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Ionic liquids as acid/base buffers in non-aqueous solvents for homogeneous catalysis: A case of selective hydrogenation of olefins and unsaturated aldehyde catalyzed by ruthenium complexes

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ABSTRACT

We present a novel approach to tune acidity/basicity in non-aqueous and low-water media by using a class of ionic liquids (ILs) with buffering characteristics, which was readily synthesized by the reaction of 1-alkyl-3-methylimidazolium hydroxide ([RMIM]OH) base moieties with a serials of binary or polybasic acids and defined as ionic liquid-buffers (IL-buffers). We have performed controlled experiments of hydrogenation of olefins and trans-cinnamaldehyde, catalyzed by [RuCl₂(PPh₃)₃] in non-aqueous media such as DMF and ILs in the presence of IL-buffers. Remarkable buffer dependence of the formation and catalytic behavior of ruthenium hydrides were evidenced by the kinetic studies and NMR measurements. The hydride [RuHCl(PPh₃)₃], being favorably formed in the presence of the IL-buffer with lower log₁₀([Base]/[Acid]), exhibited higher activity in the reduction of the C=C bond against the carbonyl functionality of *trans*-cinnamaldehyde. While the hydride $[RuH_4(PPh_3)_3]$, being preponderantly formed in the presence of the IL-buffer with higher log₁₀([Base]/[Acid]) showed activity and higher selectivity towards the C=O reduction. Consequently, the hydrogenation performance of olefins and trans-cinnamaldehyde in non-aqueous system could be adjusted by adding the different IL-buffers. It is envisioned that the ability of IL-buffers to alter and precisely control the catalytic active species in non-aqueous or low-water systems might find appreciable applications for both fundamental studies and syntheses where the reactions are acid/base-sensitive.

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1. Introduction

It is well-known that many chemical reactions are pH-related, that is, the outcome and even the nature of the products may be altered appreciably if the pH changes significantly during the process of reaction [1–10]. This is especially true in biochemical reactions where the pH is important to the proper metabolism and functioning of animals and plants [11,12]. Also, accumulated examples of pH-dependent selective hydrogenation catalyzed by transition-metal complexes in aqueous media have been reported by several groups. The ability to vary the activity and selectivity of a water-soluble catalyst by modulating pH became one of the unique aspects of aqueous-phase catalysis [1–7]. Some of them showed valuable catalytic performance in aqueous solutions or aqueous/organic biphasic systems.

Nevertheless, the effect of acid–base conditions in non-aqueous media has not received the attention that it deserves. The reports on the pH control *via* buffers in non-aqueous media such as organic solvents and ionic liquids (ILs) still need increasing. Often the reactions in non-aqueous media have been investigated without controlling the pH of the system. The use of buffering systems involving highly hydrophobic acids and their sodium salts, and highly hydrophobic bases and their hydrochlorides, has been proposed [13–16]. Indeed, these systems can efficiently buffer organic solvent media. Unfortunately, they were found to have only limited solubility in some of non-polar solvents commonly used for biocatalysis. To overcome this restriction, Halling and co-workers developed more hydrophobic buffer systems consisting of functionalized and dendritic polybenzylethers [17]. These molecules are able to buffer the ionization state of enzymes in solvents like toluene, and can be used to evaluate the "pH profile" of biocatalysts in low-water systems. Other systems such as solid-state acid-base buffers can also be used for controlling the ionization state of the enzyme in organic solvents [18-21].

ILs are known as designed liquids with controllable physical/ chemical properties and specific functions, which have been attracting considerable interest over past decade [22–34]. They are often used as the medium for selective and enzymatic reactions [22–36]. Recently, we have synthesized a new class of ILs with





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bufferic characteristics, defined as ionic liquid buffers (IL-buffers) [37]. They are miscible with non-aqueous polar solvents such as methanol, DMF, and dichloromethane and also with the ILs like [BMIM][PF₆] and [BMIM][BF₄]. Preliminary results indicated that the IL-buffers were able to control the formations of ruthenium complexes and thus vary the catalytic performance of hydrogenation in DMF and ILs. The present study extends the facile synthesis of a series of IL-buffers and demonstrates their acid/base controllability in connection to the formations of rutheniumhydride complexes in non-aqueous media. We choose the selective hydrogenation of olefins and *trans*-cinnamaldehyde (CAL), as a probe reaction for the purpose of elucidating the relationship between the ruthenium species and their catalytic performances in IL-buffered non-aqueous solvents by the means of ¹H and ³¹P NMR characterizations.

2. Experimental

2.1. Materials

trans-Cinnamaldehyde and styrene (Sigma–Aldrich) were passed through a silica column before use. Cyclohexene (99%, Alfa Aesar) and 1-hexene (98%, Fluka) were used as received without further purification. DMF was purified by drying overnight over KOH pellets and then distilled under reduced pressure. The complexes [RuCl₂(PPh₃)₃], [RuHCl(PPh₃)₃], [RuH₂(PPh₃)₄] and [RuH₄(PPh₃)₃] were synthesized by the known procedure and identified by their NMR spectra [38–40].

2.2. Characterizations

Thermal gravimetric analysis (TGA) was performed with Simultaneous Thermal Analysis-STA 409EP. The water contents in the ILs were detected by Karl–Fischer titration (Metrohm LTD., Model 787 KF Titrino). The NMR measurements of reaction mixtures were performed on a Bruker AV 400 instrument using an inner capillary filled with D₂O or CDCl₃ for ¹H NMR and 85% H₃PO₄ for ³¹P NMR. The IR measurement of sample was performed on a Nicolet Advatar 360 instrument, analyzed by OMNIC version 4.1.

2.3. Synthesis of IL-buffers

Aqueous solution of [RMIM]OH was prepared by passing the corresponding imidazolium halide ([RMIM]X) through a column filled in anion-exchange resin, as described in the literature [37,41]. The aqueous [RMIM]OH was then neutralized with serials of acids (phosphoric acid or phthalic acid) in a beaker and the pH of the solution was adjusted to the desired value. The solution was evaporated at 50 °C under reduced pressure to give a viscous liquid, which was then vacuum-dried at 50 °C for 18 h to afford the IL-buffer product. According to the titration profiles of [BMI-M]OH with acids such as phosphoric acid and phthalic acid in organic solvents, we synthesis IL-buffers by reaction of [BMIM]OH base moieties with acids at different $\log_{10}([Base]/[Acid])$ as described above.

2.4. Samples prepared for NMR measurements

In a typical measurement, calculated amounts of ruthenium complex precursor, PPh₃, solvent and IL-buffer were introduced to a stainless steel autoclave of 60 mL and then flushed with hydrogen (99.999% purity) consecutively three times. The autoclave was then filled with hydrogen to the desired pressure. The mixture was stirred at 800 rpm and required temperature. The autoclave was put in an ice-water bath and released the pressure carefully

after 1 h. The mixture was soon transferred to NMR tube in Ar atmosphere using an inner capillary filled with D_2O or $CDCl_3$.

2.5. Catalytic hydrogenation

The reaction was carried out in a stainless steel autoclave of 60 mL capacity. Typically, calculated amounts of substrate, ruthenium complex precursor, PPh₃, solvent and IL-buffer were introduced to the autoclave and then flushed with hydrogen (99.999% purity) consecutively for three times. The autoclave was then filled with hydrogen to the desired pressure. The reaction mixture was stirred at 800 rpm and required temperature. After the reaction, the autoclave was put in an ice-water bath and released the pressure carefully. The organic phase were analyzed using a capillary column (KB-Wax, 60 m × 0.32 mm × 0.32 µm) for the products of *trans*-cinnamaldehyde and a capillary column (SE-30, 30 m × 0.32 mm × 0.25 µm) for the products of other olefins with flame ionic detector (FID) and quantitated by the corrected normalization analyzing.

3. Results and discussion

3.1. Synthesis and characterization of IL-buffers

We noted that the titration profiles of 1-alkyl-3-methylimidazolium hydroxides ([RMIM]OH) with organic or inorganic binary/ polybasic acids such as phthalic acid (H₂P), tartaric acid (H₂T) and phosphoric acid (H₃PO₄) in organic solvents expressed a buffering-like region and the region is similar to that of conventional acid/base bufferic counterparts (Fig. 1). Thus, we considered that it was possible to synthesize a kind of buffer-like ILs by neutralization of aqueous-solutions of [RMIM]OH with aqueous solutions of acids in a calculated molar ratio as illustrated in Fig. 2. According to the literature methods with slight modification, the [RMIM]OH moieties were produced by anion exchange of the corresponding imidazolium chlorides, which were obtained by the reaction of methylimidazole with an equivalent of the appropriate alkyl chlorides [41,42]. The final yields of the target compounds ranged from 91% to 93%. The samples were characterized using ¹H NMR and electrospray ionization (ESI) mass spectrometry. In addition, we have measured the differential scanning calorimetry (DSC), ther-



Fig. 1. Titration curve for a serials of 0.1 mol L^{-1} acids vs. 0.1 mol L^{-1} [BMIM]OH in MeOH. (a) Phosphoric acid; (b) succinic acid; (c) malic acid; (d) tartaric acid. The electrode is standardized with two aqueous primary standard buffer solutions. Because of the unknown liquid junction potential, measurements of pH in non-aqueous solvents are referred to as "apparent pH".



Fig. 2. Schematic representation of synthetic pathway for IL-buffers.

mal gravimetric analysis (TGA) and miscibilities of the samples (Figs. 1S–11S in the Supplementary material) [37]. All the characterization data were consistent with the expected compositions and structures. We then defined this kind of ionic liquids as IL-buffers. Accordingly, we have synthesized a series of IL-buffers with different apparent pH by changing the acids as illustrated in Fig. 2. It has been indicated, however, that the solids were obtained at room temperature when the molar ratio of [RMIM]OH over acids was set at 2:1 for H_2P or H_2T and 3:1 for H_3PO_4 , which showed no buffering characteristics at all.

The solubility of the IL-buffers in organic solvents was similar to that of conventional ILs like 1-butyl-3-methylimidazolium tetra-fluoroborate ($[BMIM][BF_4]$) and 1-butyl-3-methylimidazolium hexafluorophosphate ($[BMIM][PF_6]$), miscible with polar solvents such as methanol, DMF, and dichloromethane and also with the ILs like $[BMIM][PF_6]$ and $[BMIM][BF_4]$ [37]. For a given anion, it seems that the variation in the imidazolium cation has less effect on the thermal stability of the corresponding IL-buffers. The water content, apparent pH, buffer value, and dilution value of the IL-buf-

 Table 1

 The water content, apparent pH, buffer value, and dilution value of the IL-buffers^a

Substance	Water content (%)	Apparent pH	Buffer value ^b	Dilution value
[BMIM][HP]	0.49	4.01	0.0182 (0.016)	+0.03 (+0.052)
[OMIM][HP]	0.24	4.01	0.0181	0.03
[BMIM][HT]	0.95	3.56	0.0307 (0.027)	0.04 (-0.049)
$[BMIM][H_2PO_4]^d$	0.48	2.62	0.0107	0.09
[BMIM] ₂ [HPO ₄] ^e	0.35	8.50	0.0064	0.1
[BMIM][BF ₄]	0.49			
DMF	0.28			

^a Abbreviations: BMIM = 1-butyl-3-methylimidazole, OMIM = 1-octyl-3-methylimidazole, HP = hydrogen phthalate, HT = hydrogen tartrate. BF₄ = tetrafluoroborate. Data in parentheses are those of inorganic counterparts from Ref. [43].

^b The buffer value was defined as the number of moles of strong base required to change the pH of 1 L of solution by one unit.

^c Change of pH on dilution with an equal volume of water.

^d The $log_{10}([Base]/[Acid])$ was set at -0.073.

^e The log₁₀([Base]/[Acid]) was set at 0.232.

fers are summarized in Table 1, indicating that the behaviors of the IL-buffers are exactly in agreement with that of inorganic counterparts.

3.2. Influence of IL-buffers on the selective hydrogenation of olefins

To confirm the buffering ability and exploit the usability of the ILs synthesized, we initially performed the hydrogenation of cyclohexene catalyzed by $[RuCl_2(PPh_3)_3]$ in non-aqueous media such as DMF and $[BMIM][BF_4]$ in the presence of different molar ratio of [BMIM]OH and H_2P . Plots of the reaction TOF (mol-product mol-Ru⁻¹ h⁻¹) against the $log_{10}([Base]/[Acid])$ are shown in Fig. 3. No



Fig. 3. Base–acid molar ratio effect on catalytic hydrogenation of cyclohexene in DMF and [BMIM][BF₄]. Reaction conditions: $[RuCl_2(PPh_3)_3] = 12.0 \text{ mg}$; IL-buffer [BMIM][HP] with different molar ratio of [Base] and [Acid] = 50 mg; solvent = 2.0 mL; olefin = 1.0 mL; hydrogen pressure = 2.5 MPa; stirring speed = 800 rpm; temperature = 50 °C; reaction time = 5 h.

by-products of the reactions were detected by the capillary GC. A steep decrease in catalytic activity in term of TOF occurred in the log₁₀([Base]/[Acid]) ranging at 0.15–0.3, implying the meaningful effect of pH value on the reaction rate. It was also remarkable that in [BMIM][BF₄] the catalytic activity did not fall to zero in the log₁₀([Base]/[Acid]) above 0.28. This observation pointed to somewhat more complex equilibria than a simple disappearance of [HRuCl(PPh₃)₃] with increasing basicity. In principle, the coordination of phthalate or tartrate could not be ruled out either. Evidences in the hydrogenations of hexene and styrene also revealed that the catalytic activities were strongly dependence of the log₁₀([Base]/[Acid]) in the non-aqueous media as shown in Table 2. The lower reactivity of the internal olefin compared with the terminal one was analogous to what has been observed in the hydrogenation reactions by the [RuCl₂(PPh₃)₃] complex in homogeneous catalysis [38].

It is well established that the hydrogenation of CAL occurs through the classical pathway shown in Fig. 4. The reaction was then carried out at 60 °C using [RuCl₂(PPh₃)₃] as catalyst in DMF, in which the acid/base was controlled by using two kinds of IL-buffers generated from [BMIMOH] and [H₃PO₄] in the log₁₀([Base]/ [Acid]) at -0.073 and 0.232, which were denoted as [BMIM][H₂₋ PO₄] and [BMIM]₂[HPO₄], respectively. The reaction rate decreased in the presence of IL-buffers as compared with that in the absence of buffers, but the product selectivities were apparently IL-buffer dependence (Table 3). To exclude the possibility of controversial contradiction in conversion and selectivity generally existed in the catalytic reactions, the product distribution of CAL hydrogenation was determined both as a function of PPh₃ excess at constant acid/base molar ratio (Figs. 12S-14S in the Supplementary material) and as that of conversion at constant PPh₃. In the case of with and without IL-buffers, the CAL conversion and also the selectivity to unsaturated alcohol (UOL, the reduction product of C=O bond) increased with increasing P/Ru ratio, but the selectivity to UOL was lower than 45% even in the case of $PPh_3/Ru = 9.0$ when the reaction was conducted in the absence of IL-buffer or in the presence of IL-buffer [BMIM][H₂PO₄] with log₁₀([Base]/[Acid]) at -0.073. Contrast to these results, the selectivity to UOL could in-

Table 2

Hydrogenation of olefins in DMF buffered by [BMIM][HP]^a

Substrate	$Log_{10}([Base]/[Acid]) = 0.0^{b}$		$Log_{10}([Base]/[Acid]) = 0.315^{c}$	
	Conversion (%)	TOF (h^{-1})	Conversion (%)	TOF (h^{-1})
1-Hexene	97.8	1251	58.8	374
Styrene	55.3	769	40.6	282
Cyclohexene	2.3	36	0.7	6

^a Hydrogen pressure = 0.5 MPa; other conditions are the same as in Fig. 3.

^b Reaction time = 30 min; TOF = turnover frequency, in mole of product yield per mole of Ru per hour (mol-product mol-Ru⁻¹ h⁻¹).

^c Reaction time = 60 min.



Fig. 4. Hydrogenation reaction of trans-cinnamaldehyde (CAL).

crease to as high as 86.7% when the reaction was buffered by $[BMIM]_2[HPO_4]$ with $log_{10}([Base]/[Acid])$ at 0.232 was added into the system. Plots of CAL conversion vs. the product selectivity at

Table 3

Hydrogenation of *trans*-cinnamaldehyde by [RuCl₂(PPh₃)₃] in DMF in the absence and presence of IL-buffers

IL-buffer	Conversion (%)	Selectivity (%)			TOF (h^{-1})
		UOL	SAL	SOL	
[BMIM][H ₂ PO ₄] ^a [BMIM] ₂ [HPO ₄] ^b No buffer	65.5 36.6 97.9	12.2 84.9 32.0	60.2 7.2 6.5	27.6 8.0 61.5	59.7 33.4 89.3

Reaction conditions: $[RuCl_2(PPh_3)_3] = 10.42 \mu mol, excess PPh_3 = 0.03 mmol (Over$ all, P/Ru = 6.0 molar ratio), CAL = 0.95 mmol, DMF = 1.0 mL, temperature = 60 °C,hydrogen pressure = 2.0 MPa, stirring speed = 800 rpm, reaction time = 1 h.

^a $[BMIM][H_2PO_4]$ in the $log_{10}([Base]/[Acid])$ at -0.073 = 10.0 mg.

 b [BMIM]₂[HPO₄] in the log₁₀([Base]/[Acid]) at 0.232 = 30.0 mg.



Fig. 5. Selective hydrogenation of *trans*-cinnamaldehyde (CAL) catalyzed by $[RuCl_2(PPh_3)_3]$ in the presence of IL-buffer $[BMIM][H_2PO_4]$ with $log_{10}([Base]/[Acid])$ at -0.073. Reaction conditions: $[RuCl_2(PPh_3)_3] = 10.42 \mu mol$, P/Ru = 6.0 (molar ratio), CAL = 0.95 mmol, IL-buffer = 30.0 mg, DMF = 1.0 mL, hydrogen pressure = 2.0 MPa, stirring speed = 800 rpm, temperature = 60 °C. \blacksquare : selectivity to UOL; \bullet : selectivity to SAL; \blacktriangle : selectivity to SOL.



Fig. 6. Selective hydrogenation of *trans*-cinnamaldehyde (CAL) catalyzed by [RuCl₂(PPh₃)₃] in the presence of IL-buffer [BMIM]₂[HPO₄] with log₁₀([Base]/[Acid]) at 0.232. Reaction conditions: IL-buffer = 10.0 mg, others are the same as in Fig. 5. ■: selectivity to UOL; ●: selectivity to SAL; ▲: selectivity to SOL.

the constant molar ratio of PPh₃/Ru = 6.0 in the presence of different IL-buffers are displayed in Figs. 5–7. It can be seen that the major product was saturated aldehyde (SAL, the reduction product of C=C bond) and its selectivity was almost independent of CAL conversion when the reaction was buffered by [BMIM][H₂PO₄] with $log_{10}([Base]/[Acid])$ at -0.073 (Fig. 5). However, the major product was inverted to UOL with a selectivity up to 87.3% even in the case of higher CAL conversion when the reaction was controlled by [BMIM]₂[HPO₄] with $log_{10}([Base]/[Acid])$ at 0.232 (Fig. 6). In the case of without any IL-buffers, the selectivity to UOL was slightly higher than that to SAL, but both were never larger than 45%



Fig. 7. Selective hydrogenation of *trans*-cinnamaldehyde (CAL) catalyzed by $[RuCl_2(PPh_3)_3]$ in the absence of IL-buffer. Reaction conditions are the same as in Fig. 5. \blacksquare : selectivity to UOL; \bullet : selectivity to SAL; \blacktriangle : selectivity to SOL.

(Fig. 7). The above results convinced that the reaction selectivities were essentially governed by the IL-buffers with the different log₁₀([Base]/[Acid]).

3.3. Influence of IL-buffers on the formation of ruthenium hydrides

The influence of different [Base]/[Acid] pairs and their molar ratio on the proton species during the hydrogenation of [RuCl₂(PPh₃)₃] has been measured in the solutions by ¹H NMR. In the absence of IL-buffer, the ¹H NMR spectra at high field of the reaction solution gave resonances at -12.7 and -17.8 ppm (Fig. 8A) when the stoichiometric complex was hydrogenated at 60 °C for 1 h. Whereas the spectra of hydride species became simple when the excess of PPh₃ was added, exhibiting a quartet at -17.8 ppm, which was straightforwardly assigned to the proton of Ru-H in the hydride species [HRuCl(PPh₃)₃] by referring to literature [39] and comparison with the authentic complex. When the reaction solution of the stoichiometric complex was buffered with the IL-buffer $[BMIM][H_2PO_4]$ in the $log_{10}([Base]/[Acid])$ at -0.073, the ¹H NMR spectra at the high field showed an additional triplet signal at -28.3 (t) ppm besides the ones at -12.7 ppm (s) and -17.8 ppm (q) (Fig. 8B). The clarifications for the signals at -12.7and -28.3 ppm were not clear enough, but they disappeared once adding excess PPh₃. In this case, a new signal appeared at -7.2 ppm, but its intensity was relatively weak and almost unchanged when increasing PPh₃. When the complex solution was buffered by [BMIM]₂[HPO₄] in the log₁₀([Base]/[Acid]) at 0.232, the ¹H NMR spectra showed three resonances at -7.2, -17.8 and -28.3 ppm (Fig. 8C). When the excess PPh₃ was added, the signal at -28.3 ppm disappeared while the relative intensity of the remained resonance at -7.2 ppm became dominance over the one at -17.8 ppm. Analogue ¹H NMR spectra were obtained in the reaction solution buffered by [BMIM][HP] with different log₁₀([Base]/[Acid]) (Figs. 15S–16S in the Supplementary material) [37]. In addition, the spectra in [BMIM][BF₄] were somewhat in



Fig. 8. ¹H NMR spectra at high field of ruthenium hydrides derived from $[RuCl_2(PPh_3)_3]$ under the conditions of hydrogen pressure 2.0 MPa and 60 °C for 1 h in the absence of IL-buffer and presence of IL-buffers $[BMIM][H_2PO_4]$ and $[BMIM]_2[HPO_4]$. (A) $[RuCl_2(PPh_3)_3] = 0.01 \text{ mol/L}$, without IL-buffer, DMF = 1.0 mL: (a-1) P/Ru = 3.0 (molar ratio); (a-2) P/Ru = 6.0 (molar ratio); (a-3) P/Ru = 9.0 (molar ratio). (B) $[RuCl_2(PPh_3)_3] = 0.01 \text{ mol/L}$, $[BMIM][H_2PO_4]$ with $log_{10}[Base]/[Acid]$ at -0.073 = 10.0 mg, DMF = 1.0 mL: (b-1) P/Ru = 3.0 (molar ratio); (b-2) P/Ru = 6.0 (molar ratio). (C) $[RuCl_2(PPh_3)_3] = 0.03 \text{ mol/L}$, $[BMIM]_2[HPO_4]$ with $log_{10}[Base]/[Acid]$ at 0.232 = 30.0 mg, DMF = 1.0 mL: (c-1) P/Ru = 3.0 (molar ratio); (c-2) P/Ru = 6.0 (molar ratio); (c-3) P/Ru = 9.0 (molar ratio).

agreement with those above but the spin-couplings were more complicated [37].

In order to make an assignment for the ruthenium hydride at -7.2 ppm, we synthesized [RuH₂(PPh₃)₄] and [RuH₄(PPh₃)₃] according to the known methods [40]. The ¹H NMR spectra at high field of [RuH₂(PPh₃)₄] and [RuH₄(PPh₃)₃] in DMF showed a quartet signal at -10.7 ppm and a singlet one at -7.2 ppm, respectively (Figs. 17S–19S in the Supplementary material). In the process of ¹H NMR and IR measurements under nitrogen atmosphere, we noticed that [RuH₄(PPh₃)₃] in DMF underwent a rapid substitution by N₂ to generate a species of [RuH₂(PPh₃)₃(N₂)], which showed a weak resonance at -12.6 ppm due to Ru-H in the ¹H NMR spectrum, and a sharp absorption at 2147 cm⁻¹ due to $v_{(N-N)}$ in the IR spectrum (Fig. 20S in the Supplementary material). The loss of a dihydrogen ligand was believed through a η^2 -dihydrogen complex [RuH₂(η^2 -H₂)(PPh₃)₃] intermediate under N₂ atmosphere [44].

Therefore, the results implied that in the case of excess PPh₃ two kinds of ruthenium hydrides, giving ¹H NMR signals at -17.8 and -7.2 ppm, were formed during the hydrogenation of [RuCl₂(PPh₃)₃] in the presence of IL-buffers and their relative intensities were in connection to the values of log₁₀([Base]/[Acid]) in the IL-buffers. The hydride [RuHCl(PPh₃)₃], with ¹H NMR resonance at -17.8 ppm, was favorably formed in the absence of IL-buffer and presence of IL-buffer [BMIM][H₂PO₄] in the log₁₀([Base]/[Acid]) at -0.073. The hydride [RuH₄(PPh₃)₃], with ¹H NMR resonance at -7.2 ppm, was predominately formed in the presence of IL-buffer [BMIM]₂[HPO₄] in the log₁₀([Base]/[Acid]) at 0.232.

3.4. Catalytic mechanism in the presence of IL-buffers in non-aqueous media

It is known that the selective hydrogenation of CAL could be completely inverted by minor changes in a aqueous solution pH, shifting the equilibrium between the ruthenium hydrides [RuHCl(TPPMS)₃] and [RuH₂(TPPMS)₄] when using water-soluble complex [RuCl₂(TPPMS)₂]₂ as the catalyst [1–7]. In aqueous system it was established that the water-soluble complex [RuCl₂-(TPPMS)₂]₂ could be dominantly converted to [RuHCl(TPPMS)₃] at



Fig. 9. A possible catalytic mechanism of ruthenium complex in the presence of ILbuffers in non-aqueous media.

pH lower than 3.3, and $[RuH_2(TPPMS)_4]$ at pH larger than 7. The species $[RuHCl(TPPMS)_3]$ catalyzed the slow but selective hydrogenation of the C=C bond in CAL, while the one $[RuH_2(TPPMS)_4]$ was active and selective for the reduction of C=O bond. However, in the case of excess PPh₃ the pseudo quartet at -10.3 ppm due to $[RuH_2(PPh_3)_4]$ was not observed in DMF either in the presence or absence of IL-buffers (Fig. 8). Also, no impressive selectivity to UOL was achieved if the stoichiometric $[RuCl_2(PPh_3)_3]$ was used as catalyst in the presence or absence of IL-buffers (Figs. 12S–14S Supplementary material).

Taking the results of kinetic studies and NMR measurements into account, we are able to propose a plausible catalytic mechanism, which is different from that in aqueous system, for selective hydrogenation of CAL in non-aqueous media when the system was controlled by the IL-buffers as shown in Fig. 9. In the presence of IL-buffer and an excess of PPh₃ under H₂ atmosphere, the complex $[RuCl_2(PPh_3)_3]$ in DMF could undergo a consecutive equilibrium reactions. The likely species [RuHCl(PPh₃)₃] was formed in the presence of IL-buffer with log₁₀([Base]/[Acid]) at -0.073 and absence of IL-buffer. Such hydride was more active for the reduction of C=C functionalities than for that of C=O bond. Hydrogenation of $[RuCl_2(PPh_3)_3]$ in the presence of IL-buffer with $log_{10}([Base]/[Acid])$ at 0.232 could cause the formation of [RuHCl(PPh₃)₃] as an intermediate at first, but it would be readily transferred to the hydride [RuH₄(PPh₃)₃]. Such hydride was believed to be essentially responsible for the reduction of C=O bond. In fact, in non-aqueous media like THF, the species [RuH₄(PPh₃)₃] has also been found active and efficient for the catalytic hydrogenation of cyclohexanone [45].

4. Conclusions

We have presented a facile method for the synthesis of the ILbuffers by the reactions of [BMIM]OH with organic/inorganic binary/polybasic acids. We have performed controlled experiments to explore the potential application of IL-buffers for controlling acid/base in non-aqueous media and found a remarkable buffer dependence of the rutheniumhydride complexes in their formations and catalytic behaviors in the selective hydrogenation of olefins and unsaturated aldehyde. We have shown that in nonaqueous media, the hydrides $[RuHCl(PPh_3)_3]$ and $[RuH_4(PPh_3)_3]$ were preponderantly formed in the presence of IL-buffers at lower or higher log₁₀([Base]/[Acid]), which, respectively, exhibited activity and selectivity for the hydrogenations of C=C and C=O bonds. As an extension of our ongoing research, the IL-buffers are also found to be able to tune the ionization state of enzyme in nonaqueous solvents and ILs and hence control its activity, which will be reported in due course.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2008.06.028.

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