 (s, D_c).

Deuteration of trans-Stilbene

trans-Stilbene (180 mg, 0.998 mmol), RuHCl(CO)(PPh₃)₃ (29.0 mg, 30.4 μ mol, 3.05 mol%), D₂O (161 μ L, 9.01 mmol); reaction time: 4.5 h; yield: 154 mg (84.5%). Theoretical percentage of deuteration at the vinyl position=90.1%.



¹H NMR (400 MHz, CDCl₃, 25 °C): δ =7.53-7.52 (m, 4H, Ph), 7.39-7.35 (m, 4H, Ph), 7.29-7.25 (m, 2H, Ph), 7.11 (br, s, 0.35H, CH=CH); ²D NMR (61.2 MHz, acetone-*d*₆, 25 °C): δ =7.33 (br, s, CD=CD).

Deuteration of cis-Stilbene



cis-Stilbene (97%, 184 µL, 1.00 mmol), RuHCl(CO)(PPh₃)₃ (28.6 mg; 30.0 µmol, 3 mol%), D₂O (161 µL, 9.01 mmol); reaction time: 4.5 h; yield: 134 mg (73.5%). *cis*-Stilbene was isomerized to *trans*- stilbene in the reaction. Theoretical percentage of deuteration at the vinyl position=90.0%. ¹H NMR (400 MHz, CDCl₃, 25°C): δ =7.54–7.51 (m, 4H, Ph), 7.4–7.34 (m, 4H, Ph), 7.27–7.25 (m, 2H, Ph), 7.11 (br s, 0.36H, *CH*=*CH*); ²D NMR (61.2 MHz, acetone-*d*₆, 25°C): δ =7.33 (br s, CD=CD).

Deuteration of *trans*-β-Methylstyrene



trans-β-Methylstyrene (130 μL, 1.00 mmol), RuHCl(CO)-(PPh₃)₃ (29.0 mg, 30.4 μmol, 3.04 mol%), D₂O (402 μL, 22.5 mmol); reaction time: 10 h; yield: 98 mg (81.5%). Theoretical percentage of deuteration at the vinyl and alkyl position = 90.0%. ¹H NMR (300 MHz, CDCl₃, 25 °C): δ = 7.39– 7.30 (m, 4H, Ph), 7.25–7.19 (m, 1H, Ph), 6.44 (br, 0.126 H, PhCH_a), 6.26 (br, 0.12 H, =*CH*_b), 1.88 (br, 0.404 H, CHD₂); ²D NMR (61.2 MHz, dichloromethane + CDCl₃, 25 °C): δ = 6.38 (s, 1 D, D_a), 6.23 (s, 1 D, D_b), 1.79 (s, 2.99 D, CD₃).

Deuteration of β-Ethylstyrene



β-Ethylstyrene (133 mg, 1.01 mmol), RuHCl(CO)(PPh₃)₃ (28 mg, 29.39 µmol, 2.91 mol%), D₂O (563 µL, 31.5 mmol); reaction time: 10 h; yield: 116 mg (83.3%). Theoretical percentage of deuteration at the vinyl and alkyl positions= 90.0%. ¹H NMR (400 MHz, acetone-*d*, 25 °C): δ = 7.34–7.19 (m, 5H, Ph), 6.38 (br, 0.125 H, PhCH_a=), 6.31 (br, 0.125 H, =CH_b), 2.16 [br, 0.24 H, CH(D)], 1.01 (br, 0.4 H, CHD₂); ²D NMR (61.2 MHz, acetone+CDCl₃, 25 °C): δ = 6.25 (br, 2D, D_a and D_b), 2.23 (br, 2D, CD₂), 0.97 (br, 3D, CD₃).

Deuteration of 4-Vinylbenzoic Acid



4-Vinylbenzoic acid (97%, 76.4 mg, 0.500 mmol), RuHCl(CO)(PPh₃)₃ (14.4 mg, 15.1 µmol, 3.02 mol%), D₂O (161 μ L, 9.01 mmol), dioxane (1 mL); reaction time: 3.5 h. After the reaction, the product was extracted with chloroform. The combined organic extract was dried over MgSO₄. After removal of the solvent, the solid was re-dissolved in ethanol and filtered to remove the catalyst. The solvent of filtration was removed to obtain the final product; yield: 66.6 mg (90%). Theoretical percentage of deuteration at the vinyl position = 90.0%. ¹H NMR (400 MHz, acetone- d_6 , 25°C): $\delta = 8.16$ (d, J = 8.4 Hz, 2H), 7.73 (d, J = 8.4 Hz, 2H), 6.96 (br, 0.15 H, $=CH_a$), 6.08 (br, 0.14 H, $=CH_c$), 5.52 (br, 0.12 H, = CH_b); ²D NMR (61.4 MHz, acetone + acetone- d_6 , 25 °C): $\delta = 6.99$ (s, D_a), 6.11 (s, D_c), 5.54 (s, D_b).

Deuteration of Cyclooctene



The H/D exchange experiment was carried out in 2 steps. 1st step: cyclooctene (1.10 mL, 8.44 mmol), RuHCl(CO)- $(PPh_3)_3$ (322 mg, 338 µmol, 4.0 mol%), D₂O (4.30 mL, 240 mmol); reaction time: 40 h. 2nd step: cyclooctene (product from step 1, 1.10 mL, 8.44 mmol), RuHCl(CO)(PPh₃)₃ (333 mg, 350 µmol, 4.1 mol%), D₂O (4.30 mL, 240.4 mmol); reaction time: 44 h; overall yield: 360 mg (39%). Theoretical percentage of deuteration at the vinyl and alkyl positions cannot be determined since the reaction proceeds via two steps. ¹H NMR (400 MHz, CDCl₃, 25 °C): $\delta = 5.61$ (s, 2H, CH=), 2.09 (s, 3.72H, =CDCHD), 1.43 (s, 7.70H, other CHD); ${}^{13}C{}^{1}H$ NMR (100.6 MHz, CDCl₃, 25 °C): $\delta = 129.89$ (residual =CH), 129.56 (t, J = 23.14 Hz, =CD of deuterated COE), 28.2 (m, CD₂ of deuterated COE), 24.86 (m, CD₂ of deuterated COE). Normal ¹³C{¹H} NMR integration cannot be used for quantitative analysis. In this work, the intensities of the ¹³C signals of =CH and =CD have been determined by inverse gated decoupling ¹³C[¹H] NMR. The relaxation time d_1 is set to 12 sec and the number of scans is 4116. Based on the =CH/=CD intensity ratio of 0.52:3.04, it was estimated that the vinyl carbon has ca. 85.4% of deuterium. ²D NMR (61.25 MHz, CH₂Cl₂, 25 °C): $\delta = 5.59$ (s, 1 D), 2.03 (s, 2D), 1.38 (s, 4D).

Attempted Deuteration of trans-a-Methylstyrene

trans-α-Methylstyrene (99%, 195 mg, 0.994 mmol), RuHCl(CO)(PPh₃)₃ (28.5 mg, 29.9 µmol, 3.01 mol%), D₂O (320 µL, 17.9 mmol); reaction time: 18 h. No H/D exchange was observed and starting material was recovered (156 mg, 80.0%). ¹H NMR (400 MHz, CDCl₃, 25 °C): δ =7.55-7.24 (m, 10 H, Ph), 6.84 (s, 1 H, =CH), 2.29 (s, 3 H, PhCMe=).

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